

## Thermal properties and stability of cassava starch films cross-linked with tetraethylene glycol diacrylate

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### Abstract

The thermal stability of starch cross-linked with tetraethylene glycol diacrylate was studied under nitrogen atmosphere by thermogravimetry (TG) and infrared spectroscopy (FTIR). The cross-linking reaction was confirmed by the increase in intensity of the absorption band at ca. 3330 cm<sup>-1</sup> indicating the reinforcement of hydrogen bonds and the appearance of a new band at 1726 cm<sup>-1</sup> associated with the carbonyl group of the cross-linking agent. After cross-linking the solubility of starch in water decreased to the range 9%–16%. The thermogravimetric curves of pure and cross-linked starches showed an initial stage of degradation (up to ca. 150 °C) associated with the loss of water. The main stage of degradation occurred in the range 250–400 °C corresponding to ca. 60%–70% mass loss. The activation energy (*E*) for the degradation process increased from 145 kJ mol<sup>-1</sup> (pure starch) to 195 kJ mol<sup>-1</sup> and 198 kJ mol<sup>-1</sup> for starch treated for 60 min by UV (30 °C) and at 90 °C, suggesting high stability after cross-linking. A higher value (240 kJ mol<sup>-1</sup>) was obtained for starch treated by UV for 120 min. The main volatile products determined by FTIR which correspond to hydrocarbons and carbonyl groups are apparently associated with the scission of weak bonds in the chain (probably branched groups) and the scission of stronger bonds (glycosidic linkages), respectively.

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**Keywords:** Cassava starch; Thermal stability; Activation energy; Cross-linking effect

### 1. Introduction

Starch is a renewable biopolymer of amylose (linear  $\alpha$ -(1 → 4) linked D-glucopyranosyl residues) and amylopectin (composed of linear chains of (1 → 4)- $\alpha$ -D-glucose residues connected through (1 → 6)- $\alpha$ -linkages). Starch has gained considerable interest because it is

inexpensive, available in large amounts from different sources and has provided a viable alternative to replace synthetic polymers, decreasing in consequence the environmental pollution [1–3]. Because starch itself is very brittle and has poor mechanical properties most of the applications have been associated with starch modifications including plasticisers, cross-linking agents and blending with other polymers [4–9]. Depending on the process, a higher temperature is needed affecting, in consequence, the thermal stability of the starch. Many polysaccharides have been analysed in terms of their thermal degradation, mainly considering the mechanism

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of chain breakdown, volatile products and activation energy. For example, cellulose and cellulose derivatives have been extensively studied in terms of the processes of degradation, reaction products of degradation and pyrolysis under different conditions [10–13]. Sodium hyaluronate, xanthan and methylcellulose were compared considering the kinetic (activation energy) and thermogravimetric parameters associated with the thermal degradation under nitrogen atmosphere [14]. The activation energy was also analysed for the process of thermal degradation of chitosan and a mercaptan derivative of chitosan under nitrogen and air atmospheres [15]. In general, depolymerisation processes (including thermal degradation) for polysaccharides are commonly described by equations which consider that the chain scission of the glycosidic linkage follows a pseudo first-order reaction [16,17]. However, the mechanism of thermal degradation of polysaccharides, such as starch, depends on the products of degradation, formation of radicals and temperature for the chain breakdown.

Considering that cassava starch is produced in large quantities and, in general, has been used as a raw material for different processes in food industries, in this study the thermal stability of starch films was evaluated before and after cross-linking with tetraethylene glycol diacrylate by two different methods: (i) UV irradiation at 30 °C and (ii) thermally at 90 °C. Kinetic and thermogravimetric parameters and volatile products for the thermal degradation of starch were analysed.

## 2. Experimental

### 2.1. Materials

The cassava starch (named Polysize55) was kindly donated by Poliamidos (Curitiba, Brazil) and was used as received. The percentage of amylose determined by titration was 16%. The molecular weight determined by light scattering was in the range  $10^6$  g mol<sup>-1</sup>– $10^8$  g mol<sup>-1</sup> depending on the solvent and temperature. Tetraethylene glycol diacrylate was purchased from Aldrich (St. Louis, USA) and was used without further purification.

### 2.2. Film preparation

Cassava starch films were prepared by casting from solutions in the concentration 1.5% (m/v) in distilled water. For both cross-linking methods the tetraethylene glycol diacrylate was added in the proportion of 5% (m/v) to the starch solution. In the UV cross-linking, first the starch solution was heated to 75 °C–80 °C (gelatinization temperature) for 40 min under stirring, cooled to room temperature and the cross-linking agent

was added. The samples were kept in the absence of light during the irradiation process ( $\lambda = 230$  nm) which was carried out for periods of 30 min, 60 min and 120 min at 30 °C. For the thermal process (90 °C) starch and the cross-linking agent were mixed before the starch gelatinization. All the solutions after irradiation or heating (90 °C) were spread on Teflon plates for solvent evaporation (casting process) to obtain the films. The films were stored in a desiccator under vacuum until analysis.

### 2.3. Thermogravimetry

The thermogravimetric analysis was performed with a Shimadzu (TGA-50) instrument. The measurements were performed at heating rates of 10 °C min<sup>-1</sup>, 20 °C min<sup>-1</sup> and 40 °C min<sup>-1</sup> under nitrogen (50 cm<sup>3</sup> min<sup>-1</sup>). The thermogravimetric data were analysed by the Ozawa's method [18] and the activation energy ( $E$ ) was determined from the slope of the plot of  $\log \beta$  (heating rate) versus  $1/T$  as defined by the Arrhenius equation [19].

### 2.4. Infrared spectroscopy

The FTIR spectra of pure and cross-linked starch samples (films) were obtained in KBr support with a 16 PC Perkin Elmer instrument with a resolution of 4 cm<sup>-1</sup>, in the range 4000 cm<sup>-1</sup>–400 cm<sup>-1</sup>. For the analysis of gas products, samples of ca. 150 mg were submitted to degradation in a tubular oven connected to the infrared equipment. The samples were heated under nitrogen (50 cm<sup>3</sup> min<sup>-1</sup>) at a heating rate of 10 °C min<sup>-1</sup>.

## 3. Results and discussion

### 3.1. Cross-linked starch characterization

Fig. 1 shows the FTIR spectra of starch before and after thermal cross-linking considering two wave number regions: (I) 4000 cm<sup>-1</sup>–2400 cm<sup>-1</sup> and (II) 2000 cm<sup>-1</sup>–400 cm<sup>-1</sup>. In region I, spectrum A (dotted line) shows a broad band at 3600 cm<sup>-1</sup>–3000 cm<sup>-1</sup>, in which the main absorption band (3530 cm<sup>-1</sup>) is related to free hydroxyl groups of pure starch. The shoulder at ca. 3300 cm<sup>-1</sup>–3200 cm<sup>-1</sup> indicates the presence of intramolecular hydrogen bonding for this system. The absorption band at ca. 2930 cm<sup>-1</sup> refers to the C–H stretching present in the starch. In the spectra related to cross-linked starch (B–D) a shift of the main absorption band to ca. 3330 cm<sup>-1</sup> is observed indicating the reinforcement of hydrogen bonds with covalent bonds (ether linkages). In the region 2000 cm<sup>-1</sup>–400 cm<sup>-1</sup>, the main absorption bands related to non-cross-linked

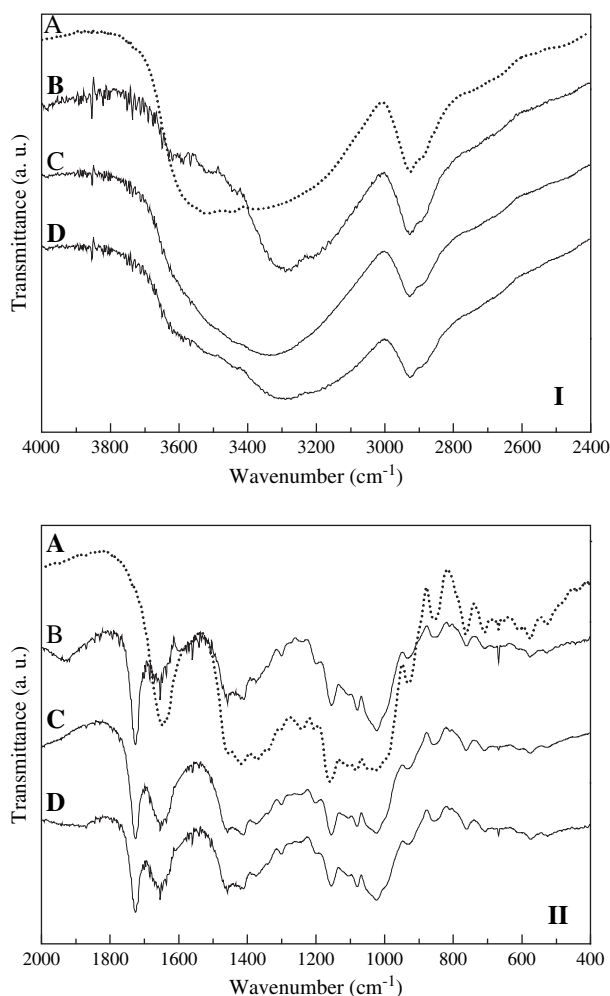


Fig. 1. FTIR spectra in the wave number regions 4000–2400  $\text{cm}^{-1}$  (I) and 2000–400  $\text{cm}^{-1}$  (II) for (A) pure starch and starch cross-linked at 90 °C with 5% of tetraethylene glycol acrylate for 30 min (B), 60 min (C) and 120 min (D).

starch (spectra A, dotted line) correspond to bound water at 1645  $\text{cm}^{-1}$ , C–H bending at 1400  $\text{cm}^{-1}$ –1460  $\text{cm}^{-1}$  and bands associated with C–O, C–C and C–O–H in the region 1200  $\text{cm}^{-1}$ –900  $\text{cm}^{-1}$ . The band position associated with the scissoring mode of residual water depends, in general, on the polysaccharide crystallinity. For example, in crystalline trehalose (a disaccharide) the band related to the water absorption appears at 1685  $\text{cm}^{-1}$ , indicating the presence of stronger hydrogen bonding [20]. For amorphous trehalose, an absorption band at 1645  $\text{cm}^{-1}$  is observed. The bands associated with C–O and C–O–H had been assigned to the glycosidic linkage [21]. In spectra B–D (cross-linked starch) a new band is observed at 1726  $\text{cm}^{-1}$  associated with the carbonyl group of the cross-linking agent used in this study. With cross-linking the absorption band at 1645  $\text{cm}^{-1}$  shifts to 1653  $\text{cm}^{-1}$  probably due to the presence of stronger hydrogen bonding as reported for crystalline trehalose [20]. Small frequency shifts ( $\sim 4 \text{ cm}^{-1}$ ) can also be observed for the

bands in the region 1200  $\text{cm}^{-1}$ –900  $\text{cm}^{-1}$  indicating a change in the level of hydrogen bonding with the cross-linking.

In order to confirm the cross-linking of the starch, the solubility in water considering different treatment times at 90 °C and UV (30 °C) was analysed. Non-cross-linked starch films swell very fast losing their resistance after a few hours. The solubility of cross-linked starch was analysed after 36 h of stirring in distilled water. Under these conditions, the percentage of soluble starch after cross-linking at 90 °C was 15.8%. After treatment by UV (2 h) the solubility was only 9.0%. Under both conditions the films remained intact. These results suggest the efficiency of cross-linking for both methods used.

### 3.2. Thermogravimetry

In Fig. 2, the thermogravimetric curves of starch before (solid line) and after (dotted line) cross-linking by UV irradiation and at 90 °C (dashed line) are shown. Despite some differences in terms of the presence of bound water and residual mass, similar profiles in the curves of mass loss were observed. The percentage of bound water varies from 11% to 15% and the residual mass at 600 °C from 15% to  $\sim 20\%$ . For non-cross-linked cassava starch, the main stage of degradation, which corresponds to  $\sim 70\%$  of mass loss, starts at  $\sim 250 \text{ °C}$  and the residual mass is 15% at 600 °C. Apparently the residual mass is related to the nature of the starch, impurities and inorganic components. Athawale and Lele [22] determined for maize starch 75.5% of mass loss in the main stage of degradation. However, for the same starch the cited authors described as  $\sim 2\%$  the residual mass at 495 °C.

For cross-linked cassava starch the degradation starts at  $\sim 300 \text{ °C}$ . The main stages of degradation correspond

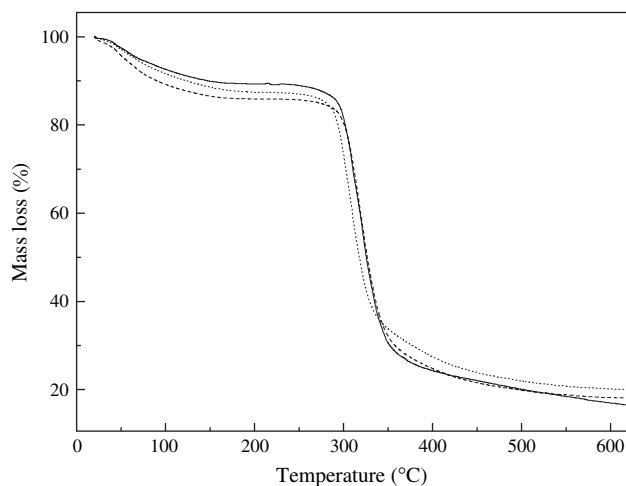


Fig. 2. Thermogravimetric curves for starch before (solid line) and after (dotted line) cross-linking by UV irradiation and at 90 °C (dashed line).

to 55% and 60% for the starch cross-linked by UV irradiation (dotted line) and at 90 °C (dashed line), respectively. The residual mass at 600 °C for the starch cross-linked by both methods is ~20%.

### 3.3. Activation energy

The apparent activation energy ( $E$ ) was determined using Ozawa's method [18] in which the temperature dependence of the degradation reaction may be expressed in terms of Eq. (1) (Arrhenius equation [19])

$$k = A \exp(-E/RT) \quad (1)$$

where  $k$  is the rate constant,  $R$  the gas constant and  $T$  the temperature (K). This method requires at the least three thermogravimetric (TG) curves at different heating rates ( $\beta$ ). In Fig. 3, the TG curves at  $\beta = 10, 20$  and  $40 \text{ }^\circ\text{C min}^{-1}$  for starch cross-linked with 5% of tetraethylene glycol acrylate by UV irradiation (60 min) are shown as an example. As observed, the TG curves shift towards higher temperatures as the heating rate increases due to the shorter time required for a sample to reach a given temperature at a faster heating rate [23]. Considering the region defined by the dashed lines (ca. 15%–65% weight loss) in Fig. 3 and the three heating rates at constant degree of conversion, the activation energy can be determined by plotting  $\beta$  versus the inverse of the temperature according to Eq. (2).

$$\log \beta = -0.457E/RT \quad (2)$$

Thus, the plots of  $\log \beta$  versus  $1/T$  (Fig. 4) for the cross-linked starch mentioned above were linear with the slope equal to  $-E/R$ .

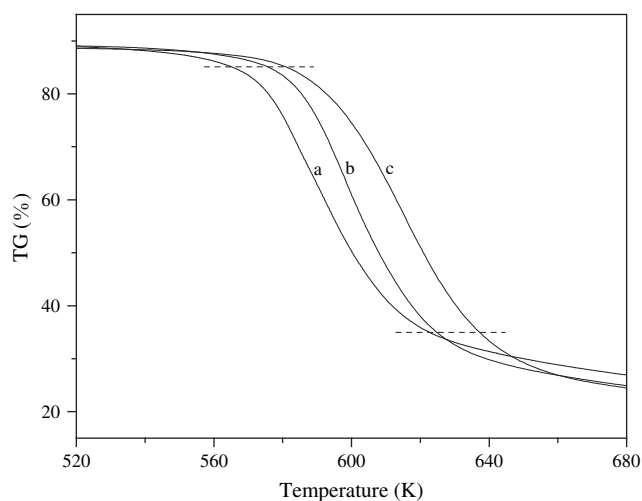


Fig. 3. Thermogravimetric curves of starch cross-linked with 5% of tetraethylene glycol acrylate by UV irradiation (60 min) at heating rates: (a) 10, (b) 20 and (c)  $40 \text{ }^\circ\text{C min}^{-1}$ .

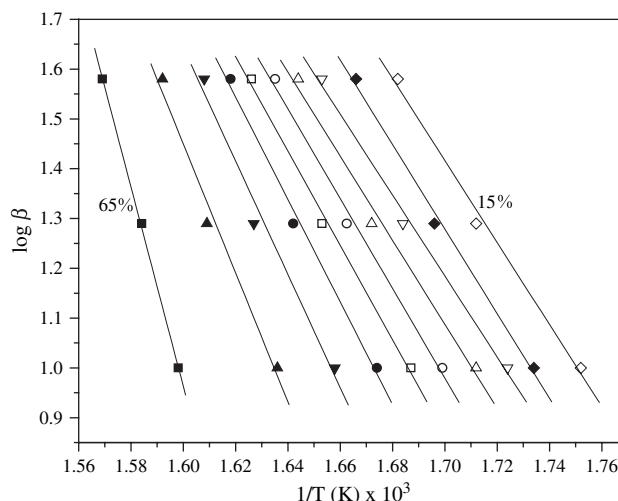


Fig. 4. Plots of  $\log \beta$  versus  $1/T$  with weight loss from 15% to 65% ( $\beta = 10, 20$  and  $40 \text{ }^\circ\text{C min}^{-1}$ ).

In Table 1 the activation energy of various polysaccharides, considering different reaction media are shown. For non-cross-linking polysaccharides great differences were first identified in terms of  $E$  values between the reaction conducted under nitrogen or air atmosphere. Under air the  $E$  values were lower than  $100 \text{ kJ mol}^{-1}$  (except for chitosan) suggesting a favorable chain breakdown under this condition. Under nitrogen,  $E$  values in the range  $130 \text{ kJ mol}^{-1}$ – $150 \text{ kJ mol}^{-1}$  and  $170 \text{ kJ mol}^{-1}$ – $200 \text{ kJ mol}^{-1}$  were observed, indicating an effect associated with the structural characteristics. For example, the activation energy value which was  $195 \text{ kJ mol}^{-1}$  for cellulose decreased to  $140 \text{ kJ mol}^{-1}$  for methylcellulose due to the presence of methyl groups.

Table 1

Comparative values of activation energy for thermal degradation of different polysaccharides

| Polysaccharides       | $E$ ( $\text{kJ mol}^{-1}$ ) | Atmosphere | Reference  |
|-----------------------|------------------------------|------------|------------|
| Cellulose             | 59                           | Air        | [28]       |
|                       | 84                           | Air        | [29]       |
|                       | 195                          | Nitrogen   | [30]       |
| D-Glucose             | 174                          | Nitrogen   | [30]       |
| Corn starch           | 50                           | Air        | [28]       |
| Xanthan               | 130                          | Nitrogen   | [14]       |
| Sodium hyaluronate    | 135                          | Nitrogen   | [14]       |
| Methylcellulose       | 140                          | Nitrogen   | [14]       |
| Chitosan              | 181                          | Nitrogen   | [15]       |
|                       | 160                          | Air        | [15]       |
| <i>Cassava starch</i> |                              |            |            |
| Pure                  | 145                          | Nitrogen   | This study |
| Cross-linked          |                              |            |            |
|                       |                              |            |            |
| 30 min (UV)           | 226                          | Nitrogen   | This study |
| 30 min (90 °C)        | 187                          | Nitrogen   | This study |
| 60 min (UV)           | 195                          | Nitrogen   | This study |
| 60 min (90 °C)        | 198                          | Nitrogen   | This study |
| 120 min (UV)          | 240                          | Nitrogen   | This study |
| 120 min (90 °C)       | 148                          | Nitrogen   | This study |

Another apparent effect is that related to charged polysaccharides. In general, the thermal stability increased with a decrease in the charge of the macromolecules. As shown in Table 1, charged polysaccharides such as sodium hyaluronate have lower  $E$  values in comparison to cellulose which is neutral. This effect was previously described by Khomutov et al. [24] in studies of thermooxidative degradation of an ionic polysaccharide.

For pure cassava starch an activation energy value of  $145 \text{ kJ mol}^{-1}$  was determined in this study. This value is of the same magnitude as those described in the literature for methylcellulose (modified cellulose) and sodium hyaluronate (charged macromolecule). However, for cross-linked starch,  $E$  values up to  $240 \text{ kJ mol}^{-1}$  were determined. The  $E$  values for the samples exposed to UV were higher suggesting high stability. Apparently, this behaviour indicates a higher efficiency of cross-linking in agreement with the low solubility (9%) as previously discussed. The  $E$  values for cross-linked starch shown in Table 1 indicate firstly that these films acquired a structure with stronger links in the chain. At the same time,  $E$  values higher than  $100 \text{ kJ mol}^{-1}$  suggest that the chain scission occurs randomly, as described for other systems in the literature [14,19,25–27].

### 3.4. Products of degradation

Different reports in the literature have described processes of polysaccharide degradation considering mainly the products of degradation and reaction mechanism [10–12,14,31–39]. For example, the mechanism of cellulose degradation, which is one of the most extensively studied polysaccharides, was described considering the water evolution from cellulose after heating to different temperatures in the presence of air [10]. The authors observed up to ca.  $300 \text{ }^\circ\text{C}$  the formation of anhydrocellulose and above the appearance of furanic species as the products of thermal degradation. Under nitrogen, Richards [11] identified at  $350 \text{ }^\circ\text{C}$ , glycolaldehyde, formic acid, 1-hydroxypropan-2-one, acetic acid and ethylene glycol as the main reaction products for the degradation of cellulose (filter paper). Results obtained by Radlein et al. [38] indicated that at temperatures lower than  $300 \text{ }^\circ\text{C}$  the pyrolysis of cellulose produced mainly char and gases, confirming previous results described by Shafizadeh [39] who suggested that up to  $300 \text{ }^\circ\text{C}$  a reduction in the degree of polymerisation, elimination of water, formation of carbonyl, carboxyl and hydroperoxide groups (in the presence of air), and evolution of carbon mono- and dioxide occurred. Villetti et al. [14] analysed by FTIR the residual products of the thermal degradation of sodium hyaluronate. The analysis at  $280 \text{ }^\circ\text{C}$  (the temperature of maximum degradation rate) resulted in the appearance of bands associated with exocyclic groups ( $1150 \text{ cm}^{-1}$ ,  $1079 \text{ cm}^{-1}$  and  $1042 \text{ cm}^{-1}$ ) and glycosidic

linkage in the main chain. At temperatures above  $400 \text{ }^\circ\text{C}$ , the scission of strong links in the backbone occurred.

In this study only the gas products evolved from the degradation of cross-linked starch (2 h at  $90 \text{ }^\circ\text{C}$ ) were analysed by FTIR. The FTIR spectra at different degradation temperatures are shown in Fig. 5. The main degradation reaction starts at ca.  $240 \text{ }^\circ\text{C}$  in agreement with the thermogravimetric curves (Fig. 2). Below  $240 \text{ }^\circ\text{C}$  (spectra not shown) absorption bands of low intensity were observed which are associated with adsorbed water, non-reacted tetraethylene glycol diacrylate (cross-linking agent) and low molecular weight fractions (branched chain). The presence of branched fractions of low molecular weight was reported by Colonna and Mercier [40] in pea starches. The starch studied here presented a higher level of amylopectin ( $>80\%$ ) suggesting that the gas products with C–H groups (bands at region  $3000 \text{ cm}^{-1}$ – $2850 \text{ cm}^{-1}$  and at  $1390 \text{ cm}^{-1}$ ) may be related to the presence of branched fractions of low molecular weight in the cassava starch.

At  $280 \text{ }^\circ\text{C}$ , absorption bands associated with free OH ( $3670 \text{ cm}^{-1}$ , primary alcohols), C–H stretching ( $3000 \text{ cm}^{-1}$ – $2850 \text{ cm}^{-1}$ ,  $1240 \text{ cm}^{-1}$ , and  $890 \text{ cm}^{-1}$ ),  $\text{CO}_2$  ( $2360 \text{ cm}^{-1}$  and  $668 \text{ cm}^{-1}$ ), CO ( $2175 \text{ cm}^{-1}$  and  $2108 \text{ cm}^{-1}$ ),

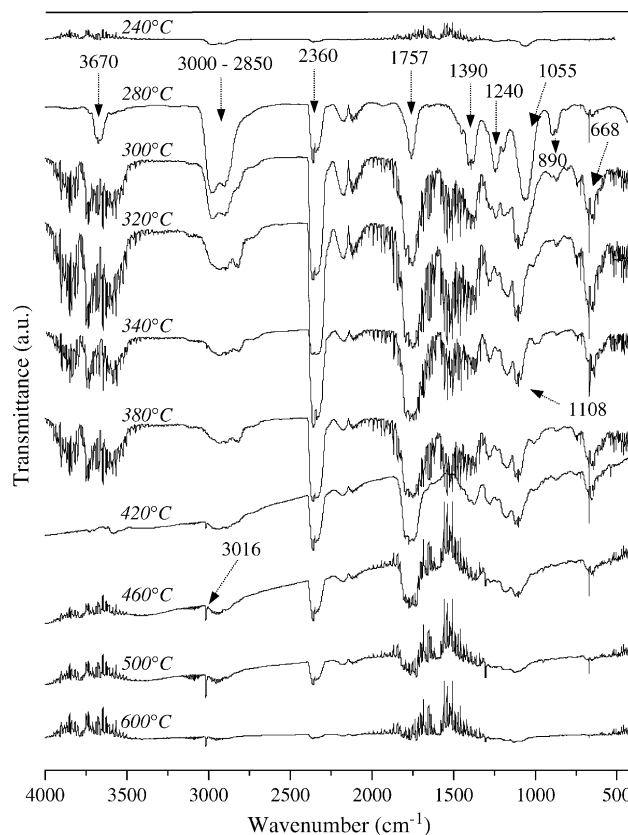


Fig. 5. FTIR spectra for the volatile products of starch cross-linked at  $90 \text{ }^\circ\text{C}$  with 5% of tetraethylene glycol diacrylate during thermal degradation at different temperatures.



C=O ( $1757\text{ cm}^{-1}$ ), CH<sub>3</sub> bending modes ( $1390\text{ cm}^{-1}$ ), CH<sub>2</sub> stretching ( $1240\text{ cm}^{-1}$ ) and C–O (C–O–C) stretching ( $1055\text{ cm}^{-1}$ , glycosidic linkage), were observed. At  $300\text{ }^{\circ}\text{C}$  a considerable decrease in the intensities of the absorption bands related to C–H and C–O–H groups associated with weak bond chain scission was observed. These results are in agreement with those reported by Athawale and Lele [22] who considered the pyrolysis of maize starch. With increased temperature the band at  $1055\text{ cm}^{-1}$  shifted to  $1108\text{ cm}^{-1}$  (at  $320\text{ }^{\circ}\text{C}$ – $340\text{ }^{\circ}\text{C}$ ) due to the chain scission, the formation of carbonyl compounds was thus increasing. The appearance of the band associated with CO<sub>2</sub>, CO and C=O indicates the scission of the glycosidic linkages and strong links in the backbone of the starch. At the same time, the fine vibrational structures observed at  $\sim 1500\text{ cm}^{-1}$  are apparently associated with aliphatic products formed by the scission of the polymeric main chain [26]. The carbonyl band at ca.  $1757\text{ cm}^{-1}$  ( $280\text{ }^{\circ}\text{C}$ ) associated with the broadening of the same band at higher temperatures indicates the formation of volatile products, such as carboxylic acid esters, alkyl esters and aldehydes as the main products. These results are in agreement with the formation of volatile degradation products, such as formic acid, 1-hydroxypropan-2-one, acetic acid and ethylene glycol, previously described by Richards and Shafizadeh [32] for other polysaccharides. However, the bands associated with C–H stretching ( $3000\text{ cm}^{-1}$ – $2850\text{ cm}^{-1}$  and  $1240\text{ cm}^{-1}$ ) and CH<sub>3</sub> bending modes ( $1390\text{ cm}^{-1}$ ) practically disappeared at  $460\text{ }^{\circ}\text{C}$ , a new band at  $3016\text{ cm}^{-1}$  (symmetric =CH<sub>2</sub>) appearing which indicates that at high temperatures of degradation the formation of unsaturated volatile products also occurs.

#### 4. Conclusions

The thermal stability of starch cross-linked with tetraethylene glycol diacrylate was analysed using thermogravimetry and infrared spectroscopy. Although the thermogravimetric curves for non-cross-linked and cross-linked starches seem similar, with only one main stage of degradation, different activation energy values were observed. With the cross-linking, the  $E$  values increased from  $145\text{ kJ mol}^{-1}$  (pure starch) to  $195\text{ kJ mol}^{-1}$  and  $198\text{ kJ mol}^{-1}$  for starch treated for 60 min by UV ( $30\text{ }^{\circ}\text{C}$ ) and at  $90\text{ }^{\circ}\text{C}$ , respectively, suggesting high stability after treatment. The  $E$  values for the samples exposed to UV were higher, suggesting a greater efficiency of the cross-linking method. The increase in the  $E$  values after cross-linking also indicates changes in the mechanism of degradation which is also dependent on the products formed during the degradation process. Although  $E$  values higher than  $100\text{ kJ mol}^{-1}$

suggest a random chain scission, it seems clear that for the cross-linked starch, the main volatile products associated with hydrocarbons and carbonyl are associated with the scission of weak bonds in the chain (probably branched groups) and after the scission of stronger bonds (glycosidic linkages), respectively.

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