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Tosylation Optimization, Characterization and Pyrolysis Kinetics of Cellulose Tosylate

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Cellulose tosylates with different degree of substitution (DS) were prepared by reacting cellulose in DMAc/LiCl with *p*-tosyl chloride at 8 °C in the presence of triethylamine. The effects of number of mole of tosyl chloride (A), number of mole of base (triethylamine) (B) and reaction time (C) on DS were studied by Response Surface Methodology (RSM) known as Box-Behnken Design (BBD). It was found that A is the main factor influencing DS and the interaction between B and C is negligible. An optimal DS value of 2.79 was obtained with A = 6.96 and B = 2.99 mol eq. at a reaction time C = 24 h. The synthetic polymers were characterized by elemental analyses, FT-IR, NMR and SEM spectroscopy. The results indicated that the cellulose was successfully tosylated with various DS. Cellulose tosylate with DS = 0.5 and DS = 2 were subjected to thermo-gravimetric analysis under inert atmosphere. The kinetic parameters were determined by Coats-Redfern method. Thermal analyses and kinetics indicates that the lower DS of tosyl group the higher thermal stability is. Thus, cellulose lose its stability after esterification with *p*-tosyl chloride.

Introduction

Cellulose, the most common organic compound on Earth, is the major structural component of the cell wall of most plants, many forms of algae. It is mainly used to produce paper products such as cotton, linen, and rayon for clothes, cellulose esters for a plastic used in films and eyeglass frames, and nitrocellulose for explosives.[1–3] The knowledge of morphology and structure of the cellulose molecule in the solid state lead to understand its chemical and physical properties.[4] Cellulose structure is a linear homo-biopolymer composed of repeat units of the monomer glucose. The presence of the hydroxyl groups (-OH) in an anhydroglucose unit (AGU) of cellulose predetermines the occurrence of a system of inter- and intra-chain hydrogen bonds in the native polymer. This strongly limits the solubility of cellulose in water and typical organic solvents.[5] However, Special solvents were developed to dissolve cellulose both for shaping and homogeneous chemical modification of the biopolymer.[6] The most important aqueous media such as NaOH–CS_2 and *N*-methylmorpholine *N*-oxide monohydrate have disadvantages concerning the environmental impact, chemical stability and difficult recycling. Non-aqueous media like DMAc/LiCl,[7] ionic liquids (ILs) and IL/Co-solvent were applied as the homogeneous media for cellulose modification in lab scale but these solvents system seem improper for large scale processing.[8–11] The principle aim in research on cellulose fonctionalization is of course the synthesis of new macromolecular species and the description of their properties. Cellulose bio-polymer is mostly used due to its neutrality and its wide applications in food medical products, pharmaceutical industries, packaging, textile, etc.

The cellulose tosylate ester is one of the most promising derivatives for the creation of new polymeric materials by nucleophilic displacement (SN) reactions and thereby it can open up new paths for the utilization of cellulose.[12–14] The tosyl group serves as leaving group in displacement reactions or as protecting group in further modifications of the remaining free OH groups.[13]

The kinetics of degradation of materials is essential for investigating thermal stability of compounds. Thus, it is very useful to understand the mechanisms controlling the interaction between chemical and physical processes. Degradation kinetics can be studied by several methods, but one of the most popular and simplest techniques widely used in the literature is the thermogravimetric analysis.[15] The kinetic parameters, apparent activation energy and frequency factor, can be calculated by different methods such as Friedman method,[16–19] and Coats–Redfern method.[20] Many researchers have examined characteristics of thermal degradation including kinetic parameters on cellulose and cellulose derivatives.[21] Therefore, these results are not directly comparable since

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different methods were used under different conditions and heating rates.

In the current work, we tried to modify the hydroxyl groups (6-OH, 2-OH and 3-OH) of microcrystalline cellulose (MCC) in DMAc/LiCl (8%) by *p*-tosyl chloride (TsCl) to synthesis cellulose tosylate with various degree of substitution (DS). This reaction is affected by reaction time, molar ratio of reactant/AGU and the amount of base. These parameters can enhance or reduce the DS of obtained product. Indeed, a system can have a large number of parameters but generally only a group of them are important or significant for control the DS of cellulose ester. Screening experience practices cost-effective design to determine important factors to identify optimal conditions and maximize DS. Recently, research work on esterification reactions has been based on the optimization of reaction conditions.[22–26] It is also useful to applying the Response Surface Methodology (RSM) experimental scheme. RSM is a group of statistical techniques for design, experiential modeling and process optimization, where the studied responses are influenced by several RMS parameters.[27,28] Optimization was performed by plotting three-dimensional response surfaces, in which the degree of DS was as the relevant responses. The main purpose of RSM is to check the optimum operational conditions for a given system or to determine a region that satisfies the operational specifications. It might then be possible to obtain a second-order polynomial prediction equation or some other mathematical equations to describe the experimental data obtained at some particular combination of input variables.

The primary aim of this study is to determine the optimal reaction conditions for synthesis of cellulose tosylate in DMAc/LiCl solvent system by conversion of the -OH groups of MCC through the use of a Box Behnken design and RSM techniques. This optimization was based on the maximization of DS. Currently, there are no published studies related to the optimization of reaction conditions for synthesis of cellulose tosylate in DMAc/LiCl using design experiments to our knowledge. In addition, most of published works were conducted using conventional methods of optimization, i.e. investigating a process by varying one factor whilst maintaining all other factors involved at constant levels; such methods are time-consuming and of low efficiency in optimizing a given process. Furthermore, the conventional optimization process cannot give an indication of the interactive effects between any two factors in a multi-variable system. Response surface methodology can avoid the limitations of conventional methods and is commonly used in many fields. The obtained products were characterized by means of elemental analysis as well as FT-IR and NMR spectroscopies.

The secondary aim of this paper is to determine the kinetic parameters, activation energy (E_a) and pre-exponential factor (A), of pure MCC and cellulose tosylate with DS values of 0.5 and 2. In addition, the effect of DS of tosyl groups on thermal decomposition of cellulose tosylate is discussed. For this purpose, thermal decomposition and thermal behavior results of these samples is investigated using thermo-gravimetric analysis (TGA). Determination of the mechanism and kinetics of thermal degradation of materials developed from cellulose are important because designing systems based on the pyrolysis of cellulosic materials requires good understanding of the kinetic of these processes. Consequently, to reach the kinetic parameters from thermogravimetric data, we opted for Coats Redfern method given its precision in the determination of degradation mechanisms for one single heating rate.

Results and Discussion

Synthesis of cellulose tosylate

Cellulose tosylate was synthesized as shown in Figure 1. There are three hydroxyl groups in microcrystalline cellulose chains, a primary hydroxyl at C-6 and a secondary hydroxyl at C-2 and at C-3. The C6-OH, C1-OH and C3-OH are preferred, respectively, for the tosylation reaction of MCC in DMAc/LiCl (8%) system

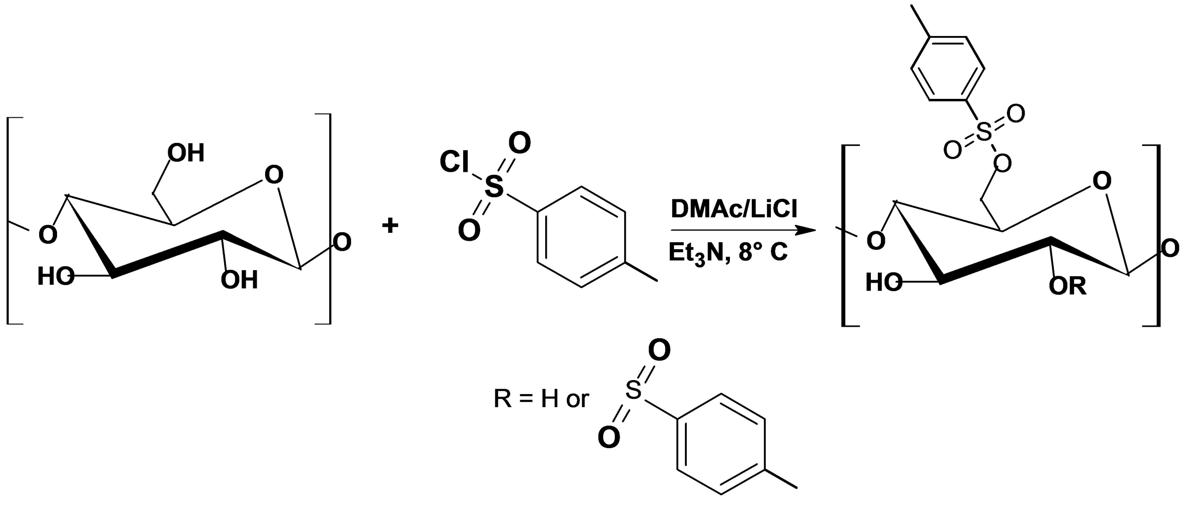

Figure 1. Reaction scheme showing the synthesis of cellulose tosylate.

solvent due to the lack of steric hindrance against neighboring acetamide groups and lack of intramolecular hydrogen bonds with neighboring repeating units. The reaction was carried out homogeneously at 8 °C for 24 h in the presence of triethylamine (Et_3N) as a base. The cellulose tosylate esters are valuable intermediates for various subsequent reactions in the design of advanced cellulosic materials.

Modeling results

The responses of 15 experimental runs are shown in Table 1. The response that evaluated is the degree of substitution (DS) of cellulose tosylate derivatives. The results were studied using the analysis of variance (ANOVA) presented in Table 2.

The high F value located in the ANOVA Table shows that the model is significant. In addition, ANOVA specifies which of the parameters are concerned. We used 95% confidence to assess the ability to predict the model. A P-value shows than 0.05 shows a significant factor, however a P-value greater than 0.1 shows an irrelevant factor. For the current work, the variables A, B, C, AB, AC, A^2, B^2 and C^2 are all relevant variables for the DS. The remaining factor (BC) is not relevant. Also, despite not being significant, was included in the final model. The final model obtained is represented by Equation (1):

$$DS = 0.5133 + 0.8237\,A + 0.1975\,B + 0.2837\,C + 0.14\,AB + 0.2375\,AC + 0.202\,A^2 + \mathbf{0.1795\,B^2} + \mathbf{0.1795\,C^2} \tag{1}$$

The statistical analysis (Table 3) indicates that the model has a very acceptable estimation capacity, it is reasonable and statistically very significant, with an $R^2_{adj} = 99.57\%$ and a p-value of 0.647. This shows that the theoretical model does not explain only 0.42% of the total variations.

The predicted DS was plotted against the experimental results, as shown in Figure 2, where the regression line shows that the experimental and predicted results are very close. Consequently, it can be concluded that the data are within the confidence limits, and that the model has an adequate adjust respect to the real data.

Optimize Response

The mathematical model above is found for plotting the contour plots and the response surfaces. Figure 3 shown the contour plot and the response surface curves in the plan: {n (Tosyl chloride)*n (Base)}; {n (Tosyl chloride)*Reaction time} and

Table 1. Matrix of the Box-Behnken experimental design of degree of substitution.

Run	**A** (mol eq.)	**B** mol eq.	**C** (h)	**DS_{exp}** -
1	4(0)	3(1)	10(-1)	0.89
2	7(1)	1(-1)	17(0)	1.39
3	4(0)	2(0)	17(0)	0.59
4	1(-1)	1(-1)	17(0)	0.05
5	4(0)	3(1)	24(1)	1.42
6	7(1)	2(0)	24(1)	2.3
7	4(0)	2(0)	17(0)	0.53
8	4(0)	2(0)	17(0)	0.50
9	7(1)	2(0)	10(-1)	1.29
10	1(-1)	2(0)	24(1)	0.15
11	1(-1)	2(0)	10(-1)	0.09
12	7(1)	3(1)	17(0)	2.02
13	1(-1)	3(1)	17(0)	0.12
14	4(0)	1(-1)	10(-1)	0.38
15	4(0)	1(-1)	24(1)	1.05

Table 2. Analysis of variance (ANOVA) for DS.

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A: Number of mole of TsCl	5.42851	1	5.42851	3333.78	0.0000
B: Number of mole of base	0.31205	1	0.31205	191.64	0.0000
C: Reaction time	0.644112	1	0.644112	395.57	0.0000
AA	0.150785	1	0.150785	92.60	0.0002
AB	0.0784	1	0.0784	48.15	0.0010
AC	0.225625	1	0.225625	138.56	0.0001
BB	0.119078	1	0.119078	73.13	0.0004
BC	0.0049	1	0.0049	3.01	0.1433
CC	0.216385	1	0.216385	132.89	0.0001
Total error	0.00814167	5	0.00162833		
Total (corr.)	7.12476	14			

Table 3. Response coefficient values and statistics.

R^2	99.81%
R^2_{adj}	99.57%
Standard Error of Est	0.046
Mean absolute error	0.022
Durbin-Watson statistic	2.197 (P = 0,647)

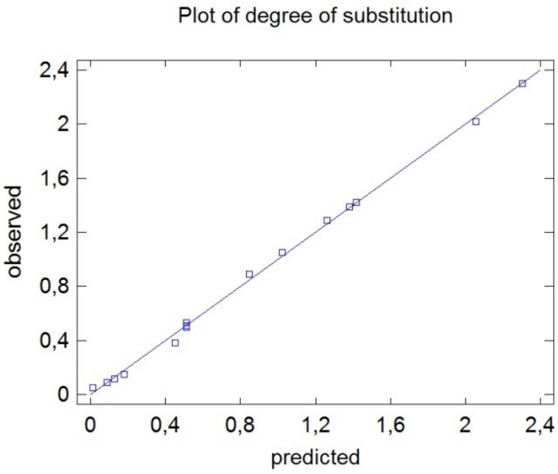

Figure 2. Plot of DS of cellulose ester.

{n (Base)*Reaction time}. Parameters not displayed have been set to their average value (0).

Figure 3 (a) displays the interaction of mole ratio of tosyl chloride/anhydroglucose units and number of mole of base, where the reaction time was constant at 17 h. The estimated response surface reinforces the influence of those parameters. Figure 3 (b) showed the combined effect of mole ratio of tosyl chloride/AGU and reaction time on DS, where the number of mole of base was constant at 2 molar equivalents. It indicated that both factors have a significant effect on the response. But the mole ratio of tosyl chloride/AGU is the most relevant factor, since its increase causes an increase of DS values from 1.3 to over 2.3. Figure 3 (c) showed the combined effect of number of mole of base and reaction time, where the mole ratio of tosyl chloride/AGU was constant at 4 molar equivalents. Moving along number of mole of base axis does not change well in response compared to others parameters.

The procedure used in this work helps to determine the combination of experimental parameters, which optimize the response. Maximizing Equation (1) leads to the optimal values of each factor, which gives the desirable DS, displayed in Table 4. The confirmation run was realized. The predicted theoretical response was a DS of 2.79, and the confirmation run was 2.71. This value shows that the model developed has the power to predict the response with high precision and that it is very suitable for experimental data.

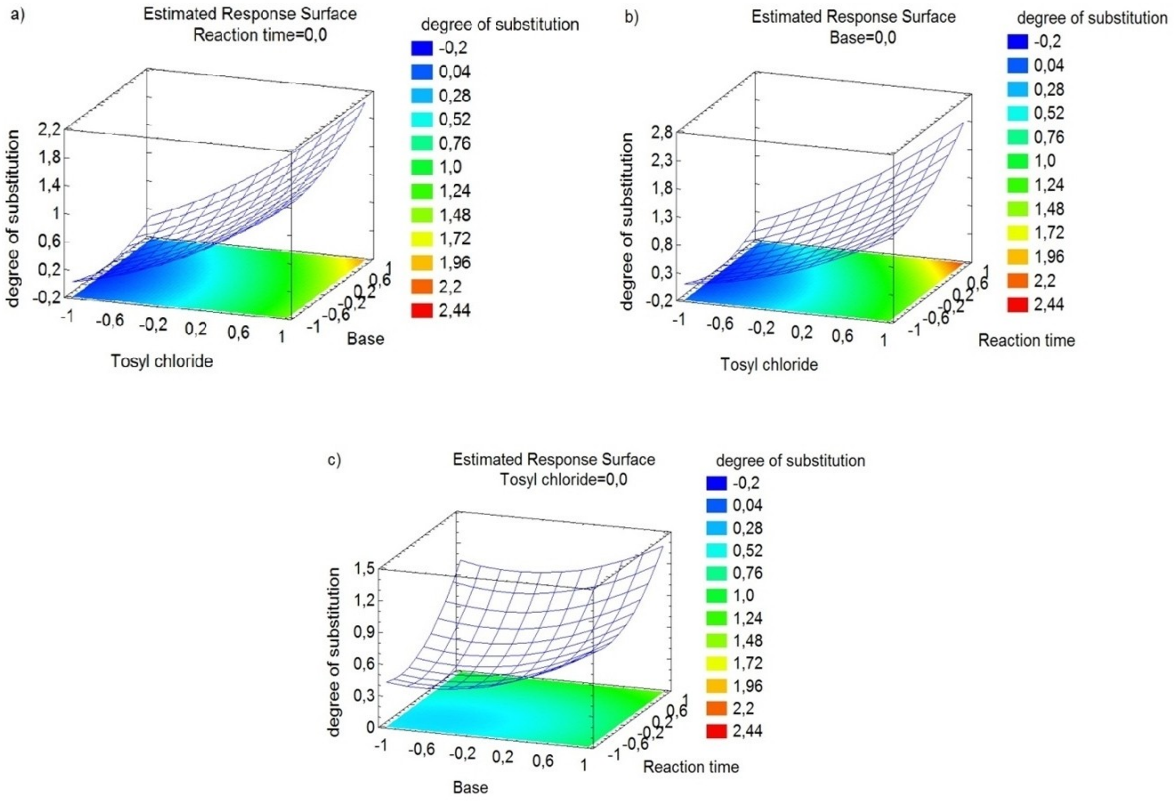

Figure 3. Estimated Response Surface and Contour plots
a: Reaction time = 17 hours, b: n (base) = 2 mol eq., and c: n (Tosyl chloride) = 4 mol eq.

Table 4. Optimal parameter values.

Parameters	Coded variable	Optimal values	Real values	Maximize DS optimum value
Number of mole of tosyl chloride (mol eq.)	A	0.9874	6.96 mol eq.	2.79
Number of mole of base (mol eq.)	B	0.9999	2.99 mol eq.	
Reaction time (h)	C	1.0	24 h	

The optimal DS value of 2.79 obtained in this study was apparently higher than it was reported in previous studies. Celluloses tosylates with DS values between 0.4 and 2.3 were prepared by reacting cellulose, with a degree of polymerization in the range 280–5100, dissolved in DMAc/LiCl with tosyl chloride of molar ratio/AGU ranging from 0.6 to 9.0 within 24 h at 8 °C.[29] Similarly, Schmidt et al. prepared a tosylated cellulose, in an eco-friendly medium NaOH-urea, with DS values ranging from 0.43 to 1.68 with a molar ratio of tosyl chloride/AGU in the range 3–7 mol eq.[12] The variation of DS values in literatures may be due to the nature of cellulose and its degree of polymerization, and to the difference in reaction conditions such as molar ratio of reactant and catalyst/AGU, reaction medium, temperature and reaction time, etc.

Characterization

FT-IR Spectroscopy

FT-IR spectra of the MCC, and cellulose tosylate are shown in Figure 4. It can be seen that spectrum of the cellulose tosylate provide a clear evidence of tosylation by showing the presence of some important peaks at 813 cm^{-1} for aromatic ring (C–H) stretching, 1116 cm^{-1} for (C–O-C) asymmetric stretching and ring asymmetric stretching for cellulose. The appeared peaks at 1172 and 1370 cm^{-1} correspond, respectively, to (SO_2) group symmetric and asymmetric stretching, 1500 and 1456 cm^{-1} for aromatic (C–C) stretching. While, the peaks at approximately 3459 and 2924 cm^{-1} indicated the presence OH group and C–H of MCC. These results proved that the cellulose tosylate was obtained successfully in these reaction conditions.

NMR spectroscopy

The ^{13}C NMR and ^{1}H-NMR spectra for cellulose tosylate are shown in Figure 5. In the ^{13}C NMR spectrum, the signals at δ 21.15 ppm and δ 125.46–144.90 ppm were assigned to p-CH_3 and aromatic carbons of the tosyl groups, respectively. The signals at δ 60.25–102.85 ppm were attributed to the carbons of cellulose backbone.[29, 30, 31]

In the ^{1}H-NMR spectrum, the signal at δ 2.43 ppm is assigned to 3 protons for methyl of the tosyl groups, the appeared signals at δ 7.12–7.82 ppm were attributed to the 4 phenyl protons of tosyl groups, in addition the signals at δ 3.3–5 ppm were assigned to 7 protons for cellulose backbone. These results indicated the successful synthesis of cellulose tosylate.

Scanning Electron Microscopy (SEM)

Figure 6 displays the morphological structure of MCC (a) and cellulose tosylate derivative (b). The SEM images of the surface of MCC and cellulose tosylate show clear differences between them. The microcrystalline cellulose is principally composed of platelet-like cellulose micro-fibrils, created a spherical agglomeration. However, the surface structure of cellulose tosylate (b)

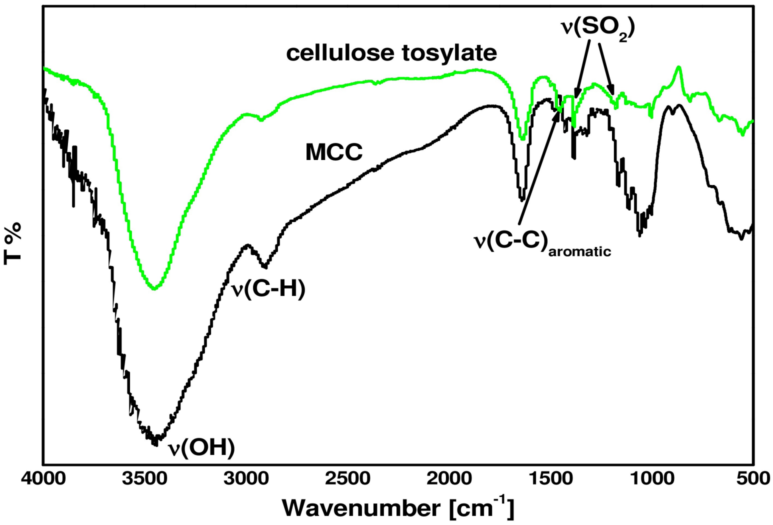

Figure 4. Infrared spectrum of cellulose and cellulose tosylate.

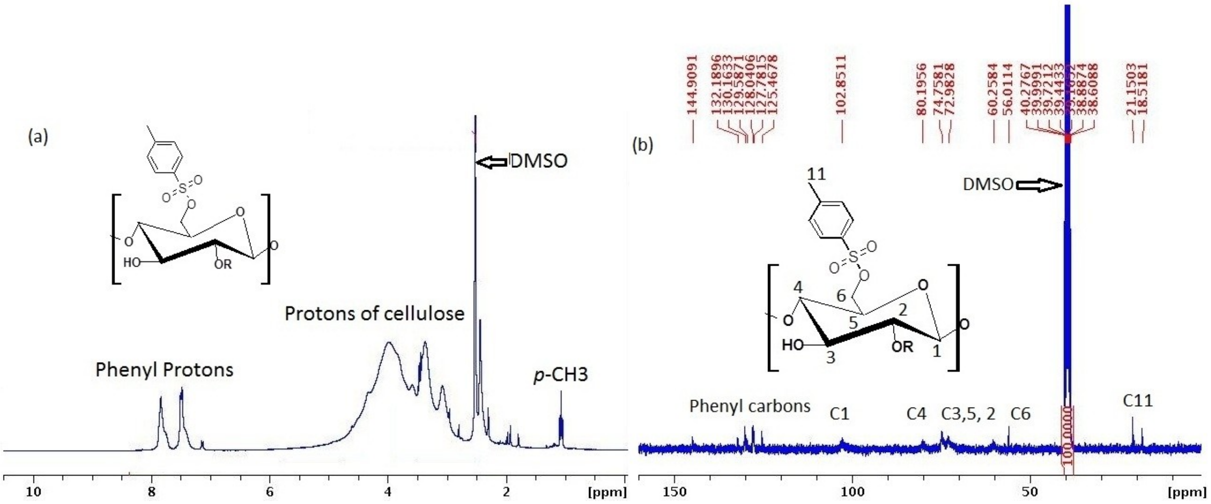

Figure 5. ^{1}H NMR (a) and ^{13}C NMR (b) for cellulose tosylate.

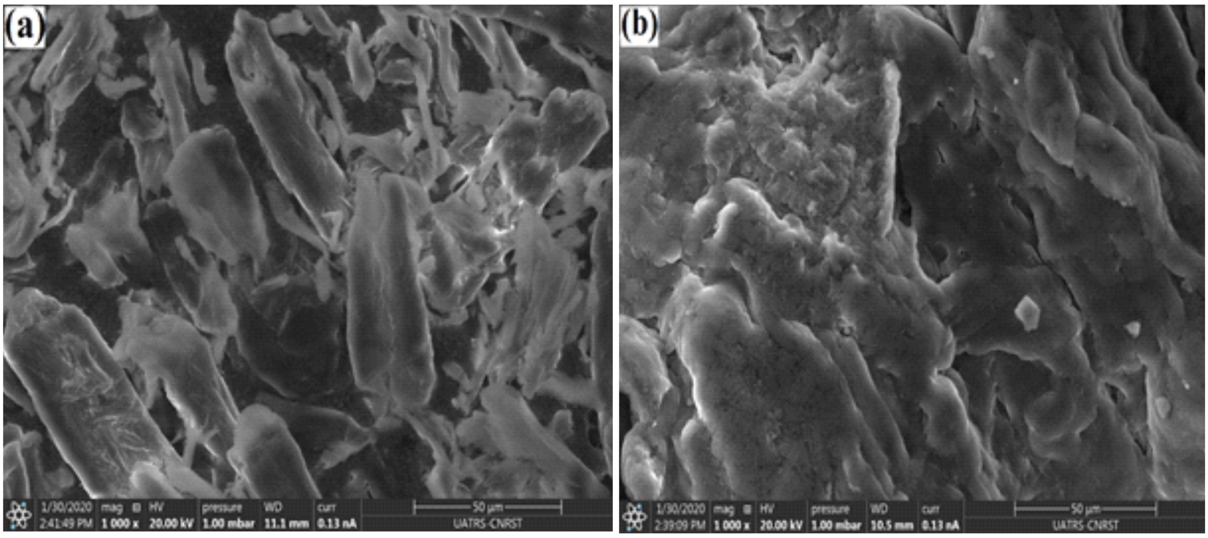

Figure 6. SEM microphotographs of MCC (a) and cellulose tosylate derivative (b), (magnification x1000).

is loose and porous, the surface roughness of cellulose tosylate were increased than unmodified MCC. Interruption of the backbone of cellulose tosylate polymer can explain this observation as a result of reaction of hydroxyl group (-OH) of MCC with *p*-tosyl chloride and breaking of hydrogen bonds of MCC, in addition this change of the morphology of cellulose tosylate as a consequence of the hydrophobic phenyl groups newly introduced. We speculated that loose and porous structure result in weaker thermal stability of cellulose tosylate.

Thermogravimetric analysis (TGA-DTG)

Interesting results appear from thermal analysis of the MCC (a) and cellulose tosylate with DS = 0.5 (b) and DS = 2 (c) which were studied by thermo-gravimetric analysis (TGA-DTG) in a range of temperature (room temperature- 500 °C) under inert atmosphere (Figure 7). This Figure shows that the thermal stability of cellulose tosylate varies with DS. The temperature for 5% weight loss for the unmodified MCC is higher than that of the cellulose tosylate with DS values of 0.5 and 2. A decrease in thermal stability could promote an earlier a departure of water of the polymers and generate a protective char layer on the surface of the polymers at a lower temperature.[32] The first region of thermal decomposition of polymers range from room temperature to 105 °C is due to the departure of free water of the polymer.[33] The MCC sample (a) degrades between 270 and 360 °C and the speed of mass loss has a peak around 304 °C (mass loss 49%), these results are consistent with those of the literature.[34–36] As anticipated, the TGA and DTG spectra of the cellulose tosylate (b and c) are different from those of the

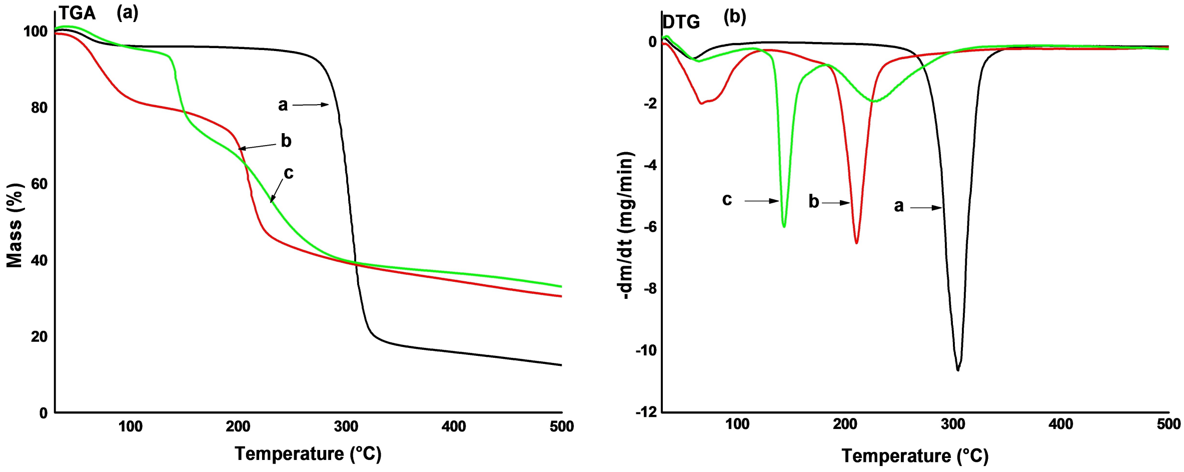

Figure 7. Comparison of the thermo-gravimetric analysis TGA-DTG data for different samples: MCC (a), Cellulose tosylate with DS = 0.5 (b) and DS = 2 (c).

unmodified microcrystalline cellulose. The TGA curve of cellulose tosylate of DS = 0.5 is characterized by a clearly visible decomposition at a temperature range of 178 to 266 °C, mass loss about 41%, with peak of speed of mass loss around of 210 °C. The TGA and DTG spectra for cellulose tosylate of DS = 2 can be decomposed into two stages.

The first one is degrade between 122 and 180 °C with a DTG peak centered at 143 °C (mass loss 15%). The second stage of degradation is located between 180 and 302 °C with a maximum mass loss speed at 226 °C (mass loss 43%), is related to slower decomposition processes. This indicates that the content of grafted tosyl group on cellulose backbone is an important factor influencing the thermal degradation, i.e., the lower DS leads to a higher thermal stability. The effect of the DS of tosyl group on the decomposition temperature of synthesized material is clearly seen.

Kinetic parameters estimation

Curves indicating the solid-state mechanisms $-\mathrm{Ln}(g(\alpha)/T^2)$ as function $1/T^2$for MCC (a), and cellulose tosylate with DS = 0.5 (b) and DS = 2 (c) are given in Figures 8. These plots indicate that MCC and modified cellulose breakdown in two stages even through different temperature range. The values of activation energy (E_a), frequency factor (A) and correlation factors R^2 are listed in Tables 5 and 6, respectively for first and second degradation step. According to the aforementioned tables, the parameters A and E_a evolve in the same direction and their values depends on the degradation mode for both MCC and cellulose tosylate. Moreover, for the first decomposition stage, it appears from Table 5 that the best correlation coefficients are obtained for the mode **F0** and **F1** for microcrystalline cellulose, **F1** for cellulose tosylate with DS = 0.5. The value of the activation energy for the latter 'cellulose tosylate with DS = 0.5' is almost 5 times lower than that of microcrystalline cellulose (Table 5). The presence of tosylate group would have an accelerating effect on the thermal decomposition. For cellulose tosylate with a DS value of 2, the activation energy values are negative for all examined degradation modes (Table 5). This indicates that the mechanism is complex. With respect to the second degradation step, the degradation mechanisms with the best mathematical fit are **P2** and **P3** for microcrystalline cellulose, **F0, F1, P2, P3** and **A3** for cellulose tosylate with DS = 0.5 and **F1, F2, P2** and **P3** for cellulose tosylate with a DS of 2. This latter requires slightly less energy to thermally decompose than cellulose tosylate with DS = 0.5

Table 5. Thermal kinetic results for MCC and cellulose tosylate first region of pyrolysis.

DM	*MCC*			*Cellulose tosylate with DS = 0.5*			*Cellulose tosylate with DS = 2*		
	R^2	E_a	Ln A	R^2	E_a	Ln A	R^2	E_a	Ln A
F1	0.669	38.777	10.538	0.969	8.0615	-1.0882	0.927	-306.996	-
F0	0.698	36.568	11.086	0.980	-157.092	-	0.933	-294.319	-14.534
F2	0.636	41.389	9.8863	0.955	-183.903	-	0.921	-320.291	-
F3	0.590	39.209	9.5435	0.934	-199.424	-	0.914	-334.202	-
R2	0.675	33.728	12.330	0.976	-160.129	-	0.9301	-300.580	-
R3	0.672	33.897	12.687	0.975	-161.983	-	0.929	-302.701	-
P3	0.401	5.743	14.207	0.966	-39.710	-	0.9167	-86.776	-
D3	0.608	20.552	13.083	0.966	-105.859	-	0.926	-196.540	-
P2	0.572	12.543	13.959	0.976	-68.199	-	0.925	-138.662	-
A2	0.547	13.477	13.768	0.962	-74.733	-	0.922	-143.220	-
A3	0.388	6.401	14.132	0.952	-43.607	-	0.910	-91.002	-

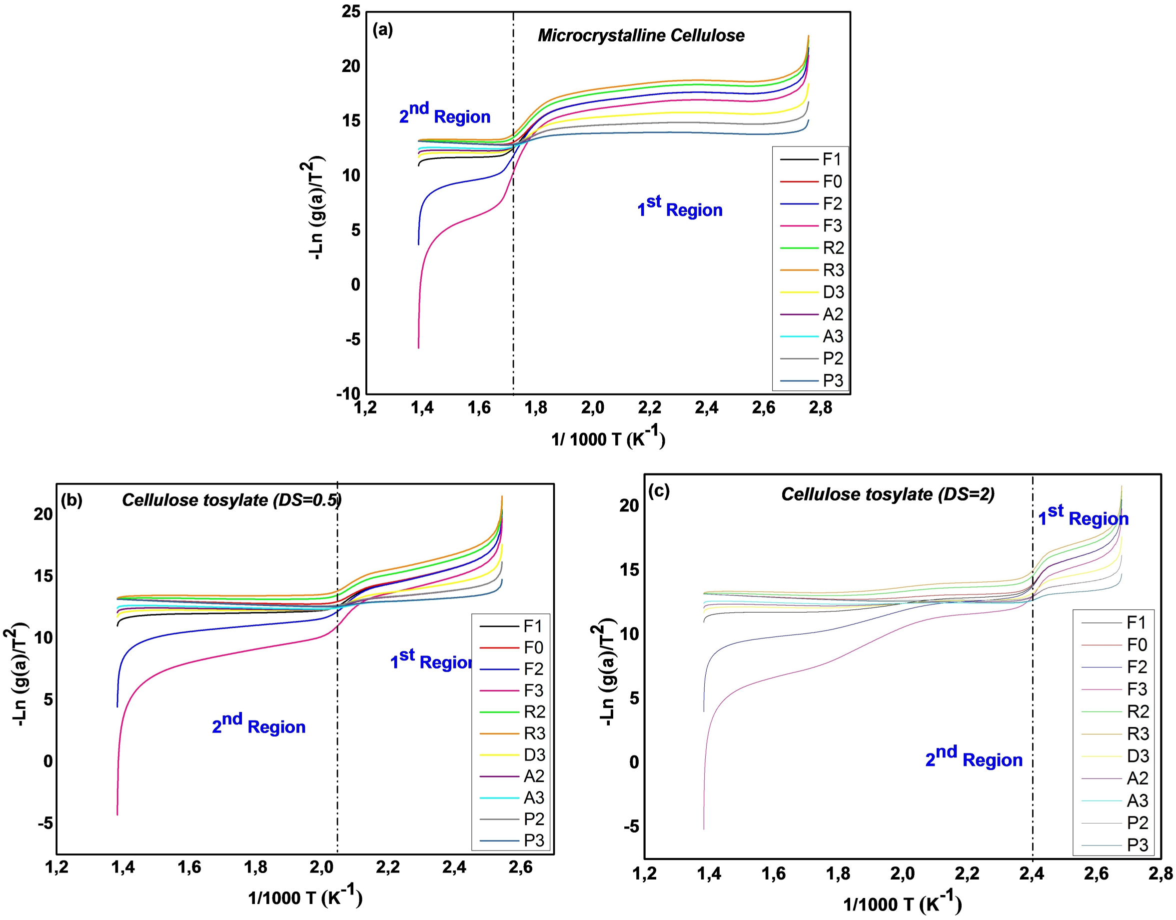

Figure 8. Curves indicating the solid-state mechanisms of MCC (a) and cellulose tosylate with DS = 0.5 (b) and DS = 2 (c) degradation under inert atmosphere.

Table 6. Thermal kinetic results for MCC and cellulose tosylate second region of pyrolysis.

DM	*MCC*			*Cellulose tosylate with DS = 0.5*			*Cellulose tosylate with DS = 2*		
	R^2	E_a	Ln A	R^2	E_a	Ln A	R^2	E_a	Ln A
F1	0.7608	9.4883	12.367	0.906	5.566	12.784	0.898	13.771	11.900
F0	0.966	-92.416	-	0.938	13.816	16.847	-	-	-
F2	0.939	-141.305	-	0.912	-72.709	-	0.982	38.901	6.126
F3	0.934	-343.965	-	0.987	-117.973	-	0.977	-175.360	-
R2	0.534	7.391	15.765	0.315	2.465	14.499	0.556	-13.515	-
R3	0.0374	-1.748	-	0.336	-3.184	-	0.728	-19.494	-
P3	0.995	25.355	18.133	0.991	21.214	17.773	0.910	15.279	16.870
D3	0.268	-6.408	-	0.204	-1.972	-	0.782	-15.301	-
P2	0.991	24.334	18.023	0.986	19.436	17.567	0.755	11.284	16.274
A2	0.0167	9.091	14.668	0.736	4.747	14.517	0.443	-5.693	-
A3	0.8209	9.682	15.586	0.974	11.467	16.067	0.409	3.914	14.241

which in its turn requires less energy to degrade than microcrystalline cellulose. Compared values being those obtained by **P2** and **P3** modes (Table 6). There are differences between our kinetic parameters values and those in literature reviews.[37,38] These differences can be attributed to the nature of cellulose and its degree of polymerization (DP), to different calculation methods and to experimental conditions.

Conclusion

In the present work, cellulose tosylates with various DS were synthesized by the tosylation of MCC with *p*-tosyl chloride in DMAc/LiCl solvent system at 8 °C. The response surface methodology model was used to study the influences of different parameters, number of mole of tosyl chloride, number of mole of base (triethylamine) and reaction time, and their interactions on the DS of cellulose tosylate synthesized. The model obtained by RSM was a quadratic polynomial equation with a R^2_{adj} equal to 99.57%. It was concluded that the main factor affecting DS was n(TsCl) and the interaction between n (base) and reaction time is negligible but the interaction between n(TsCl) and reaction time is great. Therefore, the n (base) has weak effect on the reaction DS compared to other parameters. An optimum DS of reaction of 2.79 was found for a n(TsCl) of 5 mol eq., a n(base) of 4.1 mol eq., and 24 h for reaction time, which was found by an independent experimental test. The structure of the obtained products was confirmed by elemental analyses, FT-IR and NMR spectroscopy.

MCC and cellulose tosylate with DS values of 0.5 and 2 were subjected to thermo-gravimetric analysis under inert atmosphere in order to approach the mechanisms and kinetics of their thermal degradation. Decomposition processes of the samples proceed in three main stages: water evaporation, active and passive pyrolysis. The stability of cellulose and cellulose tosylate were evaluated, Coats–Redfern method was used for calculation of the activation energy of degradation. The thermal stability decrease by introducing tosyl groups compared to unmodified MCC, this is an evidence of a significant tosylation of cellulose and the formation of a chemical bond between these compounds confirming that the reaction has occurred.

Supporting Information Summary

The experimental section is provided in Supporting Information.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Acylation · Cellulose tosylate · Kinetics · Optimization · Polymers

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