

# Kinetic Thermal Degradation of Cellulose, Polybutylene Succinate and a Green Composite: Comparative Study

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**Abstract** Polybutylene succinate (PBS), classed as biopolymer, was synthesized by condensation of succinic acid with a lower excess of (1, 4) butanediol. The synthesized polymer was analyzed by FTIR, RMN, DSC and ATG/ATD. Thermal degradation kinetics was investigated for cellulose, polybutylene succinate, physical blend of both polymers (cellulose (80%) + PBS (20%)) and compared with polycaprolactone by dynamic thermogravimetry, under nitrogen atmosphere from room temperature to 480 °C, at constant nominal heating rates: 5, 10 and 15 °C/min, respectively. The Kissinger, Friedman, Flynn-Ozawa-Wall and Coatse - Redfern (modified) methods were developed and the corresponding activation energies, frequency factors and reaction orders were determined.

**Keywords:** polybutylene succinate, synthesis, characterization, cellulose, blend, polycaprolactone, thermogravimetry

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## 1. Introduction

In Morocco, plastic-industry is one of the largest chemical industrial activities in terms of quantity and diversity of application sectors, primarily dependent on fossil resources [1], these non biodegradable very long life plastics, represent a source of visual pollution, discharge soil and marine environment-pollution. The law 22.10 proposes the use of biodegradable plastics as alternative solution to overcome fossil resource plastic exploitation [2].

Biodegradable polymers, such as cellulose, were investigated in order to reduce environmental pollution caused by plastic wastes [3,4]. Cellulose is the most abundant biopolymer on earth; its primary structure is a linear homopolymer of glucose residues having D configuration and connected by  $\beta$ -(1 $\rightarrow$ 4) glycosidic linkages. The two chain ends are chemically different, one end has a D-glucopyranosyl group in which the anomeric carbon atom is involved in a glycosidic linkage, whereas the other end has a D-glucopyranose residue in which the anomeric carbon atom is free. This latter cyclic hemiacetal function is in  $\alpha$ ,  $\beta$  anomeric equilibrium via a small proportion of free aldehyde form; the degree of polymerization (DP) of native cellulose depends on its source. Indeed, the combination of procedures required to isolate, purify, and solubilize cellulose generally causes

scission of the chains [5] and the cellulose has to undergo unhealthy chemical process with harsh alkali and acid treatment to improve its properties for industry.

Polybutylene succinate (PBS) has received extensively attention, as one of the most representative and generally acknowledged biodegradable aliphatic polyester [6]. This polymer has excellent melt processability and good chemical resistance [7]. Due to its high crystallinity degree, PBS exhibits a slow biodegradation rate [8], either in polymer and co polymer [9,10,11,12,13]. Now it is well known that PBS can be produced from renewable resources, by reacting succinic acid [14-21] and 1.4 butandiol [22,23,24]. In order to improve the physical properties of PBS and contributing to reduce the overdependence on petroleum products, some methods have been reported such as adding nano clay [25,26,27]; via cross linking reaction [28,29,30], but also by blending with other polymers to reach these objectives. Researchers are now focusing their efforts more on green materials specially cellulose. Green composites obtained via mixing synthetic or/natural polymers are materials having ecofriendly attributes that are technically and economically feasible while minimizing the generation of pollution [31].

The aim of the present work is to elaborate a green composite by blending cellulose (80 %) and synthesized polybutylene succinate (20%). The thermal characteristics of cellulose, PBS and the green composites will be studied. To better understand green blend polymer thermal

stability, all results will be compared with PCL thermal degradation data. Polycaprolactone (PCL) is a much known biodegradable polymer derived from petroleum resources. PCL is intensively studied in terms of its synthesis and properties evaluation. Its importance owes to its potential applications in various medical and non-medical fields like agriculture, medicine, pharmacy, and also as environmentally friendly materials in packaging industry.

## 2. Materials and Methods

### 2.1. Materials

Cellulose (Mn = 300 g/mol), polycaprolactone (Mn = 10000 g/mol), 1, 4 - butanediol, succinic acid, paratoluene sulfonic acid (APTS), acetic anhydride, titanium butoxide, pyridine, phenolphthalein, Potassium hydroxide, toluene, dichloromethane and ether were purchased from Sigma–Aldrich Chemical Co. All reagents were used as received.

### 2.2. Polybutylene Succinate Synthesis

The polybutylene succinate was synthesized in two steps, by melting condensation using 1, 4 - butanediol, succinic acid and paratoluene sulfonic acid. In a three-necked round bottom flask equipped by Dean Stark, we introduced 1, 4 - butanediol (0.06 mol), succinic acid (0.05 mol), paratoluene sulfonic acid (APTS) (0.1%) and 20 ml of toluene. The mixture was maintained under continuous stirring at 140 °C during 24 hours to obtain oligomers compounds. The organic solvent was eliminated, we used rotary evaporator connected pump to create a vacuum. After removing the organic solvent Titanium Butoxide (0.1%) catalyst was added to the mixture by maintaining constant stirring, the temperature was carried out at 240 °C under vacuum for another 6 hours. The reaction mixture was dissolved in dichloromethane and precipitate in ether excess. White polymer was removed by filtration and kept at 60°C under vacuum for 24 hours.

### 2.3. Blend (cellulose (80%) + polybutylene succinate (20%)) Preparation

An amount of cellulose (80%) and Polybutylene succinate (20%) was added to dichloromethane under constant stirring for 3 hours at room temperature. The mixture was poured in Petri dish, and kept at room temperature for solvent evaporation over night then dried in desiccator containing a desiccant powder (P<sub>2</sub>O<sub>5</sub>) for 24 hours under vacuum and a blend material was formed.

## 2.4. Characterization

### 2.4.1. Thermogravimetric Analysis TGA/DTA

Thermogravimetric analysis (TGA) was carried out with Shimadzu TA 60 (Oujda- Morocco). Samples were placed in alumina crucibles and were heated from room temperature to 480 °C under 50 ml/min N<sub>2</sub> flow. Alumina crucible was used as reference. Nominal heating rates of 5, 10 and 15 °C/min were settled, and continuous records of sample temperature, sample weight, its first derivative and heat flow were recorded.

### 2.4.2. Rayon X analysis DRX

The rayon X analysis was carried out with Shimadzu RX (Oujda – Morocco)

### 2.4.3. Calorimetric Analysis

Differential scanning calorimetric (DSC) analysis were performed by a TA DSC Q20 (United State). About 10 mg of sample was placed in sealed aluminum capsules. Samples were subjected to two scan from - 40 to 200 °C with a rate of 10 °C /min. The crystallinity degree (X<sub>c</sub>) [32], is calculated using the equation 1:

$$X_c (\%) = \frac{\Delta H_m}{(w_{poly} \times \Delta H_{100})} \times 100 \quad (1)$$

ΔH<sub>m</sub>: Polymer melting enthalpy calculated from second scan,

W<sub>poly</sub>: Massic fraction of polymer in blend (20%)

ΔH<sub>100</sub>: Melting enthalpy of polymer 100% cristallin

### 2.4.4. Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra were recorded using FTIR B8400S Shimadzu (Oujda- Morocco) between 4000 and 600 cm<sup>-1</sup> at resolution of 4 cm<sup>-1</sup>, using potassium bromide pellet method.

### 2.4.5. Nuclear Magnetic Resonance (<sup>1</sup>H-NMR)

The NMR spectra were recorded in UATARS - CNRST – RABAT- MOROCCO using BRUKER 250 MHZ spectrometer. Deuterated chloroform (CDCL<sub>3</sub>) with trifluoroacetic acid are used as solvent and tetramethylsilane (TMS) as internal reference.

### 2.4.6. Hydroxyl Value and Molecular Weight Number Average

The polymer must be exactly weighted between (1 and 2 g) placed in a 250 ml flask, then 20 ml of the acetylating mixture (1 × V acetic anhydride and pyridine 3 × V) added, and the mixture is stirred until complete dissolution of the material was reached. The content was refluxed for 30 min, then the solution was cooled down at room temperature and 50 ml cold water was added. The free acetic acid was titrated with standard potassium hydroxide (1 N) using phenolphthalein as indicator. The procedure was repeated for blank titration under similar condition [33].

$$\text{Hydroxyl Value} = \frac{56.1 \times N \times (B - A)}{W} \quad (2)$$

N: Potassium hydroxide normality.

A: Volume of Potassium hydroxide solution used for titration.

B: Volume of Potassium hydroxide solution used for blank titration.

W: Weight of Copolymer sample taken.

The average number of molecular weight was calculated using the following expression:

$$Mn = \frac{103 \times W}{N \times (V - V_0)} \quad (3)$$

Where:

W: Weight of copolymer.

N: Titer of a solution of Potassium hydroxide in ethanol.

V: Volume of titrated solution.

$V_0$ : Blank volume of titrated solution.

### 2.4.7. Thermal Degradation: Theoretical Approach

The thermal degradation kinetics can provide useful information for polymeric materials processing and use conditions optimization. TGA/DTA use in kinetic parameters determination has broadly raised interest during last years. Moreover, the possibility of using different thermal histories can provide further informations on the kinetic nature of the degradation process. Isothermal or dynamic TGA tests at constant

heating rates can be used to study the thermal decomposition of polymeric materials. Mathematical models of thermal decomposition reactions make possible the understanding of the whole process and the quantitative conclusions are useful for practical applications from apparent kinetic parameter. The Kissinger [34], Friedman [35], Flynn-Ozawa-Wall [36] and Coatse-Redfern (modified) [37] methods were developed Table 1, the corresponding activation energies, frequency factors and reaction orders were determined [38].

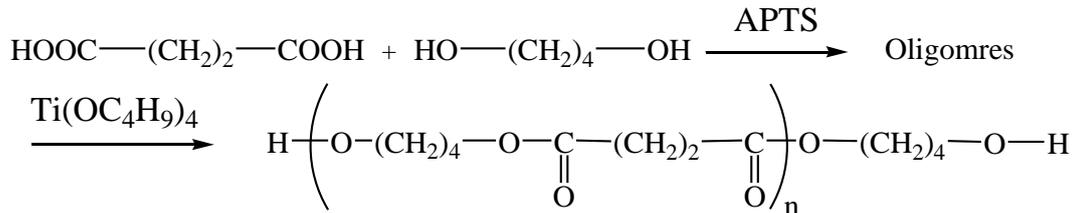
Table 1. Kinetic methods

| Methods                   | Equations   | Plots  |
|---------------------------|---|--|
| Friedman                  | $\text{Ln} \frac{d\alpha}{dt} = \text{Ln}[Af(\alpha)] + (-\frac{E_a}{RT})$  | $Y = \text{Ln}(\frac{d\alpha}{dt}), X = \frac{1}{T}$ [35]      |
| Kissinger                 | $\text{Ln}(\frac{\beta}{T_p^2}) = (-\frac{E_a}{RT_p}) + \text{Ln}(\frac{AR}{E_a})$                                  | $Y = \text{Ln}(\frac{\beta}{T_p^2}), X = \frac{1}{T_p^2}$ [34] |
| Flynn-Wall-Ozawa          | $\text{Ln}(\beta) = -\frac{E_a}{RT} + \text{const}$   | $Y = \text{Ln}(\beta), X = \frac{1}{T}$ [36]                   |
| Coatse-Redfern (modified) | $\text{Ln}[\frac{\beta}{T^2(1-\frac{2RT}{E_a})}] = \text{Ln}[\frac{-AR}{E_a \text{Ln}(1-\alpha)}] - \frac{E_a}{RT}$ | $Y = \text{Ln}(\frac{\beta}{T^2}), X = \frac{1}{T}$ [37]       |

## 3. Results and Discussion

### 3.1. Synthesized of Polybutylene Succinate

Synthesis of Polybutylene succinate by classical polycondensation reaction is presented in Scheme 1:



Scheme 1. Synthesis of Polybutylene succinate (PBS) by polycondensation reaction

#### 3.1.1. FTIR Characterization

The FTIR spectrum of Polybutylene succinate presented in Figure 1 shows an absorption band at  $2947\text{cm}^{-1}$  assigned to the C-H bond stretching. The band intense appeared at  $1716\text{cm}^{-1}$  correspond to carbonyl C=O stretching vibration characterizing the formation of ester group. Furthermore,

the peak present at  $1341\text{cm}^{-1}$  is assigned to -COO- bond stretching vibration. The signal at  $1158\text{cm}^{-1}$  is a characteristic of C-O-C stretching vibration in the repeated -OCH<sub>2</sub>CH<sub>2</sub> unit. These vibration bands described below that the polycondensation reaction was successful and the polycondensat was obtained with a high yield.

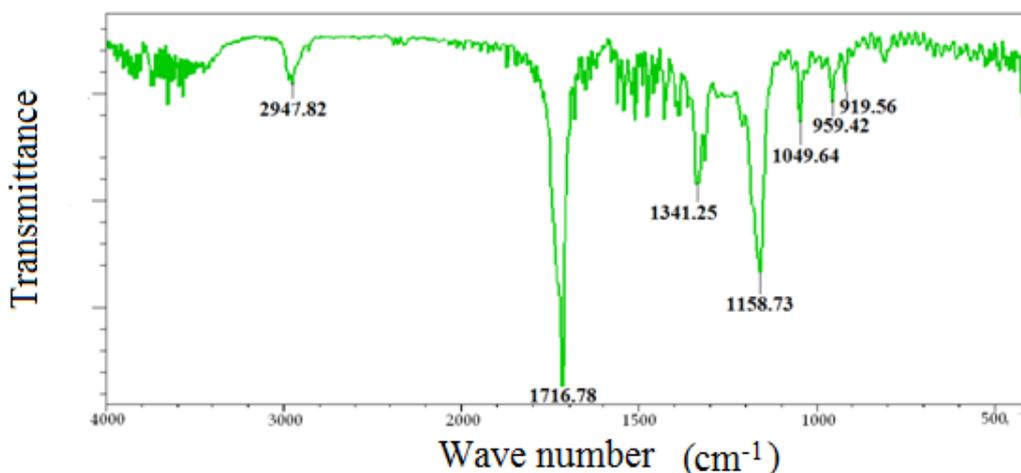


Figure 1. FTIR spectrum of Polybutylene Succinate synthesized

3.1.2. <sup>1</sup>H-NMR Characterization

The <sup>1</sup>H-NMR spectrum of Polybutylene Succinate is shown in Figure 2. For the analysis by the NMR method, the different structural units in the NMR spectrum are distinguished. The peak present at 2.65 ppm is attributed to the methylene protons of the succinic acid unit (a). The peak at 4.3 ppm is attributed to methylene protons of -

CH<sub>2</sub>-OCO- group (c). Furthermore, the centered methylene protons of 1, 4 - butanediol (b) gives a multiply at 1.6 ppm. The little peak at 3.4 ppm is attributed to methylene proton of CH<sub>2</sub>-O- at the chain extremity. The triply appearing at 4.3 ppm shows clearly that the reaction takes place between the diol and the diacid.

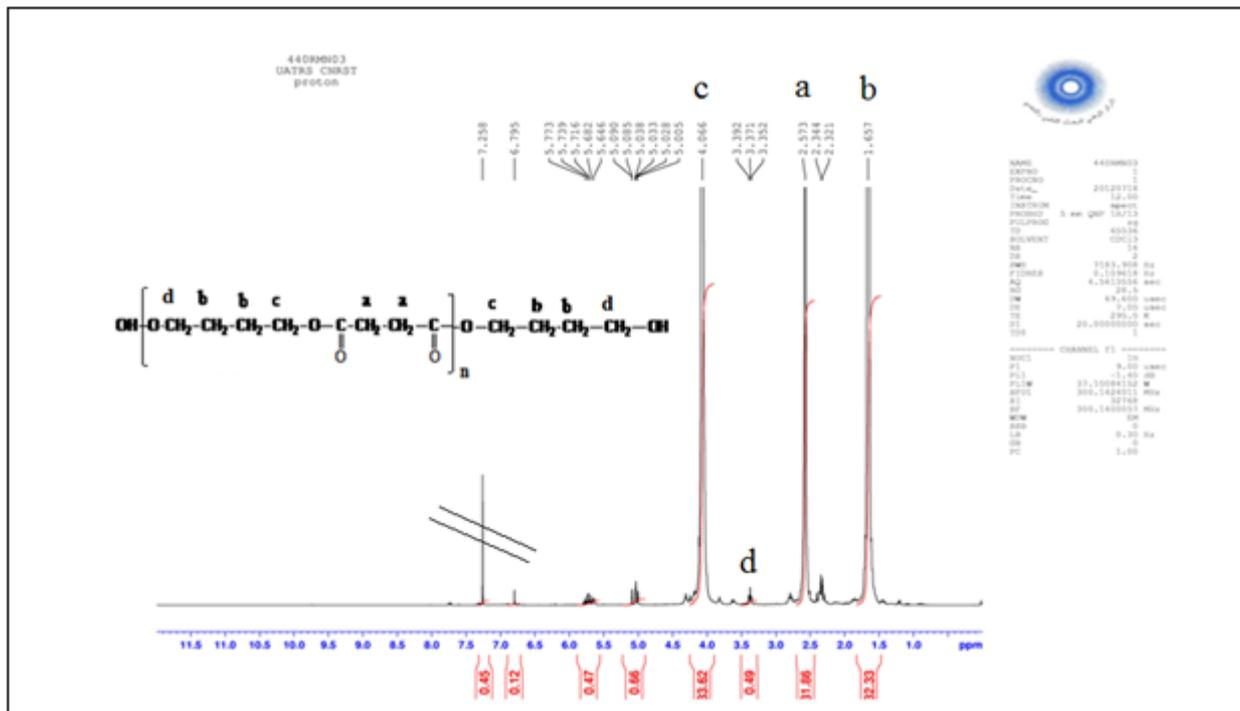


Figure 2. <sup>1</sup>H-NMR spectrum of the polybutylene succinate

3.1.3. DSC Analysis

In the Figure 3, during DSC run the main melting peak is at T<sub>m</sub> ≈ 111 °C, The same results were obtained by K. Chrissafis and al [40]. The main crystallization peaks are

relatively obtained at around T<sub>c</sub> = 62.5 °C. We observed a little crystallization peak at T<sub>c</sub> = 90.2°C followed by pre-melting inflexion at T<sub>pm</sub> = 100°C.

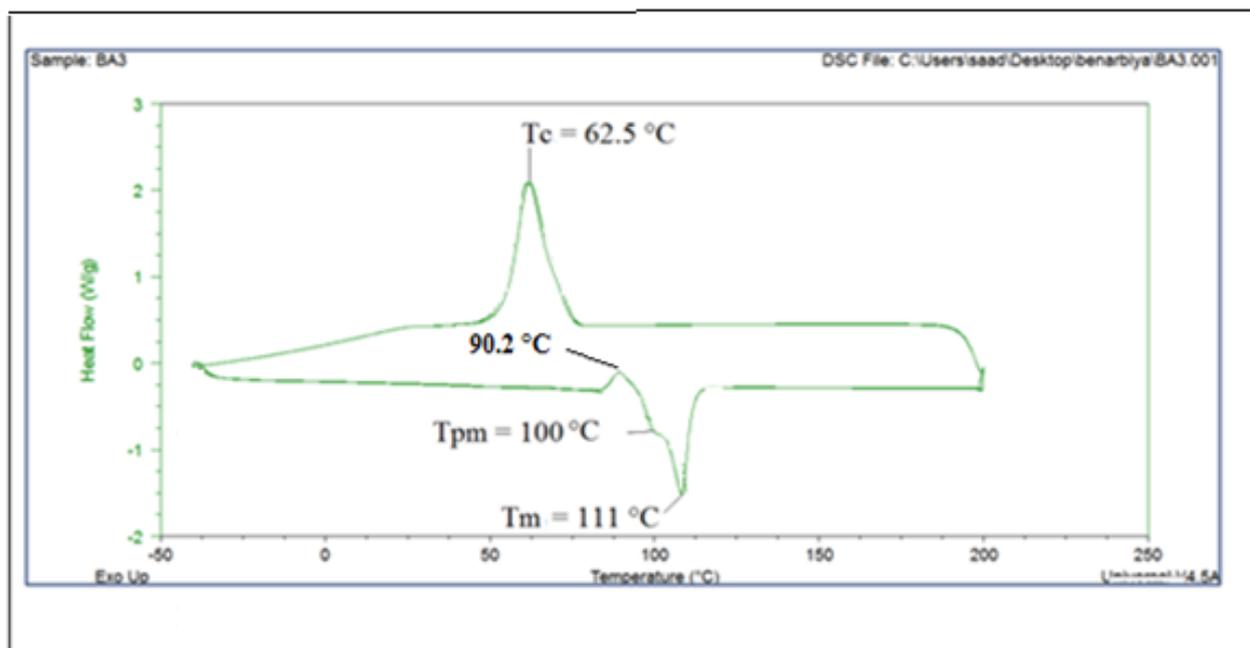


Figure 3. DSC thermograms of the polybutylene succinate

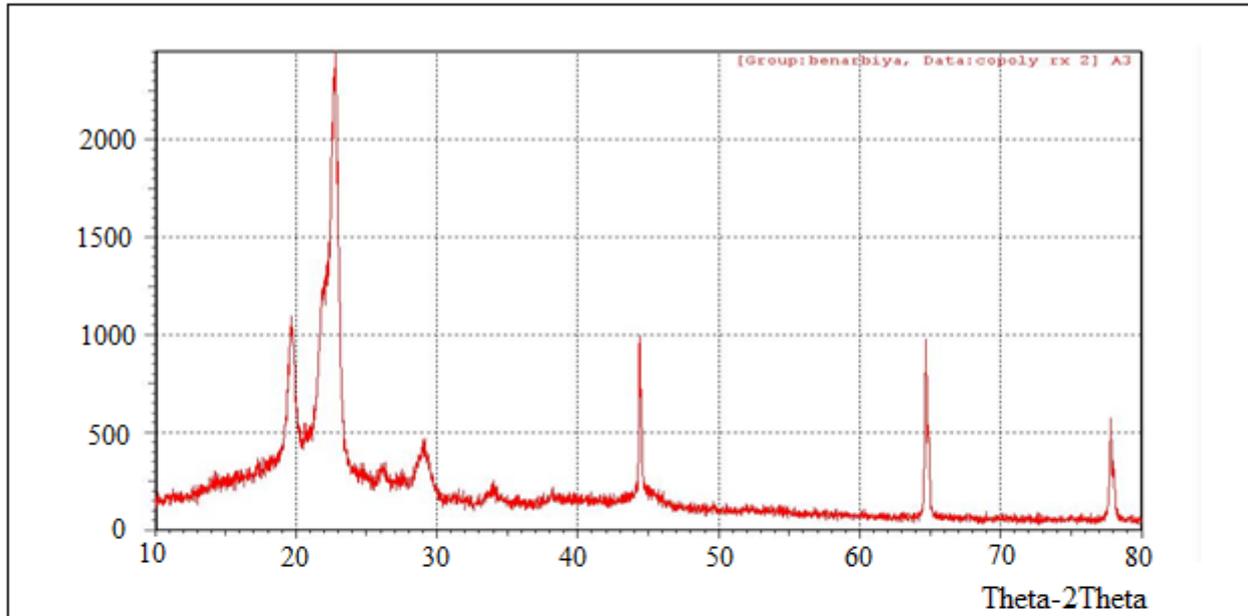


Figure 4.a. RX spectrum of polybutylene succinate

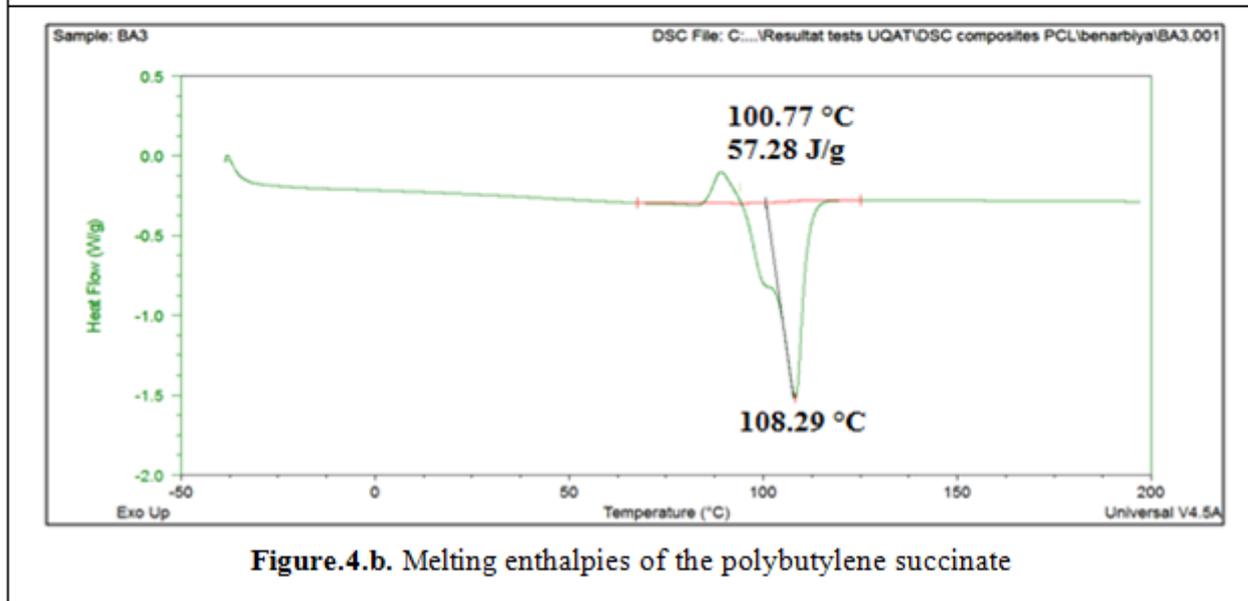


Figure 4.b. Melting enthalpies of the polybutylene succinate

Figure 4. (a) RX spectrum of polybutylene succinate, (b) Melting enthalpies of the polybutylene succinate

From the Figure 4.a, the polybutylene succinate present height crystallinity and from the Figure.4.b, the crystallinity degree ( $X_c$ ) in blend was calculated according to the equation 1:

$$X_c (\%) = \frac{\Delta H_m}{(w_{poly} \times \Delta H_{100})} \times 100 = 25.85\% \quad (1)$$

(\*  $X_c$  (%): crystallinity degree in blend

Where  $\Delta H_m = 57.28$  J/g is the melting enthalpy calculated from second scan,  $w_{poly}$  is the polymer massic fraction in the blend (20%) and it is well known that  $\Delta H_{100} = 110.3$  J/g melting enthalpy of polybutylene succinate 100% crystallin [41].

Table 2. Structure and properties of the prepared polyester.

| Tm (°C) | $\Delta H_f$ J/g | $X_c$ (%) | Mn (g/mol) | Hydroxyl Number |
|---------|------------------|-----------|------------|-----------------|
| 111     | 57.28            | 25.85     | 1040       | 1.34            |

### 3.2. FTIR Characterization of the Commercial Cellulose and Polycaprolactone

#### 3.2.1. FTIR Characterization of the Commercial Cellulose

From FTIR spectrum of the cellulose (Figure 5), the absorption band at  $3391\text{cm}^{-1}$  is assigned to hydroxyl

groups stretching. Bands at  $2906\text{cm}^{-1}$  and  $1373\text{cm}^{-1}$  are assigned to stretching and deformation vibrations of C-H group in glucose unit. The absorption band at  $898\text{cm}^{-1}$  is characteristic of  $\beta$ -glycosidic linkage between glucose units. The signal at  $1061\text{cm}^{-1}$  is assigned to -C-O- group of secondary alcohols and ethers functions existing in the cellulose chain backbone.

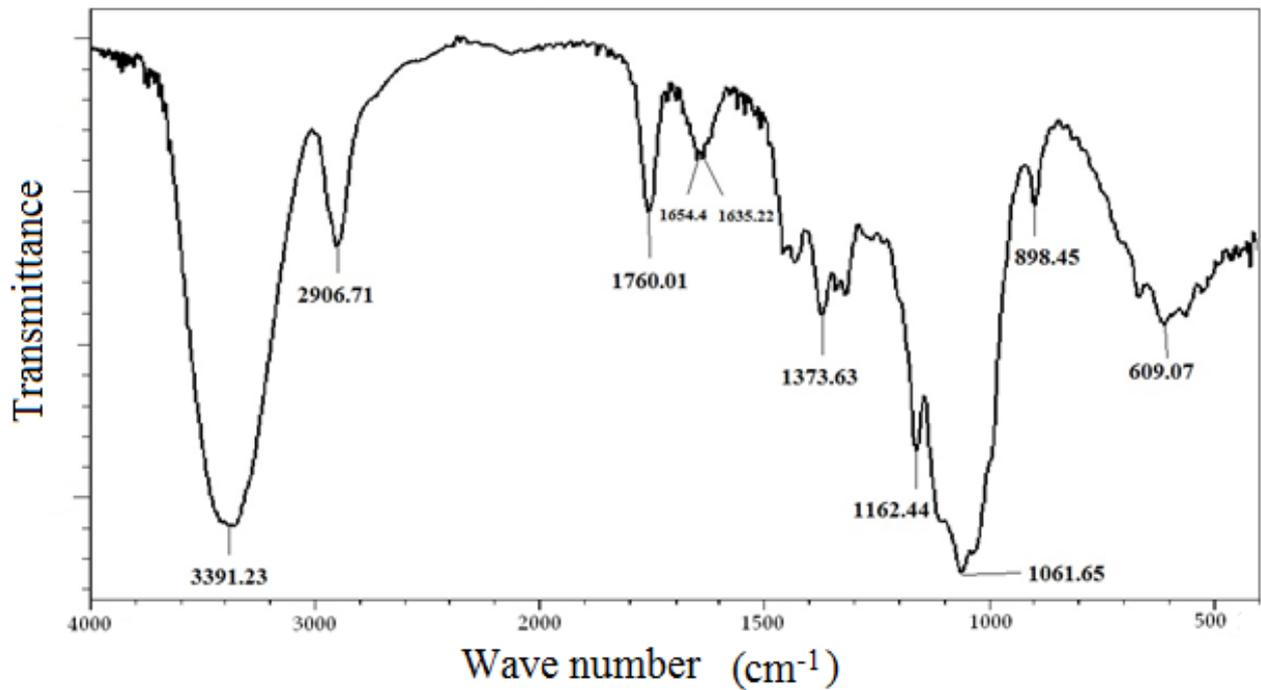


Figure 5. FTIR spectrum of the commercial cellulose

### 3.2.2. FTIR Characterization of the Commercial Polycaprolactone

From *FTIR* spectrum of the chosen polycaprolactone (Figure 6), we remarked the following bands. The absorption band at  $2940\text{ cm}^{-1}$  is assigned to the C–H hydroxyl groups asymmetric stretching. The band at

$2860\text{ cm}^{-1}$  is assigned to C–H hydroxyl groups symmetric stretching. The absorption band at  $1722\text{ cm}^{-1}$  is assigned to  $\text{C}=\text{O}$  stretching vibrations of the ester carbonyl group. The absorption at  $1238\text{ cm}^{-1}$  is assigned to C–O–C asymmetric stretching, but, the signal at  $1160\text{ cm}^{-1}$  is assigned to  $\text{C–O–C}$  symmetric stretching.

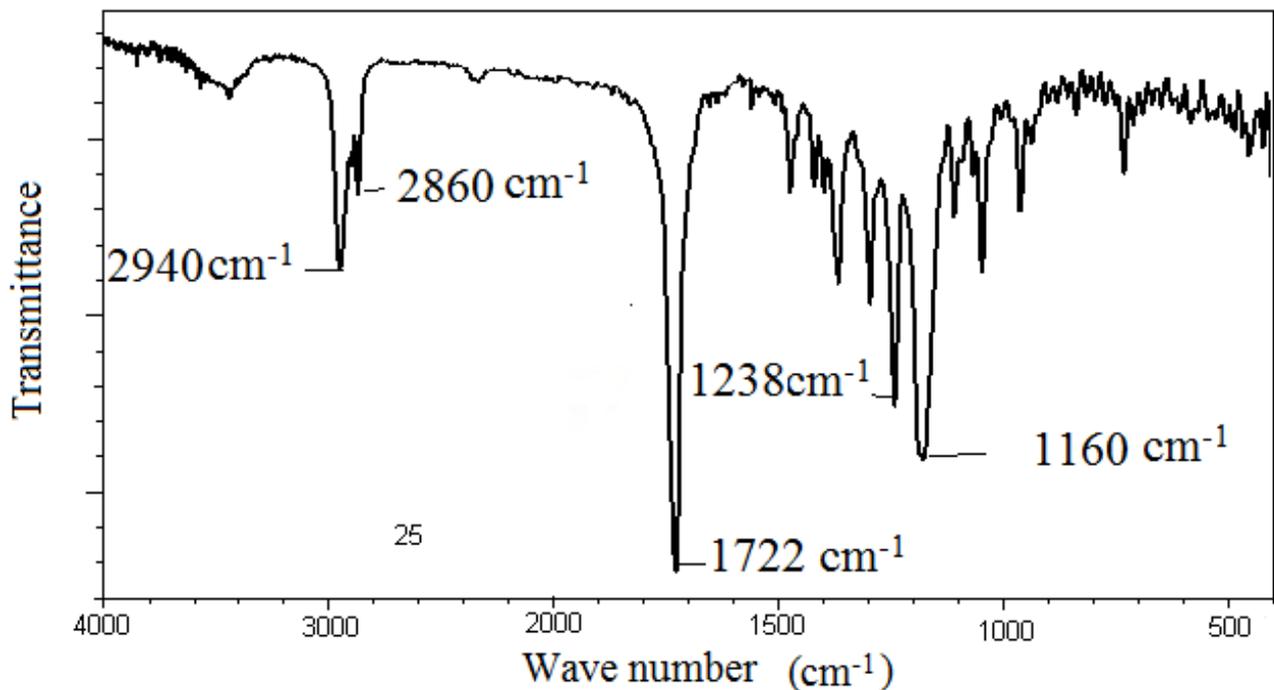


Figure 6. FTIR spectrum of the commercial polycaprolactone

### 3.2.3. FTIR Characterization of the Cellulose(80%)/PBS (20%) Composite

From the *FTIR* spectrum of the physical blend (cellulose (80%) and Polybutylene succinate (20%))

reported in the Figure 7, we remarked that all characteristic bands of the polymer functional groups are depicted, but the intensity of  $\text{C}=\text{O}$  stretching vibrations of the ester carbonyl group is lower than the intensity in pure Polybutylene succinate.

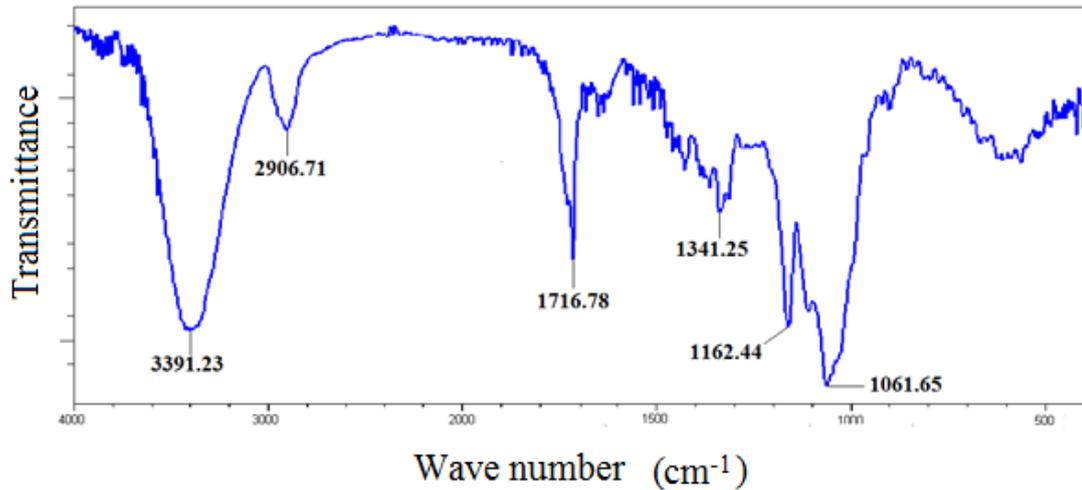


Figure 7. FTIR spectrum of the cellulose (80%)/PBS (20%) blend

### 3.3. Thermal Kinetic Studies

#### 3.3.1. Comparative Thermal Degradation Kinetic Studies of Cellulose, Polybutylene Succinate and physical Blend of both Polymers

Thermal degradation of polybutylene succinate, cellulose and physical blend of both polymers was studied by their mass loss during heating. From thermogravimetric curves (TGA) (Figure 8), it can be seen that cellulose presents a relatively lower thermostability. The polybutylene succinate presents relatively good thermostability, since no significant weight loss occurred until 300 °C, and the weight loss of -

2.92% is observed at  $T^{\circ} = 306.30$  °C. The physical blend between cellulose (80%) and polybutylene succinate (20%) presents - 2.92% weight loss at 65.10 °C. If we compare between cellulose and the blend, we can see that thermostability temperature increases about 15.85 °C for the same percentage (- 2.92%), and we can note that adding only 20% of polybutylene succinate to the cellulose (80%) increases the thermostability. It is also interesting to promote the biodegradability properties of PBS by physical blending [40,41,42]. The variations of DTA results for polybutylene succinate and physical blend of cellulose ((80%) and poly (butylene succinate) (20%)) are reported in Table 3.

Table 3. Differential thermal analysis (DTA) variations of cellulose, polybutylene succinate and the physical blend of both polymers at heating rate ( $\beta$ : 10 °C/min).

| Samples<br>$\beta = 10$ °C/min | $T_i$  | Char yield<br>at 480 °C | DTA peak<br>maxima<br>temperature (°C) | Nature of<br>DTA peak | DTA peak range<br>(°C) | DTG peak<br>maxima<br>temperature (°C) | Mn(g/mol) |
|--------------------------------|--------|-------------------------|--|-----------------------|------------------------|--|-----------|
| Cellulose 100 %                | 49.25  | 3.62 %                  | 56.65                                  | Endo                  | 30.00 - 96.56          | 350.10                                 | 300       |
|                                |        |                         | 360.85                                 | Endo                  | 115.53 - 392.46        |  |           |
| PBS<br>100 %                   | 306.30 | 1.27 %                  | 112.79                                 | Endo                  | 69.08 - 154.60         | 395.52                                 | 1040      |
|                                |        |                         | 393.79                                 | Endo                  | 343.92 - 437.27        |  |           |
| Cellulose 80%<br>+PBS20 %      | 65.10  | 3.90 %                  | 63.49                                  | Endo                  | 33.14 - 92.32          | 354.35                                 | ----      |
|                                |        |                         | 110.08                                 | Endo                  | 97.04 - 127.07         |  |           |
|                                |        |                         | 358.02                                 | Endo                  | 310.53 - 382.08        |  |           |
|                                |        |                         | 389.64                                 | Endo                  | 382.08 - 418.60        |  |           |

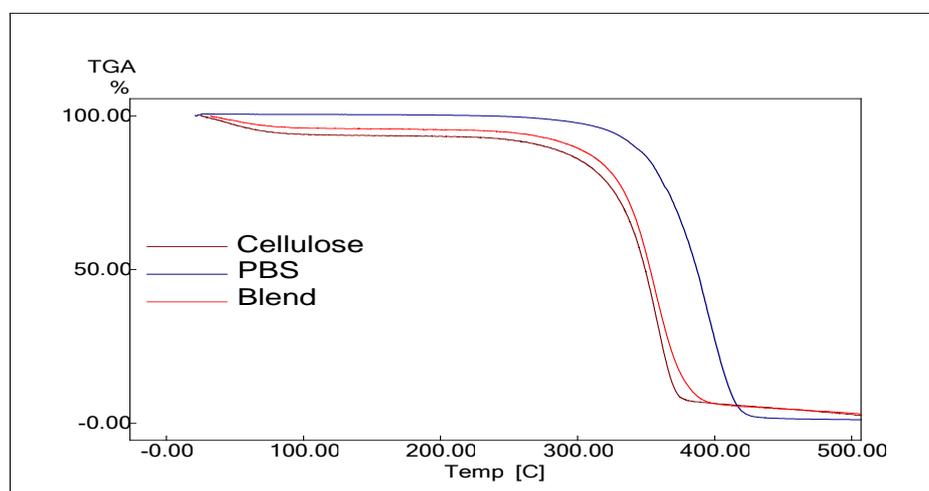
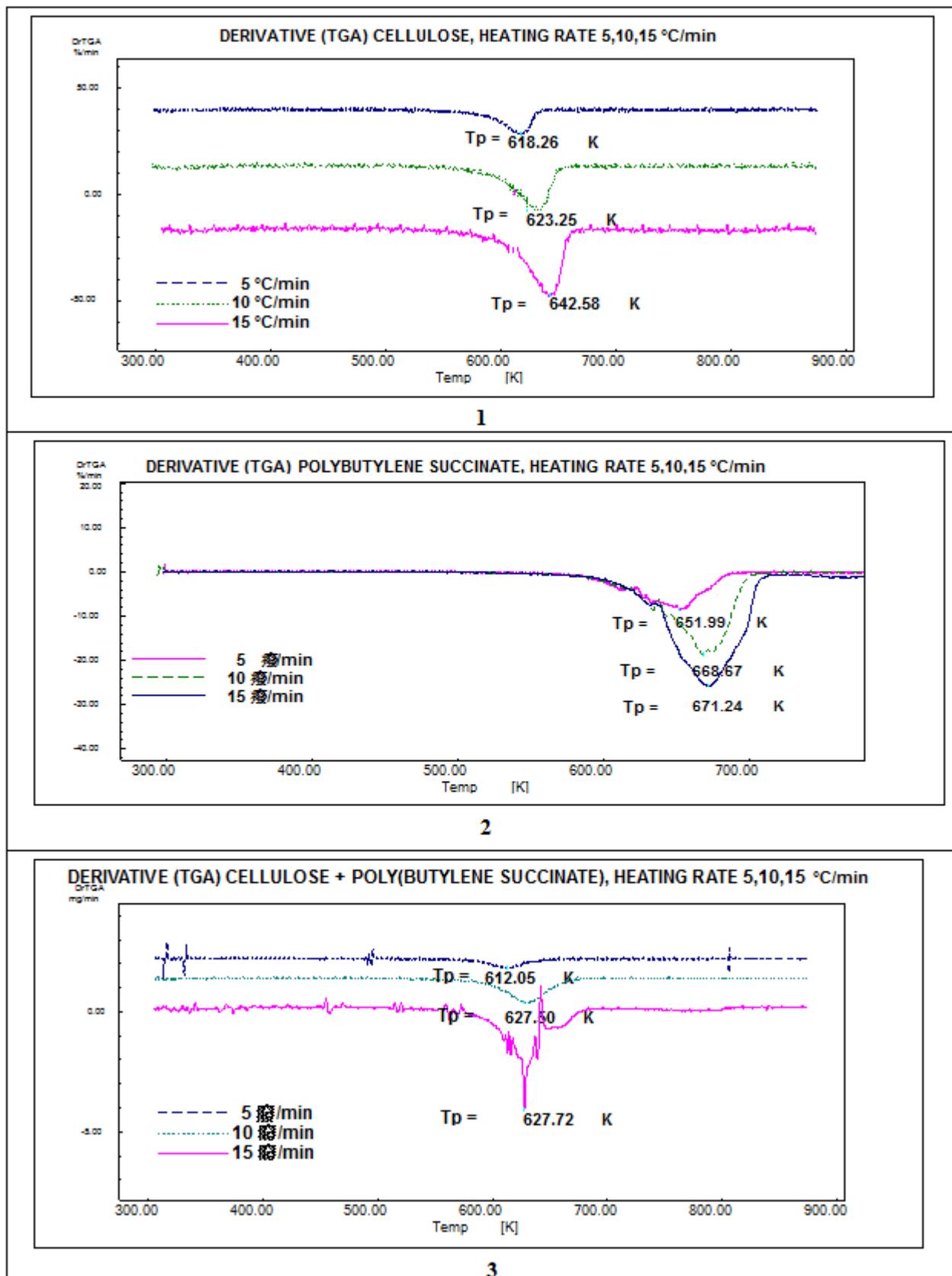


Figure 8. TGA dynamic thermograms of Cellulose, PBS, and physical blend of both polymers at heating rate ( $\beta$ : 10 °C/min)



**Figure 9.** Derivative thermogrammes DrTG curves of (1) cellulose, (2) Polybutylene succinate and (3) the physical blend of both polymers at different heating rates  $\beta$ : 5 °C/min; 10 °C/min and 15 °C/min. ;  $T_p$  is the fastest decomposing temperature used by Kissinger equation

Since, every isoconversional method has different errors, the use of more than one method can give a range of values for the activation energy at every particular value of  $\alpha$ . In our studies we used four methods. Degradation activation energy of the studied cellulose,

Polybutylene succinate and the physical blend of cellulose ((80%) and polybutylene succinate (20%)) were estimated using Ozawa, Flynn and Wall (OFW) (Figure 10), Friedman (Figure 11), Coatse-Redfern (modified) (Figure 12) and

Kissinger (Figure 13) methods. All results are presented in Table 4 –Table 7.

From the data in Table 4-Table 7, activation energies values calculated by Ozawa method and Coatse-Redfern (modified) method are close for cellulose, polybutylene succinate and the physical blend of cellulose ((80%) and polybutylene succinate (20%)) with acceptable correlation coefficient close and superior to 90% in major cases, the little difference can be explained by a systematic error due

to improper integration [19]. Activation energies calculated by Friedman is the double with acceptable values of correlation coefficient. The activation energy calculated by Kissinger method is the lowest in the case of cellulose with coefficient of determination  $R^2 = 0.763$  and physical blend of cellulose ((80%) and polybutylene succinate (20%)) with coefficient of determination  $R^2 = 0.861$ . In our studies, we used activation energies calculated by OFW method.

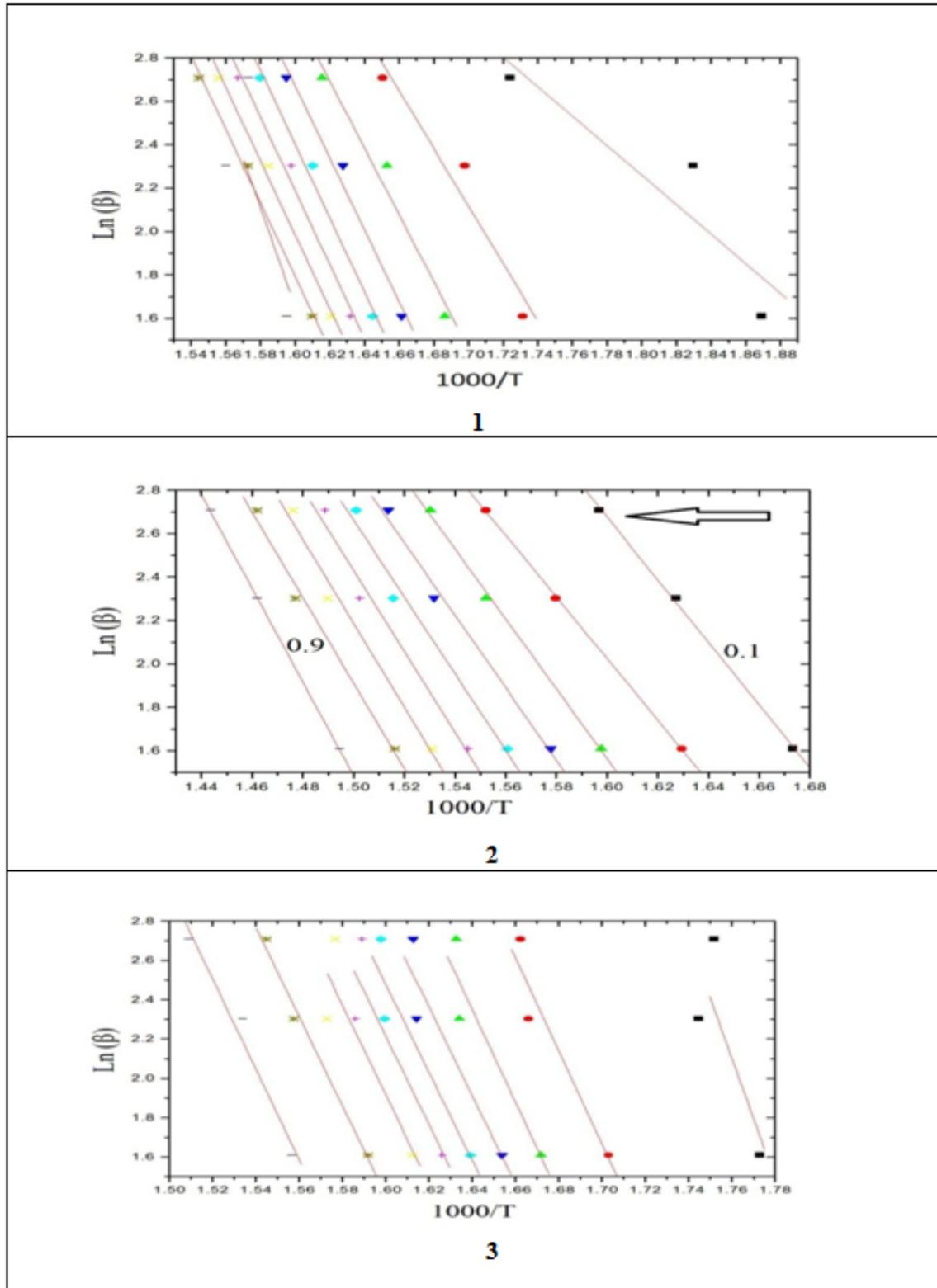
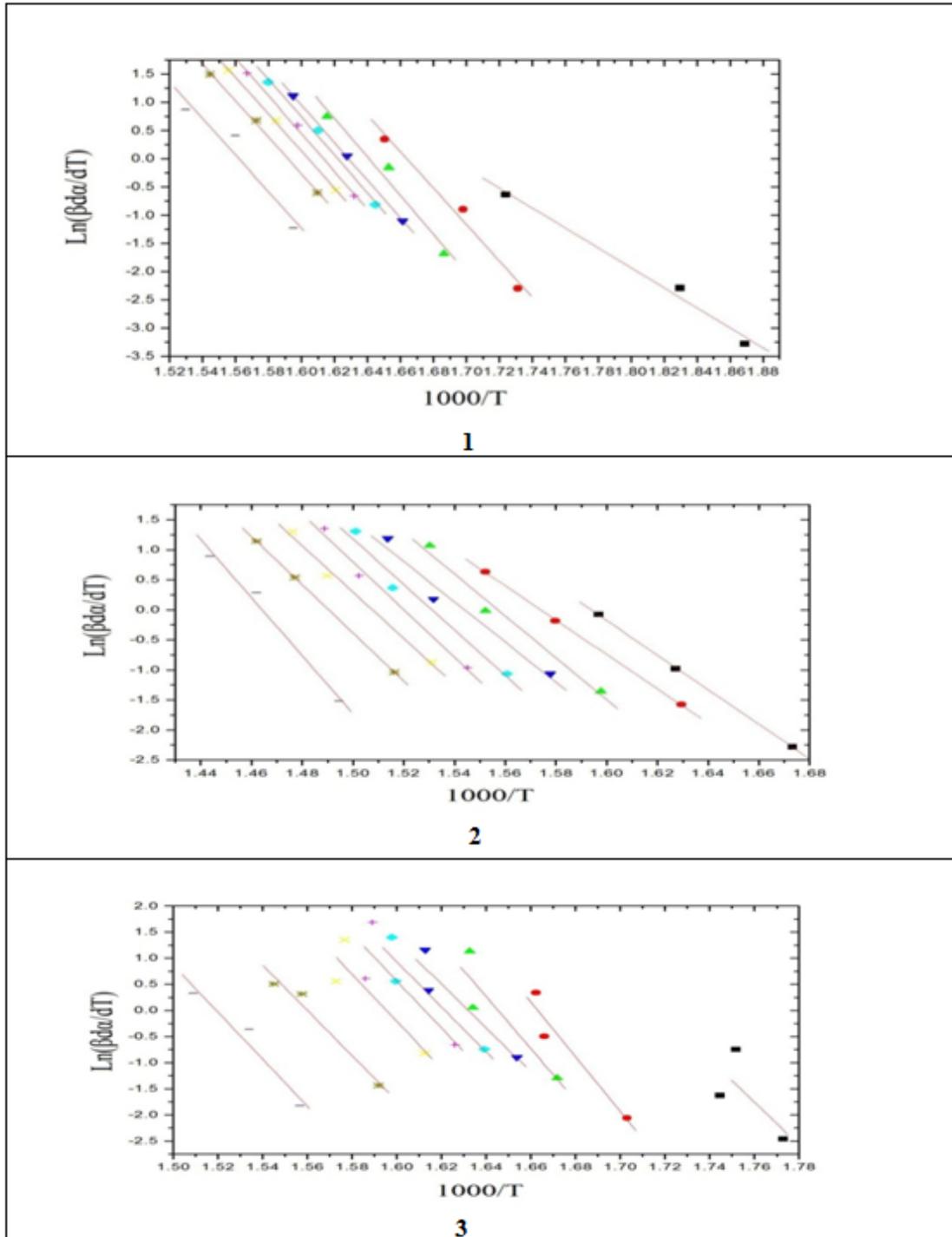


Figure 10. Ozawa plots of (1) cellulose, (2) polybutylene succinate, (3) blend of cellulose (80%) and polybutylene succinate (20%), fractional extent of reaction:  $\alpha = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$

**Table 4. Activation energies ( $E_a$ ) of cellulose, polybutylene succinate and Blend (cellulose 80%, PBS 20%) using fit of plots Flynn-Wall-Ozawa (FWO) method**

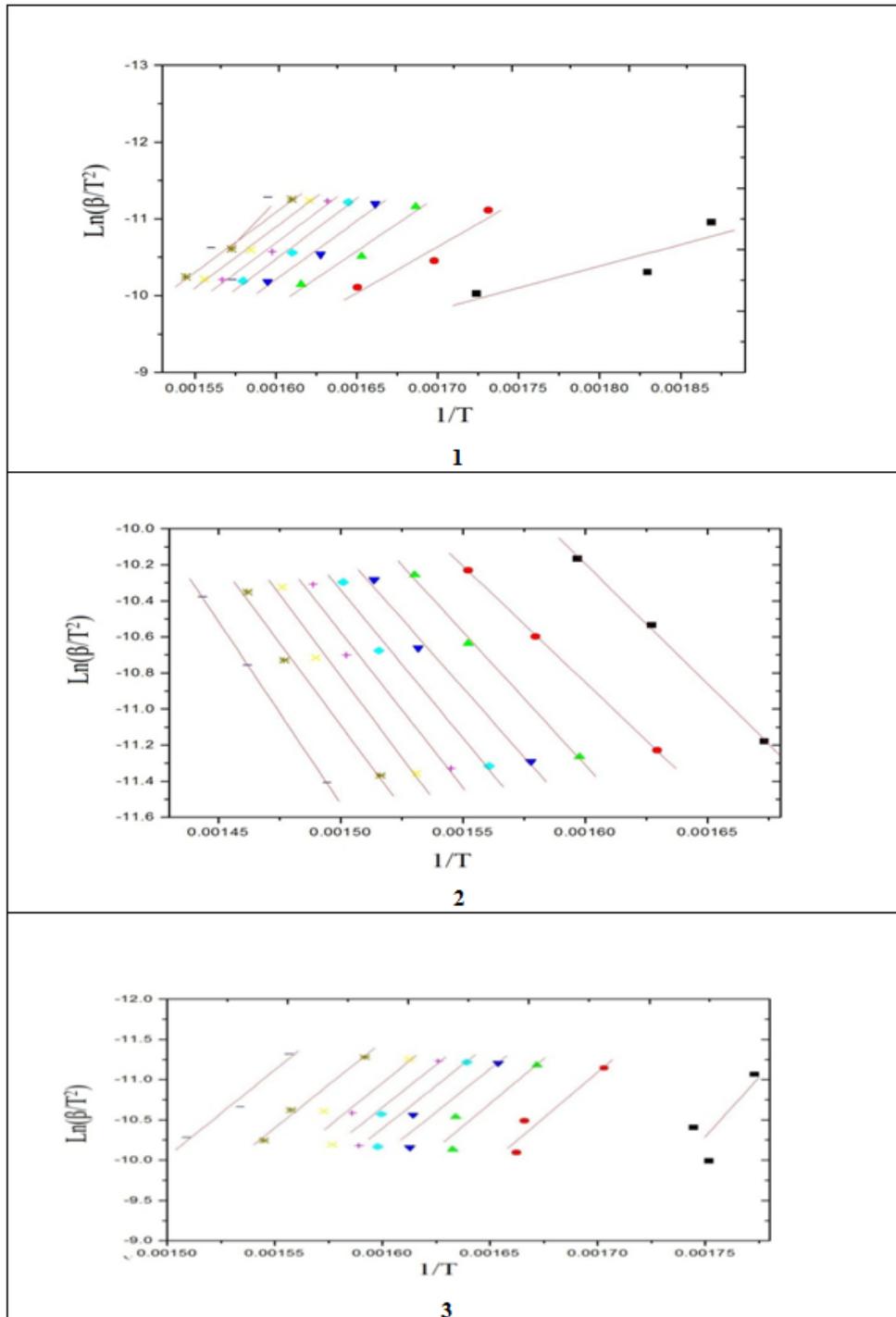
| A    | Cellulose             |       | Polybutylene succinate |       | Blend (cellulose 80%, PBS 20%) |       |
|------|-----------------------|-------|------------------------|-------|--------------------------------|-------|
|      | $E_{a(FWO)}$ (Kj/mol) | $R^2$ | $E_{a(FWO)}$ (Kj/mol)  | $R^2$ | $E_{a(FWO)}$ (Kj/mol)          | $R^2$ |
| 0.1  | 56.49                 | 0.842 | 119.91                 | 0.998 | 255.70                         | 0.663 |
| 0.2  | 109.97                | 0.937 | 117.88                 | 0.999 | 196.63                         | 0.919 |
| 0.3  | 128.13                | 0.967 | 133.95                 | 0.997 | 196.02                         | 0.888 |
| 0.4  | 137.44                | 0.980 | 138.94                 | 0.990 | 187.01                         | 0.888 |
| 0.5  | 141.16                | 0.987 | 147.02                 | 0.981 | 186.39                         | 0.891 |
| 0.6  | 141.07                | 0.985 | 155.35                 | 0.980 | 187.52                         | 0.817 |
| 0.7  | 141.40                | 0.992 | 160.54                 | 0.983 | 189.47                         | 0.803 |
| 0.8  | 140.69                | 0.994 | 163.68                 | 0.989 | 188.57                         | 0.987 |
| 0.9  | 190.06                | 0.534 | 179.07                 | 0.999 | 190.55                         | 0.968 |
| Mean | 131.82                |       | 146.26                 |       | 197.54                         |       |



**Figure 11. Friedman plots of (1) cellulose, (2) polybutylene succinate and (3) blend of cellulose (80%) and polybutylene succinate (20%), fractional extent of reaction:  $\alpha = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$**

**Table 5. Activation energies ( $E_a$ ) of cellulose, polybutylene succinate and their blend (cellulose 80%, PBS 20%) using fit of plots Friedman (F) method**

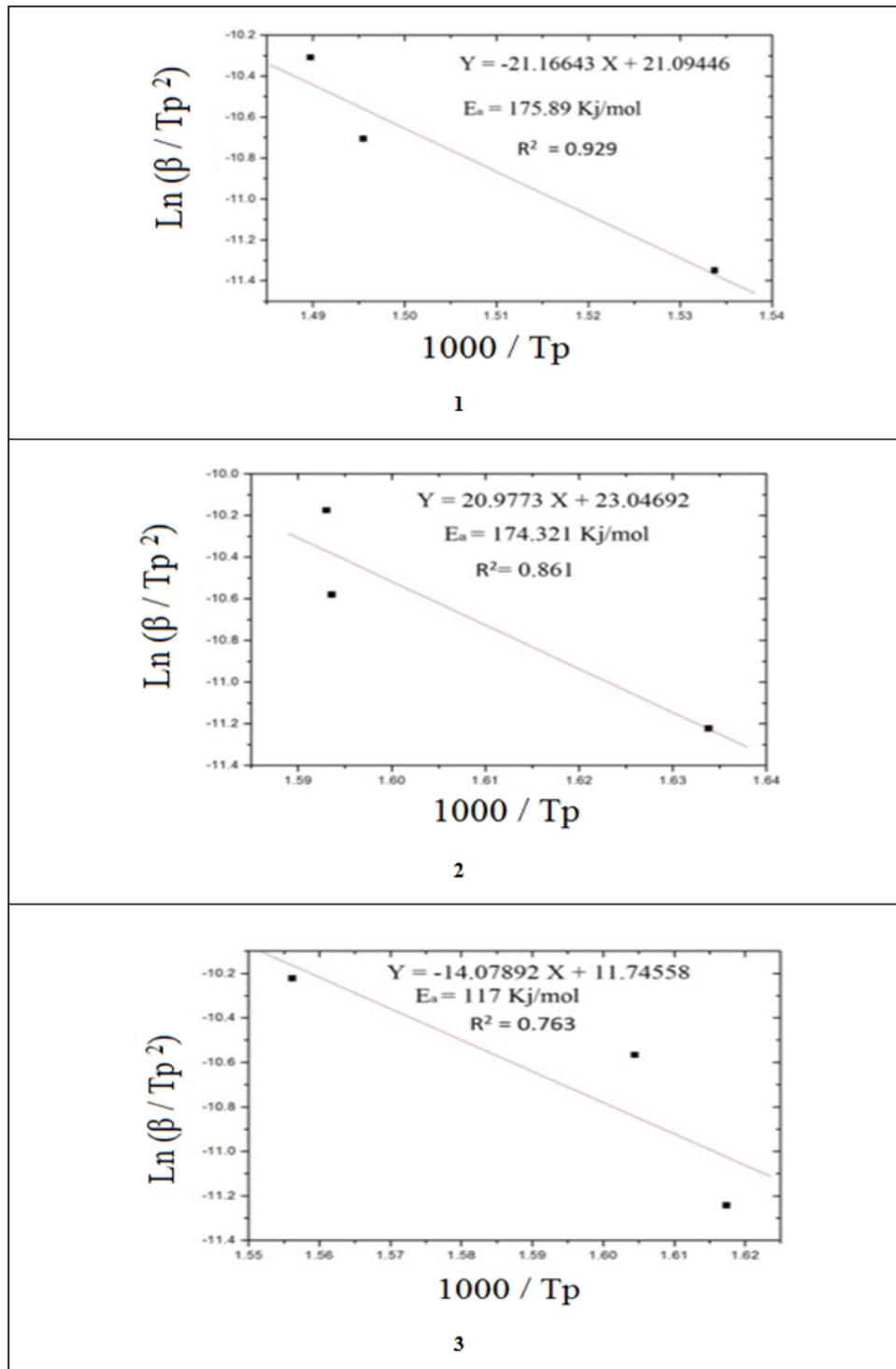
| A    | Cellulose      |       | Polybutylene succinate |       | Blend (cellulose 80%, PBS 20%) |       |
|------|----------------|-------|------------------------|-------|--------------------------------|-------|
|      | $E_f$ (Kj/mol) | $R^2$ | $E_f$ (Kj/mol)         | $R^2$ | $E_f$ (Kj/mol)                 | $R^2$ |
| 0.1  | 147.08         | 0.986 | 239.21                 | 0.999 | 343.11                         | 0.5   |
| 0.2  | 268.14         | 0.981 | 237.26                 | 0.999 | 434.04                         | 0.932 |
| 0.3  | 283.87         | 0.968 | 290.30                 | 0.980 | 414.58                         | 0.827 |
| 0.4  | 276.99         | 0.999 | 278.15                 | 0.965 | 348.48                         | 0.883 |
| 0.5  | 278.63         | 0.993 | 314.68                 | 0.972 | 358.97                         | 0.874 |
| 0.6  | 278.37         | 0.996 | 330.76                 | 0.988 | 374.28                         | 0.730 |
| 0.7  | 272.36         | 0.999 | 320.50                 | 0.990 | 375.29                         | 0.805 |
| 0.8  | 268.57         | 0.997 | 333.31                 | 0.999 | 360.42                         | 0.971 |
| 0.9  | 269.49         | 0.928 | 400.94                 | 0.986 | 373.43                         | 0.948 |
| Mean | 260.38         |       | 305.01                 |       | 375.84                         |       |



**Figure 12.** Coatsse-Redfern (modified) plots of (1) cellulose, (2) polybutylene succinate and (3) blend of cellulose (80%) and polybutylene succinate (20%), fractional extent of reaction:  $\alpha = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$

**Table 6. Activation energies ( $E_a$ ) of cellulose, polybutylene succinate and their blend (cellulose 80%, PBS 20%) using fit of plots Coatse-Redfern (CR) (modified) method:**

| A    | Cellulose           |       | Polybutylene succinate |       | Blend (cellulose 80%, PBS 20%) |       |
|------|---------------------|-------|------------------------|-------|--------------------------------|-------|
|      | $E_a$ (CR) (Kj/mol) | $R^2$ | $E_a$ (CR) (Kj/mol)    | $R^2$ | $E_a$ (CR) (Kj/mol)            | $R^2$ |
| 0.1  | 46.87               | 0.784 | 110.64                 | 0.998 | 245.91                         | 0.643 |
| 0.2  | 100.19              | 0.923 | 107.11                 | 0.999 | 187.60                         | 0.916 |
| 0.3  | 118.24              | 0.965 | 122.85                 | 0.996 | 185.55                         | 0.876 |
| 0.4  | 126.68              | 0.974 | 127.23                 | 0.988 | 176.89                         | 0.876 |
| 0.5  | 131.64              | 0.985 | 136.41                 | 0.980 | 176.26                         | 0.879 |
| 0.6  | 131.49              | 0.982 | 143.45                 | 0.975 | 176.84                         | 0.801 |
| 0.7  | 131.66              | 0.993 | 150.32                 | 0.978 | 179.64                         | 0.780 |
| 0.8  | 129.37              | 0.993 | 151.57                 | 0.989 | 177.71                         | 0.987 |
| 0.9  | 181.00              | 0.511 | 168.02                 | 0.999 | 179.23                         | 0.967 |
| Mean | 121.90              |       | 135.28                 |       | 187.29                         |       |



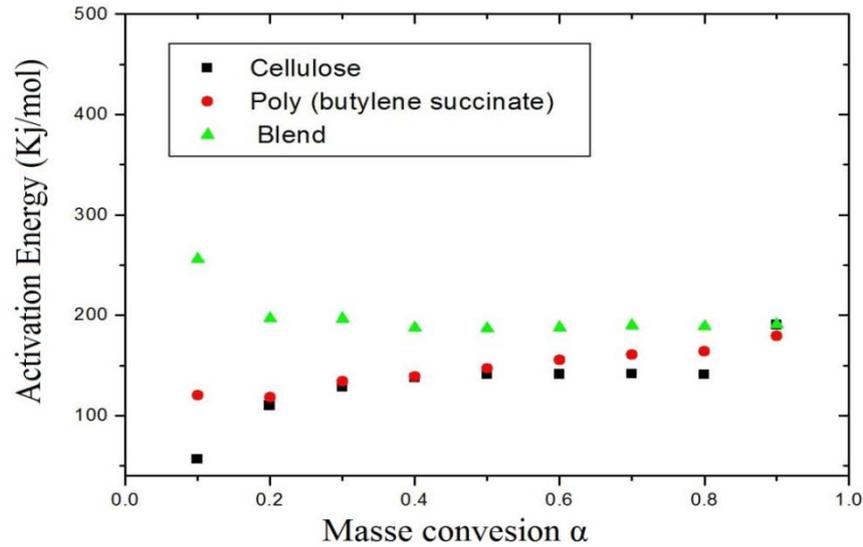
**Figure 13.** Kissinger plots of (1) cellulose, (2) polybutylene succinate and (3) blend of cellulose (80%) and polybutylene succinate (20%)

**Table 7.** Activation energies ( $E_a$ ) of cellulose, polybutylene succinate and their blend (cellulose 80%, PBS 20%) using fit of plots Kissinger (K) methods.

|   | Cellulose           |       | Polybutylene succinate |       | Blend (cellulose 80%, PBS 20%) |       |
|---|---------------------|-------|------------------------|-------|--------------------------------|-------|
| A | $E_{a(K)}$ (Kj/mol) | $R^2$ | $E_{a(K)}$ (Kj/mol)    | $R^2$ | $E_{a(K)}$ (Kj/mol)            | $R^2$ |
|   | 117.00              | 0.763 | 175.89                 | 0.929 | 174.32                         | 0.861 |

The terms  $1/T_p$  and  $\ln(\beta/T_p^2)$  could be obtained from DrTG results of heating rate (Figure 9). Therefore,  $1/T_p$  was represented in (x) axis and  $\ln(\beta/T_p^2)$  denoted as (y) axis. After three heating rates, the three values of  $T_p$  were substituted into the equation (11), a graph and a linear regression equation could be acquired. Calculated

activation energy is reported in Table 7. In case of cellulose,  $E_a=117.00$  Kj/mol with a correlation coefficient of 0.763, for polybutylene succinate,  $E_a=175.89$  Kj/mol with a correlation coefficient of 0.929, and for the blend of cellulose (80%) and polybutylene succinate (20%)  $E_a=174.32$  Kj/mol with correlation coefficient of 0.861.



**Figure 14.** Dependence of activation energy ( $E_a$ ) on mass conversion ( $\alpha$ ), as calculated by OFW methods for cellulose, polybutylene succinate and blend of cellulose (80%) and polybutylene succinate (20%)

According to the graph in Figure 14, the activation energy of the blend [cellulose (80%) and polybutylene succinate (20%)] has the largest value:

- For  $0.1 \leq \alpha \leq 0.2$   $E_{aBlend}$  decrease >  $E_{a(PBS)}$  stable,  $E_{aCellulose}$  increase,
- For  $0.2 \leq \alpha \leq 0.5$   $E_{aBlend} > E_{a(PBS)} \approx E_{aCellulose}$
- For  $0.6 \leq \alpha \leq 0.8$   $E_{aBlend} > E_{a(PBS)}$  increase >  $E_{aCellulose}$  decrease
- For  $\alpha = 0.9$   $E_{aBlend} \approx E_{a(PBS)} \approx E_{aCellulose}$

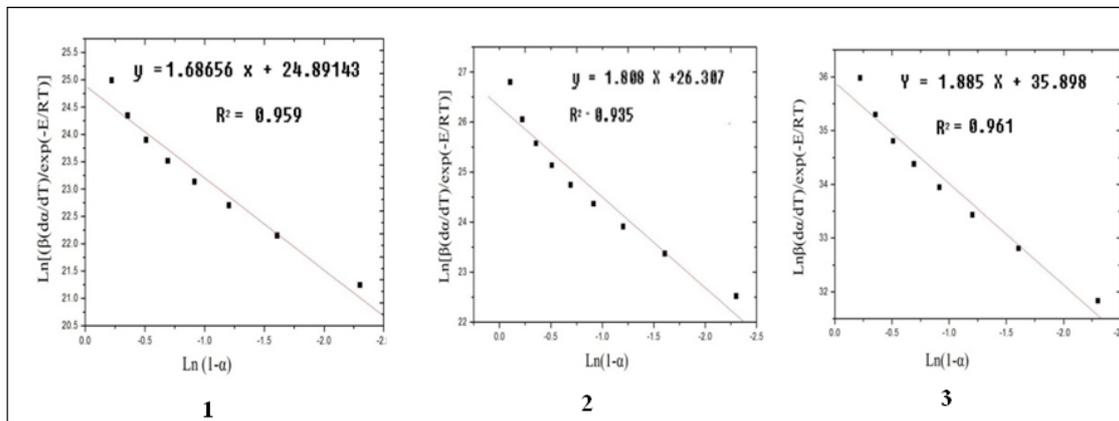
\*  $E_{aCellulose}$  = activation energy ( $E_a$ ) on the mass conversion ( $\alpha$ ), as calculated by OFW method for the cellulose

\*  $E_{a(PBS)}$  = activation energy ( $E_a$ ) on the mass conversion ( $\alpha$ ), as calculated by OFW method for the poly (butylene succinate).

\*  $E_{aBlend}$  = activation energy ( $E_a$ ) on the mass conversion ( $\alpha$ ), as calculated by OFW method for the blend [cellulose (80%) and poly (butylene succinate) (20%)].

Reaction order (n) and pre-exponential factor (A) were determined in our approach by the use of equation 10.

$$\ln \frac{\left(\frac{\beta d\alpha}{dT}\right)}{\exp\left(-\frac{E_a}{RT}\right)} = n \ln(1-\alpha) + \ln(A) \quad (10)$$



**Figure 15.** Relationship between  $\ln \frac{\left(\frac{\beta d\alpha}{dT}\right)}{\exp\left(-\frac{E_a}{RT}\right)}$  and  $\ln(1-\alpha)$  at  $\beta=10$  °C/min for pyrolysis of the Cellulose(1), the PBS(2) and the physical blend [Cellulose (80%) + PBS (20%)](3): experimental and correlated results [43]

By using Microcal Origin as informatics software and linear fit as application of these software (Figure 15), we found that for cellulose  $n = 1.68$  and  $\ln(A) = 24.89$ , and pre exponential factor  $A = 6.45 \cdot 10^{10} \text{ min}^{-1}$ , for polybutylene succinate  $n = 1.8$  and  $\ln(A) = 26.30$  and

pre-exponential factor  $A = 2.6 \cdot 10^{11} \text{ min}^{-1}$ , for the blend [cellulose (80%) and polybutylene succinate (20%)]  $n = 1.88$  and  $\ln(A) = 35.89$  and pre exponential factor  $A = 3.89 \cdot 10^{15}$ . All results are summarized in Table 8.

**Table 8. calculated values of activation energy, exponent n and pre-exponential factor for the thermal reaction mechanism of cellulose, PBS and the physical blend (Cellulose (80%) + PBS (20%))**

| Sample                               | $E_a$ (Kj) | n    | Pre-exponential factor A (min <sup>-1</sup> ) |
|--------------------------------------|------------|------|---|
| Cellulose                            | 131.82     | 1.68 | $6.45 \cdot 10^{10}$                          |
| Polybutylene succinate               | 146.26     | 1.80 | $2.6 \cdot 10^{11}$                           |
| Blend of Cellulose (80%) + PBS (20%) | 197.54     | 1.88 | $3.89 \cdot 10^{15}$                          |

The results show that the blend increases the activation energy of thermal degradation and the reaction rate is close to second order. It also promotes the rate of thermal degradation with high value of pre-exponential factor of  $3.89 \cdot 10^{15} \text{ min}^{-1}$  including most of two states of general degradation mechanism: thermal disorganization of the structural blend polymer, which allows rapid thermal degradation of carbonic chains.

**3.3.2. Comparative Thermal Degradation Kinetic Studies between the Blend [cellulose (80%) + PBS (20%)] and Polycaprolactone (PCL)**

Thermal degradation of PCL was recently studied [44, 45, 46]. Persenaire et al. proposed a degradation mechanism based on the results obtained from high-resolution thermogravimetric analysis coupled to mass spectrometry (MS) and Fourier transform infrared spectrometry [44]. They concluded that PCL degradation proceeds via elimination reaction which produces CO<sub>2</sub>, CO and 5-hexenoic acid, and via unzipping depolymerization to form ε-caprolactone.

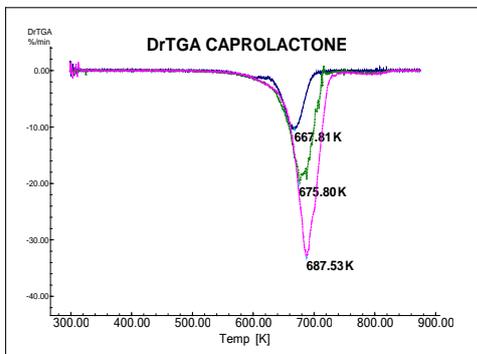
**Table 9. Activation energies of polycaprolactone using fit plots by Kissinger methods.**

| Sample           | Activation energy (Kj/mol) |                   | $\alpha_{max}$ | $R^2$ |
|------------------|----------------------------|-------------------|----------------|-------|
|                  | Kissinger method           | (second reaction) |                |       |
| Polycaprolactone | 195.91                     |                   | 0.63           | 0.931 |

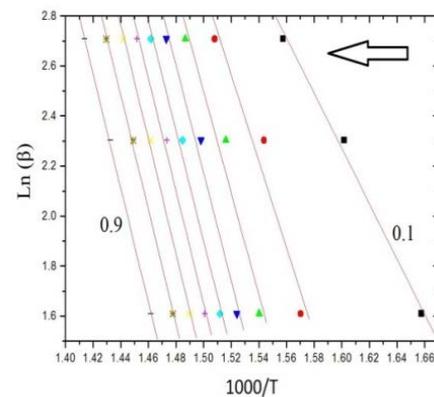
\* Where  $\alpha_{max}$  is the conversion corresponding to the maximum of a differential kinetic curve.

**Table 10. Activation energies (Ea) of the polycaprolactone using fit of plots Flynn-Wall-Ozawa (FWO) method**

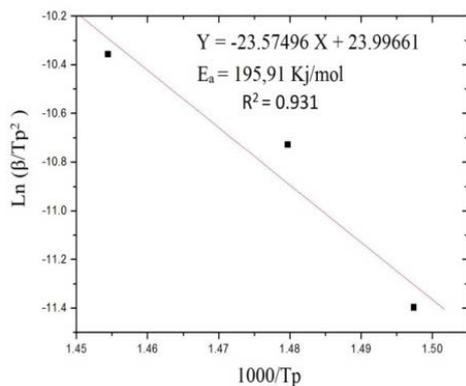
| Conversion $\alpha$ | Activation energy (Kj/mol) |       | $R^2$ |
|---------------------|----------------------------|-------|-------|
|                     | Ozawa method               |       |       |
| 0.1                 | 91.78                      | 0.992 |       |
| 0.2                 | 143.75                     | 0.946 |       |
| 0.3                 | 168.78                     | 0.958 |       |
| 0.4                 | 179.39                     | 0.980 |       |
| 0.5                 | 183.29                     | 0.989 |       |
| 0.6                 | 187.44                     | 0.993 |       |
| 0.7                 | 191.05                     | 0.997 |       |
| 0.8                 | 190.54                     | 0.998 |       |
| 0.9                 | 190.60                     | 0.999 |       |
| Mean                | 169.63                     | ---   |       |



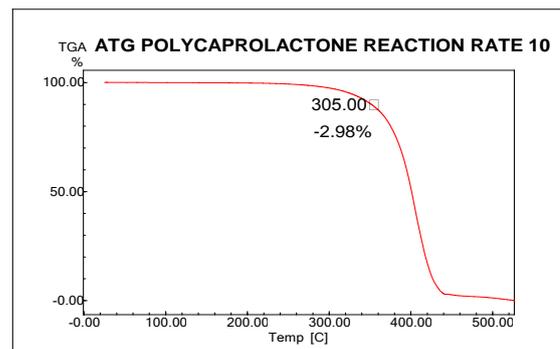
**Figure 16.** DrTGA DTG curves of polycaprolactone at different heating rates  $\beta$ : 5 °C/min; 10 °C/min and 15 °C/min. ; Tp is the most rapidly decomposing temperature used by Kissinger equation



**Figure 18.** Ozawa plots of polycaprolactone fractional extent of reaction:  $\alpha = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$



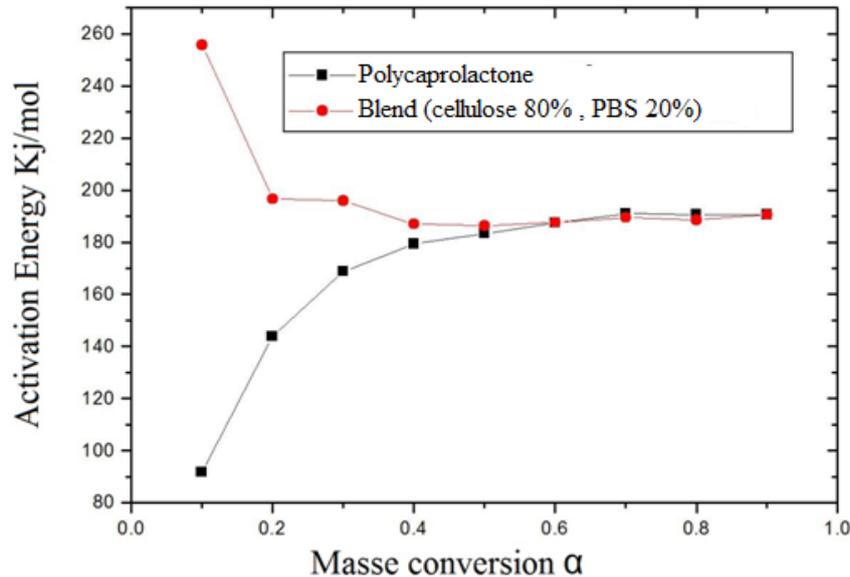
**Figure 17.** Kissinger plots of polycaprolactone



**Figure 19.** TGA dynamic thermograms polycaprolactone at heating rates  $\beta$ : 10 °C/min

In the case of PCL, the terms  $1/T_p$  and  $\ln(\beta/T_p^2)$  could be obtained from DrTG results (Figure 16). Thus,  $1/T_p$  was represented in (x) axis and  $\ln(\beta/T_p^2)$  denoted as (y) axis (Figure 17). Using three heating rate values and by substituting three  $T_p$  values into the equation (13), a graph and a linear regression equation could be acquired. The

Kissinger activation energy ( $E_a = 195.91$  KJ/mol) was determined for the reaction (Table 9) with a correlation coefficient value of 0.931 and  $\alpha_{max} = 0.63$ . The values calculated by Kissinger method were nearest to values of the activations energy (169.63 KJ/mol) calculated by Ozawa method (Figure 18) and Table 10.



**Figure 20.** Activation energy ( $E_a$ ) dependence on mass conversion ( $\alpha$ ), as calculated by OFW method for the blend [cellulose 80%, polybutylene succinate 20%] and polycaprolactone

From Figure 20, the physical blend has the highest activation energy and takes place between fractional extent of reaction  $\alpha = 0.1$  to  $0.4$ . An inverse thermal character of the activation energies between blend polymer and commercial polycaprolactone was remarked. The energies of the blend [cellulose (80%) + polybutylene succinate (20%)] decreases while activation energies of commercial polycaprolactone increases. Between fractional extent of reaction  $\alpha = 0.5$  to  $0.9$  activation energies of the blend [cellulose (80%), polybutylene succinate (20%)] and commercial polycaprolactone take the same allure.

## 4. Conclusion

In the present study, biodegradable polyester (polybutylene succinate) was prepared, then a green composite were elaborated by blending cellulose (80%) and polybutylene succinate (20%). Both polymers are biodegradable and renewable. Thermal degradation kinetics was investigated for cellulose, polybutylene succinate, physical blend of both polymers (cellulose (80%) + PBS (20%)) and compared with commercial polycaprolactone by dynamic thermogravimetry, under nitrogen atmosphere from room temperature to  $480^\circ\text{C}$ , at constant nominal heating rates: 5, 10 and  $15^\circ\text{C}/\text{min}$ , respectively. Kinetic analysis methodology consists on the combination of four different methods. Namely Friedman, Flynn-Wall-Ozawa, Kissinger, and Coats-Redfern modified methods have been successfully applied and have allowed the determination of cellulose, PBS and green composite kinetic triplet evolution. We recorded that the values of activation energies for the green

composite blend [cellulose (80%) and synthesized polybutylene succinate (20%)] and polycaprolactone are inverse between  $\alpha = (0.1- 0.4)$  and have the same values between  $\alpha = (0.5- 0.9)$ .

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