(REFEREED RESEARCH)

AN EASY AND ACCURATE METHOD FOR DETERMINING DEGREE OF SUBSTITUTION ON CARBOXYMETHYLATED COTTON FABRIC

KARBOKSİMETİLLENMİŞ PAMUKLU KUMAŞLARDA SUBSTİTÜSYON DERECESİNİ TESPİT ETMEK İÇİN KOLAY VE HASSAS BİR YÖNTEM

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ABSTRACT

Carboxymethyl cellulose (CMC) is a common cellulose ether used in many industries including food, pharmaceuticals and personal care, chemicals, drilling fluids, paper as well as textile. The degree of substitution (DS) affects final CMC properties primarily, and thus it must be precisely measured before use. There are various methods for determination of DS when CMC is in powder form, however, methods for determination on the fabric are limited to back titration. Conventional titrimetric methods include reactions with a variety of chemicals and timely titration practices whose accuracy depend mainly on high level of expertise of the operator. An easy-to-apply alternative method with high repeatability is thus needed. In this study, a quick method comprising staining with a well-known dyestuff, namely Methylene Blue, followed by short rinsing-drying, and K/S measurement with spectrometer is offered for determination of degree of substitution of CMC. A precisely followed titration procedure is also carried out. It is shown that the results of newly offered method correlates very well with those of titration method. This alternative method is easier to apply, offers visual evidence and dyeing solution can be used again by addition of expended chemicals and dyestuff, if desired.

Keywords: Carboxymethyl cellulose, degree of substitution, carboxymethylation, titration, methylene blue

ÖZET

Karboksimetil selüloz (CMC), gıda, farmasötik ve kişisel bakım, kimyasal, sondaj sıvıları, kâğıt ve tekstil gibi pek çok endüstride kullanılan yaygın bir selüloz eteridir. Sübstitüsyon derecesi (DS) karboksimetil selülozun nihai özelliklerini etkileyen en önemli faktördür ve bu nedenle kullanım öncesi hassas şekilde ölçülmelidir. Karboksimetil selüloz toz halde olduğunda sübstitüsyon derecesini tespit etmek için kullanılan pek çok yöntem mevcuttur, ancak kumaş üzerinde tespit ters titrasyon ile sınırlıdır. Konvansiyonel titrasyon esaslı yöntemler pek çok kimyasalın kullanılması ve uzun süren titrasyon işlemleri gerektirmektedir ve bu yöntemle elde edilen sonuçların doğruluğu için işlemi yapan operatörün yüksek seviyede tecrübeli olmasına gerek duyulmaktadır. Bu nedenle, yüksek tekrarlanabilirliğe sahip ve uygulanması kolay alternatif yönteme ihtiyaç duyulmaktadır. Bu çalışmada, karboksimetil selülozun sübstitüsyon derecesinin tespiti için Metilen Mavisi isimli iyi bilinen bir boyarmadde ile lekeleme, kısa süreli durulama ve kurutmanın ardından spektrofotometre ile K/S değerinin tespitini içeren hızlı bir yöntem önerilmektedir. Hassasça yürütülen bir titrasyon prosedürü de çalışılmıştır. Yeni önerilen yöntemle elde edilen sonuçların titrasyon yöntemiyle elde edilenlerle yüksek korelasyona sahip olduğu gösterilmiştir. Titrasyon ile kıyaslandığında, bu alternatif yöntemin uygulanması daha kolaydır, görsel kanıt sunmaktadır ve istendiği takdirde harcanan kimyasallar ve boyarmadde ilave edilerek boyama çözeltisinin tekrar kullanımı mümkündür.

Anahtar Kelimeler: Karboksimetil selüloz, sübstitüsyon derecesi, karboksimetilasyon, titrasyon, metilen mavisi

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1. Introduction

Chemical functionalization of cellulose aims to improve the properties of the macromolecule for different purposes to be used in a variety of applications. The conventional sources of cellulose include cotton linters and wood pulp, however, renewable raw materials such as weeds, fibers, bamboos, and wastes from agriculture and forests are gaining importance. Etherification of cellulose through methylation, carboxymethylation, cynaoethylation, hydroxypropylation, single or mixed, is one of the most important routes of cellulose functionalization [1]. Cellulose ethers have a lower degree of polimerization and crystallinity compared to cellulose. Cellulose ethers can be classified according to their solubility properties; water soluble cellulose ether types, including methylcellulose, methyl hydroxyl propyl cellulose, hydroxypropylcellulose, water-soluble ethylhy droxyethylcellulose, sodium carboxymethylcellulose (NaCMC), and hydroxyethylcellulose, or organic-solvent-soluble types including ethylhydroxyethylcellulose and ethylcellulose. Cellulose ethers of moderate to high molecular weight are insoluble in water. As a rule, as DS increases, the polymers gradually pass through a stage of solubility in dilute alkali (those with a DS of up to 1.0), then through a water-soluble stage (about DS 1.0-2.3), and finally attain an organic-solvent-soluble stage (DS 2.3-3.0). However, sodium salt of carboxymethylcellulose is water soluble, a property enhanced by its ionic nature. Carboxymethyl cellulose (CMC) is nearly always sold as sodium salt of carboxymethylcellulose and is used in this readily soluble form. The acid form is insoluble. It has an average degree of substitution of 0.75, and a maximum viscosity of 4000 cP for 1% concentration. Due to having sodium salt of weak acid groups, the viscosity of CMC increases below pH4, when free acid is formed. CMC in which every carboxyl (–COOH) group has been reacted to form the sodium salt will have a pH of 8.25. Thanks to its ionic character, NaCMC has higher moisture absorption than other cellulose ethers, directly proportional to its DS. Among cellulose ethers, sodium salt of CMC (NaCMC) has a wide range industrial applications, especially in food, paper, pharmaceutical, cosmetics, as well as in textile industries [2]. Many studies are conducted in order to synthesize CMC derivatives, including photo-active CMC derivatives [3], those prepared from Tunisian vine stem [4], from water hyacinth [5], from sugarcane bagasse [6], and from pretreated corn stover [7]. A detailed review on history of and previous studies about manufacturing of CMC is given by Ambjörnsson et al [8].

Thanks to both swelling and chemical modification of cellulose during CMC production, the ordered structure of cellulose loosens, due to disruption of the intermolecular hydrogen bonding, causing an increase in accessibility of molecules [2]. Depending on the degree of substitution (DS), even water solubility can be achieved [9-10]. Most properties of CMCs in applications depend on three parameters, namely molecular weight of polymer, average number of carboxymethyl substituents per anhydroglucose unit (or degree of substitution) and the distribution of carboxymethyl substituents along the polymer chain [2].

CMC (see Figure 1) is commonly used in textile industry as size [12], thickening agent [13], migration inhibitor, dispersing agent, soil-release agent, and foam stabilizer [14]. Moreover, by substituting the available sites on cotton in fabric form, fabric properties are improved giving possibility for further processing of cotton fabric with a variety of chemicals [15-16]. Due to its strong anionic character, NaCMC is also used for removal of cationic dyestuffs from effluents after textile dyeing, and its usefulness for a variety of dyestuffs is reported [17-19].

CMC is mostly produced using a two-step process including alkalization and etherification; alkalization mostly achieved using sodium hydroxide and etherification using chloroacetic acid. However, alternative chemicals including dimethyl sulfoxide/tetrabutylammonium fluoride are also offered for the latter [20]. The order of application of these two steps may alternate [21-24] or a mixture of these may be used [10, 25] according to the desired properties on final product, always followed by acidification in a dilute aqueous hydrochloric, sulfuric or acetic acid solution. The resulting material is very swellable and has highly acidic carboxyl groups [26] giving enhancements in water retention, moisture regain, soil release, tensile strength and elongation at break [23, 25, 27]. A very good review of studies on carboxymethylation is given by Racz, Deak, and Borsa [10].

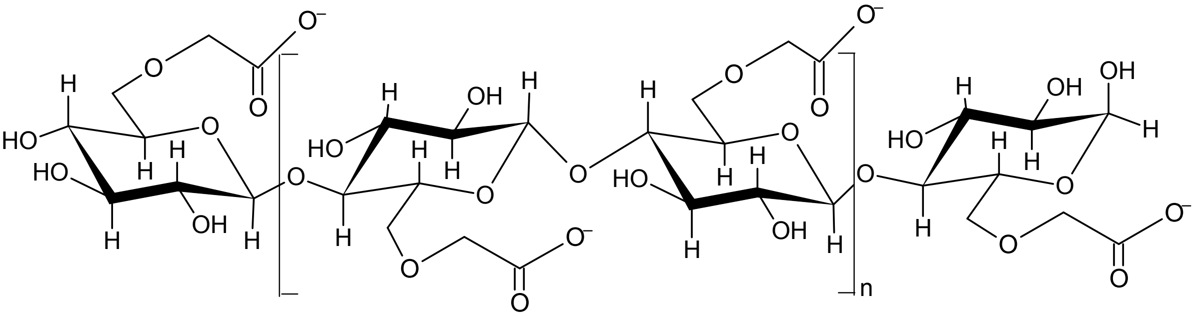

Figure 1. Molecular structure of carboxymethylated cellulose [11].

CMC having low DS value is water insoluble and suitable as adsorbent for dye removal from aqueous solution in a broader pH range [28]. When carboxymethylation is applied on cotton substrate, the fabric offers higher reactivity possibilities and less chemical use in further reactions, i.e. dyeing or crosslinking. The effects of application processes (pad-dry, pad-batch, pad-cure), amount of NaOH, soaking times, chemical concentrations and preparation methods on DS of cotton fabric are reported elsewhere in detail [29].

Accurate determination of DS of CMC is very important, as DS is the leading measure determining the properties of the product. CMC is mostly used in its powder form, thus there are various methods developed for determination of DS of CMC in powder form. The classical methods use the acidity of the carboxylic groups. They are based on conversion of the salt form to the free acid form and vice versa [30]. The acid form of the CM polysaccharide is obtained by a treatment of the sodium salt form of the polymer dispersed in ethanol with concentrated hydrogen chloride, and it can be titrated with a sodium hydroxide solution of known molarity [31]. Most common method is the back titration method [32]. The sodium salt of the polymer is converted to the free acid form, followed by addition of a known amount of NaOH, which produces sodium carboxylate. DS is calculated by back titration of the excess of NaOH. However, methods based on back titration demand highly experienced personnel and use of finely tuned low-concentration chemicals. The interaction of the CM groups with salt ions leading to quantitative precipitation of the polymers with copper salt and back titration of the excess of Cu ions gives the DS as well [33]. However, use of copper in laboratory practices bring additional laboratory waste load. In addition, many studies about the determination of DS applying various procedures as, e.g., titration of the anionic polymers with cationic polyelectrolytes forming insoluble polymeric salts have been investigated [34-35]. These methods are applicable for samples with DS values of up to 1.5. At higher DS various problems with regard to the necessary stoichiometric interactions appear. These sources of error are excluded in the spectroscopic and chromatographic methods provided the signals of the spectra and chromatograms can be suitably assigned and quantified. The modern methods also give information about the functionalization pattern of the polyglucan derivatives. However, it should be mentioned that the classical methods are still very useful because there is no need for expensive equipment. Following the procedure carefully, reproducible DS values can be obtained [36]. Other alternatives to classical methods are also offered. One method for precise determination of DS of CMC offered by Aggeryd and Olin is based on potentiometric titration. The precision of the whole method was reported to reach to as small as ±0.01D.S. [37]. A novel method offered by Oudhoff et al. for determination of DS of CMC is based on capillary zone electrophoresis. Thanks to this method, not only average DS value but also its dispersity could be established for technical CMC samples [38]. Another method, offered by Kennedy et al., comprises use of poly(hexamethylenebiguanidinium chloride) for quantitative determination of pectin and CMC in solution in terms of average charge density [39]. However, the use of such novel methods are limited due to their demand for developed equipment and use of uncommon and expensive chemicals.

On the other hand, when CMC is produced on fabric, methods for determination of DS are rather limited to back titration. An example is that offered by Hashem et.al. [15]. This method comprises of timely preparation and titration practices; steeping the fabric to be tested in HCl for 16 hours (or overnight), rinsing, drying, cutting and weighing each sample, followed by separately steeping in dilute NaOH solution for four hours and finally titration of each with dilute HCl. Care must be taken while following such a procedure in order not to interfere with the reported DS; moisture content of the sample to be tested, concentrations of the chemicals, drop size during titration which determines the precision of the measurement, the amount of solution taken out of the container on wet fabric before titration, and the correction factor that must be considered depending on the operator are some of the factors influencing the reported DS. An alternative method includes the use of conductivity meter as an alternative to or together with phenolphthalein indicator to determine the pH of the end point, however, the preparation and testing procedures are similar [11].

Turning the substrate from fabric form into a loosened form, and applying classical methods does not appear to be the solution. Moreover, long preparation and testing time for fabric samples are not acceptable in today’s fast production practices. Thus, a more acceptable and reproducible alternative method comprising the use of common chemicals and equipment is highly demanded. Hence in this study, a quick method comprising staining with a commonly used dyestuff, namely Methylene Blue, followed by short rinsing-drying, and K/S measurement with spectrometer is offered for determination of DS of carboxymethylated cotton fabric. Higher K/S shows that color strength is higher which is a direct result of attachment of Methylene Blue to the carboxymethyl sites available on the fabric, and thus the higher K/S the higher number of carboxymethyl sites on cotton fabric. A precisely followed titration procedure is also carried out. It is shown that the newly offered method correlates very well with titration method. This method is more practical and useful than conventional methods based on back-titration, because it is less time-consuming and more objective. In addition, it is easier to apply, more accurate and demands less amount of chemicals and laboratory work than conventional methods.

2. MATERIALS AND METHOD

2.1. Materials

A 100% cotton fabric having standard plain weave (Testfabrics Inc., style 400, 44”- 45”, 78 X 76, ISO 105/F02) is used in the experiment. The measured average unit weight of fabric is 102.0 g/m^2. The fabric did not have absorbency for an observation time of 60 seconds prior to bleaching [40].

For bleaching, hydrogen peroxide (50%, Fisher Chemicals Company), sodium hydroxide (50%, Fisher Chemicals Company), ethylene diamine tetraacetic acid (Questal Special, BASF Chemical Company), wetting agent (Nonionic surfactant, Kieralon N-F, BASF Chemical

Company), and stabilizer (sodium silicate, Prestogen N-D, BASF Chemicals Company) are used. Chemicals used for carboxymethylation are chloroacetic acid (Flakes, Merck Chemical Company), sodium hydroxide (50%, Fisher Chemicals Company), and sodium carbonate (reagent grade). Chemicals used for titration are phenolphthalein (Powder, Merck Chemical Company), hydrochloric acid (37% v/v for preparation of 0.5% aqueous HCl solution and 0.5N for titration, Merck Chemical Company), and sodium hydroxide (0.5N, Merck Chemical Company). Silver nitrate (VWR Chemical Company) is used for drop test. For staining, Methylene Blue (Merck Chemical Company, C.I. 52015), NaOH (50%, Fisher Chemicals Company), and potassium phosphate (reagent grade ≥98%, Sigma Aldrich) are used. Unless reported otherwise, weight on weight statement is used for all recipe percentages.

2.2. Applied Processes

2.2.1. Reaction

Before processing, cotton fabric was shown not to present sufficient absorbency, and thus, it is bleached before any subsequent wet process. Bleaching was carried by using 3g/L NaOH, 6g/L H_2O_2, 1g/L ethylene diamine tetraacetic acid (EDTA), 1g/L wetting agent and 1g/L stabilizer in a Jet dyeing machine with a liquor ratio (L.R.) of 1:8. All chemicals were added to bleaching liquor and reaction was started at 30°C by a temperature increase of 3°C/min. After the reaction temperature of 98°C was reached, bleaching was followed for 1 hour. Bleached fabric was rinsed for 10 minutes. Bleaching procedure is shown in Figure 2.

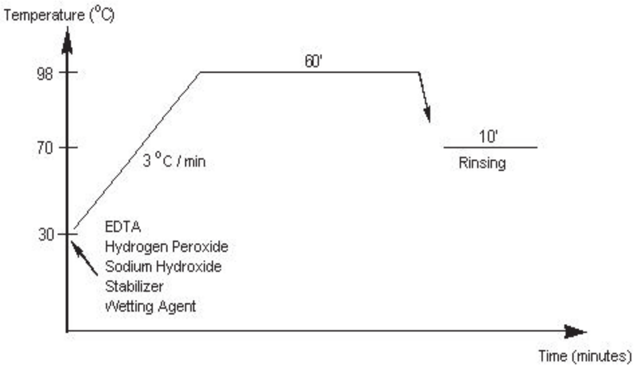

Figure 2. Bleaching procedure.

2.2.2. Carboxymethylation

After bleaching, cotton fabric was carboxymethylated using an optimized two-step process offered by Bilgen [11]. The fabric is firstly treated with 20% NaOH using pad-dry method with prior soaking in the solution for 10 minutes at room temperature. It is then padded to 100% wet-pick-up. The samples are then dried in oven under tension for 10 minutes. Secondly, the fabric is treated with sodium salt of chloroacetic acid (sodium chloroacetate-SCA), using pad-batch method, as it was shown to offer better quality for further processing when compared to other methods, probably due to better distribution of COO$^-$ sites throughout the fabric, rather than limited reaction on both surfaces of the fabric due to rapid removal of water as a result of drying of fabric in open form [24]. Both padding processes were performed using an ATC-F-350 vertical laboratory padder. SCA is prepared by preparation of chloroacetic acid solution of demanded concentration (0.5 to 2.5M), followed by portionwise adding of sodium carbonate while vigorously stirring until bubble formation (due to release of carbondioxide formed) cannot be observed. The fabric is soaked in SCA solution for five minutes at room temperature, followed by padding to 100% wet-pick-up. It is held in the sealed polyethylene bag at 70°C in an oven for one hour. Maximum care was taken in order to remove the air inside the bag. The fabric is rinsed in hot deionized water three times and then once with cold water. Finally, the samples are soaked in 2g/L acetic acid solution, centrifuged and dried at room temperature. The acetic acid neutralizes any residual alkali in the fabric. This is necessary as alkali is very difficult to wash out of cotton fabric.

2.2.3. Evaluation

A method to more rapidly determine the degree of carboxymethylation (or degree of substitution) was developed by dyeing the treated fabric with a cationic dye, namely Methylene Blue. Since a higher level of substitution produces more negatively charged functional groups, there are more sites with affinity for the positive charges of a cationic dye. In order to attach as many as possible dyestuff to the samples (to bind with COO$^-$) a dyeing procedure was performed at 100°C, using a saturated dyebath containing 7.68g Methylene Blue, 29.8mL 1.0N NaOH, and 6.8g potassium phosphate. Fabric samples were added to dyebath for one minute, then removed and rinsed under running tap water until all unfixed dye was removed as indicated by the color of the wash water. Washing was performed for approximately 10 minutes.

2.3. Testing

Prior to carboxymethylation, in order to present that sufficient absorbency is achieved after bleaching absorbency test was applied to cotton fabric. Moreover, after causticization and before steeping in SCA solution, as well as after carboxymethylation samples were tested for alkaline content in order to show that there is negligible amount of residual alkaline left on the fabric [41].

Following carboxymethylation, fabrics were evaluated to determine the degree of substitution of the partially carboxymethylated cellulose. 5cm x 5cm fabric specimen is immersed in 100mL of 0.5% aqueous HCl solution for 16 hours. The samples were then rinsed with deionized water until the HCl is totally removed from the sample. A silver nitrate drop test was performed to ensure that there is no chloride left in the rinse water. After rinsing, the samples are dried at room temperature. Approximately 0.25 gram specimens were prepared and placed in 25.0mL of 0.05N NaOH solution for four hours at room temperature. The solution container is carefully sealed to ensure that the NaOH did not react with CO_2 in the atmosphere. A blank solution of 25mL was included as control. After four hours, the solution was titrated with 0.05N HCl solution. Phenolphthalein was used to determine the end point. The amount of the titrant used for each sample was recorded. In order to increase the precision of the method, the amount of titrant used is calculated by weighing the titrant left, and calculating the amount used. The carboxyl content was then calculated using the following equation:

where V_{blank} is the volume of HCl used for titration of blank solution, V_{sample} is the volume of HCl used for titration of sample solution, and N_{HCl} is the normality of HCl titrant.

Carboxymethyl content is a measure of anionic sites in the cellulose chain. Knowing the mmole CM content per 100 grams of cotton and as molecular weight of anhydro glucose unit is 162g/mole, the average amount of anionic sites per anhydro glucose unit (AGU) or degree of substitution (DS) can easily be calculated as follows:

The color values of dyed fabric samples were measured on a Datacolor 3890 spectrophotometer (Datacolor International, USA) using D65 illuminant with 10' angle standard observer. The ultraviolet (UV) component was excluded and the specular component was included. After folding the sample twice, four measurements were taken on the sample with a 90° sample rotation before each measurement. The average of these four measurements was calculated.

3. Results and Discussion

Prior to carboxymethylation, absorbency test was applied to cotton fabric, and it was observed that the average absorbency time was lower than one seconds which is acceptable for further processing. Alkali content of fabric samples after NaOH treatment and carboxymethylation was 185.1 and 0.1, respectively. It is apparent from those results that only a small portion of residual alkali is left on the fabric after carboxymethylation was completed, and the fabric is ready for testing.

CM contents for 50 different samples, five groups of 10 samples separately treated with 0.5M, 1.0M, 1.5M, 2.0M, and 2.5M SCA, are given in Table 1. It is apparent from the data on Table 1 that the measured CM values for samples vary on a small range, regardless of the molarity of SCA applied between 0.5M and 2.5M, presenting high level of care given during preparation of samples and testing, with standard deviations ranging from $\sigma = 0.1717$ to $\sigma = 0.3349$. Moreover, data on K/S measurements showed that the amount of MB fixed on carboxymethylated fabric does not vary much from trial to trial for a given molarity of SCA, presenting very low standard deviations ranging between $\sigma = 0.0138$ and $\sigma = 0.0338$.

Using the data on Table 1, the fit between DS and K/S was calculated using Minitab$^{(R)}$ 17 package program, and presented in Figure 3. It is apparent from Figure 3 that the correlation between DS and K/S is very high, with a Pearson correlation value of 0.989 (p-value=0.000, standard deviation=0.00381205). A high correlation value close to 1.0 with a low standard deviation is the representative of a high correlation, and that the formula given in Equation 3 can be used with very high level of significance.

$$\text{CM content (mmoles/100 grams)} = 100 \,.\, (V_{blank}-V_{sample})_{HCl} \,.\, N_{HCl}/0.25 \qquad \textbf{(1)}$$

$$\text{DS} = \text{CM content (mmole/100g)} \times 162\text{(g/mole)}/(1000\text{(mmole/mole)} \times 100\text{g}) \qquad \textbf{(2)}$$

$$\text{DS} = 0.03430 * \text{K/S} - 0.06180 \qquad \textbf{(3)}$$

Table 1. CM content, DS, and K/S values for fabrics treated with SCA.

SCA (M)	CM content (mmoles/100g cotton)			DS (calculated from average CM)			K/S		
	Average	Standard deviation	%CV	Average	Standard deviation	%CV	Average	Standard deviation	%CV
0.5	19.868	0.2365	1.19	0.03219	0.00038	1.18	2.8327	0.0338	1.19
1.0	28.224	0.2604	0.92	0.04572	0.00042	0.92	3.2046	0.0296	0.92
1.5	38.611	0.1736	0.45	0.06255	0.00028	0.45	3.4495	0.0155	0.45
2.0	52.436	0.1717	0.32	0.08495	0.00028	0.33	4.2022	0.0138	0.33
2.5	63.410	0.3349	0.52	0.10272	0.00054	0.53	4.8874	0.0258	0.53

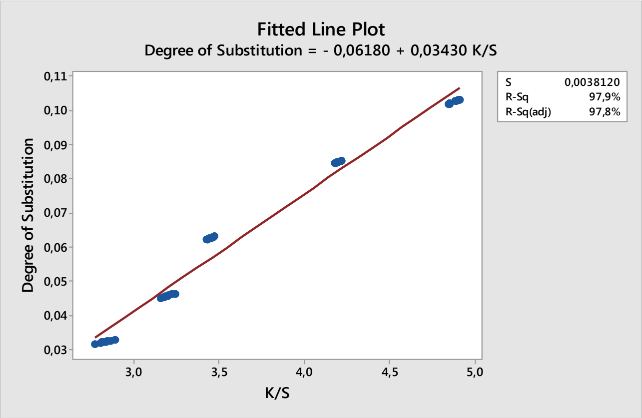

Figure 3. The fit between K/S and DS

CONCLUSION

In conventional titrimetric method for determination of DS in fabric form, there is an idle time of up to 20 hours during which each sample to be tested is kept in different chemical solutions. Moreover, during each measurement, careful observation is needed in order to end addition of drops of much diluted solution. Readings must be made carefully. For this reason, in order to increase repeatability and accuracy, all measurements must be made by the same operator who has high expertise. Common practice includes at least four samples tested one after another to reach an average value. However, the newly offered method is highly objective. A single solution is prepared, used for staining samples at any dimension. Procedures take shorter than titrimetric method, as low as one minute for staining after boiling temperature is reached, followed by rinsing under running tap water, drying and measurement using spectrophotometer. The K/S values were obtained from the measurement of the percentage reflectance at the wavelength of maximum absorption. K/S values for each sample correlated with the dye fixed on the fabric, which is directly related to the degree of substitution on the cellulose molecule. Moreover, depending on the dimensions of the sample, a higher amount of readings can be made by shifting or simply plying the colored sample which offers additional information on the distribution of the COO^- sites throughout the sample which offers additional information on efficacy of carboxymethylation method applied. This alternative method is easier to apply, offer visual evidence and dyeing solution can be used again by addition of expended chemicals and dyestuff, if desired.

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