Finishing of cellulosic fabrics with Chitosan/polyethylene glycol-siloxane to improve their Performance and antibacterial properties

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Abstract: Finishing agent; chitosan/polyethylene glycol-dimethyl siloxane (CS-PEG-DMS) was used for the treatment of cellulosic fabrics (dyed and white) to impart antibacterial activity and to enhance the performance properties, like crease recovery angle (CRA) and tensile strength (TS) too. The effect of chitosan, polyethylene glycol-dimethyl siloxane, Butantetracarboxylic acid (BTCA), sodium hypophosite (SHP) concentrations were studied and optimized to incorporate the finishing agent chemically with the cellulosic fabrics. The treated fabrics show high antibacterial activity against gram -ve, and gram + ve bacteria species (Escherichia coli and Staphylococcus aureus respectively). In addition, the performance of the finished fabrics was improved.

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1. Introduction

Clothing and textile materials are considered a suitable media for the growth of different kinds of bacteria and fungi too. These microorganisms can live on textile materials for long time and under suitable conditions, they can be converted to pathogenic species, which cause diseases to population. In order to reduce this bacterial infection in healthcare that may be caused by the textile/clothing materials, antibacterial textiles is considered the best solution for these problems [1-8].

Modification of textile surface can create a new functionality to the fabrics with new properties as well as, keeping comfort and mechanical strength to the fabric structures [5,8,9]. Currently, multifunctional properties of textile materials are necessary to the textile industry markets [9].

Chitosan is ß-(1-4) - linked polysaccharide. Chitosan is the deacetylated derivative of chitin [10] which is classified as the second abundant natural polysaccharides in nature extracted from the shells of crabs, shrimps and other animal and non-animal sources like aspergillus niger, pencellium, and schizophyllum commune [8]. Chitosan have many different unique properties like biodegradability, biocompatibility, and nontoxicity, that has long been used as a biomaterial in pharmaceutical, textiles, agricultural and bio-medical applications, such as wound healing, and drug delivery system [8]. Because of its cationic nature, chitosan has very good biological activity against different types of gram positive, gram negative bacteria, and different fungus [4].

Polyethylene glycol (PEG) has different important properties e.g. non-toxic, water solubility [11-14]. Polyethylene glycol (PEG) has been used in different industrial applications such as textiles, pharmaceutical and medical fields due to the chemical, physical, and biological advantages, including solubility in wide range of organic solvent and water. Polyethylene glycols is easy for chemical modification to obtained different functional end groups (carboxylic, aldehydes, amino, iodide, and methoxy) [12], [15-21], and the absence of antigen-city and immunogenicity, which permit polyethylene glycol to be used for bio-medical and biotechnological applications.

Recently, many co-works have extensively investigated the modification of biopolymer chitosan with polyethylene glycol, to improve the solubility of chitosan in water, and different organic solvents as well [22-24]. Polydimethyl siloxane has a small surface energy [24] in addition to it has many interesting properties such as, non- toxic, highly

permeable for air and oxygen, has good thermal stability in addition to the highly oxidation stability which considered as smart compound [25].

The aim of this present work is to prepare finishing agent of chitosan/Polyethylene glycol-dimethylsiloxane (CS/PEG-DMS), then optimize the conditions (concentration of chitosan (CS), concentration of PEG-DMS, and the crosslinking BTCA/ polyhypophosite) to treat the cellulosic fabrics to have functional cellulosic textile with antibacterial activity with highly durability as well.

2. Experimental

2.1. Materials

Chitosan degree of deacetylation (75 %) was obtained from Sigma-Aldrich Company, triethylene glycol and dimethyldichloro siloxane from Fluke Chemical Company, Xylene, BTCA, sodium hypophosphite and pyridine were of laboratory grade chemicals.

2.2. Methods

2.2.1. Preparation of polyethylene glycol -dimethyl siloxane (PEG-DMS).

In three necked flask equipped with mechanical stirrer, pressure dropping funnel, one mole of dimethyldichorosilane was reacted with one mole of tri-ethylene glycol in presence of the mixture of xylene and pyridine, the latter was used as acid acceptor. The reaction was carried out under inert atmosphere and genteelly heating at 30 ◦C for 1 hr. After that, the temperature was raised gradually until 80 ◦C for 4 hours and the temperature was kept at100 ◦C for 3 hours to produce (PEG-DMS).

2.2.2. Testing and analysis of the CS/PEG-DMS

Scanning electron microscopy (SEM) was used for characterization the morphology of the textile surfaces before and after modification. Sample images were taken by using; Tescan VEGA II LSU electron microscope (Tuscan USA Inc.). All images were taken at these conditions: voltage 2.44–10 kV, detector: SE. the magnification 300–20000 times, vacuum high, the distance between sample and objective: 4 - 5 mm.

The nitrogen percent was determined using the kjeldahl method [26]. Creasy recovery angle was determined by using AATCC method Vol.70, 1998. Elongation at break was evaluated according to the ASTM precedes D-2296-66T. Tensile strength was determined by the strip method according to ASTM method D2256- 66T [27]. The durability of the treated cellulosic fabrics was determined by using the AATCC Test method 61(2A)-1996.

The treated textile fabrics were subjected to laundry for 20 cycles using soap as detergent with full water level at 40 ^{0}C for 15 minutes and dried for 50 minute at 50 ^{0}C in an oven and sterilized by heat at 105 ^{0}C. Antibacterial activity was evaluated in term of disc diffusion method with some modification for screening the cellulosic fabrics [28] as described: "Nutrient agar for bacteria 0.1ml of an appropriate dilution of the test culture was used, cellulosic fabric samples (0.1cm diameter) were placed on the surface of the incubated plates at 35 ^{0}C for 24 h, Diameter of plates inhibition zone (mm) including the disc diameter was measured for each treatment" [28].

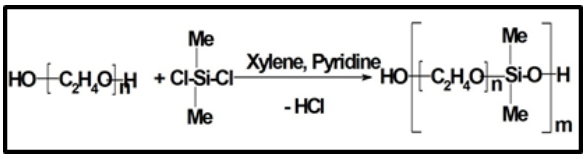
2.2.3. Application of the prepared CS/PEG-DMS on to cellulosic fabrics.

All white, dyed untreated cellulosic fabrics were immersed in a solution containing a mixture of BTCA as cross-linking agent, sodium hypophosphite as catalyst (SHP), chitosan, and polyethylene glycol-dimethylsiloxane (PEG-DMS).

3. Results and discussion

3.1. Preparation of Polyethylene glycol-dimethyl Siloxane (PEG -DMS).

The (PEG-DMS) compound is prepared through the reaction of dimethyldichlorosilane with tri-ethylene glycol in presence of pyridine as acid acceptor through the following equation. By change the chain of the monomer of ethylene glycol we obtained different molecular weight of the adduct.



Where; n: molecular weight of tri-ethylene glycol; m: 1- 25 repeating units.

3.1.2. Treatment of the cellulosic fabrics with CS/PEG-DMS.

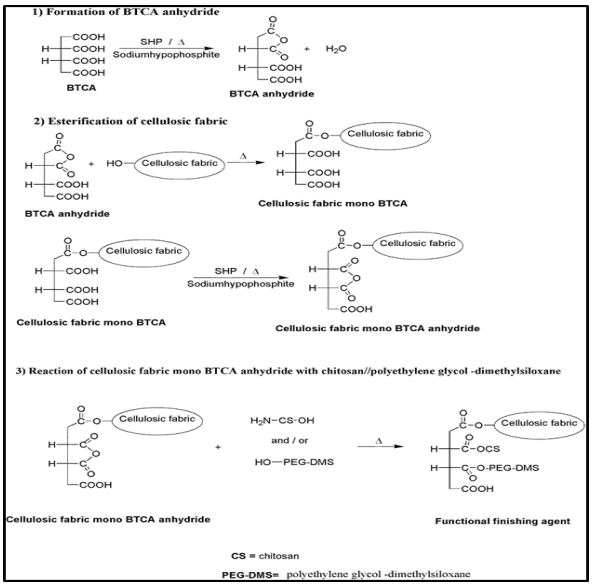
Chitosan / Polyethylene glycol-dimethylsioxane (CS/PEG-DMS) was used as finishing agent with multi-effects when used for the treatment of cellulosic fabrics (white and dyed fabrics) along with BTCA and sodium hypophosphite monohydrate (SHP) as catalyst. Factors affecting the treatment such as concentration of chitosan, siloxane derivatives, and BTCA and sodium hypophosite were studied. The performance and chemical properties of the treated fabrics are discussed below.

3.1.2.1. Effect of (BTCA) as crosslinking agent

Chitosan/ polyethylene glycol-dimethyl siloxane was used as finishing agent for the cellulosic fabrics using the pad-dry cure method in presence of (BTCA) as crosslinking agent and sodium hypophosphite (SHP) as a catalyst (as shown in Scheme 1).

Figure 1 shows the effect of butanetetracarboxylic acid (BTCA) concentration on

the nitrogen content (N %) which reflect the fixation of CS/PEG-DMS finishing agent on to cellulosic fabrics. The mechanical properties of the treated textiles such as crease recovery angel (CRA) and tensile strength (TS) of are illustrated in Figure 1. On the contrary, the nitrogen percent decreases sharply after washing of the finished fabrics, In the presence of low concentration of BTCA. Crease recovery angle (CRA) increased with increasing butenetetracerboxylic acid concentration from 3 to 9 % which is expected, due to the crosslinking of cellulose chains with BTCA. TS decreased with increasing the concentration of BTCA, this can be explained by the effect of acidic effect of BTCA in presence of SHP at high temperature.



Scheme 1: proposed crosslinking mechanism of chitosan /cellulose fabrics/polyethylene glycol-diemthyl siloxane.

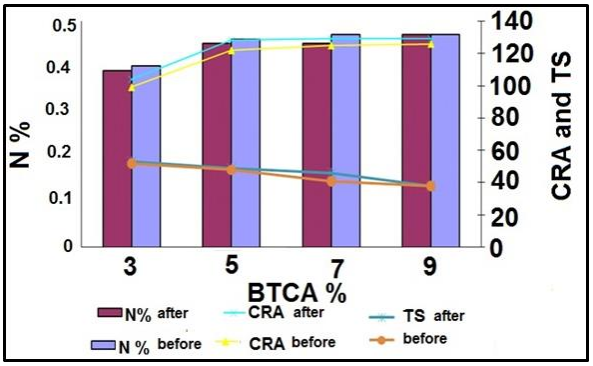


Figure1. The effect of BTCA conc. on the N%, CRA and TS
Experimental conditions: 1 % chitosan, 5 % PEG/DMS, 3 % SHP, (3-9 %) BTCA, dried at 80 °C for 10 min. curing at 160 °C for 2 min.

3.1.2.2. Effect of sodium hybophosite (SHP) concentration

Figure 2 shows the effect of SHP concentration on the results of nitrogen percent (%), crease recovery angel (CRA), and tensile strength (TS) of the treated samples. The treatment formulation was as follows, 1 % chitosan, 5 % PEG/DMS, SHP, 5 % BTCA, dried at 80 °C for 10 min. curing at 160 °C for 2 min. From the results obtained in Figure 2 it is clear that, by increasing the SHP concentration from 3 - 9 %, an enhancement of N % after washing occurred. Also the CRA increased by increasing the concentration of SHP while TS decreased with increasing of SH from 3 - 9 % which is attributed to the effect of high concentration of catalyst at high curing temperature on the cellulosic fabrics.

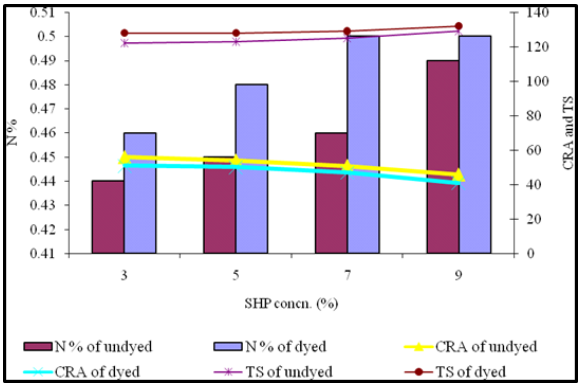


Figure 2. The effect of SHP con on the N%, CRA and TS.
Experimental condition: 1 % chitosan, 5 % PEG/DMS, 5 % BTCA, dried at 80 °C for 10 min. curing at 160 °C for 2 min.

3.1.2.3. Effect of chitosan concentration on the finishing of cellulosic Fabrics

White and dyed cellulosic fabrics were subjected to an aqueous solution of the finishing agent which contain different concentrations of chitosan and (BTCA) along with SHP as the corresponding catalyst. The finished fabrics were then characterized through measuring the nitrogen content (N %) before and after washing in order to evaluate the content of chitosan impregnated on to cotton fabric structure. Figure 3 shows the impregnated quantity of chitosan, described as Nitrogen percent, after washing, increased by increasing the finishing agent concentration till 1 %, then decrease again. Crease recovery angle is marginally increased and the tensile strength is almost constant irrespective to the concentration of chitosan.

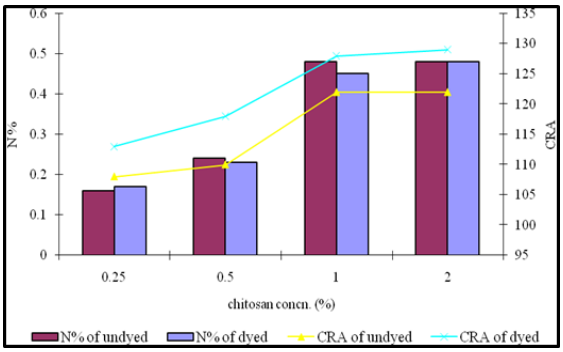


Figure 3. The effect of chitosan concentration on the nitrogen percent (N %) and crease recovery angle (CRA)
Experimental condition: 5 % PEG/DMS, 5 % BTCA, dried at 80 ºC for 10 min. curing at 160 ºC for 2 min.

3.1.2.4. Antibacterial activity of chitosan/ polyethylene glycol-dimethyl siloxane.

Cellulosic fabrics were treated using the finishing formulation; chitosan/ polyethylene glycol-dimethyl siloxane along with BTCA acid and SHP. Cellulosic Fabrics were padded with the previous solutions to a wet pick up of 100 %, followed by drying and curing at 160 ^{0}C for 2 minutes. The efficacy of the antibacterial activity for the treated fabrics was evaluated against S. aurous and E. coli as bacteria species. These bacteria were selected, as they are the most bacteria found in most of wound infection. Figure 4 shows the effect of durability on the antibacterial activity of the finished fabrics. As shown, the antibacterial activity increases by increasing the concentration of the finishing agent, until 2 %. The antibacterial activity of the dyed fabrics seem to be lower than the white fabrics after subjecting to the finishing agent.

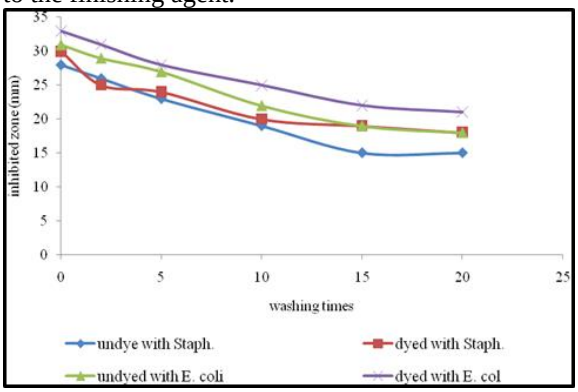


Figure 4: Effect of durability on the antibacterial activity of the finished fabrics.
Experimental condition: 1% chitosan, 5 % PEG/DMS, 5 % BTCA, dried at 80 oC for 10 min. curing at 160ºC for 2 min.

3.1.2.5. Scanning electron microscope of cellulosic fabrics treated with CS/PEG-DMS.

Figure 5 (a and b) show the scanning electron microscope for cellulosic fabrics before and after treatment with chitosan/polyethylene glycol-dimethyl siloxane (CS/PEG-DMS). It can be clearly seen the formation of smooth layer on the fabric surface (Figure 5b).

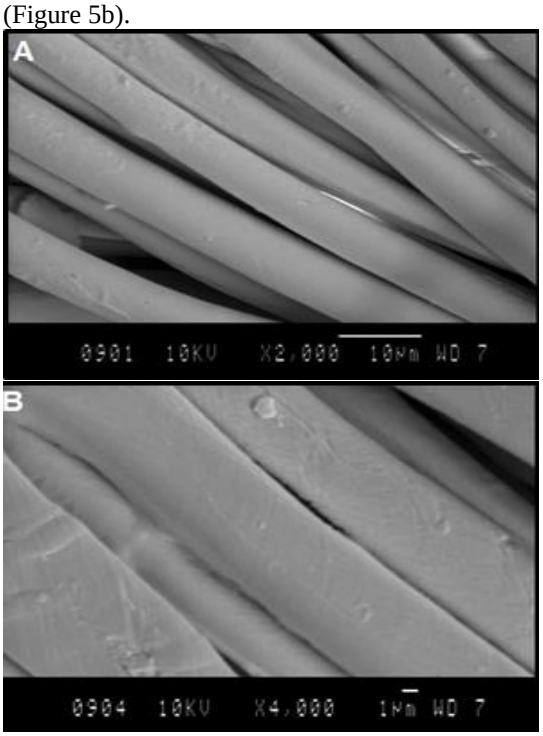


Figure 5: scan electron microscope of untreated cellulosic fabrics (a); cellulosic fabrics treated with chitosan/polyethylene glycol-dimethylsiloxane

4. Conclusion

Chitosan/ polyethylene glycol dimethylsiloxane (CS/PEG-DMS) solution was prepared and used as finishing agent for cellulosic fabrics by pad-dry-cure method to impart highly performance properties and antibacterial activity as well into. BTCA and SHP were used as crosslinking and catalyst respectively. The antibacterial activity of the cellulosic fabrics was evaluated against two types of bacterial; E. coli and St. aurous. The treated cellulosic fabrics can be used for different medical application especially for health care and hygiene products purposes.

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References

[1] Qian L, Sun G. Durable and Regenerable Antibacterial Textiles: Synthesis and Applications of 3-Methylol-2,2,5,5-tetramethylimidazolidin-4-one (MTMIO). Journal of Applied Polymer Science. 2003;89:2418-25.

[2] Fouda MMG, El-Aassar MR, Al-Deyab SS. Antibacterial activity of carboxymethyl chitosan/polyethylene oxide nanofibers embedded silver nanoparticles. Carbohydrate Polymers. 2013;92(2):1012-7.

[3] Hebeish A, El-Naggar ME, Fouda MMG, Ramadan MA, Al-Deyab SS, El-Rafie MH. Highly effective antibacterial textiles containing green synthesized silver nanoparticles. Carbohydrate Polymers. 2011;86(2):936-40.

[4] Hebeish A, Abdel-Mohdy FA, Fouda MMG, Elsaid Z, Essam S, Tammam GH, et al. Green synthesis of easy care and antibacterial cellulosic fabrics fabrics. Carbohydrate Polymers. 2011;86(4):1684-91.

[5] Abdel-Halim ES, Abdel-Mohdy FA, Fouda MMG, El-Sawy SM, Hamdy IA, Al-Deyab SS. Antibacterial activity of monochlorotriazinyl-beta-cyclodextrin/chlorohexidin diacetate finished cellulosic fabrics fabrics. Carbohydrate Polymers. 2011;86(3):1389-94.

[6] Abdel-Halim ES, Fouda MMG, Hamdy I, Abdel-Mohdy FA, El-Sawy SM. Incorporation of chlorohexidin diacetate into cellulosic fabrics fabrics grafted with glycidyl methacrylate and cyclodextrin. Carbohydrate Polymers. 2010;79(1):47-53.

[7] Fouda MMG, El Shafei A, Sharaf S, Hebeish A. Microwave curing for producing cellulosic fabrics fabrics with easy care and antibacterial properties. Carbohydrate Polymers. 2009;77(3):651-5.

[8] El-Shafei AM, Fouda MMG, Knittel D, Schollmeyer E. Antibacterial activity of cationically modified cellulosic fabrics fabric with carboxymethyl chitosan. Journal of Applied Polymer Science. 2008;110(3):1289-96.

[9] Fouda MMG, Fahmy E. Multifunctional finish and cellulosic fabrics cellulose fabric. Carbohydrate Polymers. 2011;86(2):625-9.

[10] Fahmy HM, Fouda MMG. Crosslinking of alginic acid/chitosan matrices using polycarboxylic acids and their utilization for sodium diclofenac release. Carbohydrate Polymers. 2008;73(4):606-11.

[11] Aiba S-i. Studies on chitosan 5. Reactivity of partially N-acetylated chitosan in aqueous media. Die Makromolekulare Chemie. 1993;194(1):65-75.

[12] Harris JM, Struck EC, Case MG, Paley MS, Yalpani M, Van Alstine JM, et al. Synthesis and characterization of poly(ethylene glycol) derivatives. Journal of Polymer Science: Polymer Chemistry Edition. 1984;22(2):341-52.

[13] Jeong B, Bae YH, Kim SW. In situ gelation of PEG-PLGA-PEG triblock copolymer aqueous solutions and degradation thereof. Journal of Biomedical Materials Research. 2000;50(2):171-7.

[14] Abdel-Mohsen AM, Abdel-Rahman RM, Hrdina R, Imramovský A, Burgert L, Aly AS. Antibacterial cellulosic fabrics fabrics treated with core–shell nanoparticles. International Journal of Biological Macromolecules. 2012;50(5):1245-53.

[15] Blanton JR. Borohydride-polyethylene glycol monomethyl ether derivatives: chemo- and stereoselectivity studies under phase transfer conditions. Reactive and Functional Polymers. 1997;33(1):61-9.

[16] Pengzhan Yu, Xingqi Li, Xiunan Li, Xiuling Lu, Guanghui Maa, Zhiguo Sua. Preparative purification of polyethylene glycol derivatives with polystyrene-divinylbenzene beads as chromatographic packing. Bioorganic & Medicinal Chemistry Letters 2007;17( ):5605-9.

[17] Yu H-Y, Kang Y, Liu Y, Mi B. Grafting polyzwitterions onto polyamide by click chemistry and nucleophilic substitution on nitrogen: A novel approach to enhance membrane fouling resistance. Journal of Membrane Science. 2014;449(0):50-7.
[18] Stefanko MJ, Gun'ko YK, Rai DK, Evans P. Synthesis of functionalised polyethylene glycol derivatives of naproxen for biomedical applications. Tetrahedron. 2008;64(44):10132-9.
[19] Abdel-Mohsen AM, Aly AS, Hrdina R, Montaser AS, Hebeish A. Eco-Synthesis of PVA/Chitosan Hydrogels for Biomedical Application. J Polym Environ. 2011;19(4):1005-12.
[20] Abdel-Mohsen AM, Aly AS, Hrdina R, El-Aref A. A novel method for the preparation of silver/chitosan-O-methoxy polyethylene glycol core shell nanoparticles. J Polym Environ. 2012;20(2):459-68.
[21] Abdel-Mohsen AM, Aly AS, Hrdina R, Montaser AS, Hebeish A. Biomedical Textiles Through Multifunctioalization of Cellulosic fabrics Fabrics Using Innovative Methoxypolyethylene Glycol-N-Chitosan Graft Copolymer. J Polym Environ. 2012;20(1):104-16.
[22] Hemmilä S, Cauich-Rodríguez JV, Kreutzer J, Kallio P. Rapid, simple, and cost-effective treatments to achieve long-term hydrophilic PDMS surfaces. Applied Surface Science. 2012;258(24):9864-75.
[23] Liu G, Xiangli F, Wei W, Liu S, Jin W. Improved performance of PDMS/ceramic composite pervaporation membranes by ZSM-5 homogeneously dispersed in PDMS via a surface graft/coating approach. Chemical Engineering Journal. 2011;174(2–3):495-503.
[24] Zhang Z, Wang J, Tu Q, Nie N, Sha J, Liu W, et al. Surface modification of PDMS by surface-initiated atom transfer radical polymerization of water-soluble dendronized PEG methacrylate. Colloids and Surfaces B: Biointerfaces. 2011;88(1):85-92.
[25] Almutairi Z, Ren CL, Simon L. Evaluation of polydimethylsiloxane (PDMS) surface modification approaches for microfluidic applications. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2012;415(0):406-12.
[26] Vogel AI. Elementary practical organic chemistry, part-3, Quantitative Organic Analysis. Longman Group Ltd.2nd 1975, p. 652.
[27] ASTM Test Method D-, 1972. in Book of standard philadephia, Part, 24,.
[28] Ericson HM, Sherris JC. Report of an International collaboration Study. Acta Pthologica. Scandinvia Section B. Supplement; 1971.

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