

Study of Cotton Grafting with Hemiacetal - MCT- β -CD Derivative Using Fourier Transform Infrared Spectroscopy and Statistical Analysis

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The dihydrated forms of the 40% glyoxal solution undergo a dehydration process (in the presence of HCl), when the proportion of non-hydrated glyoxal increases. In the presence of a dilute ethanol solution, the non-hydrated glyoxal generates a hemiacetal. The presence of hemiacetal is confirmed by FT-IR analysis by increasing of the peaks at 1053 cm⁻¹, 1107 cm⁻¹ and by decreasing of the peak at 1746 cm⁻¹. The grafting of cotton with the final grafting agent obtained from the interaction of hemiacetal with MCT- β -CD, was possible using pad-dry-cure technology. The presence of MCT- β -CD on cotton fabric was confirmed by FT-IR analysis (by the peaks of 1535 cm⁻¹ and 787 cm⁻¹) and by the yellowing of the sample. Confirmation of the grafting is given both by increasing the pickup / take-up degrees and by increasing the wrinkle recovery angles (WRA). The statistical analysis of these indices indicates low values for standard deviation (SD), standard error of the mean (SEM) and the coefficient of variation (CV).

Keywords: grafting, hemiacetal, MCT- β -CD, FT-IR, statistical analysis

Glyoxal is a α -dicarbonyl compound, very reactive in any reaction medium (acid or alkaline), giving reversible polymerization reactions. In the presence of water, glyoxal gives reactions of hydration, oligomerization and disproportionation [1-3].

Anhydrous form of glyoxal is unstable having a plane structure, trans type [1]. Glyoxal is commercialized as 40% glyoxal solution; which is in fact a mixture of about 11% glyoxal (monomer), the rest consisting in monohydrated and dihydrated forms (gem-diol, dimer and trimer) [4-10]. In the form of polyhydroxy carbonyl (with at least four carbon atoms), one can find it as intra-molecular hemiacetals that generate cyclical forms of pyranoid or furanoid type [1].

Glyoxal can participate in numerous nucleophile addition reactions, generating acetals, cyanohydrins, amino alcohols, and many others [1, 11-15].

The ethanol is an important intermediate in organic synthesis because this alcohol is easily synthesized and easily transformed into other compounds. Ethanol can participate in reactions of substitution, esterification, oxidation, dehydration and reactions for formation of alloxides.

There are similarities in the behavior of carbonyl compounds in the presence of water and, respectively, in the addition of an alcohol over an aldehyde. In the case of carbonyl compounds, geminal-diol compounds are obtained, and from the interaction of alcohols with aldehydes hemiacetals or acetals are obtained. Both reactions are reversible and occur only in acid catalysis, since alcohol/ethanol is a weak nucleophile [16-17].

The reaction between glyoxal and ethanol depends on the number/nature of glyoxal hydrated forms (in 40% solution) and temperature, presence/absence of a catalyst.

Monochlorotriazinyl- β -cyclodextrin (MCT- β -CD) consists in two parts: monochlorotriazinyl cycle and β -cyclodextrin. MCT component has an increased reactivity, due to an increased basicity of the triazine heterocycle and due to the presence of the two substitutes (chlorine and ONa). Chlorine atom is able to react with a series of functional groups (OH, NH₂) from other reactants or even from textile fibers [18-21].

In this paper we studied the possibility of grafting cotton with a derivative derived from glyoxal, ethanol and MCT- β -CD. The glyoxal solution was enriched in non-hydrated glyoxal using acid catalysis. Then, the glyoxal was brought into contact with ethanol, in the presence of the same catalyst. The reaction between glyoxal and ethanol depends on the number/nature of glyoxal hydrate forms (in 40% solution), temperature, concentration of ethanol solution and presence of a catalyst. It followed the addition of MCT- β -CD solution and the use of NaOH as a catalyst. The curing phase of pad-dry-curing technology is responsible for the formation of ether bonds between grafting agent and cotton. As grafting results, wrinkle proofing effects are obtained, which are confirmed by a spectroscopic analysis, the increases in take-up degrees and WRA, respectively.

Experimental part

Materials and methods

In this work were used 100% cotton samples (with specific weight of 100 g/m²) after were desized and scoured. The chemicals used in this work were without previous purification and were obtained from Sigma Aldrich (glyoxal as 40% solution), Merck (NaOH, HCl 98%, ethanol) and Wacker-Chemie (CAVASOL W7 MCT, i.e. monochlorotriazinyl beta-cyclodextrin Na-Salt).

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Sample	Code sample	Preparing of solution for padding stage
Untreated cotton	W0	-
Cotton+ glyoxal/HCl	W1	10% glyoxal solution 0.02 mL HCl (stirring 15 min.)
Cotton+(glyoxal/HCl +ethanol)	W2	Step I 10% glyoxal solution 0.02 mL HCl (stirring 15 min.) Step II 1% ethanol (stirring 15 min.)
Cotton+[(glyoxal/HCl+ethanol) + MCT-β-CD/NaOH]	S1	Step I 10% glyoxal solution 0.02 mL HCl (stirring 15 min.) Step II 1% ethanol (stirring 15 min.) Step III 20% MCT-β-CD NaOH, pH = 12 (as catalyst)

Table 1
PROTOCOL EXPERIMENTAL

The experiments were performed according to the experimental protocol of table 1.

Each solution was added to a mini-padder and the material was squeezed to a squeeze degree, DS = 80%. This was followed by drying (100°C, 3 min.) and curing (160°C, 3 min.). Finally, the samples were washed and dried at room temperature. The equipment consisted of a mini-padder and a minitherm ERNST BENZ AG (Textilmachinen Rümlang- Zurich).

Two witness samples were used for comparison: a witness sample coming from cotton treated with glyoxal and HCl (abbreviated as W1), and the second coming from the cotton treated with the solution of glyoxal/HCl and ethanol (abbreviated as W2). It was done in this manner to notice the modifications produced by the interactions between reactants after each stage.

FT-IR analysis was realized on the Spectrophotometer FTIR IRAffinity¹-Shimadzu apparatus (Japan). The spectra were superposed with the software Spekwin 32.

The grafting effects were highlighted by take-up degrees and wrinkle-recovery angles (WRA).

Taking-up degree was gravimetrically determined as in our previous works [19, 22-24].

Wrinkle-recovery angles (WRA) were determined on Metrimplex FF-01 apparatus according to the German standard DIN 53890. Each WRA value was determined as the average of 10 measurements along two directions: warp and weft [19, 22-24].

Statistical analyses of taking-up degree and WRA values were performed because important differences are often marked by the eventual imprecision with whom these determinations were carried out. How statistical calculations are extrapolated from the sample to the population it follows that do not require a large number of experiments to draw correct conclusions and relevant. One usually calculates the standard deviation (SD). These

values were calculated using MATLAB software [25, 26]. The standard deviation SD of the set of distinctive statistic data $\{WRA_1, WRA_2, \dots, WRA_n\}$ was calculated as in our previous work [22, 23]. In the same manner was performed the calculation of SD for taking-up degrees. In fact, SD shows the degree of values dispersion. The statistical analysis was completed with other values (SEM and CV).

Yellowness index, YI

Determination of the yellowness index was necessary to measure the degradation degree of cotton samples caused by chemical exposure and processing (i.e. the presence of catalysts and especially the high temperature during the curing stage).

Yellowness index per ASTM Method E313 was calculated with eq. 1:

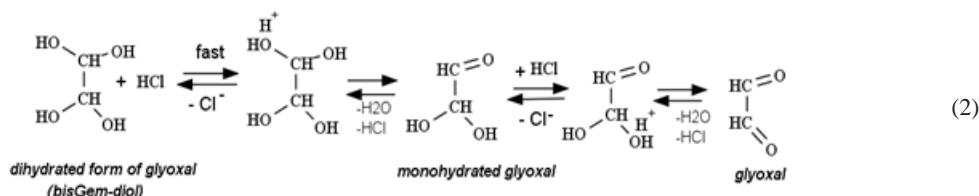
$$YI = (100 (C_x \cdot X - C_z \cdot Z))/Y \quad (1)$$

where X, Y, and Z are the CIE Tristimulus values that are determined with Spectroflash SF300/Datacolor Spectrophotometer. The coefficients C_x and C_z depend on the illuminant and observer. For the C illuminant and the 2° standard observer these coefficients have the following values: $C_x = 1.2769$ and $C_z = 1.0592$ [27].

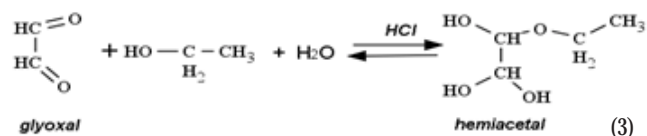
Results and discussions

Mechanism

The 40% glyoxal solution contains gem-diol, dimer and trimer dihydrated forms and only 11% anhydrous glyoxal [23]. In the presence of an inorganic acid, these dihydrated forms participate in dehydration reactions [1]. The water removal process can lead to the formation of the monohydrated or even to the non-hydrated form (eq.2).



In the presence of HCl (obtained at the end of chemical reactions 2), the addition of a diluted ethanol solution at glyoxal leads to hemiacetals or even acetals [11, 14], depending on the amount of ethanol used (eq. 3). Also in this case HCl serves as a catalyst.



In this article a small amount of ethanol (1%) was used, so according to chemical reaction 3 was obtained a hemiacetal. This hemiacetal interacts with a MCT-β-CD solution in the presence of NaOH. After the cotton is padded with the said solution, the drying and condensing/curing steps are carried out. During the curing step, a chlorine atom on a MCT triazine cycle interacts with an OH group of hemiacetals; an etheric bridge is formed that consolidates the obtained derivative which is actually the grafting agent. Grafting of cotton with this grafting agent is possible due to the high temperature during the curing step (160°C) and the presence of NaOH as a catalyst. And in

this case, ether bridges are formed between a chlorine atom (on another triazine cycle) of the grafting agent and the OH groups in the cellulose.

In conclusion, the realization of the grafting agent for this system (i.e. glyoxal/HCl + ethanol + MCT-β-CD/NaOH) involves several steps that are schematized in figure 1.

FT-IR analysis

The presence of the grafting agent onto cotton is very evident in figure 2. However, in order to understand the formation and behavior of the grafting agent, it was necessary to make *step by step grafting* and the afferent spectra are shown in figure 3.

In figure 3, the spectrum 3 belongs to the final sample (S1) and the spectra 1-2 belong to the two reference samples (W1 and W2). These samples were performed to better observe the effects of each compound existing in the studied system. For example, by comparing spectra 2 and 1, we infer the role of ethanol, and from the comparison of spectra 3 to 2 the role of MCT-β-CD is deduced.

In this system glyoxal taking into contact with ethanol in the presence of HCl. It is known that ethanol only reacts with HCl in the presence of a catalyst (ZnCl₂) to form the

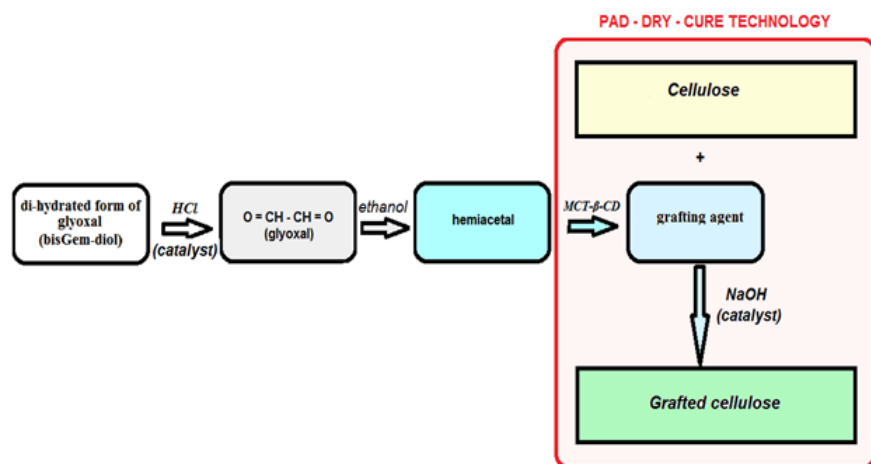


Fig. 1. Scheme of obtaining the grafting agent and its grafting on cellulose

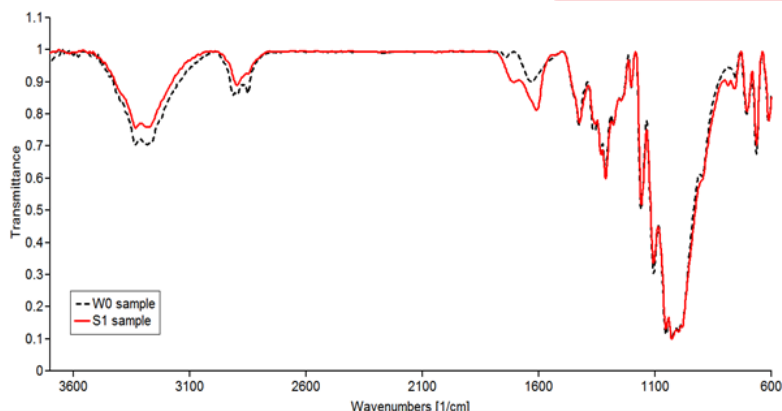


Fig. 2. FT-IR spectra for untreated cotton (W0) and sample S1 grafted with hemiacetal - MCT-β-CD derivative

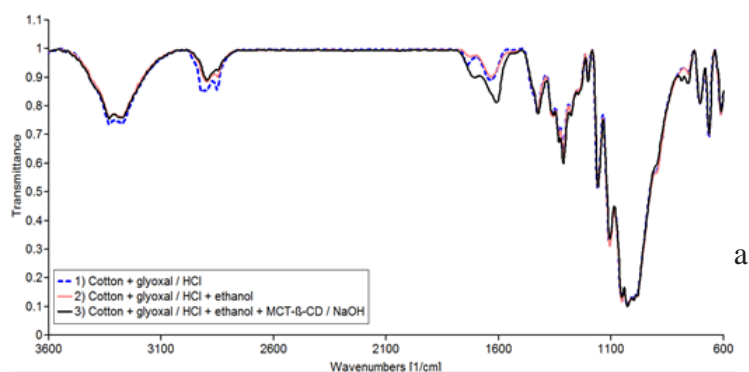


Fig. 3. FT-IR spectra for (glyoxal/HCl + ethanol) + MCT-β-CD/NaOH system: a) in the region 3600-600 cm⁻¹

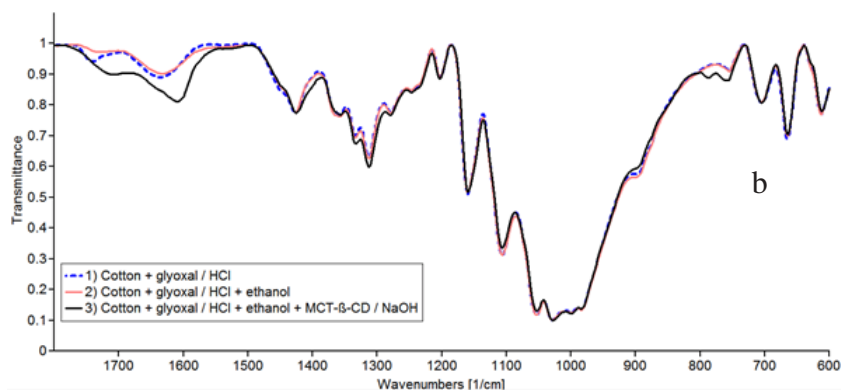


Fig. 3. FT-IR spectra for (glyoxal/HCl+ ethanol) + MCT-β-CD/NaOH system: b) detail in the region 1800-600 cm⁻¹

ethyl chloride. The absence of ZnCl₂ does not permit the reaction to occur, and ethanol will react with glyoxal. The main role of HCl is to be a catalyst. In the same time, HCl can have a destructive role leading to a slight cotton degradation; this fact can be noticed in the decrease of the afferent C-H stretching peaks (in the region 2916-2851 cm⁻¹) (fig. 3a). As a catalyst, HCl causes the elimination of H₂O from the dihydrated forms of the glyoxal and the formation of non-hydrated glyoxal (according to eq. 2). This is confirmed by the presence of a peak at 1746 cm⁻¹ (for C = O of the aldehyde type) on spectrum 1 (fig. 3b).

The absence of absorption bands specific to Cl (787 cm⁻¹) on the FT-IR spectrum of the W2 sample (i.e. cotton + glyoxal/HCl + ethanol, in fig. 3b) indicates that in this system HCl works as a catalyst.

The glyoxal reaction with 1% ethanol (in the presence of HCl) determines the formation of hemiacetals, which is confirmed by the decrease of the peak at 1746 cm⁻¹ afferent to the carbonyl group (C=O) and the increase of the peaks from 1053 and 1107 cm⁻¹ (OH) (eq. 3 and fig. 3b). This is easily observed by comparing spectra 2 to 1.

The presence of etheric bridges in the final grafting agent (obtained from the hemiacetal interaction with MCT-β-CD) as well as the existence of covalent links between the grafting agent and cotton are confirmed by the increase of the peaks at 1204 and 1159 cm⁻¹ (symmetric C-O-C and anti-symmetric stretchings [28]).

The presence of MCT-β-CD is deduced. β-CD on the cotton sample (S1) is also confirmed by the appearance of the peak 1535 cm⁻¹ assigned to C=N stretching from triazine, the increase of the height of the peak at 1630 cm⁻¹ (water absorption by β-CD), and the appearance of peaks at 787 cm⁻¹ (assigned to Cl atoms bound to MCT cycle and not involved in the chemical reaction with cellulose).

Grafting results

The grafting process is confirmed by both the FT-IR analysis (figs. 2 and 3), and by increase of taking-up degree (fig. 4) and WRA values (fig. 5).

Figure 4 confirms the idea of bigger taking-up, when many compounds are added in the impregnation bath. SD values are very small that indicate the uniformity of each studied sample set.

WRA increases as a proof of the increased length of the graft attached on cotton (fig. 5). The biggest WRA is obtained in case of the final sample (S1) which proves the attachment of the graft consisting of the hemiacetal - MCT-β-CD derivative. Figure 5 shows the WRA values obtained for the 10 samples from types W0, W1, W2 and S1 and also the size of SD.

The computation of SD and CV required the calculation of mean of WRA (table 2). Very low values for SD, SEM and CV indicate that the populations studied statistically are homogeneous.

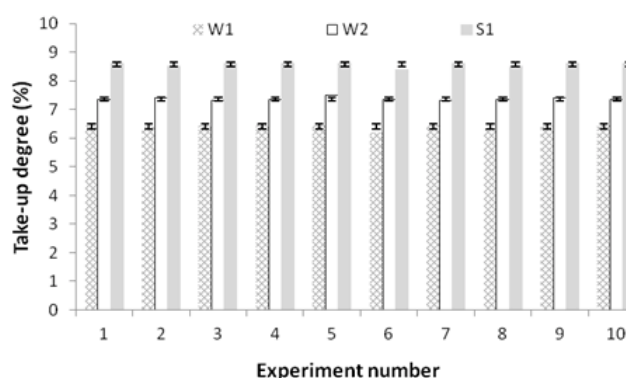


Fig. 4. Values for the take-up degrees of all 10 samples used in statistical analysis of the 3 sample sets (W1, W2 and S1) (same codes as in table 1)

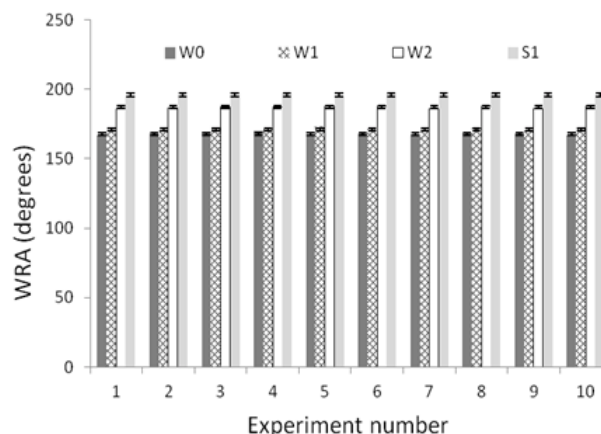


Fig. 5. WRA values for samples W0, W1, W2 and S1 and indication of error bars for standard deviation (the same coding as in table 1)

Table 2
STATISTICAL ANALYSIS RESULTS

Sample Code ^a	Statistical analysis of WRA			
	\overline{WRA} (degrees)	SD ^b	SEM ^c	CV ^d
W0	168	1.15	0.36	0.68
W1	171	1.12	0.35	0.65
W2	187	0.81	0.25	0.43
S1	196	1.09	0.35	0.56

^a Sample code is same as in Table 1;

^b SD is the standard deviation;

^c SEM is the standard error of the mean;

^d CV is the coefficient of variation.

Yellowness index, YI

The yellowness index (YI) was calculated both for standard samples (W0, W1, W2) and for final sample (S1). Each studied sample comes into contact with an inorganic

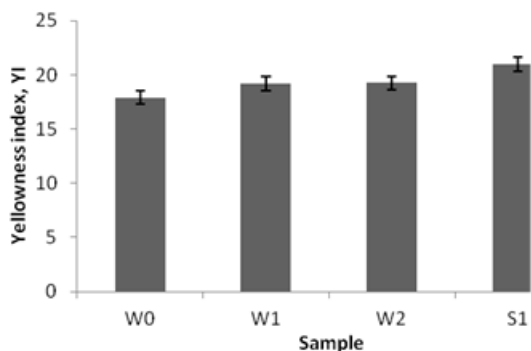


Fig. 6. The mean of Yellowness index for each studied sample (same code as in table 1)

acid/ alkaline compound (as catalysts) and high temperature during processing so there is the risk of degradation and yellowing.

In figure 6 are indicated the YI values, as arithmetic mean for the 10 samples of each type studied (W0, W1, W2, and S1).

Figure 6 indicates differences in YI values between the reference samples and the final sample (S1). The W1 sample coming into contact with HCl suffers a certain degradation, which is observable in obtaining a higher YI (YI = 19.2) than the untreated cotton sample (YI = 17.9). This degradation of W1 sample was also evidenced by the FT-IR analysis in the 2916-2851 cm^{-1} region. Instead, the presence of ethanol does not affect the sample W2 (YI = 19.26) because the ethanol does not come in direct contact with cotton but with glyoxal (when converted to hemiacetal, also in the presence of HCl as a catalyst). S1 sample has YI = 20.97 because at 160°C during curing, MCT- β -CD is lightly degraded and yellowed. Degradation is the result of dehydration of carbohydrates from β -cyclodextrin. However, yellowing decreases after rigorous washing after grafting.

Conclusions

The grafting agent is a hemiacetal-MCT- β -CD derivative. Obtaining hemiacetal is carried out by dehydration of the dihydrated forms of the glyoxal (until a high percentage of non-hydrated glyoxal is obtained) and the reaction with the dilute ethanol solution. Both reactions have the same catalyst, HCl. The grafting of cotton with hemiacetal - MCT- β -CD can be characterized by FT-IR analysis and statistical analysis. The grafting process has led to increase of wrinkle-proofing effects (i.e. take-up degrees and WRA values). The grafting effects were statistically analyzed by computing SD, SEM and CV.

The statistical analyses results indicate a great uniformity of each population studied statistical and the mean values of the wrinkle-proofing effects are representative of these populations.

The yellowing of the samples was evidenced by the yellowness index determined by the E313 method. The yellowing of samples W1 and W2 is due to the contact of the cotton sample with HCl at high temperature during grafting. The yellowing index of sample S1 is 20.97 and is the result of a slight degradation of MCT- β -CD during the curing phase of pad-dry-curing technology. The sample color S1 can return almost to the original one if after the grafting, an energetic wash is done.

References

- FRATZKE, A. R. Jr. Kinetic analysis of the dimerization and disproportionation of aqueous glyoxal. Retrospective Theses and Dissertations. Paper 7845. Iowa State University, Ames, Iowa, 1985.
- KIELHORN, J., POHLENZ-MICHEL, C., SCHMIDT, S., MANGELSDORF, I., Concise International Chemical Assessment Document 57-GLYOXAL, Geneva, 2004, p. 41.
- TONG, C., BLANCO, M., GODDARD, W. A. III, SEINFELD, J. H., Environ. Sci. Technol., **40**, 2006, p. 2323.
- ALAR, V., JURAGA, I., RUNJE, B., ALAR, Z., Mat. -wiss. u. Werkstofftech, **40**, no. 12, 2009, p. 910.
- CHASTRETTE, F., BRACOD, C., CHASTRETTE, M., MATTIODA, G., CHRISTIDIS, Y., Bull. Soc. Chim. Fr., **11**, 1983, p. 33.
- FRATZKE, A. R., REILLY, P. J., Int. J. Chem. Kinet., **18**, no. 7, 1986, p. 757.
- FRATZKE, A. R., REILLY, P. J., Int. J. Chem. Kinet., **18**, no. 7, 1986, p. 775.
- PANKAJ, D. Glyoxal: a techno-commercial profile. Chemical Weekly, 2007, p. 217
- WHIPPLE, E. B., J. Am. Chem. Soc., **92**, no. 24, 1970, p. 7183.
- MATTIODA, G., BLANC, A., GLYOXAL. Ullmann's Encyclopedia of Industrial Chemistry, Fifth Edition, Verlag Chemie, Weinheim, New York, Vol. A 12, 1989, p. 491-494.
- NENTESCU, C.D., Organic Chemistry, Didactic and Pedagogic Ed., Bucharest, 1980.
- *** Glyoxal. Brochure der Société Française, Hoechst A. G. Ed., Paris, 1984, p. 1-32.
- *** Glyoxal 40% (Aqueous Solution) - Testing for Subacute (29-Days) Inhalation Toxicity in Male and Female Wistar Rats, Report no. 94.1056, Hoechst A.G. Ed., Frankfurt, Pharma Development, Corporate Toxicology, 1995.
- CLAYDEN, J., GREEVES, N., WARREN, S., WOTHERS, P., Organic Chemistry, University Press, Oxford, 2000.
- GUPTA, N., NAAZ, R., NIGAM, G. D. Journal of Pharma and Bio Sciences, **1**, no. 4, 2010, p. 224.
- VOLLHARDT, K. PETER C., NEIL E. S. Organic Chemistry: Structure and Function. New York: W.H. Freeman and Company, 2007.
- CAREY, F. Advanced Organic Chemistry. 5th ed. Springer, 2007.
- SZEJTLI, J. Chemistry, physical and biological properties of cyclodextrins. In J. M. Lehn, J. L. Atwood, J. E. D. Davies, D. D., Macnicol & F. Vogtle (Eds.), Comprehensive supramolecular chemistry. Oxford: Pergamon (Volume 9, Chapter 2, p. 5), 1996.
- REHMANN, L., YOSHII, H., FURUTA, T. Starch/Stärke, **5**, **2003**, p.313.
- POPESCU, V., MURESAN, E.I., GRIGORIU, A.-M., Carbohydrate Polymers, **86**, no. 2, 2011, p. 600.
- POPESCU, V., SANDU, I. Rev. Chim. (Bucharest), **65**, no. 7, 2014, p. 811.
- POPESCU, V., SANDU, I. C. A., POPESCU, G., Rev. Chim. (Bucharest), **67**, no. 11, 2016, p. 2184.
- POPESCU, V., POPESCU, G., SANDU, I.C.A. Rev. Chim. (Bucharest), **68**, no.8, 2017, p. 1884.
- POPESCU, V., MURESAN, A., POPESCU, G., BALAN, M., DOBROMIR, M., Carbohydrate Polymers, **138**, 2016, p. 94.
- POPESCU, G. Programing of PCs in MATLAB; TehnoPress Ed.: Iasi, Romania, 2009.
- POPESCU, G. Numerical resolvings in MATLAB; TehnoPress Ed.: Iasi, Romania, 2009.
- *** Yellowness indices. Application note/ HunterLab, 8 no. 5, 2008, p.1.
- ZAHARIA, C., STANESCU, P.O., Mat. Plast., **51**, no. 2, 2014, p. 119

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