



Chemical Functionalization of Cellulose-Poly(Glycidyl-Methacrylate) Graft Copolymer with Two Different Poly Amino Compounds



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TWO amino-functionalized cellulose-poly(glycidyl methacrylate) graft copolymers (AM-CPGMA), based on waste cotton fibers, were prepared by the amination of selected cellulose-poly(glycidyl methacrylate) graft copolymer (CPGMA) produced at best polymerization conditions using diethylenetri-amine (DETA) and triethylenetetraamine (TETA). The different amination parameters, namely the aminating agent/epoxy molar ratio, reaction time, liquor ratio, pH and temperature were investigated, and optimum reaction conditions were established. The two prepared amino-functionalized cellulose-poly(glycidyl methacrylate) graft copolymers (AM-CPGMA) were characterized by the FT-IR, thermal gravimetric analysis (TGA), surface area measurement using Brunauer–Emmett–Teller (BET) and Barrett-Joyner-Halenda (BJH) theories and scanning electron microscope (SEM). Thus obtained results were compared with the native cellulose and its graft copolymer.

Keywords: Cotton fibers, Glycidyl methacrylate, Graft copolymerization, Amination.

Introduction

Today sorbent substances are widely applied in numerous applications e.g.; effluents treatment, metal exclusion, suitable substances for microorganism immobilizations, drug delivery, adsorption of surfactant molecules, analytical ion-exchange chromatography and many other purposes [1].

Currently, the search for environmentally friendly and inexpensive sorbents without formation of harmful substances has been considered. In light of the above, usage of natural substances has been in focus, because of less sludge formation, cheapness, high adsorption capacity, their eco-friendly properties, potential regeneration and abundance of these substances in nature [2]. The cellulosic derivatives are superior amongst various biomaterials, since they have several

unique properties such as high specific areas, light weight, variation, high flexibility, narrow pore size and biodegradability [3,4]. Cellulosic materials can be obtained using various ways, whether through oxidation, etherification, halogenation and esterification, [5], or by cross-linking and grafting methods [6,7]. Lately, cellulose graft copolymers have been considered the most efficiently and widely employed adsorbing materials for various applications based on the kind and nature of the grafted monomer.

An effective cellulosic adsorbent was obtained by grafting different materials onto cellulose such as poly (acrylonitrile) (PAN), [8] N,N-carbonyldiimidazole (CDI), [9] polyethylenimine (PEI), [10] polybenzoxazine [11].

Among all known types of monomers this one noted as glycidyl methacrylate (GMA) was

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Received 18/3/2020; 10/5/2020 Accepted

DOI: 10.21608/ejchem.2020.26122.2522

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considered superior. This may be attributed to its exceptional properties such as acidic and alkaline resistance, high tensile strength, good mechanical strength and wear resistance [12]. The most prominent property of GMA is that its structure contains a highly reactive epoxide group which gives many choices for chemical modification [13, 14].

One from this type of GMA-based resins was that resin prepared by grafting GMA onto cellulose wood pulp in presence of ceric ammonium nitrate (CAN) as initiator followed by activation by using imidazole [15–17].

Another example of resins based on GMA was titanium dioxide cellulose poly(glycidylmethacrylate) graft copolymer (CPGMA) which further aminated and ethylated [18].

In other work glycidyl methacrylate was grafted onto cellulose and the obtained resin was further functionalized with sulfosalicylic acid. This adsorbent was then examined for the adsorption of crystal violet (CV) and revealed a maximum theoretical adsorption capacity of 218.82 mg g⁻¹ [19].

The present work is a continuation of previous report [20], with the aim of synthesis and characterization of diethylenetriamine and triethylenetetramine functionalized cellulose-poly(glycidyl methacrylate) graft copolymer. Our approach to achieve this goal was first to study such factors affecting the reaction and then to characterize the produced AM-CPGMA graft copolymers.

Materials and Methodology

Aminization of grafted cellulose with two amines to prepare two different types of amino-functionalized cellulose-poly(glycidyl methacrylate) graft copolymers (AM-CPGMA) was undertaken.

Materials

- Waste cotton fiber is the cotton-fiber exhausts resulted during the different stages of textile industry, such as spinning process. It was kindly supplied by Misr Spinning and Weaving Co., Mehalla El- Kubra
- GMA [Merck], sodium hydroxide [ADWIC, Egypt], sodium carbonate [ADWIC, Egypt], carbon disulfide [Panreac], ferrous

sulfate [Sd Fine-Chem Limited], hydrogen peroxide [ADWIC, Egypt], di-ethylene-tri-amine (DETA) [Merck] and tri-ethylene-tetra-amine (TETA) [Merck], all are of analytical grade.

Methodology

Synthesis of the aimed products

The experimental procedure has been constructed of two basic groups of experiments, via graft polymerization of glycidyl-methacrylate (GMA) onto waste cotton fibers using ferrous sulfate/hydrogen peroxide initiating system, followed by aminization with two different amines, namely DETA and TETA.

Regarding the graft polymerization process, the authors have earlier investigated it thoroughly as mentioned above [20], which can briefly explained as following; a known weight of waste cotton was firstly purified by a solution containing egyptol 2mg/L, NaOH 5mg/L, Na₂CO₃ 3mg/L, for 60 mins in a solution pH ranging from 12–14 and 1:40 material-to-liquor ratio at 90 °C. Secondly the scoured sample was thiocarbonated using a mixture of 1%_(w/v) NaOH, 1%_(v/v) CS₂ and 0.2%_(w/v) egyptol for 2 hrs. and at 30 °C in aqueous solution with a material to liquor ratio equivalent to 1:25 under shaking. The thiocarbonated sample was then immersed in 0.1%_(w/v) ferrous sulphate solution at room temperature for 30 mins. following by washing with distilled water and squeezing until 7–8 times of its original weight and rapidly placed in emulsion solution of GMA 100%_(w/w), egyptol 0.2%_(w/v) and H₂O₂ 0.015%_(w/v), at 50 °C and pH 3 for 30 mins. with 1:25 material to liquor ratio. finally the grafted sample was washed with distilled water, pressed out and then kept in acetone overnight.

Referring to the aminization process, a weighted sample of the previously optimized Cellulose-poly(glycidyl-methacrylate) graft copolymer (Cell-g-PGMA), with known epoxy content [21], was treated by aqueous solution of the specified amine with definite concentration and water to material liquor ratio, followed by solution pH adjustment to the desired value. By means of a thermostatic shaking water bath, the reaction is allowed to proceed at specific temperature for a definite time. Afterwards, the sample was then pressed out using the padder, and finally washed with distilled water until filtrate neutrality. The target anionic resin is then dried in an air oven drier at 60 °C for 60 mins. The

operating parameters studied for each amine are: temperature(25-100°C); and aminating agent/ epoxy (2:1 – 16:1 molar ratio); liquor ratio (1:12.5 – 1:100)g graft cotton/ml solution; pH(2-12.6) and time (30-150 mins.).

Analysis and characterization

Analysis

- The content of free epoxy ring in CPGMA was determined using schöniger flask test [21]
- The extent of aminization reactions was monitored as per the Kjeldahl method [22] and expressed as nitrogen percent (N%) using Vapodest 20s.
- Aminization conversion and aminization percent were evaluated, via:

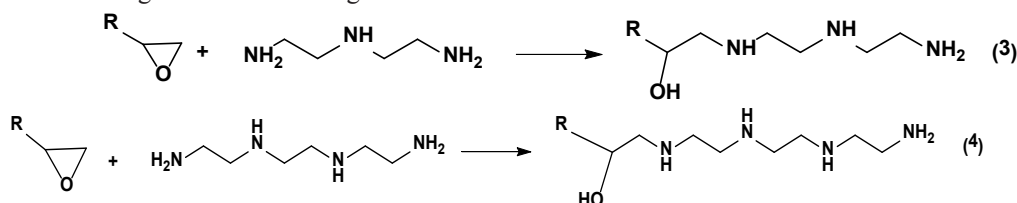
$$\text{Aminization conversion \%} = [(y_0 - y_1) / y_0] \times 100 \quad (1)$$

$$\text{Aminization \%} = [y_0 - y_1 / y_2] \times 100 \quad (2)$$

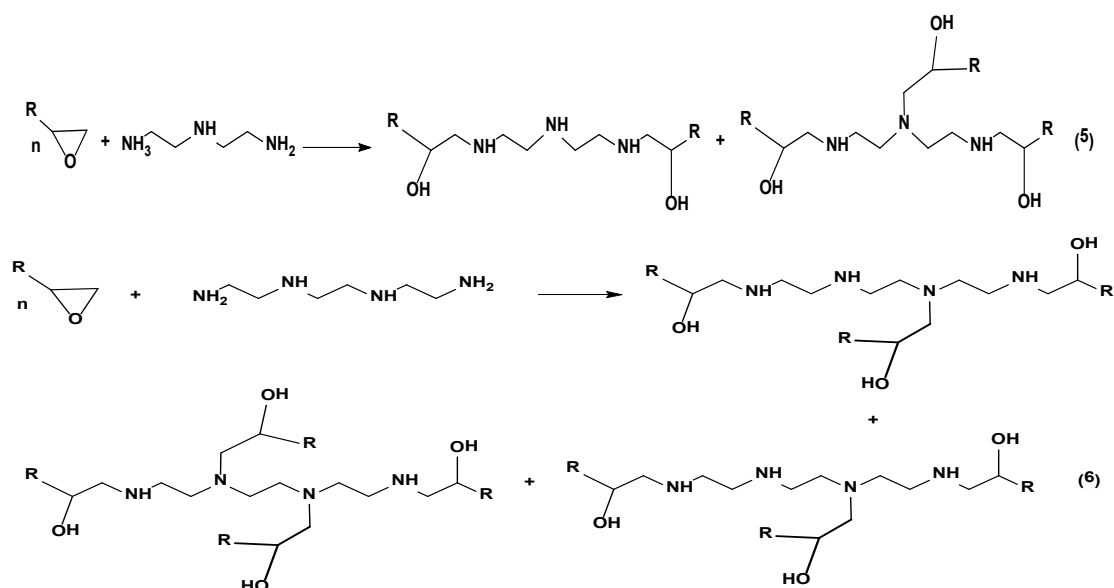
Where y_0 , y_1 and y_2 are the initial amount of charged amine, unreacted amine and epoxy content respectively.

Characterization

- Analysis by Fourier transform infra-red spectrophotometer (FT-IR) was carried out for each aminated grafted cotton using a JASCO



Likewise, the amination reaction can occur through cross linking of Cell-g-PGMA chains by the primary and secondary amino groups as following:



FT/IR6100- in the range from 400 to 4000 cm^{-1} .

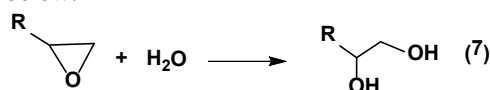
- Thermal gravimetric analysis (TGA&TDA) was conducted for the two samples by thermal analyses SDT Q600 apparatus at a rate of 10°C/ min in N_2 atmosphere.
- Surface area measurements, i.e., surface area (m^2/g), total pore volume(cc/g), average pore radius (nm) and the complete isotherm of the aminated cotton samples were evaluated using St 2 on NOVA touch 4LX [s/n:17016062702] device, based on Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) theories.
- The surface morphology of AM-CPGMA was examined using a QUANTA FEG250 scanning electron microscope (SEM) with high vacuum at accelerating voltage of 20 KV and magnification magnitude of 8000 X.

Results and Discussion

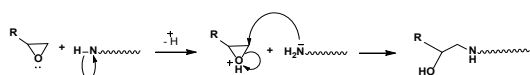
Equations

This copolymer (Cell-g-PGMA) can be functionalized to AM-CPGMA by the reaction of its epoxy groups with the targeted amines, DETA and TETA, as depicted in the following reactions:

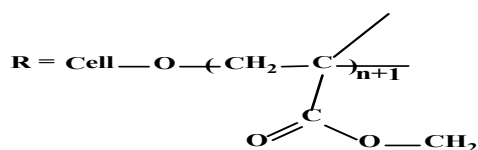
Furthermore, a side hydrolysis reaction can be elaborated during the aminization process, via the consumption of epoxy groups by water as shown below:



Suggested general mechanism of reactions



Where:



Aminization results

A batch experiment was undertaken for the preparation of cellulose-poly(glycidyl methacrylate) graft copolymer (Cell-g-PGMA), based on waste cotton fibers, at optimum conditions- shown in Table1- previously reported by the authors [20].

TABLE 1. Grafting evaluation results at the optimum grafting conditions (GMA conc. 220%_(w/w), pH 3, H₂O₂ conc., 0.015%_(w/v), T: 50 °C, liquor ratio: 1:25%_(w/v), Time:30 mins) [20].

Polymer add-on (%)	Graft yield (%)	Grafting efficiency (%)	Total conversion (%)	Epoxy content (mmol/g)
200	182	88	98	3

The dependence of investigated parameters on the target product, monitored by its nitrogen content, is reported in the following

Effect of pH

The original pH values of the reaction medium of DETA and TETA are 12.6 and 12.7 respectively. In this section, the amination extent was investigated at pH range 12.7-2 by lowering the medium pH with hydrochloric acid.

Fig. 1 indicate that the extent of aminization decreases by decreasing the original pH of DETA and TETA. This due to that by the addition of acid the reaction of Cl⁻ with the epoxy groups predominates rather than amine groups with practically no aminization [23].

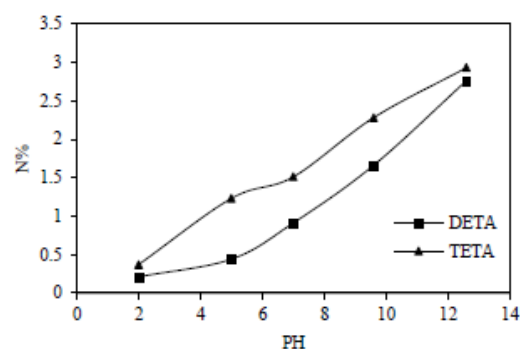


Fig. 1. Effect of pH on nitrogen percent, (Cell-g-PGMA 1g, epoxy content 1.76 mmol/g, temperature 85 °C, time 60 mins., liquor ratio 12.5:1_(v/w), amine conc. 18%_(w/v)).

Effect of temperature

As expected, raising the reaction temperature is accompanied by a sharp increase in the conversion of epoxy groups to amines within temperature range of 25°C to 80°C, as illustrated in Fig. 2.

This is recognized to the reasonable status of temperature on the enhancement of epoxy groups accessibilities due to copolymer swelling, growing the Baeyer strain in the epoxy rings and subsequent increasing its instability [24], and eventually, supplying the reactants with kinetic energy that increases their ability to collide. It is also noticed that by further raising the reaction temperature up to 100°C for both amines, the N% is leveling off. This may be interpreted as each of the aminization and side reactions (hydrolysis) proceeds with a constant ratio during the reaction path. While over 90°C most probably a higher hydrolysis rate predominate which yield the observed flattening [23].

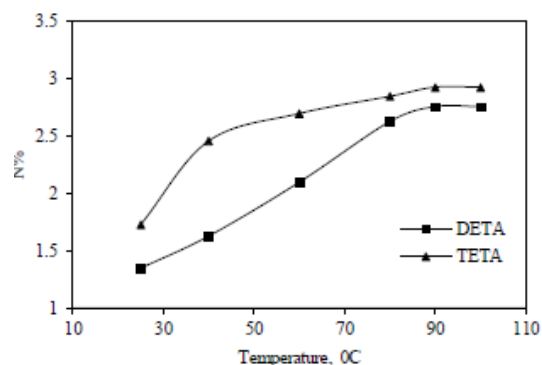


Fig. 2. Effect of temperature on nitrogen percent, (Cell-g-PGMA 1g, epoxy content 1.76 mmol/g, time 60 mins, pH 12.6, liquor ratio 12.5:1_(v/w), amine conc. 18%_(w/v)).

Effect of time

Fig. 3 demonstrates that, for both amines, the aminization reactions proceed at increasing rate up to 60 mins, and then reached a state of plateauing over that time. This indicates that the aminization reaction ceased after 1hr and the side reactions, i.e., crosslinking and hydrolysis, predominate thereafter [25]. It is also noticed that, the reaction rate with respect to TETA is faster than that with DETA, and consequently it exhibits higher aminization conversion.

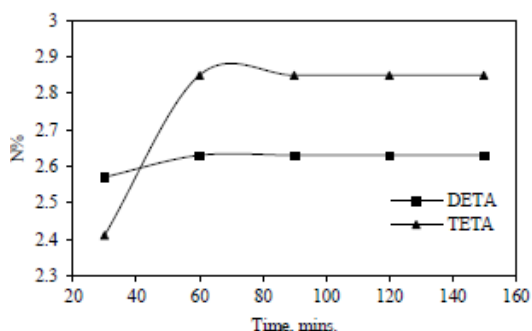


Fig. 3. Effect of time on nitrogen percent, (Cell-g-PGMA 1g, epoxy content 1.76 mmol/g, temperature 80 oC (90 oC in case of TETA), pH 12.6, liquor ratio 12.5:1(v/w), amine conc. 18%(w/v)).

Effect of liquor ratio

Dependence of nitrogen percent of aminization products on variation of the amount of reaction liquor ratio (LR), from 12.5:1_(v/w) to 100:1_(v/w), is demonstrated in Fig 4. As observed, the results show that the N% was a maximum at 12.5:1_(v/w) liquor ratio for both DETA and TETA. By increasing the liquor ratio above this value, there was a significant reduction in the N% with respect to the reaction with DETA, amounting to about 27% decrease. This was attributed to the decrease in epoxide groups' accessibility on increasing the liquor ratio, due to dilution and subsequent reduction of epoxide concentration, hence decreases the interaction between the reactants [26]. Also, it is evident from Fig. 4 that, the reaction with TETA is practically independent from the increase in LR, within the operating range studied, may be owing to its rate of solubility which remains almost constant within the investigated range.

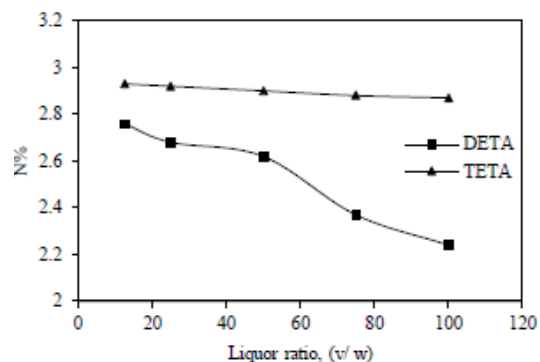


Fig. 4 . Effect of liquor ratio on nitrogen percent. (Cell-g-PGMA 1g, epoxy content 1.76 mmol/g, temperature 80 °C (90 °C in case of TETA), time 60 mins., pH 12.6, amine conc. 18%(w/v)).

Effect of the aminating agent/ epoxy molar ratio

Variation of the amount of amine to that of epoxy content, ranging from 2:1 to 16:1 molar ratio, was investigated and the results are illustrated in Fig. 5.

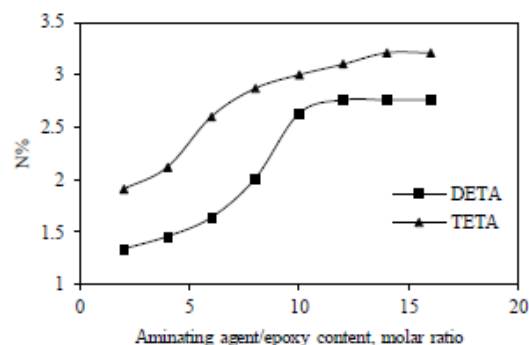


Fig. 5. Effect of aminating agent/epoxy molar ratio on nitrogen percent. (Cell-g-PGMA 1g, epoxy content 1.76 mmol/g, temperature 80 °C (90 °C in case of TETA), time 60 mins., pH 12.6, liquor ratio 12.5:1_(v/w)).

The N% increases by increasing the aminating agent/epoxy molar ratio up to 10:1, and 12:1 for DETA and TETA respectively and then levels off. This may be explained by the consumption of most of the initial epoxy content, at low aminating agent/epoxy molar ratios, in its reaction with water. Increasing the amine concentration is escorted by a significant increase in the epoxy ring opening extents and with a slight decrease in the undesired reactions extent, i.e. hydrolysis and cross-linking. The reduction in the undesired reactions extent at increasing amine concentration may be associated with: i) amine exerted a

competition to react with Cell-g-PGMA, and ii) repulsive forces increasing between cellulose-poly(glycidyl methacrylate) graft copolymer (Cell-g-PGMA) chains for cross-linking induced by the positive charges acquired on aminization. These repulsions open the structure of Cell-g-PGMA for more amine molecules to go in and carry nearby further aminization [23].

Aminization evaluation results

On the sake of comparison and in order to reduce the preparation units operation (steps) - thus reducing the product cost of the AM-CPGMA resin- two independent aminization experiments, at optimum conditions resumed in Table 2, were carried out immediately at the end of the graft polymerization process after filtration of the residual solution.

TABLE 2. Optimum aminization reaction conditions

Amine	Amine/epoxy (molar ratio)	Liquor ratio (v/w)	pH	Temperature (°C)	Time (mins.)
DETA	12:1	12.5:1	12.6	80	60
TETA	14:1	12.5:1	12.6	90	60

The aminization parameters of the prepared resins are determined from equations (1&2), and the results are depicted in Table 3.

TABLE 3. Aminization evaluation results at optimum reaction conditions

Amine	N ₁ %	N ₂ %	X ₁ %	X ₂ %	E ₁ %	E ₂ %
DETA	2.76	2.82	3.37	3.41	40	41
TETA	3.21	3.12	2.54	2.46	35.5	34.5

Where N, X and E are the nitrogen content, total conversion and aminization percentages respectively. While the subscribes 1&2 are referring to the corresponding estimate with or without washing and extraction of homopolymer from the grafted sample respectively.

As observed, the total conversions were 3.37% and 2.54% for DETA and TETA respectively, while the aminization percentages were 40% and 35.5% for DETA and TETA respectively. The low conversion percent was ascribed to the higher ratio of amine to cellulose that is required to give excessive opening of the epoxy ring. However, the

excess amine can be recovered by filtration and readjusted to the desired concentration or molar ratio to be reused in another aminization reaction.

Table 3 also indicates that approximately the same results were attained when the grafted sample was aminated rapidly after removal of polymerization solution without washing or homopolymer extraction. This is probably attributed to the role of the formed ferrous cellulose thiocarbonate, prior to grafting, which increases the chain transfer activity with reduced homopolymer formation.

Furthermore, the data show that the nitrogen percent in case of TETA was higher, while the aminization percent and total conversion were greater in case of the aminating agent DETA rather than those of TETA. This is probably due to the fact that the more the amount of primary or secondary amine groups, the greater the crosslinking bonds, the less the product is swollen and consequently the conversion and aminization percent are reduced.

Characterization

Fourier-transform infra-red spectroscopy (FT-IR)

Figure 6 illustrates the FT-IR spectra of the native, grafted and aminated cotton. Fig. 6a shows the FT-IR spectrum of the waste cotton showing a broad intense absorption band at 3428 cm⁻¹ due to O-H groups. The IR spectrum of the Cell-g-PGMA, Fig. 6b shows the absorption bands at 1729 cm⁻¹ arising from C=O stretching vibration in GMA. After aminization with DETA or TETA- Fig. 6c&d- absorption band around 1040 cm⁻¹ was more distinguished due to C-N stretching vibration of secondary N-H groups. Also the intensity of absorption band at about 3430 cm⁻¹ was increased owing to N-H stretching in both of amines. Likewise, absorption band around 1635 cm⁻¹ was more emerged due to bending of N-H groups.

The adsorption bands characteristic for remaining epoxy ring still appears after the aminization. The existence of these characteristic bands approves the grafting of cotton with GMA and chemical functionalization of the cotton-poly(glycidyl-methacrylate) graft copolymer (Cell-g-PGMA) with DETA or TETA.

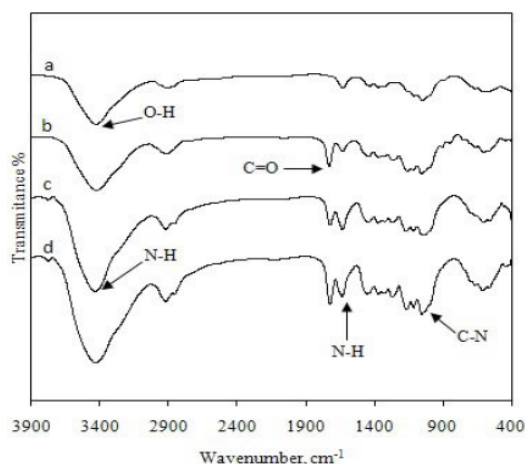


Fig. 6. FT-IR spectrum of untreated waste cotton (a), grafted cotton (b) and the aminated grafted cotton with DETA (c) and TETA (d).

Thermal gravimetric analysis & differential thermal analysis (TGA & DTG)

Figure 7a&b illustrate the thermal stability and degree of hydrophilicity of cellulose-poly(glycidyl methacrylate) graft copolymer (CPGMA) aminated with either DETA or TETA. The ratio of water content in cotton fabric was 10% that decreases to 2% after grafting as indicated by our previous work [20], and then increases again to approximately 6% after amination with either DETA or TETA; this indicates that the hydrophilicity percent decreases after the grafting step because of the hydrophobic nature of GMA, while the percent of hydrophilicity was increased by amination as a result of functionalization with hydrophilic amino groups.

The thermal profiles, of both DETA (Fig. 7a) and TETA (Fig. 7b) aminated grafted cotton, were characterized with three different zones in the range from (237-488 °C). In the first zone, (32-42 °C), almost 2.33% weight loss was observed due to water release. In the second stage (237-367 °C) the weight loss was about 60% as a result of a three overlapped decomposition stages of PGMA (210-265 °C), aminating agent (210-300 °C) and cellulose chains (237-367 °C). Finally, in the third stage about 82% weight losses was attained in the range from 367 to 488 °C as a result of formation of large quantities of volatile materials and char from the previously decomposed units. The highest decomposition percentages were at 328 and 390 °C for the second and third stages respectively.

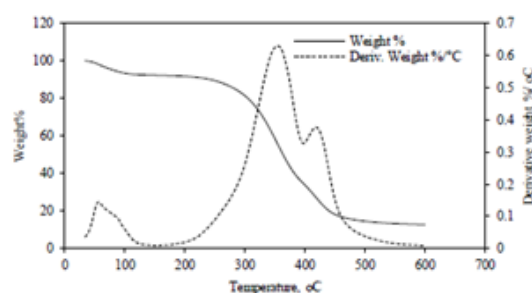


Fig. 7a TGA curves of the DETA aminated grafted cotton.

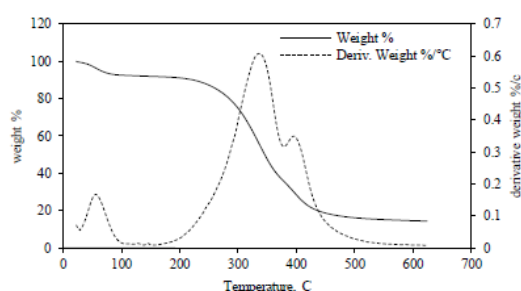


Fig. 7b. TGA curves of the TETA aminated grafted cotton.

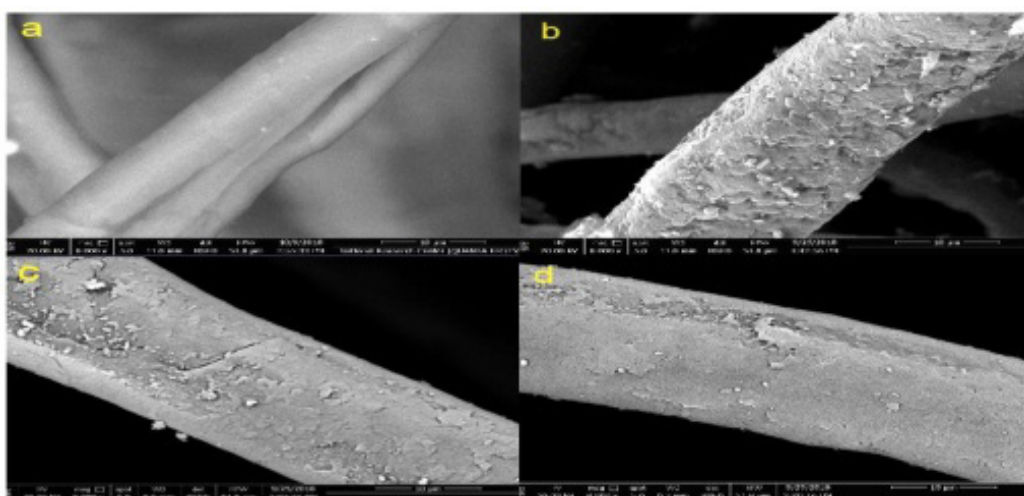
Though AM-Cell-g-PGMA has a lower thermal stability than cellulose, it still stable until 282 °C, thus it can be applied as an adsorbing material at that limit without any problems.

Surface area measurement

Table 4 demonstrates that the surface area (m²/g) and total pore volume (cc/g) of the native cotton increases after grafting and amination, while the average pore radius (nm) decreases. These results may be interpreted as follows: after amination of grafted cotton, the aminated cotton become more grindable, which result in surface area increase of cotton filaments, and thus the average pore radius decrease and total pore volume increase.

TABLE 4. Surface area, average pore radius and total pore volume of the native and the two aminated cottons

Sample	Surface area (m ² /g)	Average Pore radius (nm)	Total pore volume (cc/g)
Native cotton	20.2658	1.9236e+000	1.9492e-002
DETA -aminated cotton	40.224	9.8556e-001	2.4162e-002
TETA-aminated cotton	42.4219	9.7601e-001	3.9246e-002

**Fig. 8.** SEM images of cotton fiber (a), grafted cotton (b), DETA functionalized cotton (c) and TETA functionalized cotton (d).

Surface morphology characterization

The surface morphologies of the native, grafted and aminated cotton fiber were illustrated using scanning electron microscope (SEM). As presented in Fig. 8a, the surface of virgin cotton was to somewhat smooth. After grafting, the surface of grafted cotton, as shown in Fig. 8, revealed significant changes as the surface became rougher, revealing the grafted layer of PGMA. The consequent functionalization with DETA or TETA, illustrated in Fig. 8c&d, showed almost no additional changes to the surface morphology of cotton-poly(glycidyl-methacrylate) graft copolymer (Cell-g-PGMA).

Conclusion

Aminization of cellulose-poly(glycidyl methacrylate) graft copolymer (CPGMA), based on waste cotton fibers, was affected via reaction

with two different aminating agents, e.g. DEAT and TETA, and the best suitable operating reaction conditions were determined. The extent of aminization is expressed as percentages of nitrogen content, reaction conversion and aminization percent. Best results obtained follow the order of DETA > TETA.

Moreover, the two prepared amino-functionalized cellulose-poly(glycidyl methacrylate)graft copolymers (AM-CPGMA) were thoroughly characterized by different physical and chemical methods, that approves the chemical functionalization of CPGMA with DETA and TETA. After functionalization with such groups, the AM-CPGMA can be applied as a good ion exchange material for removal of anionic or cationic ions from it's solutions according to the medium pH.

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التفعيل الكيمياءى للسليولوز المطعم ب poly glycidyl methacrylat باستخدام نوعين مختلفين من المركبات عديدة الامين.

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في العمل الحالي تم تفعيل أحد البلمرات وهو cellulose-poly(glycidyl methacrylate) graft copolymer (CPGMA) والذي تم شرح طريقة تحضيره في عمل سابق، وذلك بإدخال مجموعات أمينيه مختلفه بغرض تطبيقها كمبادلات ايونيه لإزالة الملوثات من المخلفات السائله.

تم دراسة تأثير العوامل المختلفه للتفاعل مثل تركيز المواد المتفاعله، الزمن، الحراره، الأس الهيدروجي و نسبة المواد السائله للمواد الصلبه على خواص المبادل الايوني الناتج وكذلك تأثير هذه العوامل على كفاءته في إزالة الصبغات.

تم توصيف المنتج بالطرق الكيمائيه مثل تحديد المحتوى النيتروجيني والطرق الفيزيائيه مثل الأشعه تحت الحمراء والتحليل الحراري وقياس المساحة الكليه للسطح والتوصيف السطحي للماده.