

New Starch Hybrids via Etherification of Poly (Acrylamide)-Starch Copolymers with Acrylamide

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NOVEL starch hybrids containing acrylamide (Aam) moieties in monomeric (*i.e.* carbamoylethyl groups) and polymeric (poly acrylamide) forms were synthesized. Thus, starch was first polymerized with acrylamide to yield poly (Am)-starch composite and poly (Aam)-starch graft copolymer which represent the total polymerization products before and after removal of the homopolymer, respectively. The composite and the copolymer were then carbamoyethylated via reaction with Aam. Beside the carbamoylethyl groups, carboxyethyl groups were inevitably formed during carbamoylethylation. This and the onset of such modification on the rheological properties of the so synthesized starch hybrids signify the following. a) The extents of carbamoylethylation of the composite and the copolymer were much lower than native starch; b) The magnitude of poly(Am) content in the form of graft or homopolymer adversely affects the carbamoylethylation reaction; c) before carbamoylethylation, the composite, the copolymer and native starch exhibited non-Newtonian thixotropic behavior, d); after carbamoylethylation the etherified products were characterized by pseudoplastic behavior. The apparent viscosity of starch, starch composite and starch copolymer decreased significantly after carbamoylethylation but with the certainty that the apparent viscosity increased by increasing the carbamoylethyl and carboxyethyl groups in these starch hybrids.

Keywords: Starch, Copolymer, Acrylamide, Etherification and Composite.

A great deal of research and technical work has been carried out with a view to improve the physical and chemical characteristics of starch as a prerequisite to promote utilization of the latter. The studies reported so far are, in essence, dealt with swelling⁽¹⁾, oxidation⁽²⁻⁴⁾, hydrolysis, esterification⁽⁵⁾, etherification⁽⁶⁻⁹⁾, grafting^(10, 11) and cross-linking of starch⁽¹²⁾. Also reported are the combined hydrolysis (or oxidation) and grafting of starch^(10, 11). Major properties affected by such modifications are solubility, viscosity performance and resistance to ageing of native starch and products derived from modification.

This work is undertaken with a view to synthesize new starch hybrids containing acrylamide (Aam) moieties in monomeric and polymeric forms. To achieve the goal, poly (Aam)-starch graft copolymer was first synthesized then

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subjected to carbamoylethylation. The latter was studied under different conditions in order to establish the most appropriate conditions for carbamoylethylation of the starch copolymer. Conditions so established were employed for carbamoylethylation of the starch composite. The work was extended to study the hydrolysis of the amide groups of poly (Aam) to carboxyl groups during the carbamoylethylation treatment and the onset of this on the rheological properties of the starch products.

Experimental

Materials

Maize starch was supplied by the Egyptian Starch and Glucose Manufacturing Company, Cairo, Egypt. Acrylamide (Aam), sodium hydroxide, potassium persulphate, sodium thiosulphate, hydrochloric acid, sodium carbonate, ethanol, and acetone are of laboratory grade chemicals.

Grafting method

Unless otherwise indicated, the grafted starch was prepared by mixing 10 g starch with 100 ml water in a flask. The latter was placed in a thermostatic water bath adjusted at 65°C, and the starch /water mixture therein was subjected to continuous mechanical stirring (200 rpm) to get homogenized slurry. Aam monomer [50% based on weight of starch (ows)] was then added to the homogenized slurry while stirring. After that, the components of redox initiator system were added simultaneously. This system consisted of potassium persulphate and sodium thiosulphate with concentration of 1.1mmol/l and 3.3 mmol/l, respectively. Polymerization system was allowed to proceed for 60 min at 65°C with continuous stirring. The material to liquor ratio (M: L.R) was 1:10. After 60 min-reaction, polymerization was ceased by adding 10 ml of 0.1% hydroquinone solution. At this end, the polymerization products in the flask were neutralized using 1% sodium carbonate solution then poured over ethanol, where a precipitate was formed⁽¹²⁾. The so obtained precipitate is referred to as "composite". The latter consists of poly (Aam)-starch graft copolymer, poly (Aam) (homopolymer), oxidized starch, and unreacted starch. The homopolymer was removed from the composite according to reported method⁽¹³⁾.

Carbamoylethylation method

Unless otherwise indicated, the experimental technique adopted for carbamoylethylation of starch, starch composite and starch copolymer was as follows: Sodium hydroxide solution (5% ows), was added gradually to 100 g starch in a flask with continuous mechanical stirring (200 rpm). This was followed by addition of acrylamide (100% ows) while stirring. The latter continued till the flask contents were completely homogenized. The flask was then transferred to a thermostatic water bath and the reaction was allowed to proceed under continuous mechanical stirring at 30°C for 90 min. At this end, the reaction product was precipitated and washed several times in ethanol then dried at 50°C in an oven⁽¹⁴⁾.

Cooking process

An aqueous dispersion of starch or the modified starches under investigation was prepared at a concentration of 10% solid content. The dispersion was then homogenized before heating by making use of a mechanical stirrer (250 rpm) for 10 min. Cooking was effected by heating the sample under continuous stirring in thermostatic water bath where the temperature was raised from 25°C to 95°C in a rate of 2.5°C per min then kept constant at 95°C for 30 min cooking to bring about a paste. Temperature of this paste was lowered to 25°C; meanwhile stirring was reduced to the minimum degree within 15 min.

Analysis

The carboxyl content of starch and the modified starches before and after etherification was determined according to a reported method⁽¹⁵⁾. This method is based on acid-base titration.

The nitrogen content of starch and modified starch before and after etherification was determined according to Kjeldhal method⁽¹⁶⁾.

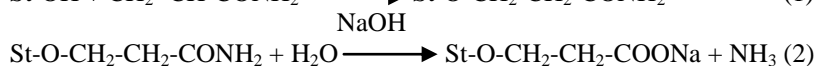
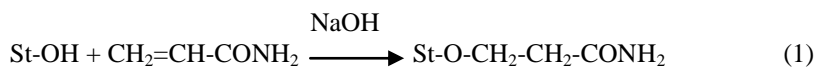
The reaction efficiency was calculated based on the sum of both carboxyl and nitrogen contents.

The rheological properties were measured using Roto-Visco RV 20 under the following experimental conditions. Rate of shear was between 129-1290 S⁻¹ and temperature 80°C. The apparent viscosity was calculated using the following formula $\eta = S\tau/D$ where:

$$\begin{aligned} \eta &= \text{Apparent viscosity (mPa.)} \\ D &= \text{Rate of shear (S}^{-1}\text{)} \\ S\tau &= \text{Shear stress (mPa.S)} \end{aligned}$$

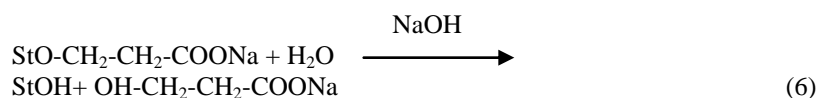
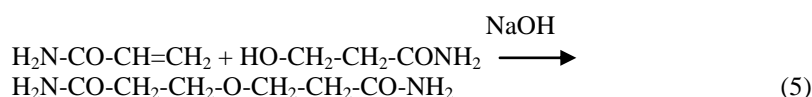
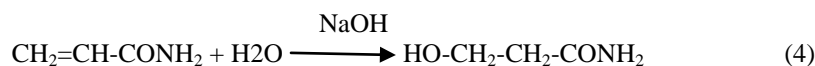
Results and Discussion*Tentative mechanisms*

In a system containing starch, acrylamide, sodium hydroxide and water, the following reactions are expected to occur:



Similar reactions would take place when starch (St-OH) is replaced by poly (Aam)-starch graft copolymer.

Furthermore, water adds to acrylamide in the presence of alkali to give amidohydroxyethylene which still further reacts with acrylamide yielding bis-2 carbamoylethyl ether ⁽¹⁾.



Poly (Aam)-starch graft copolymer was reacted with acrylamide under a variety of conditions. This was done to discover the most appropriate conditions for carbamoylethylation of the copolymer which would also be applied to the poly (Aam)-starch composite.

Sodium hydroxide concentration

Figure 1A shows the effect of sodium hydroxide concentration on the extent of carbamoylethylation reaction, expressed as nitrogen percent, when poly (Aam)-starch graft copolymer with original nitrogen content of 8.3%N was carbamoylethylated. The results disclose that the extent of the carbamoylethylation reaction increases significantly by increasing sodium hydroxide concentration up to 5% on weight of starch (ows) then decreases thereafter. Sodium hydroxide seems to perform: i) catalyzing the carbamoylethylation reaction, ii) enhancing the swellability of the copolymer thereby improving the extent of the reaction through better diffusion of reactants and iii) hydrolyzing the amide group in acrylamide, poly (Aam)-starch graft copolymer and the carbamoylethylated products derived thereof. It is logical that factors (i) and (ii) would act in favor of carbamoylethylation whereas factor (iii) would exert a reverse action.

As shown in Fig. 1A the efficiency of the carbamoylethylation reaction exhibits a trend which is similar to that obtained with the extent of the reaction. Maximum reaction efficiency is achieved at NaOH concentration of 5% ows. Above this concentration lower reaction efficiency is achieved by a virtue of the progressive action of hydrolysis at higher NaOH concentrations which may be accompanied by de-etherification. It is understandable that the reaction efficiency is based on the total amount of both nitrogen and carboxyl content of the copolymer after carbamoylethylation.

The pronounced effect of hydrolysis of the amide groups of the copolymer under the action of increasing sodium hydroxide concentration is obvious when the results of carboxyl percent are considered. The carboxyl percent (COOH %)

in Fig 1A increases significantly by increasing sodium hydroxide concentration up to 10% ows then continues to increase but marginally by further increasing NaOH concentration to 20%. It is also noted that the lower values of N% (measure for extent of reaction) are encountered by higher values of carboxyl % (measure for the extent of hydrolysis) within the NaOH concentration range of 5-20% (ows).

It is as well to emphasize that presence of measurable amount of carboxyl groups in the copolymer after carbamoylethylation regardless of NaOH concentration used is indicative of concurrent carbamoylethylation and hydrolysis. At higher NaOH concentrations the decrement in extent of the carbamoylethylation reaction is outweighed by increment in the extent of hydrolysis reaction.

Acrylamide concentration

Figure 1B shows the effect of acrylamide concentration on the extent and efficiency of the carbamoylethylation of poly (Aam)-Starch graft copolymer.

It is seen that the extent and efficiency of the carbamoylethylation reaction increase substantially as the acrylamide concentration increases up to 100% ows. Further increase in the acrylamide concentration causes no increase in the extent and efficiency of the reaction as evidenced by the constant values of N% and Carboxyl %.

The enhancement in the extent and efficiency of the reaction by increasing acrylamide concentration up to certain limit could be associated with greater availability of acrylamide molecules in the vicinity of the copolymer at higher acrylamide concentration. Since the residual starch hydroxyls in the copolymer are immobile, their reaction with acrylamide and sodium hydroxide would essentially depend upon availability of both reactant molecules in the proximity of hydroxyl of poly (Aam)-Starch graft copolymer molecule. On the other hand, leveling off of the carbamoylethylation after a certain acrylamide concentration could be interpreted in terms of reduction of reactive sites, *i.e.* hydroxyl groups, on the copolymer molecules. This means that there is a certain amount of accessible hydroxyl groups in the molecular structure of poly (Aam)-starch graft copolymer. Once these groups are blocked by the carbamoylethylation groups, further reaction becomes difficult under condition used.

Figure 1B shows the dependence of the carboxyl % (measure of the extent of conversion of amide groups via alkaline hydrolysis) of the copolymer on the acrylamide concentration. Evidently, the carboxyl % increases by increasing acrylamide concentration up to 100% ows then remains almost constant upon further increase in the acrylamide concentration; similar to the extent and efficiency of the reaction. It follows from this that the magnitude of carbamoylethylation of the copolymer determines the magnitude of the alkaline

hydrolysis. Stated in other words, alkaline hydrolysis occurs concurrent with carbamoylethylation and is favored under conditions which favor carbamoylethylation.

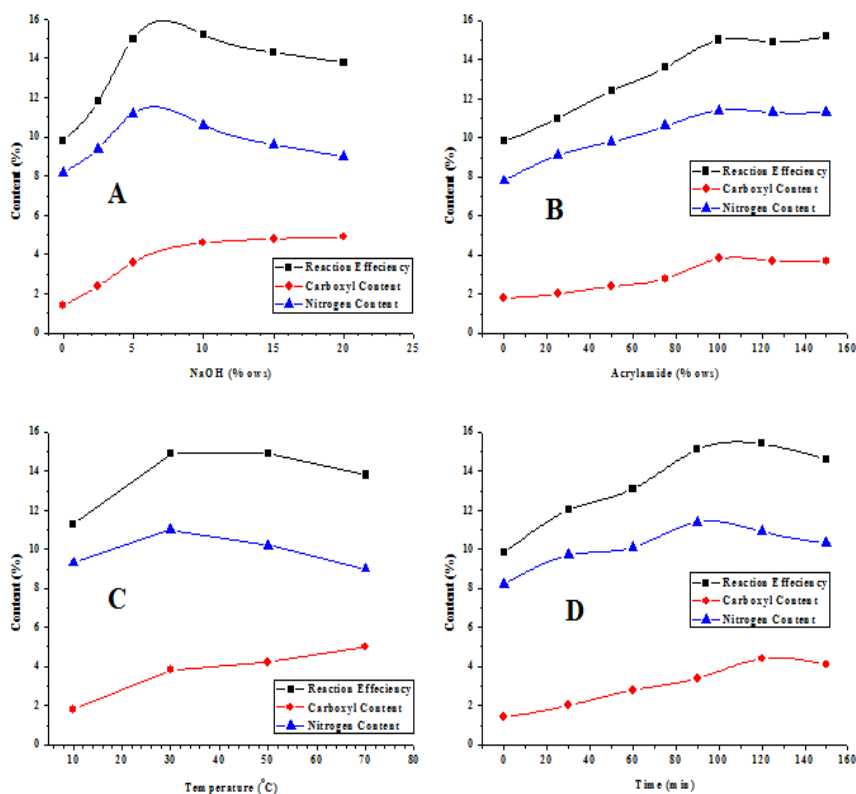


Fig. 1. Different factors affecting the carbamoylethylation of poly(Aam)-starch graft copolymer
A. Effect of sodium hydroxide concentration (Aam: 100 %ows; Temp.: 30°C; Time: 90 min.; M: L.R.: 1:10)
B. Effect of acrylamide concentration (NaOH: 5 %ows; Temp.: 30°C; Time: 90 min.; M: L.R.: 1:10)
C. Effect of temperature (NaOH: 5 %ows; Aam: 100 %ows; Time: 90 min.; M: L.R.: 1:10)
D. Effect of time (NaOH: 5 %ows; Aam: 100 %ows; Temp.: 30°C; M: L.R.: 1:10)

Effect of temperature

Figure 1C shows the effect of temperature on the extent of the carbamoylethylation reaction, expressed as N%, and efficiency of the reaction, based on nitrogen and carboxyl contents of poly (Aam)-starch graft copolymer. The results signify that the extent and efficiency of carbamoylethylation attain temperature their maximum at 30°C; then start to decrease with increasing the temperature above 30°C. It is logical that higher temperature would enhance the extent and rate of alkaline hydrolysis which, as already stated, takes place alongside the carbamoylethylation. Alkaline hydrolysis converts the amide to carboxyl groups. Indeed the results of carboxyl % shown in Fig. 1C and the trend obtained when these results are plotted versus the temperature are in full

agreement with the statement emphasizing conversion of the amide to carboxyl groups. However, the contribution of the de-etherification in reaction efficiency cannot be ruled out.

Effect of duration

Figure 1D shows the effect of reaction time on the extent and efficiency of carbamoylethylation of poly (Aam)-starch graft copolymer. It is seen that when plotted versus time, the extent and efficiency of carbamoylethylation follow similar trend, the extent of carbamoylethylation and efficiency of etherification increase by prolonging the duration of the etherification to reach the highest values after 90 min. Thereafter, they decrease indicating that longer than 90 min reaction time is meaningless since it adversely affects the carbamoylethylation reaction. Although the reaction time provides better opportunity for appropriate contact among reactants for the reaction to proceed yet longer time seems to promote alkaline hydrolysis not only of the newly introduced amide in the form of carbamoylethyl groups but also the amide groups of the graft in the poly (Aam)-starch graft copolymer. In combination with this is the plot shown in Fig. 1D of the carboxyl % versus the reaction time. As is evident, the carboxyl % of the etherified copolymer increases by increasing the duration of carbamoylethylation upto 120 min. Further prolonging the duration tends to decrease the carboxyl % suggesting de-etherification. That is, splitting off of the carboxyethyl groups of the carbamoylethylated poly (Aam)-starch graft copolymer seems to occur under the influence of longer time in presence of alkali. As a result, the carboxyl % tends to decrease.

Optimum conditions

Based on the result of Fig. 1 (A, B, C and D) discussed above, it may be concluded that the most appropriate conditions for carbamoylethylation of poly (Aam)-starch graft copolymer are as follows: sodium hydroxide 5% w/w, acrylamide 100% w/w, reaction time 90min., and temperature 30°C.

Nature of substrate

In this study the optimum conditions achieved above for carbamoylethylation of the copolymer were applied to different substrates, namely, unmodified starch as well as starch copolymers and starch composites having different nitrogen percent and carboxyl contents as indicated in Table 1. The study was undertaken with a view to shed insight on the effect of structural differences among these substrates on the extent of carbamoylethylation. Also studied was the carboxyethylation process occurring concurrently with carbamoylethylation through conversion of the carbamoylethyl groups as well as the amide groups of the copolymer and composite to carboxyethyl groups and the onset of this on the rheological properties of the carbamoylethylated products.

Nitrogen content

Figure 2 shows the nitrogen percent before and after carbamoylethylation of starch composites and starch graft copolymers. The composites and copolymers

were prepared using different concentrations of acrylamide. Obviously, the copolymers are more susceptible to carbamoylethylation than the composites. This is observed regardless of the magnitude of poly (Aam) of both substrates. Presence of poly (Aam) in the form of homopolymer which is most probably in intimate association with other components of the composites seems to be responsible for this. The homopolymer may act as a diffusion barrier for and /or mask starch hydroxyls thereby preventing their ability and accessibility to undergo the carbamoylethylation reaction.

TABLE 1. Nitrogen percent of starch- poly Aam composite and copolymer before and after etherification with Aam in alkaline medium.

[Aam] %ows	Nitrogen content (%)			
	Poly (Aam)-starch composite		Poly (Aam)-starch graft copolymer	
	BC	AC	BC	AC
5	2.3	5.3	1.3	4.5
10	3.9	6.7	2.6	5.6
20	6.8	9.3	5.3	7.9
30	8.3	10.3	6.8	9.0

Polymerization conditions: $[K_2S_2O_8/Na_2S_2O_3]=1.1/3.3$ mmol/l; time = 60 min; temp =60°C; M:L.R =1:10. Etherification conditions: $[NaOH] = 5\%$ ows; $[Aam] =100\%$ ows; time=90 min; temp =30°C; M: L.R =1:10. BC : before carbamoylethylation AC : After carbamoylethylation

Carboxyl content

Figure 3 shows the effect on the carboxyl content of the magnitude of poly (Aam) content in the copolymer and the composite substrates. Different poly (Aam) contents were obtained using different acrylamide concentrations in the polymerization medium during preparation of both substrates. The carboxyl contents of the copolymer and composite were determined before and after the copolymer and the composite were reacted with acrylamide in alkaline medium. It is seen that: a) the carboxyl content is directly related to the acrylamide concentration used in the polymerization which, in turn, determines the poly (Aam) content, b) the composite exhibits higher carboxyl content than does the copolymer and c) carboxyl content is much higher after than before etherification, *i.e.* reacting the copolymer and the composite with acrylamide in alkaline medium. These findings clearly indicate that introduction of acrylamide monomeric (as carbamoylethyl groups) or polymeric (as polyacrylamide) in the molecular structure of starch is associated with carboxyethyl groups. The latter are formed via hydrolysis of the amide groups in the acrylamide moiety-containing products; the larger the amount of acrylamide moieties, the greater the carboxyl content.

In combination with this is the alkaline condition of carbamoyethylation which would favour carboxyl group formation through alkaline hydrolysis of the amide groups. This is, rather, obvious in Fig. 3 where enhanced in the carboxyl content of the composite and the copolymer is observed after carbamoyethylation.

Reaction efficiency (total extent of etherification)

The total extent of the etherification reaction occurring between acrylamide and starch, starch composite or starch copolymer can be expressed as the sum of nitrogen and carboxyl group which are taken as a measure for carbamoyethylation and carboxyethylation extents, respectively. Results of the sum of both nitrogen and carboxyl group (expressed as mmol/100g sample) of the etherified starch products are set out in Table 2. The results bring into focus two main conclusions.

TABLE 2. Total extent of etherification (reaction efficiency) obtained when the starch, starch graft copolymer and starch composite were independently reacted with Aam in alkaline medium.

[Aam] % ows used in polymerization	Poly (Aam)-starch composite						Poly (Aam)-starch graft composite					
	BC			AC			BC			AC		
	N	COOH	R.E.	N	COOH	R.E.	N	COOH	R.E.	N	COOH	R.E.
5	164	30	194	379	60	439	93	29.0	122	321	52	373
10	279	31.5	310.5	479	70.5	549.5	179	30.9	209.9	400	62	462
20	486	32.2	518.2	664	79.9	743.9	379	31.4	410.4	564	78.1	642.1
30	680	33.8	713.8	736	91.0	827	486	32.4	518.4	643	79.4	722.4

Nitrogen content (N) and carboxyl content (COOH) expressed as mmol/100g. sample;

Reaction Efficiency (R.E.) = sum of N +COOH (mmol /100g sample).

Polymerization conditions : $[K_2S_2O_8/Na_2S_2O_3] = 1.1/3.3$ mmol/l; time =60 min; temp =60°C; M:L.R =1:10.

carbamoyethylation conditions: [NaOH] = 5% ows; [Aam] =100% ows; time=90 min; temp =30°C; M:L.R =1:10.

BC : before carbamoyethylation AC : After carbamoyethylation

Firstly, the reaction efficiency of the etherification reaction decreases by the increase in acrylamide concentration indicating that side reactions previously indicated are more pronounced at higher acrylamide concentration than does the carbamoyethylation reaction. Secondly, the starch graft copolymer displays greater reaction efficiency than the starch composite most probably owing to the presence of the homopolymer, the latter is present in intimate association with the copolymer in the composite and may act as a diffusion barrier for the etherifying agents thereby decreasing the reaction efficiency of etherification.

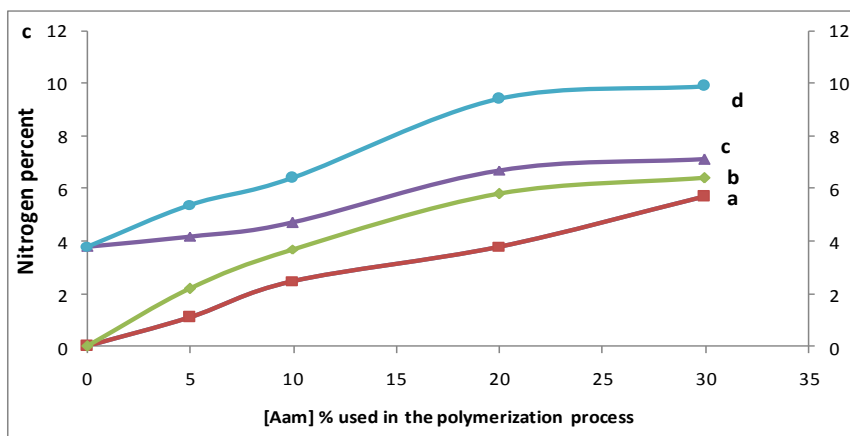


Fig. 2. Dependence of the nitrogen percent of starch –poly (Aam) composite and the copolymer before and after carbamylethylation on acrylamide concentration used for preparation of the composite.

a-Poly (Aam)-starch graft copolymer b-Poly(Aam)-starch composite
 c-Carbomylethyl poly(Aam) – starch graft copolymer
 d-Carbomylethyl poly(Aam) – starch composite

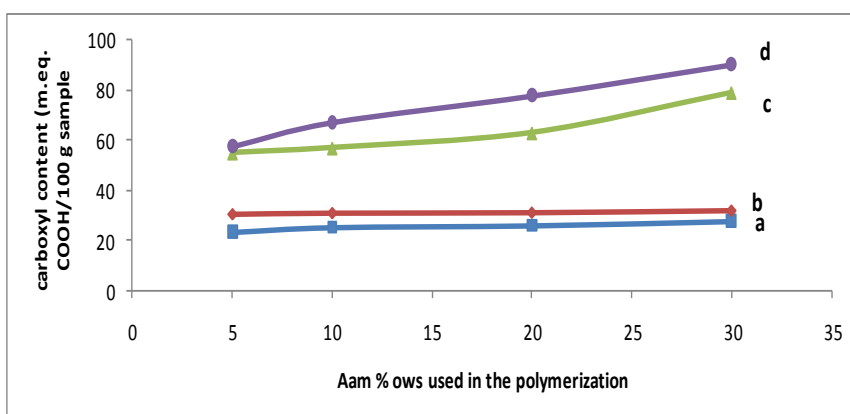


Fig. 3. Dependence of the carboxyl content of starch –poly (Aam) composite and copolymer before and after carbamylethylation on acrylamide concentration used for synthesis of the composite.

a-Poly(Aam)- starch graft copolymer b- Poly(Aam)- starch composite
 c-Carbomylethyl poly(Aam)- starch composite
 d-Carbomylethyl-poly(Aam)- starch graft copolymer

Rheological properties

shear stress versus rate of shear

It is well established that the correlation between shear stress ($S\tau$) and rate of shear (D) defining the flow curve or flow behavior of a liquid is graphically displayed in diagram of ($S\tau$) on the ordinate and D on the abscissa. This diagram is called flow curve. In this work the flow curve diagrams were produced directly

from HAAKE ROTO Visco RV 20 viscometer equipment at 80°C, for native maize starch, poly (Aam)-starch graft copolymer, starch composite when Aam was used at concentrations of 10, 20 and 30% for preparation of the composite and copolymer. It was found from the flow curve diagrams (not shown to save space) that the shear stress increases as the rate of shear increases from zero to 1290 s⁻¹. Opposite situation was encountered by decreasing the rate of shear from the maximum 1290S⁻¹ to zero. Indication of this is that the starch and the products derived thereof are characterized by non-Newtonian behavior. However, a close examination of the up and down flow curves revealed that these curves were not coincident in the case of native starch, the copolymer and the composite, indicating that these starch hybrids exhibit thixotropic behavior. On the other hand, with respect to the carbamoylethylated products derived from native starch, the copolymer and the composite were characterized by pseudoplastic behavior because the up and down flow curves were coincident. This concluded that introduction of carbamoylethyl along with carboxyethyl groups in the molecular structure of the products under investigation induces the ability of the macromolecules of these products to rebuild immediately after the applied force was removed.

Apparent viscosity

The apparent viscosities of the cooked solutions of native starch as well as those of poly (Aam)-starch graft copolymers, poly (Aam)-starch composites, carbamoylethyl poly (Aam)-starch graft copolymers and carbamoylethyl composites were measured at different rates of shear. The rate of shear ranges from 129 to 1290 S⁻¹. The measuring temperature was 80°C and the concentration of starch products was 10%.

Figure 4 shows the flow profile curves of the native starch, the copolymer and the composite before and after etherification. The latter, as already indicated involves carbamoylethylation and carboxyethylation.

Preparation of the copolymer and composite was carried out using Aam at a concentration of 10% for. A perusal at these curves reveals that the apparent viscosity decreases by increasing the rate of shear regardless of the nature of the starch products used. Nevertheless, the apparent viscosity relies on the nature of starch. For a given rate of shear of up to 1000 S⁻¹ the apparent viscosity follows the order: native starch > composite > copolymer > carbamoylethyl starch > carbamoylethyl composite > carbamoylethyl copolymer. This is also valid at rates of shear higher than 1000 S⁻¹ except that the apparent viscosity of the carbamoylethyl composite becomes equal to the apparent viscosities of carbamoylethyl copolymer.

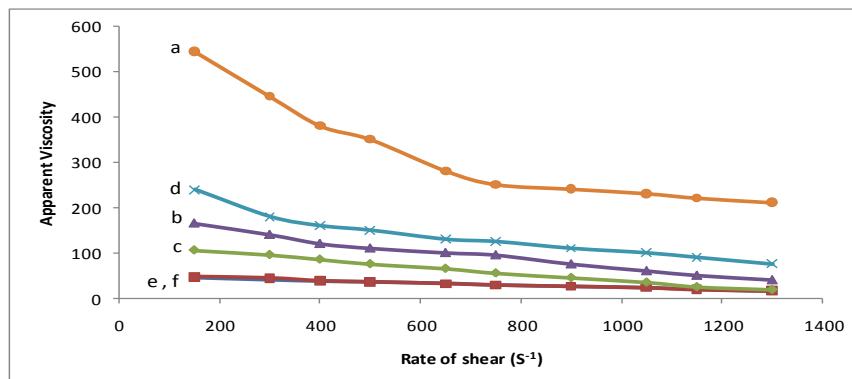


Fig. 4. Effect of rate of shear on the apparent viscosity of starch- poly (Aam) composite and copolymer before and after etherification with Aam in alkaline medium when 10% Aam was used in the polymerization reaction.
a-Native Starch b- Carbomoylethyl starch
c- Poly (Aam)- starch graft copolymer d- Poly(Aam)- starch composite
e-Carbomoylethyl poly(Aam)- starch composite
f- Carbomoylethyl-poly (Aam)- starch graft copolymer

The above order implies that the native starch undergoes oxidative degradation during the polymerization process under the influence of the initiator thereby decreasing the molecular size of starch. Such a decrease in combination with the increased solubility by the presence of poly (Aam) would account for the lower apparent viscosities of the composite and the graft copolymer when compared with native starch. Etherification causes further reduction in the molecular sizes of starch, composite and starch copolymer by oxidative degradation occurring during the carbamoylethylation and carboxyethylation process. Introduction of solubilizing groups such as carbamoylethyl and carboxyethyl groups will enhance the solubility. Hence the solubility and the low molecular mass of the etherified products are responsible for the decrease of the other apparent viscosities. It is known that the viscosity decreases when the solubility increases.

The decrease in apparent viscosity by increasing the rate of shear within the range studied (Fig. 4) deserves more classification. Shear thinning of polymer solution under investigation (containing long entangled and looping molecular chains) could be explained by considering the polymer solution before and after the shear is applied.

Before applying the shear, the polymer will maintain internal order and, correspondingly, a sizeable internal resistance against flow, *i.e.*, higher viscosity. On the other hand, with increasing shear rates, rod like particles suspended in the liquid will be turned lengthwise into the direction of the flow. Chain type molecules in a solution can disentangle, stretch and orient parallel to the driving force. Particles or molecular alignment allow particles and molecules to slip past each other more easily. This shows up as reduced viscosity.

The above shear thinning phenomenon in the field of rheology is called pseudoplasticity. This phenomenon is due to the gradual progressing structural breakdown upon deformation of the non-Newtonian system.

The decrease of pseudoplasticity by chemical modification of starch through graft copolymerization with Aam and etherification through reaction with acrylamide in alkaline medium, *i.e.* carbamoylethylation and carboxyethylation indicates that starch undergoes molecular changes under the influence of both grafting and etherification as detailed above. It is certain, however, that the magnitude of changes brought about by the etherification reaction is greater than the graft copolymerization reaction as evidenced by the lower value of the pseudoplasticity found with the former.

The above order signifies further that the presence of poly (Aam) chains with starch in the form of graft (chemically bonded) and /or in the form of homopolymer (physical entangled) lowers the mobility of the macromolecules. Thus the physical entanglement of the poly (Aam) chains with themselves as well as with starch hydroxyls together with long grafted chains and increased branching would explain the higher viscosities exhibited by the composite and the graft copolymer. On the other hand, introduction of carbamoyethyl and carboxyethyl groups in the starch backbone ruptures the physical forces (hydrogen bonds, van der Waal's forces) between the starch hydroxyls and starch-poly (Aam) chains. As a result, the viscosity is reduced.

Summary and Conclusion

Novel starch hybrids were synthesized through carbamoylethylation etherification of poly (Aam)-starch graft copolymer and poly (Aam)-starch composite using Aam as the etherifying agent in presence of NaOH. During carbamoyethylation of the composite and the copolymer carboxyethylation inevitably occurs via conversion of the carbamoylethyl groups to carboxyethyl groups. Acrylamide moieties in the starch copolymer and the composite would similarly undergo alkaline hydrolysis to carboxyethyl groups. Dependence of the etherification (carbamoylethylation and carboxyethylation) on conditions used as well as of etherification and on nature of starch substrate and the onset of this on the rheological properties of the newly synthesized starch hybrids bring into focus the following conclusions:

(1) The composite is less susceptible to carbamoylethylation than the copolymer, suggesting that the homopolymer which is intimately associated with other components of the composite acts as a diffusion barrier for the etherifying agents to reach the reactive sites (hydroxyl groups) on the starch molecules.

(2) The magnitude of poly (Aam) content in the form of graft or homopolymer or both adversely affect the etherification reaction indicating that the starch hydroxyls are the only groups amenable for etherification.

(3) In accordance with the above, the native starch is much more susceptible to carbomoylethylation than the copolymer and composite.

(4) Having studied the factors affecting etherification of the copolymer, the following conditions were formulated to constitute optimal: [NaOH]= 5% ows, [Aam]=100%, Reaction time= 90 min and temperature= 30 °C.

(5) Before etherification the composite, the copolymer and the native starch exhibit non-Newtonian thixotropic behavior.

(6) After etherification, the etherified composite, the etherified copolymer and the etherified starch are characterized by non-newtonian pseudoplastic behavior, presence of the carbomoylethyl groups and the carboxyethyl groups seem to enhance the ability of the macromolecules of the starch hybrids in question to rebuild themselves immediately after deformation under the effect of the applied force.

(7) The apparent viscosity of the native starch, starch composite and starch copolymer decreases significantly after etherification for two reasons: first , the enhancement of solubility by virtue of the solubilizing action of the introduced groups (carbomoylethyl and carboxyethyl) in the molecular structure of the starch hybrids. Second, the fall in the molecular mass of starch under the oxidative action of alkali in presence of oxygen during the etherification reaction.

Acknowledgment: The authors are indebted to late Profs. Drs. A. Bayzeed and F. El Sisi of the Textile Research Division, National Research centre, for their sound contribution in this research.

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(Received 17/ 9/ 2013 ;
accepted 27/10/ 2013)

متزاوجات جديدة من النشا بتكوين إثيرات من بوليمرات الأكريل أميد مع النشا

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تم تخليق متزاوجات جديدة من النشا تحتوى على مجموعات الأكريلاميد على هيئة بوليمرات بسيطة أو مركبة بدءا من بلمره النشا بمعالجة بالأكريلاميد ثم ادخال مجموعة كربوكسى مثيل وقد تسبب ذلك فى انخفاض فى مستوى لزوجة النشا وبوليمرات النشا المتكونة فى حين تزداد لزوجة النشا وبوليمراته بزيادة مجموعات الكاربامويل مثيل والكاربوكسى اثيل فى جزيئات متزاوجات النشا .