Carbohydrate Polymers 48 (2002) 255–261

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Some studies on starch–urea–acid reaction mechanism

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Received 4 April 2000; revised 15 January 2001; accepted 26 April 2001

Abstract

Starch reacted with urea in the absence or presence of mineral acids or mineral acid salts at 150°C for various reaction durations. The acids used were phosphoric, nitric, and sulphuric and the salts used were ammonium sulphate, ammonium nitrate, ammonium chloride and magnesium sulphate. The reaction extent was followed by monitoring nitrogen content. Carrying out the reaction of starch and urea in the presence of mineral acid or mineral acid salt gives rise to higher extents of reaction and in turn, products with higher nitrogen content and higher solubility %. The extent of reaction depends upon the nature and concentration of added acids or salts as follows: (a) sulphuric acid > nitric acid > phosphoric acid; (b) ammonium sulphate > ammonium nitrate > ammonium chloride > magnesium sulphate. The solubility of reaction products attains a value of 100% on using acids while it never exceeds 68% on using the mineral acid salts within the studied range. The nitrogen content of reaction product prepared in the presence of mineral acids is higher than the theoretical value in its absence, if all urea reacts with starch specially at longer durations indicates that there are side reactions which lower ammonia liberation.

Based on detailed investigation of the starch–urea–phosphoric acid system through monitoring the nitrogen and phosphorus contents as well as the liberated ammonia, it is envisaged that the reaction products comprises of starch carbamate, starch carbamate phosphate, starch phosphate and ammonium phosphate. It is further envisaged that the acid performs two main functions. Firstly, it prevents the amide groups of starch carbamate from reacting with adjacent amide or hydroxyl groups of the modified starch molecule through blocking these amide by the acid thereby ceasing crosslinking. Secondly, it degrades starch molecule via hydrolysis thereby lowering the molecular size of starch that enhance its solubility.

Keywords: Starch; Urea; Mineral acid; Starch carbamate; Starch carbamate phosphate; Starch phosphate; Reaction mechanism

1. Introduction

Previous reports (Abdel-Thalouth, El-Kashouti & Hebeish, 1981; Hebeish, Refai, Rageb & Abdel-Thlouth, 1991) disclosed that starch reacts with urea to yield starch carbamate as essential product. Different techniques were used, mainly, the solid state, the paste and the film techniques, for preparation of starch carbamate. The technique used determines the swellability and solubility of obtained starch carbamate which, in turn, are governed by the magnitude of crosslinking. In a recent study (Khalil, Farag, Mostafa & Hebeish, 1994), emphasis was placed on the synthesis of water soluble starch carbamate. Results obtained revealed that the solubility enhances by increasing the reaction time, the urea concentration and the nitrogen content of the starch carbamate up to a certain limit and then decreases. More specifically, up to 15 min of reaction time, 20% urea (ows) and 1.26% N of starch carbamate acts in favour of solubility. Higher values exert an adverse effect on solubility. It is further noted that the estimated ester content is equal to the calculated one up to a nitrogen content of 1.26%. This is in contrast with sample having higher nitrogen content where the estimated ester content is higher than the calculated one indicating the occurrence of crosslinking.

As a continuity, efforts are made in this work to prepare starch carbamate with high nitrogen content and completely soluble in water. It is envisaged that this state of affairs can be achieved through blocking of the amide groups of the starch carbamate by incorporation of a mineral acid or mineral acid salt in the carbamation formulation. The present research work is designed to discover the factors which determine the magnitude of carbamation vis-a-vis crosslinking when reaction of starch with urea is conducted in presence of different mineral acids or its salts. The reaction was followed through determination of the nitrogen content of the obtained product as well as liberated ammonia. Based on the results obtained, the mechanism accounting for the reactions of starch with urea is elucidated.

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PII: S0144-8617(01)00256-9

Table 1
The nitrogen content (m atom/100 g.sample), and water solubility (%) of prepared samples by using various phosphoric acid and urea concentrations (starch, 10 g; magnesium sulphate, 0.08 g; reaction temperature, 150°C, N = nitrogen content (m atom/100 g.sample), S = solubility (%))

Reaction duration	Urea (%)															
	Phosphoric acid (mmol)															
	10												20		30	
	0		3		6		9		12		15		15		15	
	N	*S*	*N*	*S*	*N*	*S*	*N*	*S*	*N*	*S*	*N*	*S*	*N*	*S*	*N*	*S*
0.5	21	4	55	38	96	87	107	92	114	94	129	94	241	87	251	80
1	39	8	69	53	116	88	118	95	125	96	149	97	251	90	274	79
2	72	10	87	70	129	93	134	99.7	143	100	161	100	268	96	293	63
3	98	10.8	104	87	134	96	146	100	161	100	176	100	279	100	303	48
4	114	11.1	117	100	136	100	151	100	168	100	189	100	289	100	307	40

2. Experimental

2.1. Materials

Maize starch was supplied by Cairo Starch and Glucose Manufacturing Company, Egypt. Urea, phosphoric, sulphuric and nitric acids as well as ammonium chloride, ammonium nitrate, ammonium sulphate and magnesium sulphate were of analytical garde.

2.2. Preparation of starch carbamate

1 g urea and x mmol of catalyst (acids or salts) dissolved in 3 ml ethanol were added to 10 g starch and mixed well using mechanical stirrer. This mixture was transferred to a petridish, covered and heated in a ventilating oven at 150°C for different reaction duration. At the end of reaction duration the reaction product was soxhlet extracted using ethanol: water (70:30 v/v) for 16 h, then dried in an oven at 60°C.

2.3. Analysis

2.3.1. Nitrogen content

Nitrogen content, expressed as m atom/100 g sample was estimated using the microkjeldahl method (Vogel, 1975).

2.3.2. Phosphorus content

Phosphorus content, expressed as m atom/100 g sample was estimated by digesting the starch carbamate using concentrated sulphric acid and hydrogen peroxide and the formed phosphoric acid was estimated according to a reported method (Vogel, 1972).

2.3.3. Solubility %

The solubility % of the prepared samples was estimated gravimetrically by treating 1 g sample in 50 ml water at 50°C for 2 h. The sample was filtered and the filtrate was transferred into a petridish and dried in ventilating oven till constant weight.

Solubility % = the dry weight of the filterate (g) × 100.

Table 2
The nitrogen content (m atom/100 g. sample) and water solubility (%) of prepared samples by using various nitric acid and urea concentrations (starch, 10 g; magnesium sulphate, 0.08 g; reaction temperature, 150°C, N = nitrogen content (m atom/100 g.sample), S = water solubility (%))

Reaction duration (h)	Urea (%)											
	Nitric acid (mmol)											
	10								20		30	
	0		1		3		5		5		5	
	N	*S*	*N*	*S*	*N*	*S*	*N*	*S*	*N*	*S*	*N*	*S*
0.5	21	4	35	12	70	59	82	79	88	42	109	41
1	39	8	60	20	90	72	121	95	129	68	144	57
2	72	10	103	25	120	85	150	100	178	92	191	69
3	98	10.8	121	30	140	94	170	100	201	99	227	73
4	114	11.1	130	35	160	100	180	100	214	100	257	75

Table 3
The nitrogen content (m atom/100 g.sample) and water solubility (%) of prepared samples by using various sulphuric acid and urea concentrations (starch, 10 g; magnesium sulphate, 0.08 g; reaction temperature, 150°C, N = nitrogen content (m atom/100 g.sample), S = water solubility (%))

Reaction duration (h)	Urea (%)													
	Sulphuric acid (mmol)													
	10										20		30	
	0		1		2		3		4		4		4	
	N	*S*	*N*	*S*	*N*	*S*	*N*	*S*	*N*	*S*	*N*	*S*	*N*	*S*
0.5	21	4	37	10	66	23	110	67	154	94	162	38	176	35
1	39	7.5	54	23	82	31	120	76	160	98	196	76	213	52
2	72	10	83	42	110	46	140	91	168	100	222	96	257	77
3	98	10.8	107	53	132	60	158	97	180	100	231	98	296	79
4	114	11.4	125	64	153	68	170	100	chared		239	100	327	81

3. Results and discussion

It is known that when starch reacts with urea at high temperatures for long reaction time the following reactions occur (Khalil et al., 1994):

$$\mathrm{St.OH} + \mathrm{CO(NH_2)_2} \overset{\text{heat}}{\rightarrow} \mathrm{St.OCONH_2} + \mathrm{NH_3} \quad (1)$$

$$\mathrm{2St.OCONH_2} \overset{\text{heat}}{\rightarrow} \mathrm{StOCONHCOOSt} + \mathrm{NH_3} \quad (2)$$

$$\mathrm{St.OH} + \mathrm{StOCONH_2} \overset{\text{heat}}{\rightarrow} \mathrm{StOCOOSt} + \mathrm{NH_3} \quad (3)$$

where St.OH is starch

Accordingly the reaction products acquire low nitrogen content and low water solubility.

Urea reacts with mineral acids to form salts, but only one amino group takes part in the salt formation (Pavlov & Terentyev, 1969; Morrison & Boyd, 1975), and the reaction product would acquire blocked amide groups which cannot undergo further reactions with adjacent amide or hydroxyl groups of starch carbamate. In this manner, crosslinking (Eq. (2) and (3)) is diminished.

Maize starch reacted with urea and $MgSO_4$ in the presence of different concentrations of mineral acids or mineral acid salts at 150°C for various reaction time (1/2–4 h). Nitrogen content was taken as a measure of the reaction extent. Tables 1–4 show nitrogen content as well as water solubility of prepared samples in the absence and presence of acids. The results imply that:

Table 4
The nitrogen content (m atom/100 g sample) and water solubility (%) of prepared samples by using various acids (starch, 10 g; urea, 1 g; magnesium sulphate, 0.08 g; acid, 3 mmol; reaction temperature, 150°C, *N* = nitrogen content (m atom/100 gsample), *S* = water solubility (%))

Reaction duration (h)	H_3PO_4		HNO_3		H_2SO_4	
	N	*S*	*N*	*S*	*N*	*S*
0.5	58	38	61	59	76	67
1	69	63	75	75	88	76
2	87	69	95	90	107	91
3	103	87	106	93	119	95

1. The extent of reaction is greater in the presence of acids than in its absence.
2. The higher the concentration of the acid incorporated in the reaction formulation the greater the extent of the reaction.
3. In the presence of acid, the reaction is characterized by an initial fast rate which slows down with time, but the nitrogen content continues to increase as the reaction time increases within the range studied; a trend which differs from that observed in absence of acid where the nitrogen content increases gradually throughout the whole duration range.
4. The reaction extent depends upon acid type (cf. Table 4) and it follows the order: sulphuric acid > nitric acid > phosphoric acid.
5. The presence of phosphoric and nitric acids in the reaction medium with concentrations up to 15 and 5 mmol/10 g sample, respectively, allows the reaction to proceed upto 4 h, while these concentrations and duration decreased to 4 mmol/10 g sample and 3 h in the case of sulphuric acid. On using higher concentrations of sulphuric or nitric acid the reaction product was shared. This may be due to the higher dehydrating and oxidizing properties of the nitric and sulphuric acids.
6. The highest nitrogen contents in prepared samples are 189 and 180 m atom/100 g sample. These values are obtained when 15 mmol H_3PO_4/10 g starch and either 5 mmol HNO_3/10 g starch or 4 mmol H_2SO_4/10 g starch were incorporated in starch–urea reaction formulation, respectively. They are higher than the theoretical values (133, 145.5 and 146 m atom/100 g sample in presence of H_3PO_4, H_2SO_4 and HNO_3 acids, respectively) if urea reacts completely with starch to form starch carbamate. This indicates that other reactions occur beside carbamate formation.

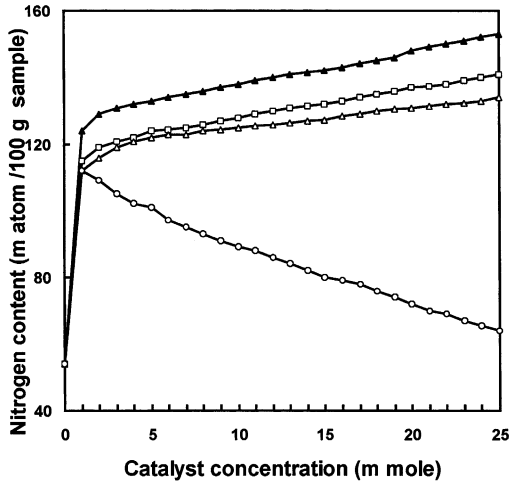

Fig. 1. The nitrogen content of the starch carbamate versus catalyst concentrations. -▲- Amm. Sulphate; -□, Amm. Nitrate; -△-, Amm. Chlorid; -○-, Mg sulphate.

7. On using mineral acid salts as a catalyst in the reaction medium reaction extent depends on the type and concentration of the salt used (cf. Fig. 1): It was found that the reaction extent increases significantly as the concentration of ammonium salt increases and follow the order $(NH_4)_2SO_4 > NH_4NO_3 > NH_4Cl$ which reflects the strength of the liberated acids. On using $MgSO_4$ the reaction extent increases significantly to attain a maximum value at 1 mmol/10 g starch then decreases sharply on increasing $MgSO_4$ concentration. This phenomenon may be explained as follows: (i) on using ammonium salts the liberated acid increases with increasing the salt concentration which acts as catalyst and increases the reaction extent ;(ii) in the case of $MgSO_4$,while the liberated acid causes the catalytic effect and increases the reaction extent, the magnesium ion has the tendency of chelate formation Hebeish, 1976; Khalil and Farag, 1998 with formed carbamate group which leads to crosslinking. The increase of magnesium sulphate concentration increases the tendency of crosslinking which prevails the action of catalytical effect of liberated acid leading to lower nitrogen content.

Table 5
Nitrogen and phosphorus contents(m atom/100 g. sample) of starch–urea–phosphoric acid reaction product prepared by using various phosphoric acid concentration (starch, 10 g; urea, 1 g; magnesium sulphate, 0.08 g; reaction temperature, 150°C, *N* = nitrogen content (m atom/100 g.sample), *P* = phosphorus content (m atom/100 g sample))

Reactin duration (h)	Phosphoric acid (mmol)					
	6		12		15	
	N	*P*	*N*	*P*	*N*	*P*
0.5	96	14.5	107	51.6	129	64.5
1	116	19.7	118	56.8	149	67.7
2	129	26.5	134	64.2	161	74.5
3	134	32.3	146	67.7	176	80.6
4	136	39.4	151	73.9	189	84.1

3.1. Reaction mechanisms

In a trial to clarify the different reactions occurring between starch and urea in presence of acids, starch carbamate was prepared in presence of phosphoric acid. The phosphorus content of different samples prepared in presence of various amounts of phosphoric acid (6–15 mmole/10 g starch) was determined. Table 5 shows the nitrogen and phosphorus contents of the prepared samples. The data show that:

1. The prepared samples contain phosphorus beside nitrogen meaning that phosphate groups have been formed simultaneously with carbamate groups from the earlier time of reaction, and the reaction extent of both carbamate and phosphate formation is very high followed by slow rate.
2. The fixed phosphate groups after 4 h equal to 76.1, 73.9 and 70% of the original amount of phosphoric acid in the reaction medium on using 6,12 and 15 mmol phosphoric acid/10 g starch, respectively.
3. The nitrogen contents of prepared samples after 4 h were 136,151 and 189 m atom/100 g sample showing that the sample prepared in presence of 6 mmol phosphoric acid/10 g starch acquires a value which is lower than the theoretical one, while those prepared at higher phosphoric acid concentrations (12 and 15 mmol/10 g sample) acquire higher nitrogen content than the theoretical value (cf. Table 5). This behavior may be explained by absorption of liberated ammonia by the phosphate groups.

Accordingly efforts are devoted to follow up critically these reactions and to bring into focus the role of the acid in the reaction mechanism. Hence three modified starches were prepared according to the following conditions: (a) starch reacted with urea in absence of a catayst; (b) starch reacted with urea in presence of $MgSO_4$ and (c) starch reacted with urea in presence of $MgSO_4 + H_3PO_4$. Librated ammonia during the reaction was monitored and the nitrogen content of the modified starch, before and after extraction, was determined. Results obtained are set out in Table 6. The data show that:

1. The liberated ammonia equals to 179,116 and 19 mmol ammonia/100 g sample for samples prepared under conditions (a),(b) and (c), respectively. This indicates that the librated ammonia in absence of catalyst is higher than half of the nitrogen content of the used urea which confirms the formation of crosslinking reactions. On the other hand the librated ammonia in presence of catalyst is lower than the theoritical value

Table 6
The liberated ammonia and the nitrogen content (m atom/100 g starch) of starch/urea reaction products in presence and absence of catalyst before and after extraction (starch, 10 g; urea, 1 g; magnesium sulphate, 0.08 g; phosphoric acid, 15 mmol; reaction temperature, 150°C; reaction time, 4 h)

Reaction condition	Liberated ammonia	Nitrogen content	
		Before extraction	After extraction
(a) Without catalyst	179	124	54
(b) With $MgSO_4$	116	184	115
(c) With $MgSO_4$ + H_3PO_4	19	246	189

indicating both catalytical effect and absorption of librated ammonia via phosphoric acid.

2. The samples prepared under conditions (a), (b) and (c) after extraction aquire nitrogen contents of 54, 115 and 189 m atom/100 g sample, respectively, which is in full agreement with the data of librated ammonia.
3. The data of librated ammonia and the nitrogen content of prepared samples in presence of phosphoric acid indicate that phosphoric acid catalizes the carbamate formation, prevent crosslinking and absorbs the librated ammonia.

On reacting starch with urea in presence of phosphoric acid, several reactions take place. Among these are:

$$H_2NCONH_2{\cdot}H_3PO_4 + St.OH \overset{heat}{\rightarrow} StOCONH_2{\cdot}H_3PO_4 + NH_3 \quad (4)$$

$$H_2NCONH_2{\cdot}H_3PO_4 \overset{heat}{\rightarrow} H_2NCONH_2 + H_3PO_4 \quad (5)$$

$$H_2NCONH_2 + St.OH \overset{heat}{\leftrightarrows} StOCONH_2 + NH_3$$

$$St.OH + H_3PO_4 \overset{heat}{\rightarrow} StPO_4H_2 + H_2O \quad (6)$$

$$StPO_4H_2 + NH_3 \rightarrow StPO_4H(NH_4) \quad (7)$$

$$StOCONH_2{\cdot}H_3PO_4 + NH_3 \rightarrow StOCONH_2(NH_4)H_2PO_4 \quad (8)$$

$$H_3PO_4 + NH_3 \rightarrow \text{ammonium phosphate} \quad (9)$$

In order to shed more insight on the reaction mechanism involved in starch–urea–phosphoric acid treatment, complete analysis of the reaction products as well as estimation of liberated ammonia during the reaction were made. The results obtained are given in Table 7.

Table 7
: Nitrogen and phosphorus contents (m atom/100 g sample) of starch/urea/phosphoric acid reaction products at various steps of the reaction process (starch, 10 g; urea, 1 g; magnesium sulphate, 0.08 g; phosphoric acid, 15 mmol; reaction temperature, 150°C; reaction time, 4 h)

Process step	Nitrogen content	Phosphorus content
Before reaction	265	120
(a) After reaction	246	120
Liberated ammonia	19	–
(b) After soxhlet extraction	189	94.5
(c) After acid treatment[a]	Zero	43.5

[a] Acid treatment (1 N HCl at room temperature over night).

The data show that:

1. The decrement in nitrogen content of reaction mixture after reaction amounts 19 m atom/100 g sample which is equal to the estimated liberated ammonia.
2. The nitrogen and phosphorus contents of the reaction product decrease by soxhlet extraction but the decrement in nitrogen is double that of phosphorus. The decrement in both nitrogen and phosphorus after extraction may be associated with removal of ammonium phosphate which is formed according to the reaction suggested by Eq. (9).
3. The nitrogen content of the reaction product after extraction is 189 m atom/100 g sample; a value which is over the theoretical if all urea reacts with starch to form starch carbamate. This implies that there are nitrogen atoms which are combined with starch in forms rather than starch carbamate.
4. Acid treatment of extracted sample leads to zero nitrogen content due to removal of carbamate and ammonium salt of the phosphate groups.
5. The phosphorus content of extracted sample decreased by acid treatment from 94.5 to 43.5 m atom/100 g sample. This indicates that phosphate groups include two types:(a) non-removable one which is starch phosphate (Eq. (6)); (b) removable phosphate which has been removed along with carbamate which is in the form of carbamate phosphate (Eq. (4)).

Based on the above mentioned data it can be concluded that the reaction products of starch–urea–phosphoric acid system are starch carbamate, starch carbamate phosphate, starch phosphate, ammonium phosphate and ammonia.

3.2. Solubility (%)

3.2.1. Effect of mineral acids and salts

Tables 1–4 show the solubility of starch carbamate samples, prepared at different conditions has been estimated. The data show that:

1. The solubility of prepared samples in presence of acids or salts are higher than that prepared in its absence.
2. The solubility depends on the catalyst type and

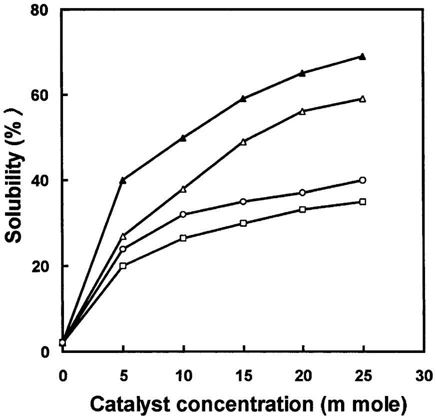

Fig. 2. The solubility of prepared starch carbamate versus catalyst concentrations. -▲- Amm. Sulphate; -□-, Amm. Nitrate; -△-, Amm. Chlorid; -○-, Mg sulphate.

concentration and follows the orders: (a) $H_2SO_4 > HNO_3 > H_3PO_4$ (cf Table 4); (b) ammonium sulphate > ammonium chloride > magnesium sulphate > ammonium nitrate (cf. Table 2).

3. The solubility increases with increasing reaction duration specially on using low acid concentration.
4. The solubility of prepared samples reachs 100% on using acids (cf. Tables 1–3) while the maximum value was 68% on using ammonium salts within the studied range (cf. Fig. 2).

3.2.2. *Effect of urea concentration*

Starch carbamate samples were prepared by using different urea concentrations (10–30% based on starch) in presence of fixed amounts of acids aiming to get samples with highs nitrogen contents. Tables 1–3 show the nitrogen contents as well as the solubility (%) of the prepared samples. The data show that:

1. The nitrogen content of prepared samples increases with increasing urea concentration but the maximum value depends on the type of used acid. The highest content (327 m atom/100 g sample) was obtained on carrying out the reaction in presence of 30% urea and 4 mmol H_2SO_4/ 10 g sample for 4 h.

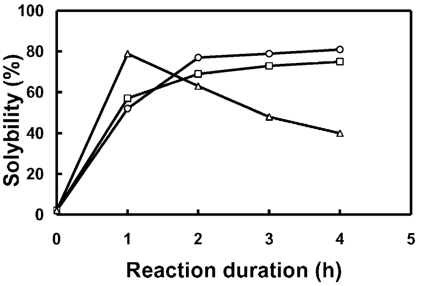

Fig. 3. The effect of acid type on the solubility of starch carbamate prepared in presence of urea (30%) -○-,sulphuric acid (4 mmol); -□-, nitric acid (5 m mole); -△-, phosphoric acid (15 mmol).

2. Solubility of prepared samples in presence of acids decreases on increasing urea concentrations This is due to higher availability for crosslinking.
3. The prepared samples using urea concentrations 10–20% acquire 100% solubility while those prepared at 30% acquire different solubility depending on the acid type and reaction duration as follows.

The solubility of prepared samples in presence of sulphuric and nitric acids increases with increasing reaction duration while the reverse occur in presence of phosphoric acid (cf. Fig. 3). These behavior may be explained as follows:

On reacting starch with excess urea in presence of acids, there are two reactions occurring: (a) hydrolytic effect due to the presence of acids and the extent depends on the strength and concentration of used. acid; (b) crosslinking reaction which depends on the amount and type of formed carbamate. On increasing urea concentration, the formed amide groups increases which accelerates the probability of crosslinking reaction leading to lower solubility values. On the other hand the strength of acid plays a good role in increasing the hydrolysis of starch molecule leading to higher solubility. Taking these in consideration: (a) within the range of 10–20% urea the hydrolytic effect is higher than the ability for crosslinking, which leads to higher solubility; (b) on using 30% urea the reflection of this concentration on the solubility depends on the strength of the used acid, i.e. in case of sulphuric acid and nitric acid the hydrolytic effect is higher than the tendency to crosslinking leading to higher solubility values while the reverse occurs in the case of phosphoric acid.

4. Conclusions

Carrying out the reaction of starch and urea in presence of mineral acid or mineral acid salt gives rise to higher extents of reaction. The extent of reaction and solubility depend upon the nature and concentration of added acid or salt. The acid performs two main functions, i.e.: (a) it prevents the amide groups of starch carbamate from reaction with adjacent amide or hydroxyl groups of the modified starch molecule thereby ceasing crosslinking, (b) it degrades starch molecule via hydrolysis thereby lowering the molecular size of starch that enhance its solubility. The reaction products of reacting starch with urea in presence of phosphoric acid comprise starch carbamate, starch carbamate phosphate, starch phosphate and ammonium phosphate.

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