Glycidyl Esters Used for Multifunctional Finishing of Textile Materials

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The study presented in this paper is related to a method for imparting multifunctional properties to the cotton fabrics by treating them with glycidyl esters of fatty acids (GEs). The treatment confers hydrophobic character, antifungal properties, soil resistance and easy soil removal properties for the cotton fabrics. The glycidyl esters used in this research were glycidyl laurate and glycidyl palmitate, obtained by the reaction of sodium laurate and sodium palmitate, respectively, with epichlorohydrin, in the presence of dimethylformamide. FTIR and SEM analysis were used to study the effect GEs have on treated cotton fibres. The hydrophobic properties of the treated samples were assessed by measurements of the water contact angles and absorption times of the water drops. Antifungal activity of the cotton samples treated with GEs was evaluated against two species of cellulolytic fungi: Phanerochaete chrysosporium and Trichoderma viridae. The effects of fabric degradation under the action of the tested fungi were highlighted by the weight loss and by the changes in colour and texture, as pointed out by the microscopic images and micro photos. The degree of soiling of the samples was assessed by the difference in colour between the soiled and washed samples. The results obtained confirm that the method used in this research allows for adding multiple desired properties of the cellulosic materials by using a single finishing agent and a single finishing treatment, thus facilitating savings in terms of energy usage and water consumption.

Keywords: antifungal activity, cotton fabrics, glycidyl esters of fatty acids, hydrophobization, soiling degree

The cotton fabrics show a high capacity to absorb and retain moisture from the surrounding environment. Although advantageous from many points of view, this feature, together with the organic components of the cotton fibres, makes them highly susceptible to fungal degradations. The degradation produced by different fungal species may cause changes in textile fabrics properties, such as loss of strength, decrease of general durability, discolorations, stains and spots. In most of the cases, the modifications appearing under the actions of the microorganisms can also lead to specific smells [1-7].

Commonly, the fungus colonies appear and grow when the textile material is deposited in poorly ventilated places and is exposed to certain conditions of humidity and temperature. The structure of the substrate and the presence of some substances used in chemical processes, such as the starch used in warp sizing, are additional factors that favour the development of fungus species on the cotton fabrics [6-10].

Due to their destination, a wide range of textile products are exposed to a complex set of factors that may lead to considerable deterioration in terms of both appearance and durability. Among these products are those intended for open air activities, such as tent canvas, hammocks, backpacks, camping furniture, but also the textile products used in transport industry or in architecture, designed for outdoor use: tarpaulin for trucks, canvas for tents and gazebos, parasols, awnings, canopies etc. During their lifetime, several types of degradation and deterioration may appear on the surface of these products, including those produced by the attacks of different fungus species or stains due to exposure to dust, mud, wet grass or different kinds of liquids that can come in contact with the textile material [11].

By applying suitable finishing treatments that help reduce the hydrophilic character of cotton fabrics and give them hydrophobic properties, the right conditions are ensured in order to reduce the soiling tendency of textile materials and to diminish their susceptibility to fungi attacks [12-25].

The study presented in this paper is related to a method for imparting multifunctional properties to the cotton fabrics, such as hydrophobic character, antifungal activity, soil resistance and easy soil removal, by applying a single finishing treatment, using a mix of glycidyl esters of fatty acids, namely glycidyl palmitate and glycidyl laurate.

Experimental part

Materials and methods

Chemicals and textile materials

The following chemicals were used for the synthesis of gycidyl esters: sodium laurate, sodium palmitate, dimethylformamide - purchased from Sigma Aldrich Co., nonionic tenside Tween 80, epichlorohydrin (1-chloro-2,3-epoxypropane) and NaOH, provided by Merck. All the chemicals were used without previous purification.

The textile material used for the study was 100% cotton plain weave fabric (170 g/m^2), desized, scoured and bleached.

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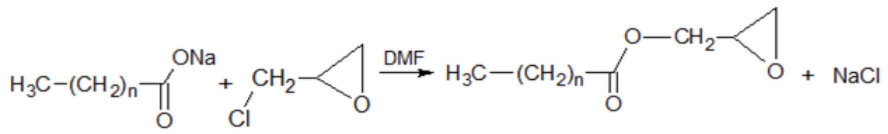
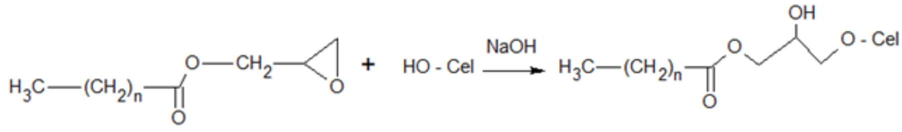


Sodium salt of fatty acid | Epichlorohydrin | Glycidyl ester of fatty acid | Sodium chloride

Scheme 1. Reaction for obtaining glycidyl esters



Glycidyl ester of fatty acid | Cellulose | Ether of cellulose

Scheme 2. Reaction of glycidyl esters of fatty acids with cellulose fibres

Synthesis of glycidyl palmitate and glycidyl laurate

Glycidyl palmitate was obtained from the reaction of sodium palmitate (0.1 mol) with epichlorohydrin (7 mL), in the presence of dimethylformamide (120 mL), heated under stirring at 105°C for 5 h. The final reaction mixture was filtered, washed with distilled water (at 60°C) and vacuum dried on a rotavapor. Glycidyl laurate was synthesized in a similar way [26].

The obtaining reaction of Glycidyl esters (glycidyl palmitate and glycidyl laurate) is illustrated in scheme 1.

Treatment of cotton fabric

The cotton fabric was treated with emulsion obtained by mixing the two esters, glycidyl palmitate (60 g/L) and glycidyl laurate (60 g/L), with 2% aqueous solution of nonionic tenside Tween 80 at 70°C.

During the first stage of the treatment, the fabric samples were impregnated with the prepared emulsion at 70°C and then pad squeezed in order to remove the excess of emulsion from them. This step was followed by impregnation in NaOH solution (10 g/L), used as a catalyst, and a subsequent pad squeezing with 100% squeezing degree. Next, the treated samples were rolled up, wrapped in polyethylene film and kept in this state for 12 h at room temperature. Afterwards, the samples were dried for 20 min at 70°C and cured at 120°C for 20 min. In the presence of NaOH as a catalyst, glycidyl esters react with hydroxyl (- OH) of cellulose and results the ether of cellulose, as show Scheme 2.

After treatment, the samples were washed with warm water to remove the loose chemical products from the cellulose fibres and then were dried.

Growth of the Fungus

The white rot fungal strains *Phanerochaete chrysosporium* and *Trichoderma viride* used in this experiment were obtained from the collection of Alexandru Ioan Cuza University of Iasi, Biology Department. All these strains were kept at 28°C on Sabouraud medium and peptone glucose agar media, respectively. Approximately 1 mL of 7 day old fresh conidia culture of the two fungi was separately inoculated on Petri dishes containing solid culture medium properly. After 5 min, the inoculums are removed and allowed to dry for 30 min, and then the textile materials were applied on these media with fungi inoculums. Thereafter, the cotton fabric samples treated with a mix of glycidyl esters of fatty acids were tested in order to evaluate their antifungal activity against these two cellulolytic fungi, being kept for 14 days at 28°C, as ensured by the thermostat.

Methods employed for characterisation of treated samples

SEM analysis

Morphological characterization of samples, before and after the treatment, was performed using scanning electron microscopy (SEM). After a pre-treatment consisting in coating the samples with a conductive layer of gold in argon plasma environment for 60 s, these were examined with a scanning electron microscope Hitachi S-3000N.

FTIR analyses

FTIR analyses were carried out using a Multiple Internal Reflectance Accessory (SPECAC, USA) with an ATR KRS-5 crystal of thallium bromide-iodide, having 25 reflexions and the investigation angle of 45°. This accessory device was attached to the Spectrophotometer FTIR IR Affinity-1 Shimadzu (Japan). The spectra registration was realized with 250 scans in the range of 4000 cm^{-1} –2800 cm^{-1} and the range of 1800 cm^{-1} – 500 cm^{-1}, respectively.

Evaluation of Hydrophobicity

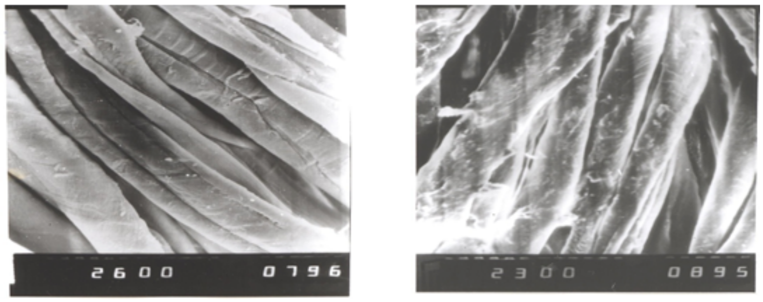
The samples hydrophobicity was put into evidence through the values of contact angle formed by water drops with the surface of treated samples and by the water absorption time. The measurements of static water contact angles were done at 22°C in ambient air using an automatic contact angle goniometer equipped with a flash camera - Kreuss Drop Shape Analysis System DSA 100 - applying a sessile drop method. For determining the water absorption time (according to AAATC Test Method 79), 10 droplets of water were poured with a micropipette on the surface of the treated samples from a height of 2 cm. The average volume of a water droplet was about 30μL. The droplets were placed in different locations on the surface of the fabric; the final result regarding the water absorption time by the fabric was considered as the average of 10 measurements.

Antifungal activity

The degradations caused by the cellulolytic action of the tested fungi on the cotton fabrics were highlighted by the weight losses and texture changes, as it results from the microscopic images and from the micro photos taken with the computerised system for microscopic analysis - MacroLab Advanced MESDAN.

Evaluation of Degree of Soiling

Two sets of treated samples and two sets of blank samples (white) were immersed in four types of aqueous soil solution: coffee, green tea, cherry compote and red wine. The samples were kept in soil solutions for 1, 5, 10,



A. B.

Fig. 1. SEM images of cotton samples before (A) and after (B) treatment with GEs

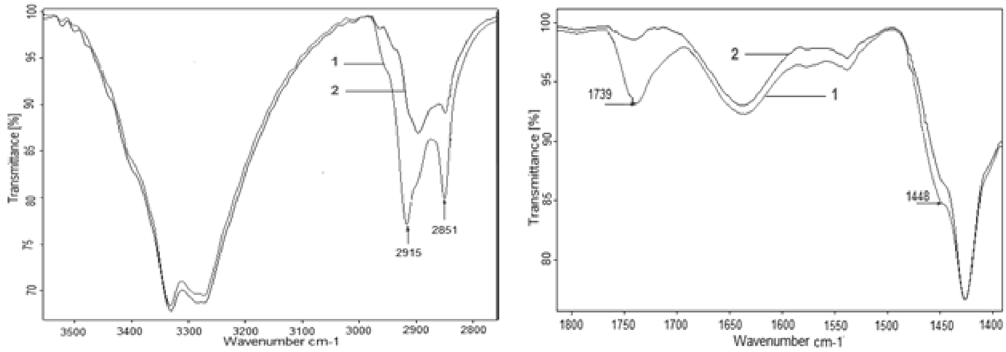


Fig. 2. FTIR spectra
1 - Treated cotton sample,
2 - Untreated cotton sample

15, 20 and 30 min respectively. Half of the soiled samples were then washed according to ISO 105-CO6:2010 method, using 4 g/L Felosan NOF. All samples were dried at 80°C.

The degree of soiling of the samples was assessed by measuring the colour difference (ΔE) between the white samples and the soiled samples (both untreated and treated). The colour measurements were performed using spectrophotometer Spectroflash 300R from DATACOLOR for illuminant D65/10 using Micromath 2000® software.

Results and discussions

SEM analysis

The change in surface properties of the cotton fabrics modified by the applied treatment and the presence of GEs on the cotton fibres is pointed out by SEM photos. The images in figure 1 show the surface morphology of the cotton samples, before (A) and after (B) treatment with GEs. As one can see in figure 1A, the untreated cotton fibres show a clean and smooth surface, while the presence of GS on the surface of treated sample is highlighted in the image in figure 1B.

FTIR analysis

The FTIR spectra in figure 2 confirm the presence of hydrophobic product on the surface of cotton fibres. The etherification reaction of glycidyl esters of fatty acids with hydroxyl (-OH) of cellulose is proved by the presence of peaks at 2915 cm^{-1} and respectively 2851 cm^{-1} that correspond to symmetric and antisymmetric stretching of CH_2 group from the hydro-carbonate chain of esters and by the absorption band located at 1739 cm^{-1} that corresponds to the esteric group of glycidyl palmitate and glycidyl laurate.

Hydrophobic properties of treated cotton fabric

The hydrophobic character of the treated samples' surface was assessed by the water contact angle values and by the absorption time of water drops placed on the fabric surface. The results displayed in table 1 show that the untreated fabric samples are strongly hydrophilic. This property is evidenced by the fast absorption of water droplets, which makes it impossible to measure the contact angle or to take pictures of water droplets deposited on the fabrics surface.

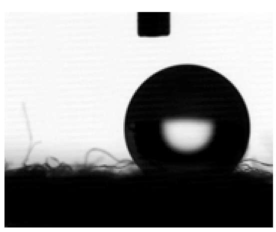
Instead, for the treated samples, the resulted value of contact angle (140 degrees) and the absorption time of water droplets (170 min) show that the cotton fabric surface has become hydrophobic after the treatment with glycidyl esters.

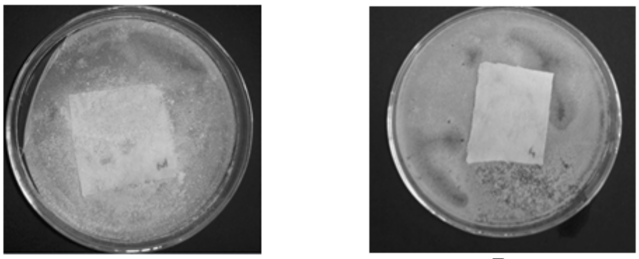
Antifungal properties of treated cotton fabric

Both treated and untreated cotton fabric samples were exposed to degradation by two fungus cultures: *P. chrysosporium* and *T. viride.* The micro photos in figure 3 show the images of cotton samples after 7 days of incubation with *P. chrysosporium* in Sabouraud culture medium.

It can be observed from the micro photos that the surfaces of the samples treated with glycidyl esters are only partial covered with the fungus spores (fig. 3B), compared to the untreated samples which are almost completely covered by spores (fig. 3A).

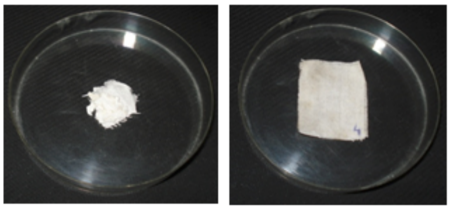
Table 1
HYDROPHOBIC PROPERTIES OF COTTON SAMPLES

Samples type	Photographic image of water drop deposited on the fabric surface	Contact angle (degrees)	Absorption time of water droplet
Treated samples		140	170 min
Untreated sample	undetermined	undetermined	2 sec



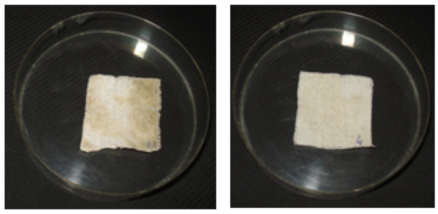
A. B.

Fig. 3. Cotton fabric samples placed on media with *P. chrysosporium* after 7 days of incubation A - Untreated cotton sample; B - Cotton sample treated with glycidyl esters



A. B.

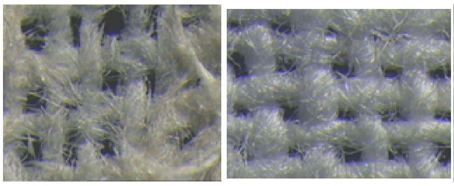
Fig. 4. Cotton fabric samples after 14 days of degradation with *P. chrysosporium*



A. B.

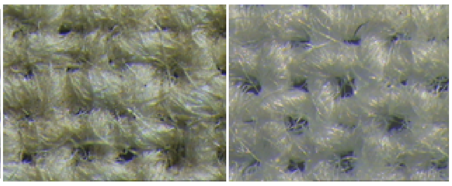
Fig. 5. Cotton fabric samples after 14 days of degradation with *T. viride*

A. Untreated cotton sample; B. Cotton sample treated with glycidyl esters



A. B.

Fig. 6. Cotton fabric samples texture, after incubation with *P. chrysosporium*



A. B.

Fig. 7. Cotton fabric samples texture, after incubation with *T. viride*

A. Untreated cotton sample; B. Cotton sample treated with glycidyl esters

Table 2
WEIGHT LOSS

Phanerochaete chrysosporium		*Trichoderma viride*	
Untreated sample	Treated sample	Untreated sample	Treated sample
50.09 %	5.52 %	27.7 %	7.52 %

After being inoculated for 14 days with the two types of fungi, the samples were washed with 4g/L detergent (Ariel) at 60°C for 30 min and then were dried at 70°C. The fungal degradations of the fabric as a consequence of cellulolytic action of the tested fungi were highlighted by changes in colour and texture.

The colour changes that appear after the inoculation period can be observed in the images presented in figures 4 and 5.

The texture changes that occurred on treated and untreated cotton samples after the fungi incubation are illustrated by microscopic images presented in figures 6 and 7.

Comparing the degradation effect of tested fungi, it can be observed that the most aggressive one was *P. chrysosporium*, the blank samples being partially destroyed as a result of the cellulolytic action of this fungus. Due to advanced degradation of the untreated sample, its strength has been significantly diminished, so that the washing process that was subsequently applied has led to yarn breakage and fabric destruction (figs. 4A and 6A).

In the case of *T. viride*, the attack was slightly less aggressive, but with equally serious consequences. The colonies of fungi developed on the sample surface are evidenced by extended coloured areas on the cotton fabric, as illustrated by the image in figure 5A. Broken fibres and frequent fungal accumulation areas are visible in figure 7A. Due to the deep degradations of cotton fibers situated on the outside layers of the yarns, their structure has been partially destroyed. The cohesion provided by the fibres twisted around the body of the yarn has been diminished and the yarns became loose and opened. This explains why the yarns' diameter for the untreated samples is visibly greater, compared to the treated samples, while the dimensions of the fabrics' pores were greatly reduced.

As for the samples treated with glycidyl esters, they show fewer changes (figs.4 B and 5B). The structure of the yarns was well preserved as well as the fabric structure, which has not undergone significant changes in terms of texture or colour (figs. 6 B and 7B).

The action of the fungi on the cotton samples before and after the treatment with glycidyl esters was also manifested through the weight loss of the fabric after the incubation with the two types of fungi and after the removal of the fungus through washing. The results presented in table 2 show that for untreated samples, the most severe degradations were produced by the attack of *P. chrysosporium,* with about 50% weight loss, followed by *T. viride* with about 28% weight loss. Instead, the weight losses of the cotton samples treated with glycidyl esters were far smaller, ranging between (5 - 7%).

Degree of Soiling

The degrees of soiling for the cotton samples, assessed as colour difference between soiled samples (treated and untreated) and unsoiled samples, are illustrated in figure

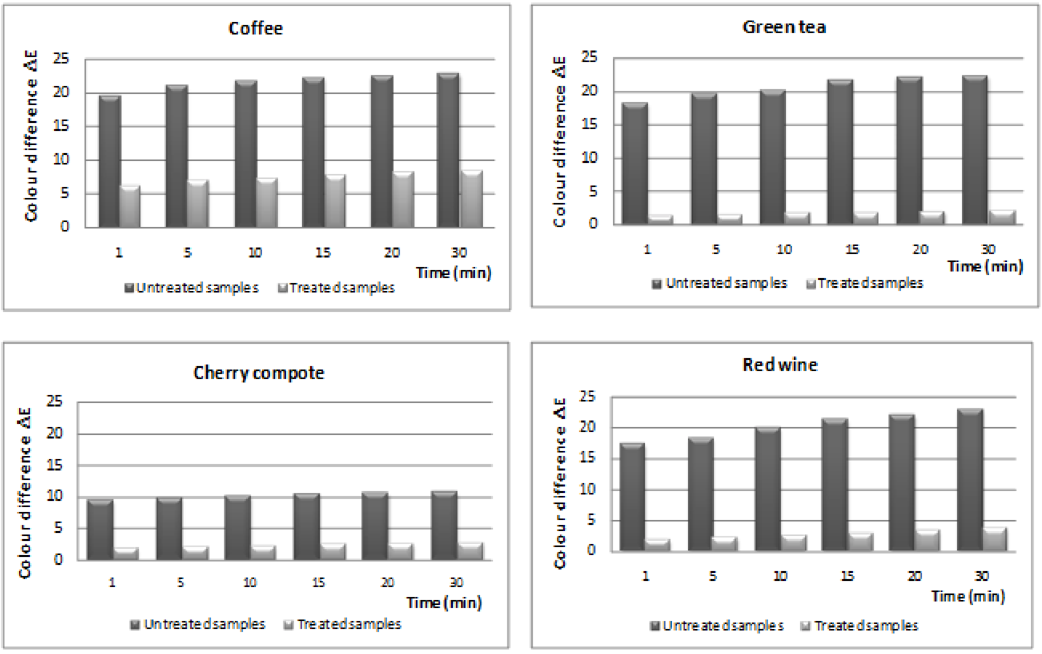


Fig. 8. Colour difference for the cotton samples soiled with the four types of soil solutions

8. Graphical representations clearly highlight the positive effect of the applied treatment on the soiling degree of the cotton samples. One can see that the cotton samples modified by treatment with GEs are much less soiled compared to the untreated cotton samples, regardless of the type of soil solution tested. Out of the four types of soil solutions used in this study, the cherry compote showed the lowest effect while the other three solutions produced a more intense soiling of the samples, the coffee being the most aggressive one. The immersion time of the samples in soil solutions directly influence the soiling degree, regardless of the type of soil solution, both for the treated and the untreated samples. These improvements concerning the soiling resistance of the tested samples are due to the hydrophobic character of the cotton fabrics' surface, obtained after the treatment with glycidil esters.

Conclusions

Treating the cotton fabrics with a mix of glycidyl esters of fatty acids confers them multifunctional properties: hydrophobic character, antifungal properties, resistance to soiling and possibility of easy soil removal. The large values of contact angle (140°) and absorption time of water droplets (170 min), confirm the hydrophobic character induced on the surface of textile support by the applied treatment.

The behaviour against two species of fungi, *Phanerochaete chrysosporium* and *Trichoderma viridae*, assessed by microscopic images and percentage of weight loss, indicates a greater degradation of untreated samples compared to treated ones, particularly under the action of *P. chrysosporium*.

The degree of soiling for the samples treated with glycidyl esters of fatty acids is lower compared to the untreated samples and certain types of dirt, such as green tea and red wine, are more easily removed by washing from the surface of treated samples.

In conclusion, the obtained results confirm the effectiveness of the method used in this research when it comes to adding multiple desired properties to the cellulosic materials by using a single finishing agent and a single finishing treatment. Therefore, it results in important savings in terms of energy usage and water consumption.

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