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N-METHYLOL POLYACRYLAMIDE CYCLODEXTRIN COMPOSITE AS A STIFFENING AGENT FOR COTTON FABRICS

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Abstract

To chemically attach β -Cyclodextrin molecules to cotton cellulose, N-methylol-acrylamide was used to synthesize a cyclodextrin containing monomer, which was then grafted onto cellulose fibers. Cyclodextrin are cyclic oligosaccharides capable of forming inclusion complex with large number of organic molecules. The aim of this work is the preparation of activated Cyclodextrin and applied it as finishing agent on cotton fabrics to improve stiffness properties, tensile strength and Crease Recovery Angle.

KEYWORD: β -cyclodextrin (CD), Acrylamide (Aam), Finishing, Crease Recovery Angle(CRA), stiffening.

Introduction

Cyclodextrin are produced by the enzymatic degradation of starch and were first isolated in 1891 by Villiers. In 1903, these characterized substances were characterized as cyclic oligosaccharides by Schadinger (1903). Cyclodextrin are cyclic oligosaccharides capable of forming inclusion complex with a large number of organic molecules. The properties of Cyclodextrin enable them to be used in a variety of different textiles application^(1,2,3). The α Cyclodextrin molecule is formed by six, β -Cyclodextrin by seven and γ Cyclodextrin by eight glycopyranose units. The Cyclodextrin consist of torus-like macrocyclic ring. All hydroxyl groups are located at the top and the bottom of this torus. Thus the cavities of the Cyclodextrin molecules possess a hydrophobic character owing to the secondary C-H bonds. The chemical structures of Cyclodextrin together with their molecular dimensions are shown in figure 1⁴⁾

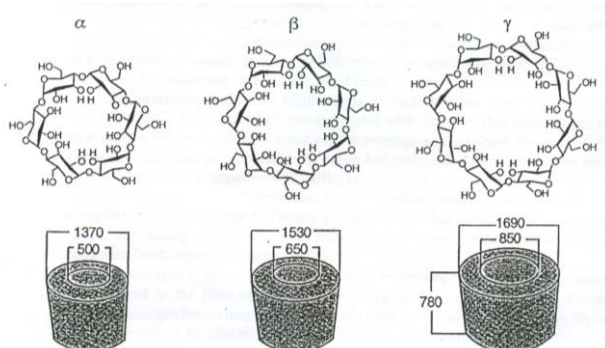


Figure 1. Chemical structures and molecular dimensions (in pm) of Cyclodextrin

Some properties of Cyclodextrin are summarized in Table 1:

Table 1. Properties of Cyclodextrin

	α -CD	β -CD	γ -CD
Number of glucose units	6	7	8
Molecular Weight (g/mol)	972	1135	1297
Solubility in water (g/dm ³) at 25 ^o C	145	18.5	232
LD ₅₀ –toxicity for mice (g/Kg)		>12.5	>16
Chemical oxygen demand (mg/g) ⁺	1100	1067	1036

CD=cyclodextrin

Two important factor concerning possible application of cyclodextrin in the textile area:

- 1) No toxic symptoms^(5,6).
- 2) Biodegradable i.e. does not cause any problems in waste water⁽⁷⁾.

In the work presented here , Cyclodextrin after grafting with acrylamide by using thiourea/potassium bromate as redox system was modified by methylation at different formaldehyde concentrations can be applied to cotton fabric to improve tensile strength , stiffness properties and crease recovery angle .

Experimental

Materials and reagents

β -Cyclodextrin is offered from Germany, acrylamide (Aam), thiourea (TU), potassium bromate (KBrO₃), sulfuric acid, sodium hydroxide, formaldehyde are of laboratory grade chemicals. Mill scoured, bleached and mercerized plain weave cotton fabric (23picksx23 picks/cm) is kindly supplied by El-Nasr company for Spinning, Weaving and Dying, Mehalla El-Kubra, Egypt.

Grafting:

Cyclodextrin (10gm) dissolved in 7.5 ml water at temperature 70°C; after complete dissolution acrylamide is added and followed by redox system at different concentration for each and the medium must be acidic by using dilute sulfuric acid.

Methylation

After the preparation of polyacrylamide Cyclodextrin composite, pH of the resultant composite is adjusted to 9.5 by soduim hydroxide. A calculated amount of formaldehyde adjusted to pH 9.5 using NaOH were added to the poly acrylamide

Cyclodextrin composite to obtain different methylation percentage (20%,40%,60%,and 80%based on weight of the polyacrylamide content of the prepared composite). The reaction was allowed to proceed under continuous stirring for 3 hours. The prepared N-methylol polyacrylamide Cyclodextrin composite is referred to as reactive composite.

Fabric treatment:

The cotton fabric was padded twice in a padding liquor Containing 0.5% ammonium chloride as catalyst then squeezed on a laboratory padding mangle to a wet pick up of ca.80% on weight of fabric. The treated fabric was then stretched back to its original dimensions on pin frame for drying (5 minutes). Curing of the treated samples were performed in a controlled laboratory oven at different temperature 140-160°C for 3 minutes. The cured fabrics were washed at 90°C for 10 minutes. Finally the fabric was dried and examined for different properties.

Analysis

In order to characterize cyclodextrin-acrylamide grafted polymer the following analyses were carried.

The percentage total conversion (%T.C) was calculated by quantitative estimation of the free double bonds of acrylamide after the polymerization according to a reported method ⁽⁸⁾.

The nitrogen percentage was measured according to Kjeldahl method ⁽⁹⁾.

The percentage grafted yield (%G.Y) was determined from nitrogen percentage.

The percentage homopolymer (%HP) and graft efficiency (G.E%) can be mathematically calculated from (%G.Y) and (%T.C) according to the equation :

$$\%G.Y = \frac{AB \times 100}{100Y - AB}$$

where A: nitrogen % ; B: molecular weight of monomer; Y: molecular weight of functional group

$$HP\% = \frac{\text{Dry weight of homopolymer} \times 100}{\text{Weight of monomer}}$$

$$G.E\% = \frac{\text{Weight of grafted polymer} \times 100}{\text{Weight of grafted polymer} + \text{weight of homopolymer}}$$

The warp tensile strength and warp elongation at break were measured by the strip method according to ASTM procedures, D-2256-66T.

The dry crease recovery angle was measured using a crease recovery type FF-07 (Metrimpex).

Stiffness is measured using Culry Type Stiffness Tester manufactured by Tokyoseiki Seesaku - Sho- Ltd. (Japan).

Free formaldehyde was measured according to Japanese Test method law 112-1973 .

Results and Discussion:

Previous reports ⁽¹⁰⁾ have disclosed that potassium bromate (oxidant) together with thiourea (reductant) forms a very effective redox system capable of initiating vinyl graft polymerization onto cellulose. As Cyclodextrin is also a polysaccharide, it is logical that grafting as well as homopolymerization will occur when CD is present in such a system along with vinyl monomer such as acrylamide.

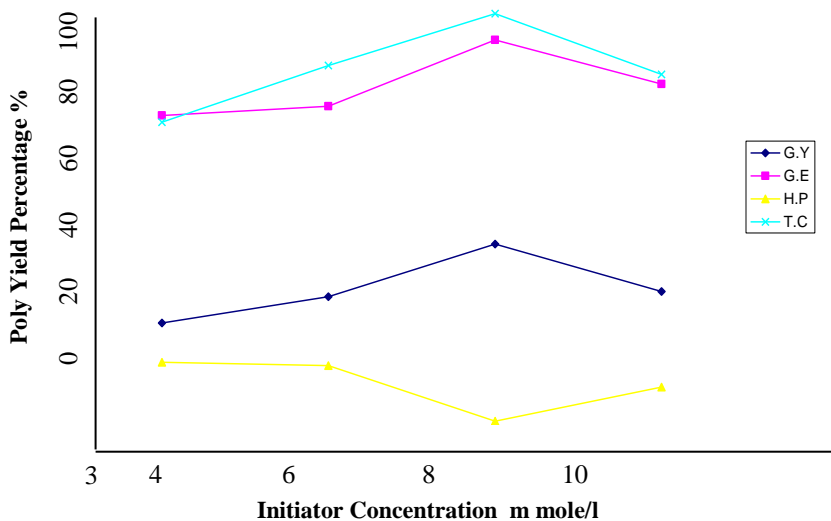
Initiator Concentration

Figure 2 shows the polymer yield percentage as a function of initiator concentration (equimolar ratio of KBrO_3/TU). The polymer yield refers to graft yield (GY%), homopolymer (HP%), total conversion (T.C%) and grafting efficiency percent (G.E%). Obviously, the grafting yield increases substantially by increasing the initiator concentration up to 8mmol/l then exhibit gradual decrease within the range studied. The opposite holds true for the homopolymer where minimum amount of homopolymer formation is observed at an initiator concentration of 8mmole/l then increase gradually thereafter. This is logical since grafting and homopolymer are two competitive reaction. That grafting prevails over homopolymerization is rather in conformation with the results of total conversion and grafting efficiency, which display trends similar to those brought about by grafting.

Enhancement in grafting by increasing initiator concentration to a certain limits is a manifestation of abundance of primary free radicals which, in turn, succeeded to create CD-macroradicals capable of initiating grafting .

Decrement in grafting and its dependents i.e. total conversion and grafting efficiency at higher initiator concentration is in accordance with previous report ^(11,12) which ascribed this decrement to fast termination at higher concentrations.

Figure 2 Effect of Initiator Concentration on Polymer Yield Percentage %

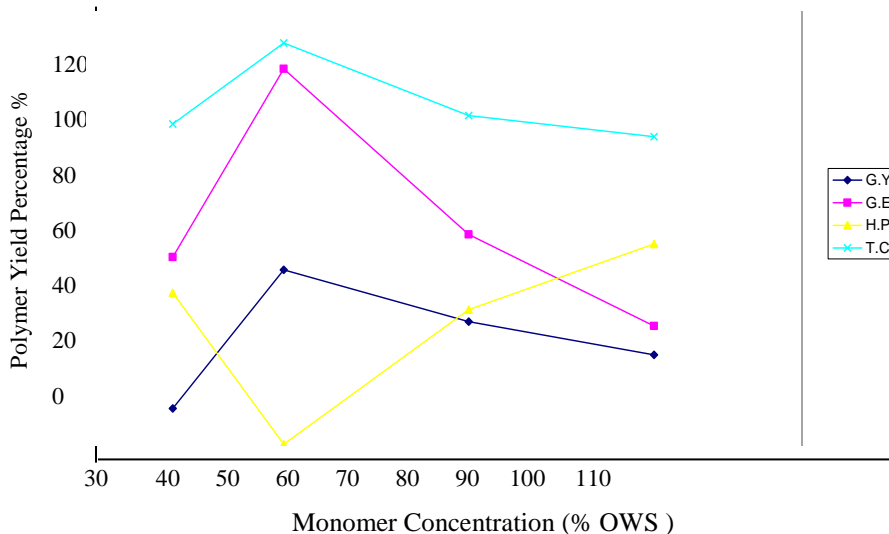


Reaction conditions: temperature, 80 C⁰; Monomer Concentration 50% (OWS); Material to Liquor, 1:7.5; Time of Reaction, 1hr.

Monomer concentration :

Figure 3 shows the polymer yield % versus the monomer concentration .The results imply that increasing the monomer concentration from 35 to 50% based on weight of CD(OWS) is accompanied by substantial increase in grafting and on further increase in monomer concentration up to 100% causes a decrease in grafting % .

The dependence of polymer yield on monomer concentration can be interpreted in terms of the diffusion controlled nature of the grafting reactions which is governed by the dilution extent. The apparent increase in G.Y%, T.C% and G.E% may be attributed to greater availability of monomer for grafting when Aam concentration 50% was used . Further increase in Aam concentration causes a decrease in these parameters.

Figure 3 Effect of Monomer Concentration on Polymer Yield Percentage %

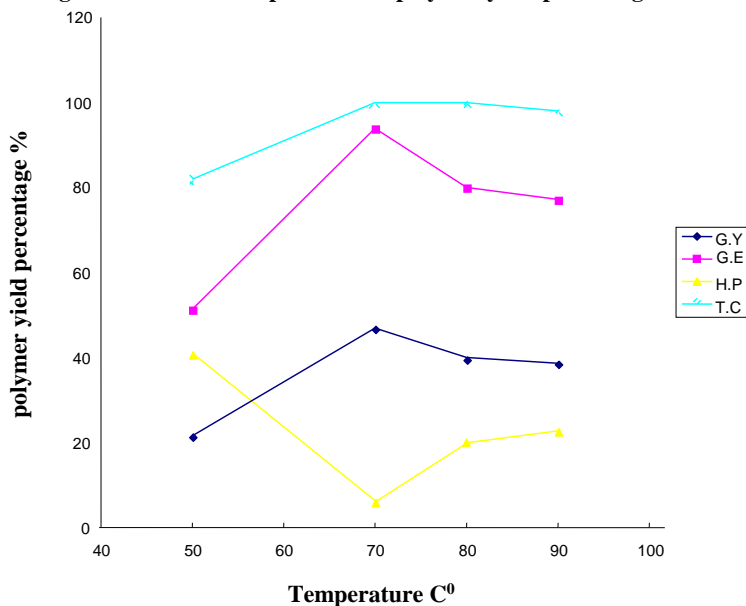
Reaction conditions : temperature, 80 C⁰; initiator concentration 8 m mole KBrO₃/ 8 m mole TU; material to liquor, 1:7.5;time of reaction,1hr.

Polymerization temperature:

Figure 4 shows the polymer yield as a function of polymerization temperature. The figure shows that the graft yield increases by raising the reaction temperature from 50C⁰ to 80C⁰ further increase in the reaction temperature leads to a decrease in the graft yield.

The increase in grafting by raising the temperature up to 80C⁰ could be associated with:

- i) Increase in the number of the free radicals formed on the CD back bone. ii) increase in propagation of the graft. iii) increase in the mobility of monomer molecules and their collision with CD macroradicals and iv) enhancement of diffusion of monomer and initiator into CD structure⁽¹³⁾. On the other hand, the decrease in the graft yield by increasing the polymerization temperature could be ascribed to fast termination rates^(14,15) along with instability of initiator salt.

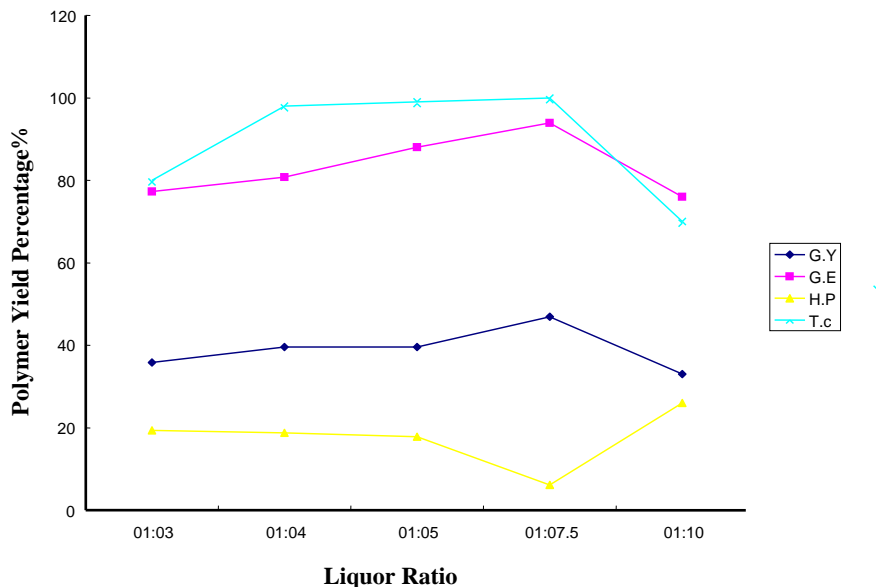
Figure 4 Effect of Temperature on polymer yield percentage %

Reaction Conditions: Monomer Concentration 50% (OWS); Initiator Concentration, 8:8 Material to Liquor 1:7.5; Time of Reaction, 1hr.

Materials to liquor ratio:

Figure 5 shows the effect of material to liquor ratio on the polymer yield. As is evidenced, increasing the liquor ratio (M:LR) to 1:7.5 increases the graft yield, total conversion and grafting efficient.

The logic for all other substrate when M:LR increase grafting decrease due to the magnitude of association of monomer and initiator with the substrate becomes significant at shorter LR but in case of CD the opposite happens because Cyclodextrin consist of a torus-like macrocyclic ring. All hydroxyl groups are located at the top and at the bottom of this tours. Thus the cavities of the Cyclodextrin molecules possess a hydrophobic character owing to the secondary C-H bonds ^(4,16)

Figure 5 Effect of liquor ratio on polymer yield percentage %

Reaction Conditions: Temperature, 80 C⁰; Initiator Concentration, 8 m mole KBrO₃ / 8m mole Tu; Monomer Concentration 50% (OWS); Time of Reaction, 1hr.

Application of poly-acrylamide-cyclodextrin graft copolymer to cotton fabric:

Based on the foregoing investigation it may be concluded that the most appropriate conditions of graft copolymerization for Aam onto Cyclodextrin composite is the use of potassium bromate/thiourea at concentration 8/8mmole/l and monomer concentration of 50% based on weight of CD at 80°C for one hour.

After grafting, methylation with different concentration of formaldehyde is carried out and the resultant product is applied to cotton fabric using 0.5% ammonium chloride as catalyst then squeezed on a laboratory padding mangle to a wet pick up of ca 80% on weight of fabric . The treated fabric was then stretched back to its original dimensions on pin frame for drying at 80C^o for 5 minutes .Curing of the treated samples were performed in a controlled laboratory oven at different temperature 140° C,

160° C for 3 minutes. The cured fabric were washed at 90°C for 10 minutes. Finally the fabric was dried and examined for different properties. The samples treated were monitored for nitrogen content, crease recovery angle, tensile strength and the elongation at break and free formaldehyde.

The results obtained are listed in Table 2. As shown from Table 2, tensile strength and crease recovery angle increase by increasing the methylol content up to 40% and decreases at methylol content 60%, 80% but it is higher than untreated fabric this due to the methylolated composite act as crosslinking cementing and coating agent. The third factor is stiffness of treated cotton fabric. The value of stiffness in mill gram increases from 20-80 methylol content more than untreated sample this could be explained in terms of formation surface polymer, which bonds the fibers together within the yarn. High stiffness gives lower CRA as expected.

The N% determined on the fabric is a direct evidence of incorporation of methylolated grafted-Aam CD in the cotton fabric as shown from Table 2 the value of N% increases by increasing methylol content from 20-80.

The free formaldehyde values as measured according to Japans test method; law 112-1973 are shown in Table 2 is very low and are comparable to international values.

Conclusions:

The grafting of Cyclodextrin with acrylamide by using thiourea/potassium bromate as redox system at the required liquor ratio was done. After grafting the grafted CD was activated by formaldehyde at pH 9 using sodium hydroxide (methylolation). The activated CD was applied as finishing on cellulose fiber to improve crease recovery angle, the tensile strength and stiffness.

The possibilities of utilization modified CD in textile finishing was studied by measuring crease recover angle, tensile strength and stiffening.

Table 2: Effect of Methylolation Percentage on Tensile Strength, Crease Recovery Angle, Stiffness and Free Formaldehyde:-

Methylolati on%	A		B		C		D		E	
	140C°	160 C°	140C°	160C°	140C°	160 C°	140C°	160 C°	140C°	160 C°
20	57(8)	54(8.5)	195	180	1946	2002	0.8983	0.9212	0.22989	0.28735
40	63(7)	62(7.5)	202	195	3680	3800	1.00689	1.1002	0.34483	0.34581
60	60(6)	59(6)	200	190	4120	4520	1.3221	1.3351	0.45978	0.46812
80	60(6)	58(6.5)	185	183	4899	4952	1.5231	1.5321	0.46920	0.4711

A, tensile strength; B, crease recovery angle; C, stiffness in mill gram; D, nitrogen content and E, free formaldehyde

Blank of a=53;b=167; c=801;d=0.1241

The value between brackets is elongation at break the blank value (8).

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الملخص العربي

تطعيم السيكلودكستيرين ثم تطبيقه كمادة تجهيز:

تم تطعيم السيكلودكستيرين باستخدام الأكريل آميد وبيادئ التفاعل برومات البوتاسيوم والثيوريا وكانت أفضل النتائج عند الظروف الآتية:

تركيز الأكريل آميد 50% بالنسبة لوزن مادة السيكلوديكستيرين - نسبة برومات البوتاسيوم إلى الثيوريا 8 مللي مول/8 مللي مول -درجة الحرارة 80 درجة مئوية- زمن التفاعل 1 ساعة -نسبة الصلب إلى السائل 1:7.5 .

تم تحويل مجموعات الأמיד (الناتجة من التطعيم عند أفضل الظروف) إلى مجموعات نشطة من خلال إدخال مجموعات الميثيلول وذلك بتفاعلها مع الفورمالدهيد بتركيزات مختلفة ويتم تفاعل المادة النشطة الناتجة مع قماش القطن في وجود كلوريد الأمونيوم كعامل مساعد.

يستخدم مترابك السيكلوديكستيرين النشط كيميائياً كمادة تجهيز على الأقمشة القطنية بغرض إكسابها خاصية الصلابة وتم قياس نسبة تصاعد الفورمالدهيد الحر فكانت لا تتعدى النسبة المسموح بها دولياً.