

# Preparation, Characterization, and Dyeing Properties of Calcium Alginate Fibers

Fangbing Lv,<sup>1,2</sup> Ping Zhu,<sup>1,2</sup> Chaoxia Wang,<sup>1</sup> Limin Zheng<sup>2</sup>

<sup>1</sup>Key Laboratory of Eco-Textile, Ministry of Education, Jiangnan University, Wuxi 214122, China

<sup>2</sup>Key Laboratory of Green Processing and Functional Textiles of New Textile Materials of Ministry of Education, Wuhan Textile University, Wuhan 430073, China

Received 15 September 2011; accepted 15 December 2011

DOI 10.1002/app.36673

Published online in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** A novel attempt has been investigated in this article to dye calcium alginate fibers with acid dyes. The calcium alginate fibers were prepared by wet spinning and their dyeing properties were studied. Scanning electron microscopy analysis revealed that the surface of calcium alginate fibers was relatively smooth and uniform with many small grooves. The X-ray diffraction results indicated that the crystallinity of the fibers was 61%. The dyeing conditions were optimized by testing the exhaustion (%). Moreover, the kinetics of dyeing calcium alginate fibers was determined as

a function of dyeing time with various acid dyes. The results also showed that the calcium alginate fibers exhibited good dyeability with the fastnesses to washing and dry rubbing around 4 grades. At the same time, the dyeing process had no significant influence on the mechanical properties of the fibers with the strength loss only around 0.3 cN/dtex. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** calcium alginate fiber; acid dye; dyeing property; dyeing fastness; mechanical property

## INTRODUCTION

Alginate is a natural unbranched binary copolymer of  $\beta$ -(1-4)-linked-D-mannuronic acid (M) and  $\alpha$ -L-guluronic acid (G) groups derived from the brown alga.<sup>1–3</sup> The interests of alginates with various M-G compositions result from their good biocompatibility and biodegradable absorbent activity.<sup>4,5</sup> The chemical structure of alginate<sup>6</sup> is displayed in Figure 1.

Alginate is water-soluble, but the alginate gel can be formed in the presence of divalent cations, such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and so on, because the cations act as ionic bridges between L-guluronic acid residues on adjacent chain segments.<sup>7,8</sup> Due to this reversible solubility, calcium alginate fibers are generally prepared by injecting a solution of sodium alginate into a bath containing calcium salt solution<sup>9–11</sup>. The fibers are extensively used in wound-care applications on account of their inherent biocompatibility, nontoxic-

ity, and potential bioactivity.<sup>12–14</sup> Especially, a moist gel is formed as a result of ions exchange between  $\text{Ca}^{2+}$  and  $\text{Na}^+$  when the fibers interact with the wound exudates.<sup>15</sup> And this eliminates fibers entrapment in the wound, which is a major cause of patient trauma at dressing change.<sup>16,17</sup>

Also, calcium alginate fibers are applicable to the manufacture of textile product and exhibit excellent characteristics including softness, strong ability of absorbing sweat, and biocompatibility. As is known, the dyeing process is crucial to the textile processing.<sup>18</sup> However, because of the ions exchange, the calcium alginate fibers are completely gelled in sodium chloride solution.<sup>19</sup> Such gelation restricts sodium chloride to be used as the accelerant in the dyeing process of calcium alginate fibers. There are few articles which have reported about the dyeing properties of calcium alginate fibers.

In this article, acid dyes were considered to be utilized due to the poor alkali resistance of the calcium alginate fibers. The research work focused on investigating the dyeing properties of calcium alginate fibers with acid dyes. The morphology and structural parameters of calcium alginate fibers were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. The dyeing conditions, including dyeing bath pH, dyeing temperature, and dye concentration, were optimized by testing the exhaustion (%). Further, the kinetics of dyeing the calcium alginate fibers was presented. The washing and dry rubbing fastnesses were also examined.

Correspondence to: P. Zhu (pzhu99@163.com).

Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 50773032, 51073122.

Contract grant sponsor: Natural Science Foundation of Hubei Province of China; contract grant number: 2009CDA033.

Contract grant sponsor: Fundamental Research Funds for the Central Universities; contract grant number: JUDCF10038.

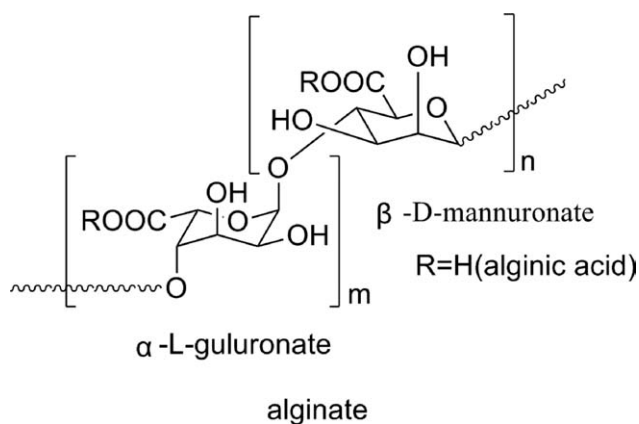


Figure 1 Chemical structure of alginate.

## EXPERIMENTAL

### Materials

Calcium alginate fibers (1.68 dtex) were prepared by the wet spinning from a solution with a laboratory spinning machine. Three acid dyes, CI Acid Red 249, CI Acid Yellow 117, and CI Acid Blue 80 with different degrees of staining on the calcium alginate fiber, were selected in this study. They were purchased from the Zhejiang Longsheng Group Co. Ltd., China. The dyes were purified by recrystallization in acetone prior to use. The chemical structures of three acid dyes were shown in Figure 2.

Acetic acid and sodium acetate which were used to adjust the dyeing bath pH were supplied by Qingdao Jiangshan Chemical Reagent Co., Ltd., China. All these chemicals were analytical grade.

### Fiber preparation

Aqueous sodium alginate was vigorously stirred at room temperature for 1 h, and filtered through a 200-mesh filter cloth under pressure. The clear filtrate was degassed in a spinning tank, and then extruded at 25°C through a 30-hole (0.08 mm diameter) viscose-type spinneret into a coagulating bath containing aqueous calcium chloride. The as-spun fibers were washed and stretched (the stretching ratio was 20%) in distilled water, then dried at 40°C for 12 h.

### Characterization of calcium alginate fibers

The calcium alginate fibers were sliced by Y172 slicer (Changzhou textile instruments factory Co., Ltd. China). Then the analysis of the cross sections and the surface of calcium alginate fibers were performed on a JSM-6390LV SEM instrument (Electronics Co., Ltd. Japan) at 5.0 kV accelerated voltage and 10–15 mm working distance. The samples were coated with platinum of 10 nm thickness.

XRD was used to investigate the supermolecular structure of calcium alginate fibers. All the samples were studied as powders. XRD data were obtained using a DMAX-250 diffractometer (Electronics Co., Ltd. Japan). Ni-filtered  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54060 \text{ \AA}$ ) generated at a voltage of 40 kV and current of 300 mA was utilized. The scanning range was varied from  $2\theta = 0^\circ$  to  $60^\circ$  with a rate of 5 degree/min.

### Dyeing procedure

To obtain uniform dyeing, the fibers were scoured in distilled water at 50°C for 30 min to remove the impurities, then rinsed in distilled water, and dried. All dyeing procedures were applied on the treated calcium alginate fibers using the exhaust dyeing method: samples were immersed into a dye bath at 40°C with a liquor ratio of 50 : 1. The dye bath was heated to a certain temperature over 30 min and the solution was held for a certain time at the dyeing temperature. The dyed samples were then rinsed in distilled water at 60°C for 30 min and dried in the air.

The calcium alginate fibers were dyed under various dye bath conditions (dyeing bath pH, dyeing temperature, and dye concentration) to investigate the effects on the dyeing properties of the calcium alginate fibers. The exhaustion (%) behavior of the acid dyes on the fibers was also investigated by the monitoring of the exhaustion (%) values of the dyed fibers as dyeing proceeded.

### Determination of dye exhaustion (%) yields

The extent of exhaustion (%) achieved for an appropriate dye concentration on the calcium alginate fibers was determined using eq. (1) by the absorbance spectroscopic analysis of the dye bath before and after dyeing.

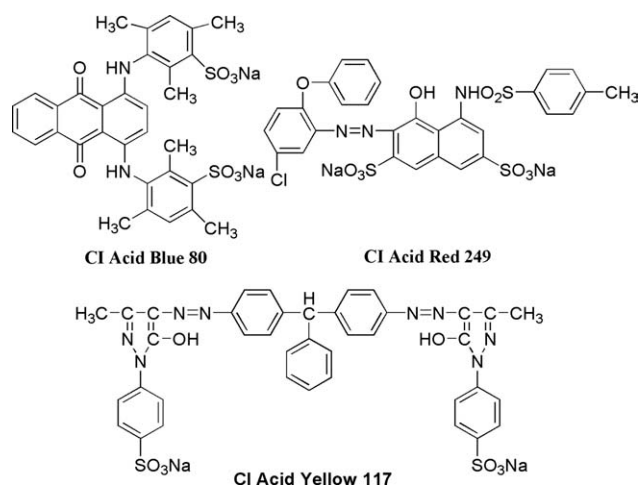


Figure 2 Chemical structures of acid dyes.

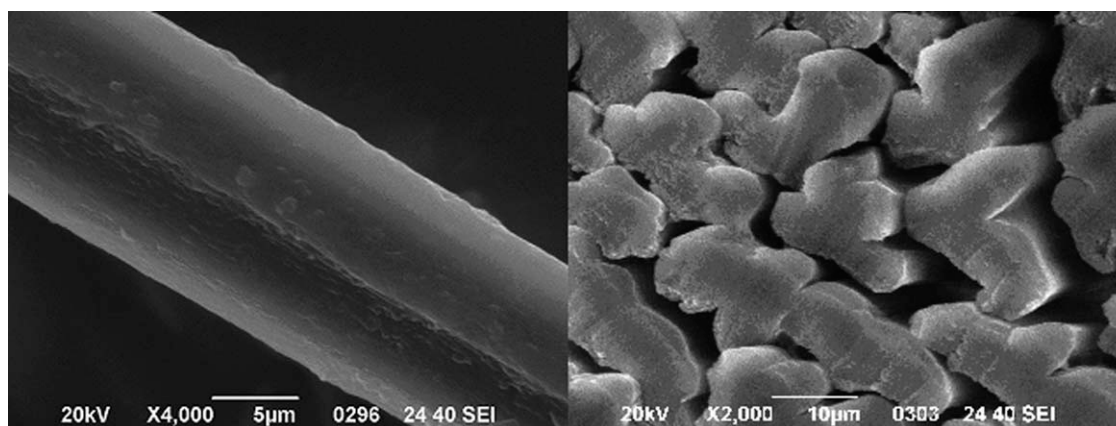


Figure 3 SEM of calcium alginate fibers: (a) surface and (b) cross-sections.

$$\text{Exhaustion}(\%) = (A_b - A_a)/A_b \quad (1)$$

where  $A_a$ : absorbance of the dyebath after dyeing;  
 $A_b$ : absorbance of the dyebath before dyeing.

#### Color fastness test

The dyed calcium alginate fibers were reduction cleared in water at 65°C for 30 min. A standard depth of 1/1 was chosen for the fastness test. The fastness tests were carried out according to the ISO-105-C06 international norms and in accordance with the AATCC 8-2001 test.<sup>20</sup> Staining and change in color were assessed using gray scales.

#### Mechanical properties test

The breaking strength of calcium alginate fibers was measured with the electronic single fiber tensile strength tester (Textechno Co., Ltd. German) and each sample was tested for 50 times with 15 mm space, 0.3 cN pretension, and a 20 mm/min stretching speed.

## RESULTS AND DISCUSSION

### Morphology of calcium alginate fibers

In order to clearly observe the morphological structure of the calcium alginate fibers, the longitudinal direction and cross section of the fibers were observed by SEM, and the results were shown in Figure 3.

From Figure 3(a), it could be seen that the surface of calcium alginate fiber was relatively smooth and uniform with many small grooves along the vertical section, which could induce the calcium alginate fibers to have high moisture absorption and excellent dye ability. Many streak patterns were evidently observed on the surface of the fibers from Figure

3(b). It was well known that both the roughness along the inner perimeters of the spinneret holes and the shrinkage upon drying of the fibers were postulated as the main reasons for the formation of these streaks.<sup>21</sup> And the calcium alginate fibers shrank as a result of dehydration and reverse diffusion of sodium and calcium cations<sup>22,23</sup> in the coagulation bath during the wet spinning process.

### Crystallinity of calcium alginate fibers

The XRD pattern of calcium alginate fibers was presented in Figure 4.

It could be found that the pattern of the fibers exhibited a sharp high peak at  $2\theta$  12.7° and two weaker diffraction peaks at  $2\theta$  23.1° and 38.9°, respectively. The result was consistent with that the diffraction of alginate showed typical peaks around 13° and 23°.<sup>24</sup> And the  $\text{Ca}^{2+}$  crosslinking with alginate facilitated the crystallization of cellulose itself. Based on the XRD analysis, the degree of crystallinity of the fibers was calculated using eq. (2)<sup>25</sup>

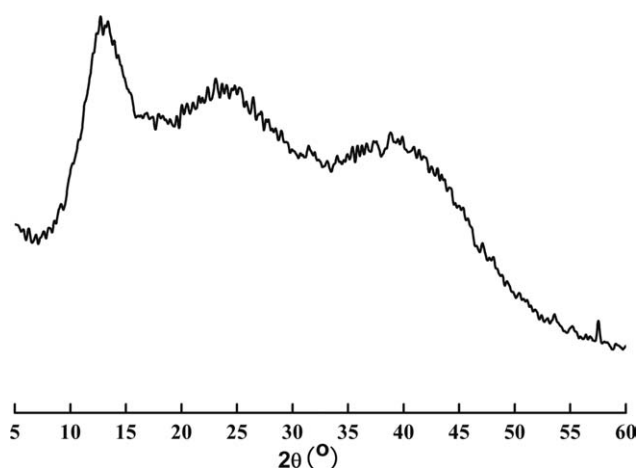
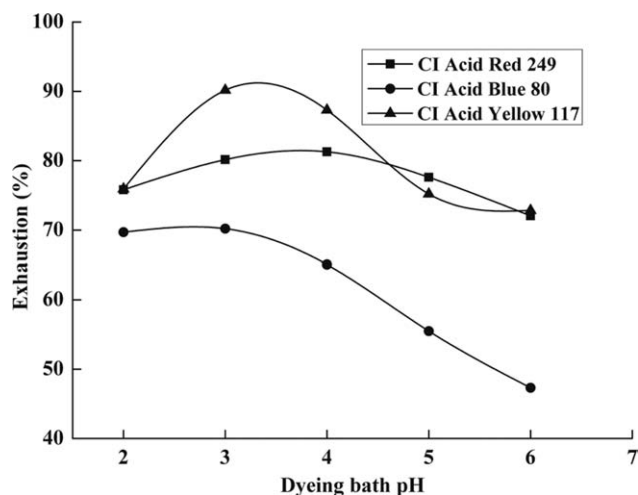


Figure 4 X-ray diffraction patterns of calcium alginate fibers.



**Figure 5** Effects of pH on exhaustion (%) of dyeing (dye 2.0% o.w.f., temperature 90°C, time 60 min).

$$CI = \frac{I_{\text{crystalline}}}{I_{\text{crystalline}} + I_{\text{amorphous}}} \times 100\% \quad (2)$$

From eq. (2) we calculated the calcium alginate fibers' crystallinity index to be 61% which could be contributed to the cross-linking between calcium ions and alginate macromolecules. In addition, the presence of  $-\text{OH}$  groups in the macromolecules of calcium alginate fibers probably formed a considerable number of hydrogen bonds, which resulted in relatively high values of crystallinity degree considering the high packing density of macromolecules. The dyeing properties varied depending upon the relative degrees of order and disorder in the structure (often described loosely as the crystalline/amorphous ratio). Generally, the higher crystallinity means a slower rate of dye diffusion with the fibers.<sup>26</sup>

### Effects of dyeing bath pH

The dye bath pH was one of the most important factors affecting the adsorption of dyes onto the calcium alginate fibers. And the effects of dyeing bath pH on the adsorption of acid dyes by the calcium alginate fibers are shown in Figure 5.

When the pH value ranged from 2 to 4, increasing pH value had a positive influence on the exhaustion (%). However, the exhaustion (%) decreased with further increasing pH value (higher than 4). It could be contributed to the chemical structure of the calcium alginate fibers.

The solidification of calcium alginate fibers took place because the water-soluble sodium alginate was transformed into water-insoluble alginate fibers. Considering the chemical structure of the calcium alginate fibers, the dyeing process could be due to the

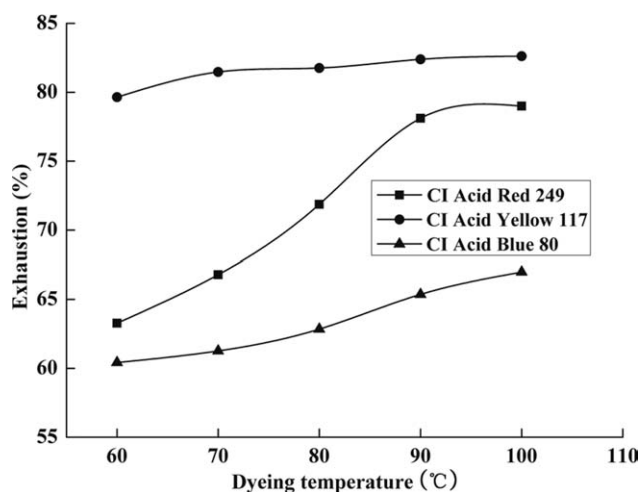
role of hydrogen bonds and Van der Waals forces between the fibers and dyes. At the same time, the ionic bonding was generated between anions of the dye molecules and calcium ions. When the pH was lower, too many hydrogen ions caused uneven dyeing. High pH value could effectively decrease the initial dyeing rate and improve level dyeing property. However, the repulsion force increased between the dyes and fibers with the pH increasing, and this repulsion force was prejudicial for dye molecules to penetrate into the fibers.

### Effects of dyeing temperature

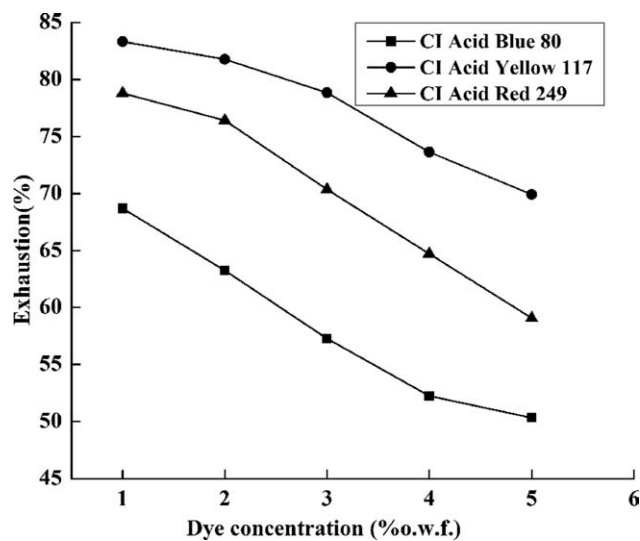
The temperature dependence on the dye ability of the calcium alginate fibers is presented in Figure 6.

An overall characteristic of higher dye ability was observed with an increase in the dyeing temperature. Although dyeing cannot take place within the crystalline regions of the fibers, it is not confined to the external surface. With the "egg-box" type of the structure appearing in the calcium alginate fibers, greater distances between macromolecules were connected. When the dyeing temperature was lower, the aggregation of dyes and the fibers' compact structure resulted in the lower exhaustion (%). The dye aggregation was reduced with the increase of the dyeing temperature, and the diffusion of the dyes into the fibers was facilitated, thus increasing the build-up property of the dyes. In this case, the exhaustion (%) was improved significantly with increasing the dyeing temperature.

It was also evident from Figure 6 that CI Acid Yellow 117 had a much slower dyeing rate than CI Acid Red 249 and CI Acid Blue 80 presumably because the shape of a dye molecule affected its diffusion rate. CI Acid Yellow 117 with high substantivity had poor migration properties, since its big



**Figure 6** Effects of temperature on exhaustion (%) of dyeing (dye 2.0% o.w.f., pH 3–4, time 60 min).



**Figure 7** Build-up properties of acid dyes on calcium alginate fibers (temperature 90°C, pH 3–4, time 60 min).

size and the strong interaction prevented the release of dyes from the initial point of attachment. Increasing the dyeing temperature would not significantly accelerate the penetration of the dyes into the cellulose matrix due to the poor migration property of CI Acid Yellow 117.

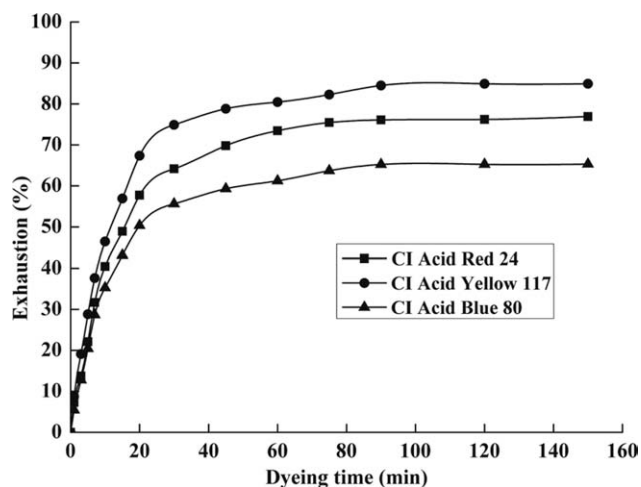
#### Effects of dye concentration

Figure 7 showed the dye concentration effects on the dyeability of the calcium alginate fibers. As expected, the exhaustion (%) decreased with increasing dye concentration.

The absorption of the dye molecules started on the less ordered surfaces of the fibers and then proceeded under favorable conditions into the interlinking region between elementary crystallites, penetrating into them from both ends. Only water-swollen intermicellar spaces and regions of lower order of the fibers were accessible to large acid dyes molecules. The molecular chains in amorphous region exhibited disorderly packing and could move easily to provide a large free volume, allowing dye molecules to diffuse easily into and out of the chains. Equilibrium between adsorption and desorption was thus displaced. As the dye concentration increased, the probability of contact between the dye molecules and fibers' surface increased. However, increasing the concentration accelerated the aggregation of the dye molecules in the dye bath, and that was prejudicial for dye molecules to penetrate into the fibers. And an excess of dye concentration would cause the waste of the dyes and water pollution.

#### Kinetics of dyeing calcium alginate fibers

Figure 8 illustrated the kinetics of dyeing the calcium alginate fibers with acid dyes.



**Figure 8** Kinetics of dyeing calcium alginate fibers with acid dyes (dye 2.0% o.w.f., temperature 90°C, pH 3–4, time 60 min).

The duration of dyeing varied from 0 to 160 min. The selectivity of the dyes for calcium alginate fibers increased significantly in the first 20 min after the dyeing process began. On the one hand, dissolved dye molecules in the bath were continuously absorbed onto and diffuse into the fibers during the dyeing process. On the other hand, dye molecules within the fibers could migrate out to deposit on the surface of fibers. With an increase in dyeing time, the adsorption capacity of the dyes gradually reduced, and then the exhaustion (%) reached saturation after 90 min. Dye adsorption at equilibrium represented the maximum sorption from the dye bath under certain conditions.

Considering the existence of large amounts of hydrogen bonds in calcium alginate fibers, high sorption properties were formed. Calcium alginate fibers exhibited relatively fast exhaustion (%) behavior presumably because of the high sorption properties and the existence of calcium ions which would bond with anions of the dyes. There is a general rule in textile dyeing: faster exhaustion (%) means uneven dyeing. However, no obvious uneven dye was observed in the dyeing results.

#### Washing and dry rubbing fastnesses

Washing and dry rubbing fastnesses for the dyed calcium alginate fibers are presented in Table I.

**TABLE I**  
Washing and Dry Rubbing Fastnesses of Calcium Alginate Fibers Dyed with Acid Dyes

| Dye                | Washing fastness (grade) | Dry rubbing fastness (grade) |
|--------------------|--------------------------|------------------------------|
| CI Acid Red 249    | 3–4                      | 3–4                          |
| CI Acid Yellow 117 | 4–5                      | 4                            |
| CI Acid Blue 80    | 3–4                      | 4                            |

**TABLE II**  
**Breaking Strength Loss of Calcium Alginate Fibers Dyed with Acid Dyes**

| Dye                | Alginate fibers (cN/dtex) | Dyed alginate fibers (cN/dtex) | Strength loss (%) |
|--------------------|---------------------------|--------------------------------|-------------------|
| CI Acid Red 249    | 2.35                      | 2.03                           | 13.49             |
| CI Acid Yellow 117 | 2.35                      | 2.04                           | 13.14             |
| CI Acid Blue 80    | 2.35                      | 2.07                           | 11.72             |

Obviously, dry rubbing fastness was slightly higher than washing fastness for the dyed calcium alginate fibers. CI Acid Yellow 117 offered both high fixation and good washing fastness presumably as a result of its higher molecular weight compared with the other two dyes, which made it less accessible to hydrolysis. And increasing dyes molecule size would increase the intensity of Van der Waals forces between the dyes and fibers. For the calcium alginate fibers, absorbed dye molecules could not easily migrate out of the fibers owing to the tight packing structure of the polymer chains. All the three dyes imparted the calcium alginate fibers good washing and dry rubbing fastness to satisfy the requirement of textile processing.

### Breaking strength loss

The breaking strength of the calcium alginate fibers before and after dyed with acid dyes is listed in Table II.

The breaking strength of calcium alginate fibers was close to that of cotton and higher than that of viscose rayon. The strength originated in the crystalline material whilst the amorphous material provided the flexibility. The calcium alginate fibers showed higher breaking strength than viscose rayon, presumably due to the higher crystallinity values.

Further it could be seen that the breaking strength decreased after the fibers were dyed with acid dyes. On the basis of an analysis of the results obtained, the decrease of breaking strength could contribute to fact that the penetration of dye molecules into the calcium alginate fibers destroyed the high packing density of fiber macromolecules. However, the dyeing process had no significant influence on the mechanical property of the calcium alginate fibers with the breaking strength decreasing slightly.

### CONCLUSIONS

A new regenerated cellulosic fiber spun by the wet process from sodium alginate solution exhibited excellent dyeing properties with acid dyes. SEM images showed that the surface of the calcium alginate fibers was relatively smooth and uniform with

many visible grooves along the vertical section. The XRD results indicated that the crystallinity of the calcium alginate fibers was 61%. The optimum dyeing process was concluded as follow: dye concentration 2% weight of fabric (o.w.f.); dyeing temperature 90°C; dyeing time 60 min; liquor ratio 50 : 1; pH value of dyeing bath 3–4. The kinetics of dyeing calcium alginate fibers demonstrated that the exhaustion (%) increased significantly with an increase in dyeing time, then gradually reached saturation. The dyed calcium alginate fibers exhibited good washing and dry rubbing fastness around 4 grades. And the breaking strength of calcium alginate fibers after dyeing decreased slightly.

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