THERMAL AND THERMOXIDATIVE DEGRADATIONS OF STARCH AND THERMOSENSITIVE STARCH-g-BAM COPOLYMERS

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Thermal degradation under N_2 atmosphere and thermoxidative degradation under air atmosphere of increasingly grafting efficiency values (i.e. *GE*%=0.0 to 35.5) for starch and starch grafted with N-*tert*-butylacrylamide thermosensitive copolymers (starch-g-BAM) by Ozawa and Kissinger methods using thermogravimetric analysis (TG) and differential scanning calorimetry techniques (DSC) at 10, 30 and 50% mass losses respectively have been studied. Influence of physical inter and intra molecular interactions on grafting and consequently on activation energy of degradation ($E_{a,d}$) was investigated using Ozawa's method, whereas linear dependence of $E_{a,d}$ on *GE*% by scaling relations using Kissinger's method was determined. Furthermore, the thermoxidative degradation induces the possibility of molecular rearrangement, cyclization and partial crosslinking that is deduced from the activation energy of degradation ($E_{a,d}$) and residual mass of TG profile. Thermal stability of starch does not alter as a result of different grafting efficiency percentages.

Keywords: *grafting efficiency, thermal and thermoxidative degradation, thermosensitive polymers*

Introduction

Thermal and thermoxidative degradation techniques have been extensively used to investigate and describe the thermal degradable fragments and degradation changes that can take place in the backbone of the segments of polymers. In addition such techniques were used to analyze and elucidate kinetic parameters, physical changes, and chemical interactions that occur throughout thermal and thermoxidative degradation processes [1–10]. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) were found to describe profound and deep insight investigation of the molecular and segmental changes of polymers especially if it is combined with mass spectrometry.

The industrial applications (i.e. biodegradable thermoplastics, sizing agents, thickeners, and napkins) [11–14] of grafted starch with N-substituted monomers that can form thermosensitive polymers such as N-*tert*-butylacrylamide, and other monomers, makes it important to study the thermal and thermoxidative degradation behavior and the kinetic parameters of this class of polymers by different techniques.

Recently we have described the synthesis and optimization of chitosan grafted with ethylmethacrylate [15] and acrylic acid [16] polymers using ceric ammonium nitrate as initiator [17], furthermore starch grafted with thermosensitive monomers such as N-*tert*-butylacrylamide was also investigated

in our laboratory [18]. The present work at the investigation of degradable products and kinetic parameters deduced from TG and DSC techniques using Kissinger [19] and Ozawa [20] methods and its relation to grafting efficiency (*GE*%) of starch grafted with N-*tert*-butylacrylamide that can form new class of thermosensitive copolymers. Furthermore, the thermal stability of starch and grafted starch copolymers are also investigated.

Experimental

Materials

N-Butylacrylamide monomer (BAM)   (>99.5%, Acros) was stored in refrigerator and was brought to room temperature before use, and Maize Starch (Food grade) used for synthesis of starch-g-BAM copolymer was supplied by Riedel-Dehaen (Germany) and Ceric ammonium nitrate (CAN) was used as a 0.1 M solution in molar nitric acid.

Preparation of Starch-g-BAM copolymer

The synthesis of the desired copolymer was described in a previous work [18] where 1.0 g of dried starch was dissolved In 75 mL distilled water and then was treated with $9.1 \cdot 10^{-4}$ M of CAN (i.e. from ~84% to 21% (mass/mass) with respect to N-*tert*-butylacrylamide monomer amount) for 15 min under N_2 atmosphere then

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a predetermined amount of N-*tert*-butylacrylamide (BAM) monomer was dropwisely added to the solution as described in Table 1, and the polymerization was proceeded at 30°C and for 240 min. After the completion of 240 min, the solution was allowed to cool and 50 mL of distilled water were added and stirred for 10 min to extract homopolymer. The precipitate was then collected, filtered and washed several times with warm distilled water, can remove excess homopolymer and can be checked by precipitation with methanol. Washing process was continued until no precipitation of homopolymer was observed [18, 21]. The percentage of grafting was evaluated using grafting efficiency (*GE*%) [22], which could be calculated from the relation.

$$GE\% = 100(W_2 - W_1)/W_3 \qquad (1)$$

where W_1, W_2 and W_3 are the masses of starch, starch-g-BAM copolymer and the BAM monomer respectively. Table 1 describes the optimum conditions for starch-g-BAM thermosensitive copolymer, which will be investigated for thermal and thermoxidative degradation processes using Ozawa and Kissinger methods.

Thermal techniques

- Thermogravimetric analysis (TG): was carried out using Shimadzu TGA-50 (Japan) under air and N_2 atmospheres from ambient temperature to 500°C at different heating rates (i.e. 5, 10, 20, and 40°C min^{-1}).
- Differential scanning calorimetry (DSC): was carried out on a Shimadzu DSC-50Q quick cooling differential scanning calorimeter under a N_2 atmosphere at a heating rate of 50°C min^{-1}. All samples in Table 1 were heated from ambient temperature to 200°C at a heating rate of 50°C min^{-1} and then the temperature was automatically fixed by computer programme at 200°C for 150 min.

Results and discussion

Methods for degradation kinetics

Kissinger's [19] and Ozawa's [20] techniques are respectively differential and integral thermal analysis methods used for the determination of activation energy of degradation ($E_{a,d}$) values at different heating rates. Kissinger's technique treat materials that pyrolyze and residue and it emphasizes on the conversion of solid into solid and gas, where the temperatures (T_{fdp}) of the first derivative peaks of TG profile (fdp denotes first derivative peak) are monitored at different heating rates. The Kissinger's equation that involves the determination of the activation energy of degradation is as follows:

$$d[\ln (B/T_{fdp}^2)]/d(1/T_{fdp}) = -E_{a,d}/R \qquad (2)$$

where B is the heating rate, T_{fdp} is the first derivative peak temperature at certain heating rate, and $E_{a,d}$ is the activation energy of degradation. Thus, a plot of $\ln(B/T_{fdp}^2)$ *vs.* $1/T_{fdp}$ yields the activation energy of degradation. Ozawa's techniques is an integral technique which implies that relationship between the logarithm of the heating rate (log$B$) and reciprocal temperature ($1/T$) at constant mass loss, yields straight lines at different heating rates, in which the apparent activation energy of degradation can be calculated from the slope of linear relationships [20]. Thus in order to manipulate the data obtained from both techniques, we choose to study the activation energy of degradation at three decomposition temperatures (i.e. temperatures which have shown first derivative peaks), which are 10, 30 and 50% mass losses respectively. The choice of such three decompositions is made based on that the maximum changes occurred within this range, and beyond 50% mass loss changes were limited and less important. Furthermore the activation energy of degradation values deduced from both techniques are correlated with grafting efficiency (*GE*%) to examine the effect of grafting on the degradation kinetic parameters.

Analysis with TG

Figure 1 shows the TG profile of starch-g-BAM copolymer (*GE*%=35.5) at different heating rates under N_2 atmosphere. It can be noticed that around 80% of the copolymer decomposes in a temperature range of 290 to 450°C, whereas under air atmosphere only 60% of the copolymer (*GE*%=35.5) was decomposed in the same temperature range.

Table 1 The optimum conditions for starch-g-BAM thermosensitive copolymer

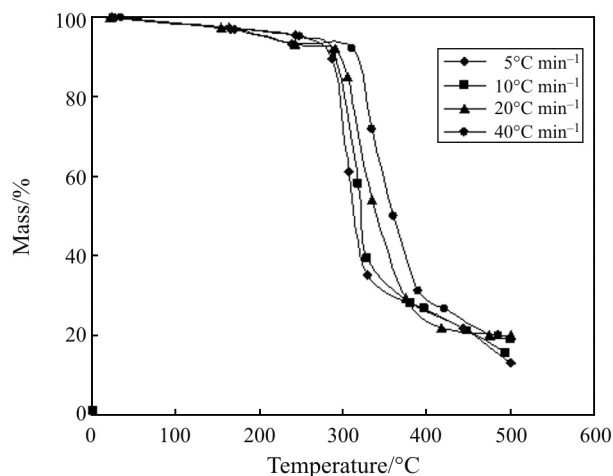| Sample	[BAM]/M	[CAN]/M	Temperature/°C	Time/min	Liquor/mL	GE%
1[a]	–	–	–	–	–	0.00
2	0.005	9.1·10^{-4}	30	240	200	18.6
3	0.010	9.1·10^{-4}	30	240	200	23.5
4	0.015	9.1·10^{-4}	30	240	200	29.5
5	0.020	9.1·10^{-4}	30	240	200	35.5

[a]Pure starch

Fig. 1 TG profile of maximum $GE\%$ (i.e. $GE\%=35.5$) of starch-g-BAM copolymer at different heating rates under N_2 atmosphere

Furthermore the decomposition temperatures ($T_{max.}$) at 30% mass loss derived from first derivative increases about 11–15°C on each incline of heating rate. Figure 2 illustrates the change of maximum decomposition temperatures as grafting efficiency increases at different heating rates.

It can be deduced from Fig. 2 that the maximum decomposition temperatures does not alter at different grafting efficiencies at constant heating rate. This implies that the grafted chains of N-*tert*-butylacrylamide (BAM) on starch does not form any chemical intermolecular forces (i.e. crosslinking) between starch chains or even between grafted poly(BAM) chains at ambient temperature or even at elevated temperatures.

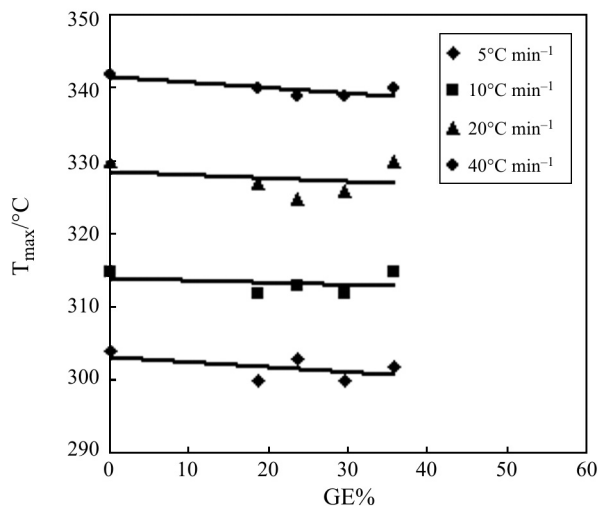Figure 3 shows the Ozawa's plot of maximum decomposition temperature (i.e. 30% mass loss) at

Fig. 2 Change of maximum decomposition temperatures ($T_{max.}$) *vs.* grafting efficiency ($GE\%$) at altered heating rates under N_2 atmosphere
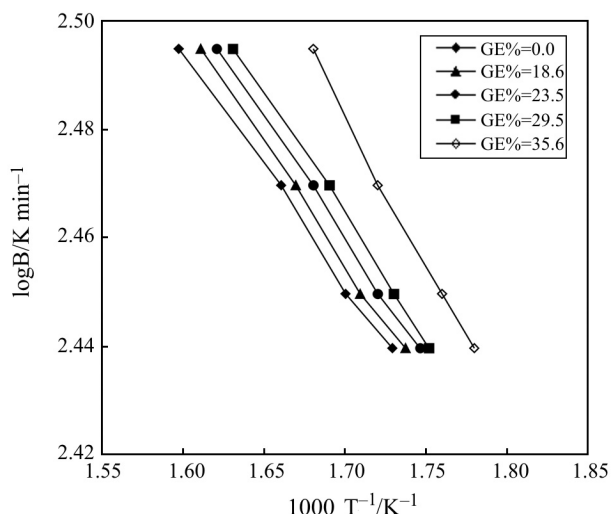

Fig. 3 Log$B$ *vs*. $1/T$ plot of the maximum decomposition temperatures (30% mass loss) at different grafting efficiencies

different grafting efficiencies, used for the determination of activation energies of degradation.

The activation energy of degradation values ($E_{a,d}$) at two mass losses (i.e. 10, and 30%) calculated using Ozawa's plot are listed in Table 2.

It can be noticed that for the 10% mass loss, the activation declines as $GE\%$ increases, up to $GE\%=23.5$, then it inclines again. This decline in activation energy is attributed to the ability of poly(BAM) chains to partly destroy some crystalline regions of starch macromolecules [18, 23], which consequently cause decrease in microhardness of polymer chains and this is reflected on the decrease in activation energy of degradation. Furthermore the small incline is explained by the increase of poly(BAM) chains a result of increase in $GE\%$, which enhance some physical intermolecular and intramolecular interactions like hydrogen bonding, which physically bind the starch and poly(BAM) chains with each other [26, 27]. At 30% mass loss there is a noticeable oscillatory behavior in the activation energy of degradation. This oscillatory behavior suggests that the activation energy of degradation values deduced from Ozawa's plots show independency on grafting efficiency.

Table 2 Activation energy of degradation values ($E_{a,d}$) at different mass losses determined under N_2 atmosphere (and under air atmosphere) using Ozawa plots

$GE\%$	$E_{a,d}$ at 10% mass loss/kJ mol^{-1}	$E_{a,d}$ at 30% mass loss/kJ mol^{-1}
0.0	7.26	3.27 (3.53)
18.6	3.10	3.41 (3.68)
23.5	1.52	3.26 (3.71)
29.5	3.33	3.52 (3.78)
35.5	3.97	3.44 (4.58)

Table 3 Activation energy of degradation values ($E_{a,d}$) at different mass losses determined under N_2 atmosphere (and under air atmosphere) using Kissinger's plots

GE%	$E_{a,d}$ at 10% mass loss/kJ mol^{-1}	$E_{a,d}$ at 30% mass loss/kJ mol^{-1}
0.0	10.45	2.49 (2.41)
18.6	5.24	2.13 (0.53)
23.5	4.98	2.02 (0.32)
29.5	4.62	1.49 (1.21)
35.5	4.03	1.20 (3.76)

Table 3 summarizes the calculated activation energy of degradation ($E_{a,d}$) using Kissinger's plots at different mass losses. It can be seen that the $E_{a,d}$ at 10 and 30% mass losses under N_2 atmosphere decreases linearly with increasing GE%. Thus using Kissinger's method, one can determine scaling relations [24] (i.e. log-log relations) between activation energy of degradation and grafting efficiency, where

$$E_a \sim (GE\%)^\alpha \qquad (3)$$

The α value which reflects the dependence of E_a on GE%, can be determined from a log-log plot, in which the α value is the slope of the linear relationship. Thus if activation energy at different mass losses (i.e. 10 and 30%) is plotted *vs*. GE%, one can determine the α values for different mass losses. Figure 4 shows the scaling relationships of at 10% and 30% mass losses. No scaling relations for 50% mass loss due to lack of activation energy values at lower GE%.

The scaling relations of 10 and 30% mass losses using Kissinger's method confirms the linear dependence of activation energy of degradation on the grafting efficiency, the values of α for 10 and 30% mass losses respectively are -0.4 and -0.9. This dependence can be explained by the role of poly(BAM) chains that bind to the crystalline regions of starch
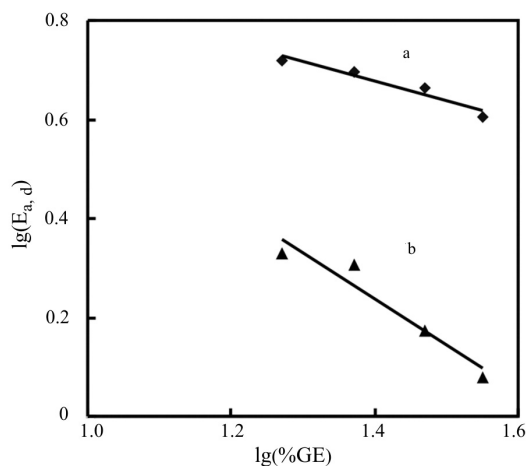
Fig. 4 Scaling relation of logE_a *vs*. log(%GE) for a – 10% and b – 30% mass loss

and consequently cause a destruction in the crystalline regions into amorphous regions. Such destruction reduces the consistency and the microhardness at the molecular level of starch macromolecules and consequently lowers the activation energy of degradation. In spite of the fact that increasing the amount of poly(BAM) chains should lead to increasing the possibilty of hydrogen bonding between starch and poly(BAM) chains, but that is considered as a minor factor with respect to destruction of crystalline regions which is the major factor that governs the consistency of the copolymer and hence the activation energy of degradation. In other words, the grafting process is acting as a catalyst that causes lowering of activation energy of degradation by destruction of crystalline regions. Thus one can conclude that using Kissinger's method, the activation energy of degradation can be studied linearly and correlated to grafting efficiency (GE%) and the α values reflect the amount of dependence of E_a on GE%.

The temperature peak at 50% mass loss derived from first derivative TG profile was not observed at GE%=0.0, 18.6 and 23.5 and was observed at GE%=29.5 and 35.5 for both Tables 2 and 3, where no conclusive remarks could be deduced.

Despite that the values of activation energy of degradation of Ozawa's and Kissinger's methods are in good agreement with each other, there exist some noticeable outputs between results of Ozawa and Kissinger's methods, for instance using Ozawa's method one can deduce the influence of physical inter and intra molecular interactions on grafting and consequently on activation energy of degradation, whereas this could not be seen in Kissinger's method. On the contrary, in Kissinger's method the destruction of crystalline region could be indirectly monitored through the linear decrease of activation energy of degradation ($E_{a,d}$) at increasing grafting efficiency (GE%), where this could not be seen in Ozawa's method.

The thermoxidative degradation of the different grafting efficiency values (GE%) under air atmosphere in Tables 2 and 3 showed only one first derivative peak at 30% mass loss, and its apparent activation energy of degradation values were increased GE% increases using Ozawa's and Kissinger's methods. Obviously that the trend of thermoxidative degradation in the presence of O_2 atmosphere is completely different than that in the presence of inert atmosphere (i.e. N_2 atmosphere). It is known that C–C bond in the tertiary butyl groups is a weak bond that is expected to break with higher probability than other stronger bonds, where its bond dissociation energy at 25°C is 335 kJ mol^{-1} [25]. Thus the presence of molecular O_2 at elevated temperatures can encourage the possibility of molecular rearrangement, cyclization, and/or partial crosslinking [25], which in

turn causes a gradual increase in activation energy of degradation as *GE*% increases.

Analysis with DSC

It has been reported that polyacrylic acid (poly(AA)) gives higher stability to starch when grafted onto it owing to hydrogen bonding between starch and poly(AA) chains [26, 27]. In Fig. 5 the different *GE*% samples were heated at heating rate of 50°C min^{-1} then at 200°C the temperature was hold for 150 min in order to study the effect grafting efficiency on the thermal stability of starch-g-BAM copolymer. It can be clearly seen from Fig. 5 that the presence of more poly(BAM) chains (i.e. higher *GE*%) does not alter the thermal stability of starch. This is mainly because there has been no chemical interactions (i.e. crosslinks) between starch and poly(BAM) chains that can change the thermal stability. Furthermore, the physical interactions effect (i.e. hydrogen bonding) was not significant in making the copolymer more thermally stable even at high *GE*%. This result is rather confirmed by Fig. 2, where the maximum decomposition temperature was found to be independent of grafting efficiency (*GE*%) at constant heating rate.
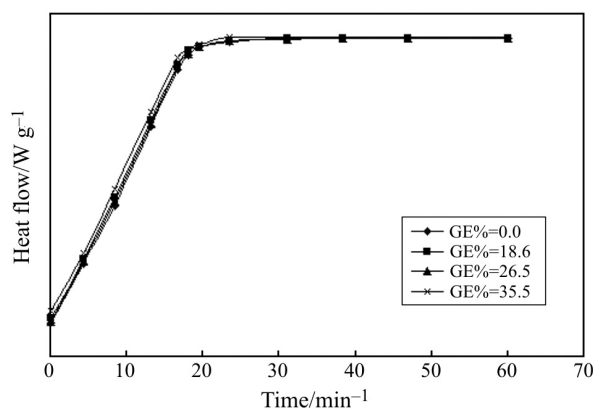

Fig. 5 DSC profile at 200°C for different grafting efficiency values in the presence of N$_2$ atmosphere

Conclusions

The thermal and thermoxidative degradation of starch and increasingly grafting efficiency of starch-g-BAM copolymer using Ozawa and Kissinger's methods showed the following conclusive remarks;

- Using Ozawa's method influence of physical inter and intra molecular interactions on grafting and consequently on activation energy of degradation (*E*$_{a,d}$) was investigated at 10% mass loss, whereas at 30% mass loss an oscillatory behavior of *E*$_{a,d}$ was observed. On the contrary, using Kissinger's

method the linear dependence of *E*$_{a,d}$ on *GE*% by scaling relations proved that the gradual increase of *GE*% causes a linear decrease in *E*$_{a,d}$ 10 and 30% mass losses respectively.

- The 60% decomposition of starch-g-BAM under air atmosphere induces the possibility of molecular rearrangement, cyclization, and/or partial crosslinking at elevated temperature, whereas that was not found in the 80% decomposition of the copolymer under N$_2$ atmosphere. This result is confirmed by the increase of activation energy of degradation (*E*$_{a,d}$) as a result of *GE*% increase under air conditions.

- The thermal stability of starch does not alter as a result of grafting of starch with increasing number of chains of poly(BAM) (i.e. increasing *GE*%).

Acknowledgements

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