



## Effect of Enzymatic Treatment of Starch Gelatinized with Urea

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THE present work is undertaken with a view to discover the effect of enzymatic hydrolysis using  $\alpha$ -amylase enzyme on different kinds of starches. This was done while starch was in the gelatinized form under the action of urea at room temperature. To achieve this goal, maize starch was subjected to gelatinization using urea at room temperature under different conditions. The latter comprise, starch concentration, urea concentration, pH value, time and temperature as well as the concentration of  $\alpha$ -amylase enzyme. The modified starches were evaluated via measuring the solubility and the apparent viscosity at various rates of shear. The modified starches were evaluated as thickeners in printing wool fabrics with acid dye and polyester using disperse dye. The results of these investigations demonstrated that the concentration of starch increases from 30 to 40 to 50g%, the apparent viscosity increases regularly irrespective of the rate of shear. The apparent viscosity increases by increasing the amount of urea. Increasing of  $\alpha$ -amylase enzyme concentration is accompanied by a decrease in the apparent viscosity at any specific rate of shear. The most suitable pH for starch modification by enzyme was found at pH 7. The temperature highly influences the apparent viscosity of maize starch at any specific rate of shear. However 80 °C can be considered as the optimum temperature in enzymatic modification of maize starch to obtain soluble starch which acquire a suitable viscosity. Generally speaking enzymatic treated starches give better results in direct printing when compared with Daico-thic or mypro gum.

**Keywords:** Enzyme, Maize starch, Urea, Acid dye, Wool fabrics.

### Introduction

Starch is a major storage product of many economically important crops such as wheat, rice, maize, tapioca, and potato.

A large-scale starch processing industry has emerged in the last century. In the past decades, we have seen a shift from the acid hydrolysis of starch to the use of starch-converting enzymes in the production of maltodextrin, modified starches, or glucose and fructose syrups. Currently, these enzymes comprise about 30% of the world's enzyme production <sup>(1)</sup>.

Besides the use in starch hydrolysis, starch-converting enzymes are also used in a number of other industrial applications, such as laundry and porcelain detergents or as anti-staling agents in baking. A number of these starch-converting enzymes belong to a single family: the  $\alpha$ -amylase family or family 13 glycosyl hydrolases. This group of enzymes share a number of common characteristics such as a  $(\beta/\alpha)_8$  barrel structure, the hydrolysis or formation of glycosidic bonds in the  $\alpha$  conformation, and a number of conserved amino acid residues in the active site. As many as 21 different reaction and product specificities are found in this family. Currently, 25 three-di-

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mensional (3D) structures of a few members of the  $\alpha$ -amylase family have been determined using protein crystallization and X-ray crystallography (2-3).

The present work is undertaken with a view to discover the effect of enzymatic hydrolysis using  $\alpha$ -amylase enzyme on different kinds of starches.

This was done while starch was in the gelatinized form under the action of urea.

## **Experimental**

### *Materials*

#### *Fabric*

Mill scoured wool fabric (100%) supplied by Misr Co. for Spinning and weaving Mehalla El-Kubra, Egypt, was used.

Polyester fabric (100%) produced by spinning and weaving Mehalla El-Kubra, Egypt, was used.

#### *Starch*

##### *Maize Starch*

Egyptian maize starch supplied by Misr Company for Starch and Glucose, Cairo, Egypt.

##### *Rice Starch*

Egyptian rice starch supplied by the Egyptian Starch Yeast and Detergents Company, Cairo, Egypt.

##### *Wheat Starch*

Egyptian wheat starch from the local Egyptian Market.

#### *Thickening agents*

Mypro gum NP-16, a-nonionic chemically modified Guar endosperm derivative, kindly supplied by Meyhall chemical AG Switzerland, was used.

Daico thick 1600, synthetic thickener was kindly supplied by Daico Company, Cairo, Egypt.

### *Dyes*

#### *Disperse dyes*

-Suncron Red S-BLSF, supplied by I.C.I, Cairo, Egypt.

-Dianix Classic Blue BG, supplied by Dystar, Cairo, Egypt.

#### *Acid dyes*

-Nylosan Red F-2B, supplied by Sandoz, Switzerland.

-Isolan Bordeayx 2S-B, supplied by Dystar, Cairo, Egypt.

### *Chemical*

Urea, sodium dihydrogen phosphate, formic acid, ammonium sulphate as well as commercial ethyl alcohol (95%) were used.

### *Enzyme*

Alpha-amylase enzyme, supplied by Novozymes A/S Krogshoejvej 362880 Bagsvaerd Denmark.

### *Methods*

#### *Enzymatic treatment of maize starch using $\alpha$ -amylase enzyme*

A calculated amount of starch was added to 100ml water and mixed well, different amounts of urea were added under continuous stirring to obtain gelatinous form of starch.

The gelatinized starch was subjected to enzymatic modification via adding amylase enzyme under different conditions. The latter comprise the amount of enzyme, pH, temperature and time to obtain pastes acquired a suitable viscosity, and the rheological properties of the pastes were measured.

After enzymatic modification the modified starch samples were precipitated using ethyl alcohol and finally subjected to purification via dissolving in water and precipitation again in ethyl alcohol to remove the remaining of enzyme.

At this end the modified starches were dried at room temperature.

#### *Preparation of the printing paste*

Two different printing pastes were prepared using Acid or Disperse dye as follows:

##### *a- On using Acid dye:*

The acid dye paste was prepared according the following recipe:

Dye	30g
Urea	50g
Thioethylene glycol	50g
Thickener	X
Water	Y
Ammonium sulphate 1:2	60g
Oxidizing agent	15
	1000gm

The thickener used was either 80g/Kg printing paste Mypro gum or enzymatic modified starch 120 or 150g/kg printing paste.

*b- On using disperse dye*

The disperse dye paste was prepared according to the following recipe:

Disperse dye	40g
Sodium dihydrogen phosphate	5g
Oxidizing agents	5 g
Thickener	X
Water	y
	1000 g

The thickener used was either 30g/Kg printing paste Synthetic thickener (Daico thic) or enzymatic modified starch 120 or 150g/kg printing paste.

*Printing Technique*

- The conventional screen printing technique was used.

*- Fixation:**a- On using Acid dye:*

Fixation of the printed goods was done by steaming for 30minutes at 100°C with saturated steam.

*b- On using Disperse dye:*

Fixation was carried out by thermofixation of polyester fabrics for 3 min at 180°C.

*- Washing:**a- On using Acid dye:*

- Washing of the printed goods was carried out as follows:

Rinsing with cold water-

Soaping at 30-40°C in 2g/l soap solution-

Rinsing with cold water-

*b- On using Disperse dye:*

Washing and reduction clear

Washing of the printed goods was carried out as follows:

-Rinsing in cold water

-Soaping at 60°C with 2g/l Hostapal CV (non ionic detergent) for 20 minutes.

-Reduction clear with 2g/l hydrosulphite, 2g/l sodium hydroxide (32.5%), 2 g/l Hostapal CV (non ionic detergent) at 40-70°C.

-Rinsing at 60-70°C.

-Cold rinsing.

*Rheological properties*

The rheological properties expressed as apparent viscosity at different rates of shear were measured using Brookfield Model DV-111 Programmable Rheometer.

*Fastness properties<sup>(4)</sup>*

Fastness properties to washing, rubbing (dry&wet), perspiration as well as light fastness were measured according to a standard method.

**Result and Discussion**

Starches are used in large quantities in various industrial applications. They are used to provide body and consistency to solutions, as a vehicle for transferring colors, as adhesives for paper and paper products, as a sizing agent in textile, and as a source of energy in human and animal diets<sup>(5)</sup>. However, natural starches often do not match the properties required for a particular end- use. Many starches show unstable viscosity when their pastes are subjected to high shearing action, heated for prolonged or subjected to freeze-thaw cycles. There is thus the necessity of modifying the starches<sup>(6-16)</sup>.

It has been reported that<sup>(17)</sup> addition of borax or urea to starch sizes brings about considerable changes in the viscosity of starch. Furthermore, the structure of the borax-starch complex and urea-complex are confirmed by thin layer chromatography. It was disclosed that these additives are not chemically bound to the starch molecules but are physically attached.

Addition of urea to starch slurry causes gelatinization of starch at room temperature. The time required to gelatinization, type of gel formed, rheological properties and apparent viscosity of starch suspension in urea solutions were studied<sup>(4)</sup>. It has been reported that, the latter did not decrease significantly after storing up to 8 weeks where that of cooked starch decreased sharply after one week of storage. Suspensions of starch in urea solutions did not show any fermentation and retrogradation during 8 weeks storage.

The present work is undertaken with a view to discover the effect of enzymatic hydrolysis using amylase enzyme on different kinds of starches. This was done while starch was in the gelatinized form under the action of urea.

To achieve this goal, maize starch was subjected to gelatinization at room temperature under different conditions.

### Effect of Starch Concentration

To investigate the effect of starch concentration, different amounts of maize starch via. 30, 40 and 50 g were added to 100ml of water containing 70g of urea at pH 7 at room temperature to obtain a highly viscous gelatinized mas of maize starch. After that 2.5ml of  $\alpha$ -amylase was add and the temperature was raized to 80°C under vigorous stirring. The mixture was left for 10 minutes at 80°C. After which, the enzymatic modified starches were cooled and its apparent viscosity at various rates of shear were measured. The results obtained are given in Table 1.

It is clear from the data of Table 1 and fig.1 that as the concentration of starch increases from 30 to 40 to 50g%, the apparent viscosity increases regularly irrespective of the rate of shear. For example if the rate of shear is held constant at 4.65 sec<sup>-1</sup> the apparent viscosity increases from 40 to 940 to 1680 centipoise by increasing the concentration of starch from 30 to 40 to 50 respectively.

On the other hand, at a constant concentration, the apparent viscosity decreases (fig.1) by increasing the rate of shear.

The dependence of the apparent viscosity to the rate of shear indicates that these pastes are non-Newtonian. While the decrease in the apparent viscosity by increasing the rate of shear indicates that, these pastes are acquiring pseudo plastic behavior.

The decrease in the apparent viscosity by increasing the rate of shear means that, if the viscosity (resistance to flow) of a solution is measured using a large applied force (shearing stress) which causes a high velocity of flow (shear rate), the apparent viscosity is less than that of the same solution determined with a smaller force and slower rate of flow. In pseudoplastic solutions no time dependence effect are observed.

From the previous data it is clear that the optimum concentration of starch is 40%.

TABLE I . Effect of starch concentration on the apparent viscosity at different rates of shear.

Conc. of Starch	Solubility in cold water	Apparent Viscosity in centipoise at rate of shear (sec <sup>-1</sup> ) of				
		4.65	9.30	14	18.6	23.3
30g	Soluble	40	35	33	30	28
40g	Soluble	940	860	607	330	210
50g	Soluble	1680	1210	983	895	798

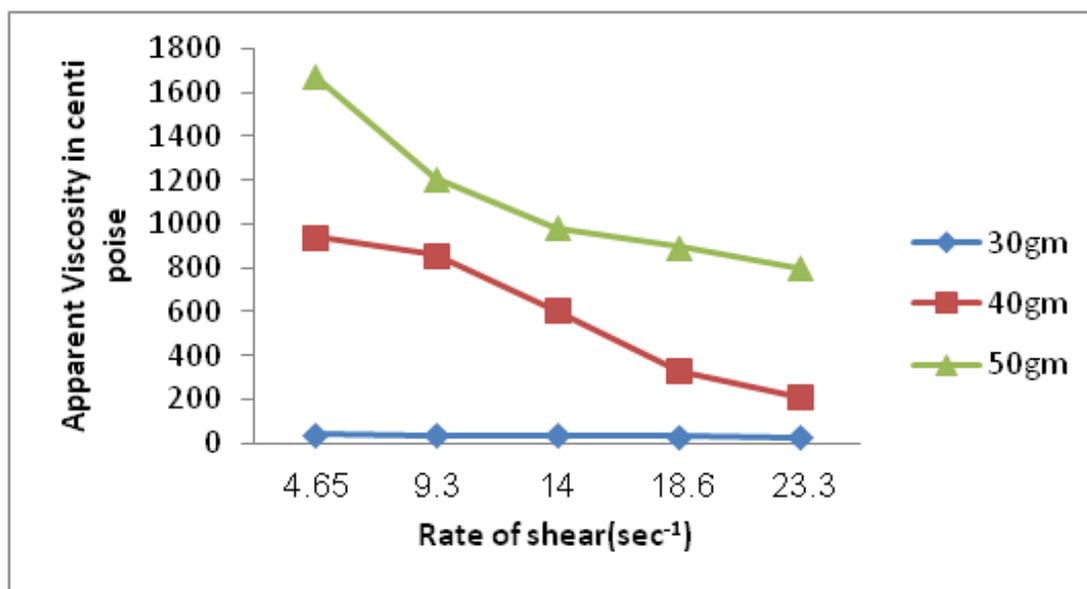


Fig.1. Dependence of the apparent viscosity on the rate of shear .

*Effect of Urea Concentration:*

To investigate the effect of urea concentration, different amount of urea (50, 60, 70 and 80g) were add to 100ml water containing 40g of maize starch at pH 7 at room temperature to obtain a highly viscous gelatinized mass of maize starch. After that 2.5ml of  $\alpha$ - amylase enzyme were added and the temperature was raised to 80°C under vigorous stirring. The mixture was left for 10 minutes at 80°C. After that, the enzymatic hydrolyzed starches were cooled and their apparent viscosities were measured. The results obtained are given in Table 2 and represented in Figure 2.

It is clear from the data of Table 2 that, in spite of the constant amount of starch in the pastes, the apparent viscosity increases by increasing the amount of urea. This phenomenon holds true at any constant specific rate of shear.

Table 2 also clarify that at any specific concentration of urea the apparent viscosity decreases by increasing the rate of shear.

From the previous data it is clear that the optimum concentration of urea is 70%.the current data also indicates that, these pastes are acquiring pseudo plastic behavior.

*Effect of Enzyme Concentration*

It has been reported that, the substrate concentration is maintained at a high level, and other conditions such as pH and temperature are kept constant. Thus as the enzyme concentration is increased, so will be a rate of the enzymatic reaction. Hence it is of great interest to investigate the effect of amylase concentration on the degree of modification of maize starch expressed as solubility and viscosity.

To achieve this, 40g of maize starch were added to 100ml water containing 70gm urea and mixed well at pH 7 at room temperature, different concentrations of amylase enzyme (1, 1.5, 2 and 2.5 ml)were added. The temperature was raised to 80°C. The mixture was left at 80°C for 10min, after which it is left to cool and its viscosity was measured the results obtained are represented in Table 3 and illustrated in Figure 3. It is clear from the data Table 3 and figure 3 that the apparent viscosity of the enzymatic modified maize starch depends on both the concentration of amylase enzyme and the rate of shear at which the viscosity is measured.

TABLE 2. Effect of amylase enzyme on the apparent viscosity on using different amounts of urea at constant amount of starch.

Conc. of Urea	Solubility in cold water	Apparent Viscosity in centipoise at rate of shear ( $\text{sec}^{-1}$ ) of				
		4.65	9.30	14	18.6	23.3
50g	Soluble	610	470	390	255	160
60g	Soluble	873	525	423	305	190
70g	Soluble	940	860	607	330	210
80g	Soluble	1250	1190	1070	960	900

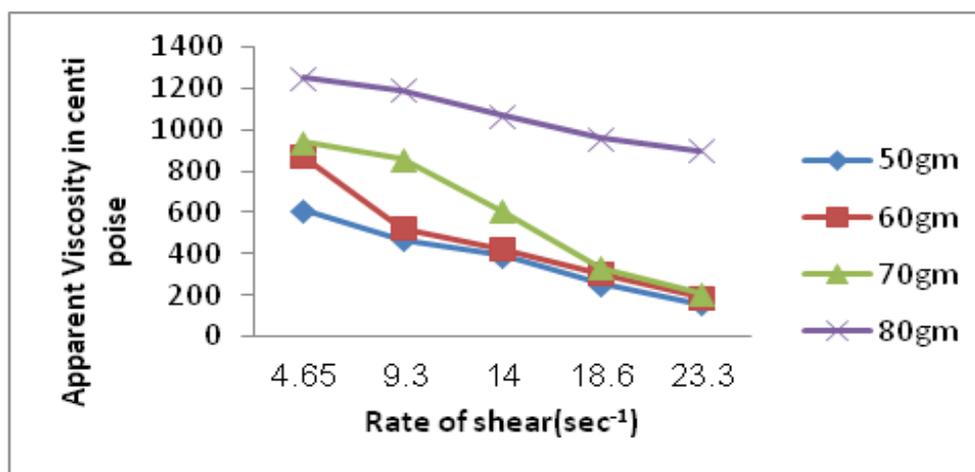


Fig. 2 . Dependence of the apparent viscosity on the concentration of urea and rate of shear.

TABLE 3. Effect of amylase concentration on the apparent viscosity of maize starch.

Conc. Of En- zyme	Solubility in cold water	Apparent Viscosity in centipoise at rate of shear ( $\text{sec}^{-1}$ ) of				
		4.65	9.30	14	18.6	23.3
1.5ml	Soluble	1240	985	890	740	670
2ml	Soluble	1100	900	833	533	490
2.5ml	Soluble	940	860	607	330	210
3ml	Soluble	610	515	457	300	190

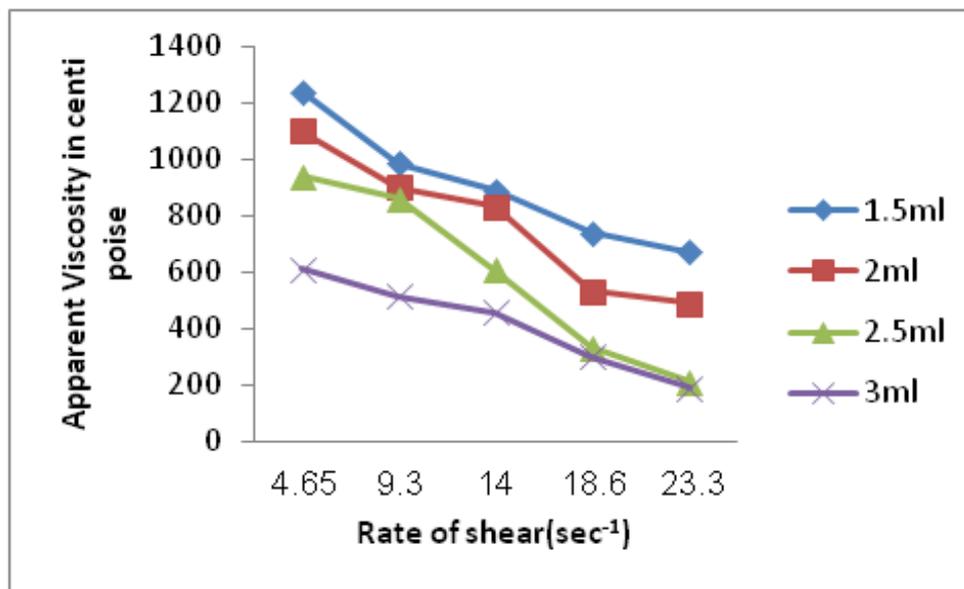


Fig.3 Dependence of the apparent viscosity on the concentration of enzyme and rate of shear.

As the concentration of enzymes increases from 1.5 to 2 to 2.5 to 3ml / 100ml water the apparent viscosity decreases. However, the magnitude of decreasing depends on rate of shear.

On the other hand, as the rate of shear increases the apparent viscosity decreases.

Fig.3. clarify that all the examined pastes are non-Newtonian pseudoplastic solutions, where its viscosity is not constant as Newtonian solutions and decreases by increasing the rate of shear.

From the previous data it is clear that the optimum concentration of amylase is 2.5ml.

#### Effect of pH:

It has been reported that an enzyme depends strongly on the pH of the medium for two major reasons: (1) the presence of essential proton-accepting groups in the catalytic center, and (2) maintenance of the overall structure of the enzyme. Proton-accepting can be directly titrated

and the dependence of the enzyme activity on pH often has the form of a bell-shaped titration curve, with a maximum usually in the neutral range (pH optimum). However, the large majority of enzymes have optimum that fall between pH 4 and 8.

To investigate the effect of pH on the rate of hydrolyses of gelatinized maize starch with amylase enzyme. 40g of maize starch were add to 100ml of water containing 70g of urea and mixed well in the high viscous mass. 2.5ml of enzyme were added and pH was adjusted to 5, 6, 7 and 8. The temperature was raised to 80°C. The mixture was left for 10min at 80°C while agitation. The mixture was cooled and its viscosity was measured. The results obtained are given in Table 4 and represented in figure 4.

It is clear from the data of Table 4 and figure 4 that the optimum pH for the current investigation is attained at 7.

TABLE 4. Effect of pH on the apparent viscosity of enzymatic hydrolyses maize starch.

pH	Solubility in cold water	Apparent Viscosity in centipoise at rate of shear ( $\text{sec}^{-1}$ ) of				
		4.65	9.30	14	18.6	23.3
5	Soluble	2170	1710	1477	1435	1300
6	Soluble	1370	890	670	470	390
7	Soluble	940	860	607	330	210
8	Soluble	1980	1850	1510	1295	1060

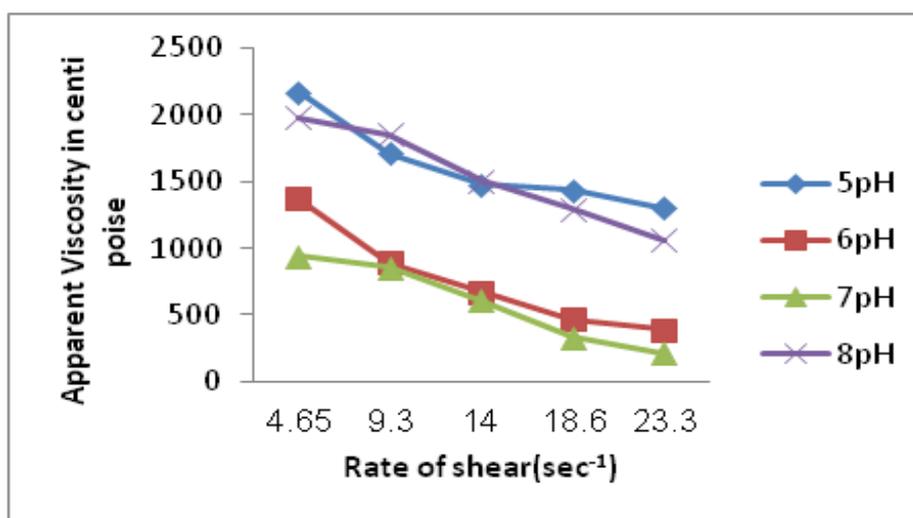


Fig.4. Dependence of the apparent viscosity on pH and rate of shear.

#### Effect of Temperature

The influence of temperature on enzymes and their activity has been reviewed by several scientists. At least over a certain range, enzymatic reactions behave like ordinary chemical reactions in that, as the temperature is increased, the rate increases too. With enzymes however, a "point of diminishing returns" is reached, since the enzyme itself will begin to suffer thermal inactivation at high temperatures.

High temperature denaturation is usually irreversible because essential weak bonding forces are broken by increased thermal vibration of the component atoms, a phenomenon that damages the three dimensional structure.

The optimum temperature depends on many factors such as purity of enzyme and substrate and the presence of activators or inhibitors.

All of the above in mind it is of great interest to investigate the effect of temperature on the current work. Hence 40g of maize starch were

added to 100ml water containing 70g urea at pH 7 and 2.5ml of enzyme. The temperature was raised to either 60, 70, 80 or 90°C and left at this temperature for 10 minutes. After which, the samples were cooled to room temperature and the viscosity were measured at different rates of shear. The results obtained are given in Table 5 and represented in Figure 5.

It is clear from the data of Table 5 that the temperature highly influences the apparent viscosity of maize starch at any specific rate of shear. For example at a rate of shear of 4.65 it decreases from 4620 to 3150 to 940 centipoise. While at 90°C it becomes highly fluid to be measured. It worthy to mention that at high temperature starch molecules are not only subjected to enzymatic degradation but also it is subjected to thermal degradation too. However 80°C can be considered as the optimum temperature in enzymatic modification of maize starch to obtain soluble starch which acquire a suitable viscosity.

TABLE 5. Effect of Temperature on the viscosity of enzymatic hydrolyzed maize starch.

Temp	Solubility in cold water	Apparent Viscosity in centipoise at rate of shear ( $\text{sec}^{-1}$ ) of				
		4.65	9.30	14	18.6	23.3
60° C	Soluble	4620	3020	2320	1883	1568
70° C	Soluble	3150	1920	1370	1058	890
80° C	Soluble	940	860	607	330	210

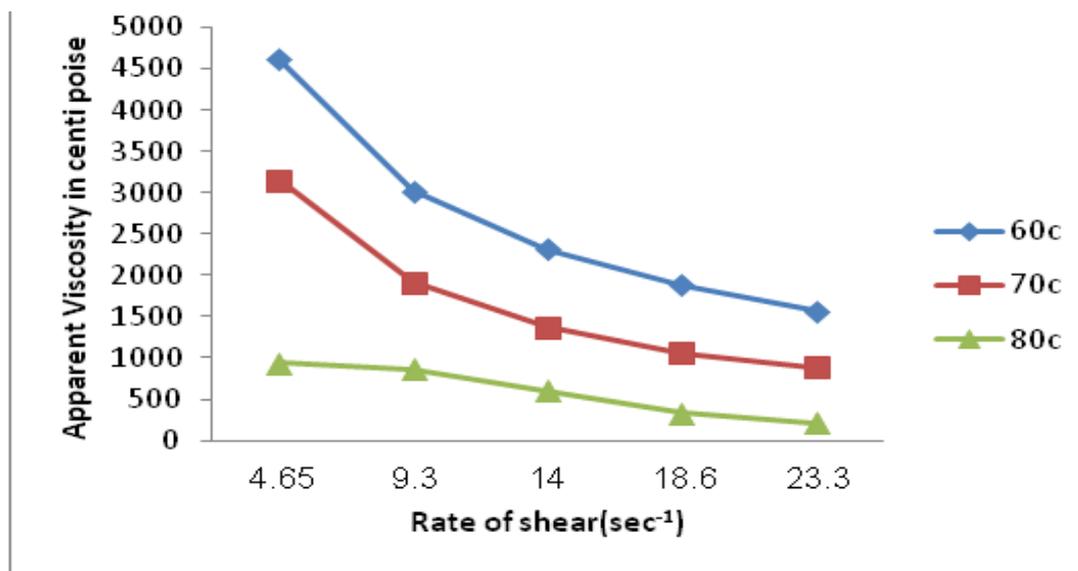


Fig.5. Dependence of the apparent viscosity on temperature and rate of shear.

#### Effect of Time

It is well known that, in the initial period of time the amount of substrate which has been transformed is directly proportional to the length of time for which the reaction has been proceeding after this initial period the rate of reaction starts to decrease and the amount of reaction is no longer directly proportional to time.

Provided the substrate is present in excess the explanation of this phenomenon is the progressive loss of enzyme activity after a period of time. This may be due to the effect of heat on the tertiary structure of the enzyme or to the formation of some product or side product of the reaction which inhibits the enzyme.

At this end, it is of great interest to investigate the effect of time of enzymatic hydrolysis maize starch. To achieve this 40g of starch were added to 100ml water containing 70g urea, the pH was adjusted to pH 7 after the addition of 2.5ml amylase enzyme. The temperature was raised to 80°C and

the mixture was kept for 7, 10 or 12.5min at 80°C.

After that the mixture was left to cool at room temperature and its viscosity was measured. The data obtained are given in Table 6 and represented in figure 6.

It is clear from the data of Table 6 that generally speaking as the time of reaction increases the apparent viscosity decreases. This phenomenon is hold true at any specific rate of shear.

While increasing the time more than 10 min, i.e. for 12.5min, the viscosity decreases and the solution become too fluid to be measured.

Also, here, Table 6 and Fig.6 illustrate that the apparent viscosity depends to the rate of shearing at which it be measured. It decreases by increasing the rate of shear i.e. it is also characterized by a Non-Newtonian behaviour.

From the previous data it is clear that the optimum time is 10min.

TABLE 6. Effect of Time enzymatic hydrolysis of starch on the apparent viscosity.

Time "min"	Solubility in cold water	Apparent Viscosity in centipoise at rate of shear ( $\text{sec}^{-1}$ ) of				
		4.65	9.30	14	18.6	23.3
5min	Soluble	1850	1200	960	815	720
7.5min	Soluble	1430	1050	700	510	470
10min	Soluble	940	860	607	330	210

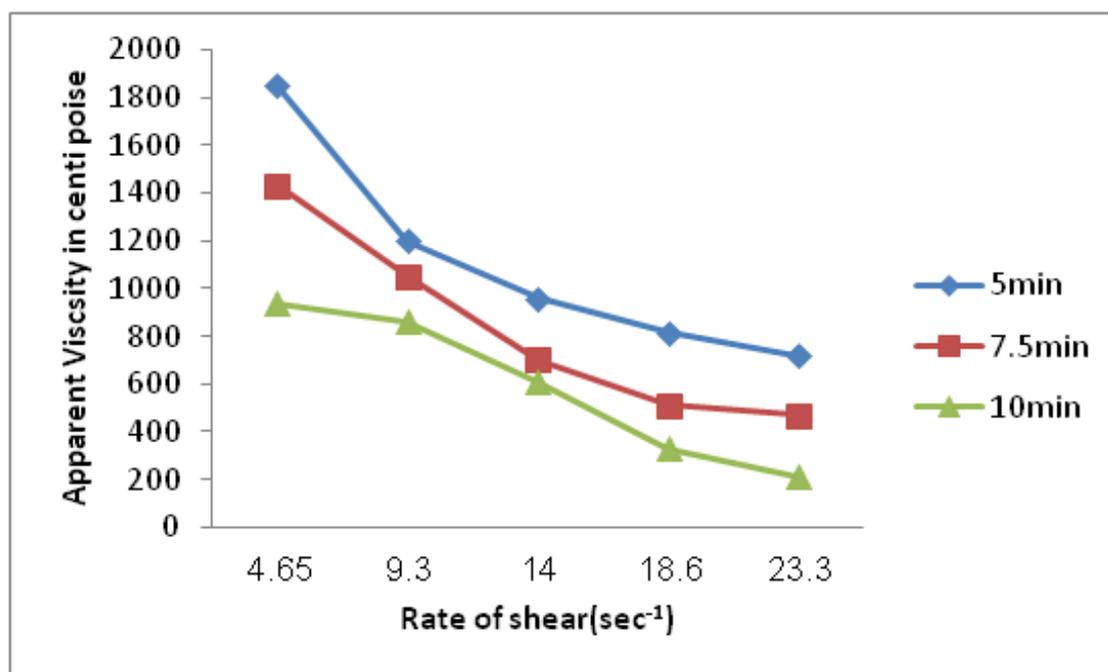


Fig.6. Dependence of the apparent viscosity on Time and rate of shear.

#### Solubility

It is clear from the foregoing data (Tables 1 to 6) that all of the prepared amylase hydrolyzed starches under the current experimental condition are water soluble, i.e. could be used safely as thickening agent for textile printing. The solubility of the enzymatic hydrolyzed starches were measured after precipitation of the modified starch from its viscous solution several time using commercial ethyl alcohol to obtain pure samples. The purified samples were dried, grinded and its solubility were measured by dissolving 10g of the dry sample in 100ml water at room temperature.

#### Effect of nature of starch

To investigate the behavior of different Kinds of starches towards gelatinization under the action of urea in the presence of enzyme. The available three kinds of starches (maize, rice and wheat) were treated under the same optimum conditions.

Hence 40g from every kind of starch (maize, rice and wheat) were added to 100ml water containing 70g urea at pH 7, and then 2.5ml of  $\alpha$ -amylase enzyme are added. The temperature was raised to 80°C and left at this temperature for 10 minutes. After which, the samples were cooled to room temperature and the viscosity were measured at different rates of shear. The results obtained are given in Table 7 and represented in Figure 7.

It is clear from Fig.7 that. Irrespective of the nature of starch, the apparent viscosity depends on the rate of shear. As the latter increases the apparent viscosity decreases. Which indicate that these pastes are characterized by non-Newtonian pseudoplastic behaviour.

However it is also clear from the data that the three kinds of starches are different in the values of their rheological behaviour.

TABLE 7 . Effect of nature of starch.

Type of starch	Solubility in cold water	Apparent Viscosity in centipoise at rate of shear (sec. <sup>-1</sup> ) of				
		4.65	9.30	14	18.6	23.3
Maize starch	Soluble	940	860	607	330	210
Rice starch	Soluble	522	436	344	175	103
Wheat starch	Soluble	877	743	511	222	165

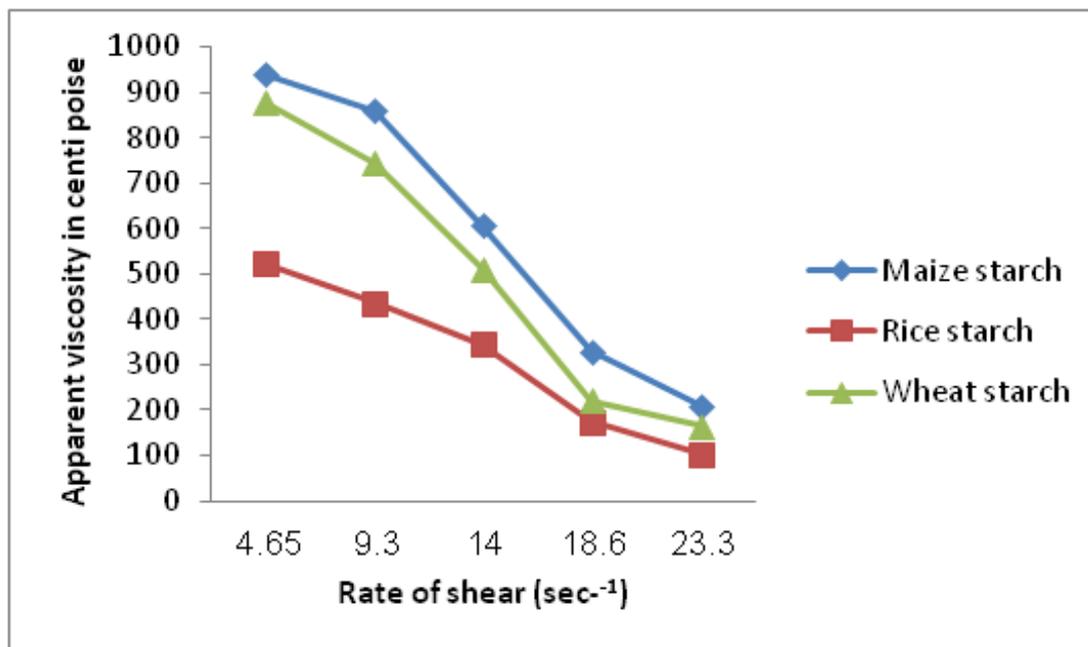


Fig.7. Dependence of the apparent viscosity on Type of starch and rate of shear.

The difference in the rheological properties and in the apparent viscosity of the three different kinds of starches may be due to the difference between them in:

- The molecular weight.
- The ratio between amylose and amylopectin.
- The ratio of the amorphous and crystalline regions.

#### Printing

The suitability of the previously modified starch samples (maize, rice and wheat) starch treated with  $\alpha$ -amylase enzyme, as thickening agents in printing was investigated. To achieve this goal. Printing pastes thickened with starch modified with  $\alpha$ -amylase enzyme were prepared according to the recipes given in the experimental section. For the sake of comparison another printing paste thickened with meipro gum containing the same components were also prepared. After

printing and drying the fabrics were subjected to fixation via either steaming at 102°C for 30 minutes, in case of wool fabric printed using acid dye (Nylosan Red F-2B and Isolan Bordeaux 2S-B) or thermofixation at 180°C for 3 minutes in case of polyester fabric printed using disperse dye (Sunron Red S-BLSF and Dianix classic Blue BG). After printing, fixation, the samples were subjected to washing followed by drying and their K/S as well as their overall color fastness properties were measured. Given below the results obtained along with the appropriate discussion.

#### Printing of Polyester Fabric using Disperse dye

To investigate the suitability of modified starches (maize, rice and wheat) starches treated with  $\alpha$ -amylase enzyme as thickeners in printing polyester fabric with disperse dye a series of printing pastes thickened with modified starches of different concentrations (12% and 15%)

containing Dianix classic Blue BG. For the sake of comparison, other paste thickened with Daico-thic was also prepared.

After printing and drying the disperse dye was fixed via thermofixation as previously mentioned in the experimental section.

At this end, the goods were washed thoroughly and their K/S and their colour fastness properties were measured. The results obtained are represented in Table 8 before and after storing of the printing pastes prior to printing for 3 days.

Generally speaking it is clear from the data Table 8 that the K/S of the freshly prepared samples printed using modified starch are higher than K/S of the samples printed using (Daico-thic).

While samples printed using modified starches after storing for 3 days is nearly identical to those obtained on using Daico-thic.

It is also clear from the data that the K/S of modified rice starch is higher than modified maize and wheat starches.

Furthermore it is also clear that the overall color fastness properties for the aforementioned modified starches before and after storing for 3 days is nearly identical to these obtained on using the commercial thickener namely Daico-thic which means that the nature of thickening agent affect the K/S and has no effect on the overall color fastness properties.

It can be concluded that enzymatic modified starches could be used as thickening agents in printing polyester fabrics with disperse dye where relatively higher K/S could be obtained than the commercial synthetic thickener namely Daico-thic. While the overall color fastness properties remain as it is  $\alpha$ -amylase enzyme convert unmodified starches to a water-soluble products. Hence, it can be used easily in preparing the printing pastes due to its solubility. The latter property of enzymatic modified starches is converted on the rubbing colour fastness properties, since it can be removed easily by washing.

The variation between the results obtained among the different starches are expected since the used three starches are different in their (1) molecular weight, (2) amylose, amylopectin ratio, (3) viscosity.....etc.

*Effect of nature of dyes on the K/S and fastness*

*properties of polyester fabric printed using maize starch*

To investigate the suitability of modified maize starch treated with  $\alpha$ -amylase enzyme as thickeners in printing polyester fabric with disperse dye a series of printing pastes thickened with modified starches of different concentrations (12% and 15%) containing Dianix classic Blue BG and Suncron Red S-BLSF. For the sake of comparison, other paste thickened with (Daico-thic) was also prepared.

After printing, drying of printed goods, the disperse dye was fixed via thermofixation as previously mentioned in the experimental section. At this end, the goods were washed thoroughly and their colour fastness and K/S properties were measured.

The results obtained are represented in Table 9 before and after storing of the printing pastes prior to printing for 3 days.

It is clear from the data that the K/S is higher for freshly modified prepared samples printed with maize starch than that samples printed on using Daico-thic regardless of the nature of the dye.

The overall color fastness to washing, to rubbing and to perspiration for the samples printed using modified maize starch is not different than that printed that printed using commercial thickener.

*Printing of Wool Fabric using Acid dye*

As previously indicated, the main aim of the present work was to investigate the suitability of modified starches (maize, rice and wheat) treated with  $\alpha$ -amylase enzyme as thickeners in printing wool fabric with acid dye. A series of printing pastes thickened with modified starches of different concentrations (12% and 15%) containing acid dye namely Isolan Bordeayx 2S-B were prepared. For the sake of comparison, other paste thickened with mypro gum was also prepared.

After printing, drying of printed goods, the acid dye printed good was fixed via steaming for 30minutes at 100°C as previously mentioned in the experimental section. At this end, the goods were washed thoroughly and their K/S and overall color fastness properties were measured.

The results obtained before and after storing of the printing pastes prior to printing for 3 days are given in Table 10.

**TABLE 8. Colour strength and fastness properties of polyester fabrics printed using modified starches of different concentrations.**

Nature of thick-ener	Concentration of thick-ener (modified starch)	Storing	K/S	Washing fastness		Rubbing fastness		Perspiration fastness			
				St.	Alt.	Dry	Wet	Acidic		Alkali	
				St.	Alt.	St.	Alt.	St.	Alt.	St.	Alt.
Daico-thic	2.5%	F	18.42	4-5	4-5	4-5	4	4-5	4-5	4-5	4-5
		S	12.64	4-5	4-5	4-5	4	4-5	4-5	4-5	4-5
	12%	F	21.32	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
		S	12.96	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
(I)	15%	F	19.80	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
		S	10.96	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
(II)	12%	F	22.44	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
		S	16	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	15%	F	20.72	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
		S	14.49	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
(III)	12%	F	18.73	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
		S	14.86	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	15%	F	16.04	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
		S	13.05	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5

- **The dye used was disperse dye namely Dianix Classic Blue BG.**

- **St.:** Staining **Alt.:** Alteration

- **F:** Fresh **S:** Storing 3 days

- **I:** Enzymatic modified Maize starch

- **II:** Enzymatic modified Rice starch

- **III:** Enzymatic modified Wheat starch

**TABLE 9. Effect of nature of dyes on the K/S and fastness properties of polyester fabric printed using maize starch.**

Nature of thick-ener	Concentration of thickener	Nature of dye	Storing	K/S	Washing fastness		Rubbing fastness		Perspiration fastness			
					St.	Alt.	Dry	Wet	Acidic		Alkali	
				St.	Alt.	St.	Alt.	St.	Alt.	St.	Alt.	
Dico-thic	2.5%	Suncron Red S-BLSF	F	3.1	4	4	4	4	4-5	4	4-5	4
			S	2.77	4	4	4	4-5	4-5	4	4-5	4
		Dianix Classic Blue BG	F	12.64	4	4	4	4	4-5	4-5	4-5	4-5
			S	9.49	4	4	4	4	4-5	4-5	4-5	4-5
Maize	12%	Suncron Red S-BLSF	F	3.21	4	4	4	4	4-5	4	4-5	4
			S	3.3	3-4	4	4	3-4	4-5	4	4-5	4
		Dianix Classic Blue BG	F	21.32	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
			S	12.96	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	15%	Suncron Red S-BLSF	F	3.7	4	4	4-5	4-5	4-5	4	4-5	4
			S	3	4	4	4-5	3-4	4-5	4	4-5	4
		Dianix Classic Blue BG	F	19.80	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
			S	10.96	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5

**St.:** Staining **Alt.:** Alteration

**F:** Fresh **S:** Storing 3 day

Generally speaking it is clear from the data Table 10 that the K/S of the samples printed using modified starches are higher than K/S of the samples printed using mypro gum. It is also clear from the data that the K/S of modified rice starch is higher than modified maize and wheat starches.

Furthermore it is also clear that the overall color fastness of the wool fabric printed using the aforementioned modified starches before and after storing for 3 days is nearly identical to these obtained on using mypro gum.

The current results is nearly the same trend of that obtained in case of printing polyester fabric with disperse dye and increases the scope of  $\alpha$ -amylase modified starches as thickening agents for both natural (wool) and synthetic fabrics (polyester).

*Effect of nature of dyes on the K/S and fastness properties of wool fabric printed using maize starch*

To investigate the suitability of modified maize starch treated with  $\alpha$ -amylase enzyme as thickeners in printing wool fabric with acid dye a series of printing pastes thickened with modified starches of different concentration (12% and 15%) containing Nylosan Red F-2B and Isolan Bodeayx 2S-B For the sake of comparison, other paste thickened with mypro gum was also prepared.

After printing, drying of printed goods, the acid dye printed goods was fixed via steaming as previously mentioned in the experimental section.

At this end, the goods were washed thoroughly and their colour fastness and K/S properties were measured.

The results obtained are represented in Table 11 before and after storing of the printing pastes prior to printing for 3 days.

It is clear from the data that the K/S is higher for freshly samples printed with modified maize starch than that printed on using mypro gum regardless of the nature of the dye. While the overall color fastness properties, i.e. for rubbing, washing and perspiration is nearly comparable.

It can be concluded that enzymatic modified starch gelatinized with urea is able to act as thickening agent in printing polyester fabric and wool fabric with Suncron Red S-BLSF and Nylosan Red F-2B dyes. Where samples printed with it acquire K/S and overall color fastness properties is nearly identical to their corresponding samples printed using commercial thickening agent namely daico-thic or mypro gum.

**TABLE 10 .Colour strength and fastness properties of wool fabrics printed using modified starches of different concentrations.**

Nature of thick-ener	Concentration of thickener (modified starch)	Storing	K/S	Washing fastness		Rubbing fastness		Perspiration fastness			
				St.	Alt.	Dry	Wet	Acidic		Alkali	
								St.	Alt.	St.	Alt.
Mypro-gum	3%	F	6.11	4	4	4	3-4	4	4	4	4
		S	5.43	4	4	4	3	4	4	4	4
(I)	12%	F	8.72	4	4	4-5	4	4	4	4	4
		S	6.38	4	4	4-5	4	4	4	4	4
		F	7.18	4	4	4-5	4	4	4	4	4
		S	4.71	4	4	4-5	3-4	4	4	4	4
(II)	12%	F	11.1	4	4	4-5	3-4	4	4	4	4
		S	7.77	4	4	4	3-4	4	4	4	4
		F	7.81	4	4	4-5	4	4	4	4	4
		S	7.76	4	4-5	4	3-4	4	4	4	4
(III)	12%	F	8.7	3-4	4	4	3-4	4	4	3-4	4
		S	6.15	4	4	4	3-4	4	4	4	4
		F	7.22	4	4	4-5	3-4	4	4	4	4
		S	4.36	4	4	4-5	4	4	4	4	4

The dye used was acid dye namely Isolan Bodeayx 2s-B  
 - St.: Staining Alt.: Alteration  
 - F: Fresh S: Storing 3 days  
 - I: Enzymatic modified Maize starch  
 - II: Enzymatic modified Rice starch  
 - III: Enzymatic modified Wheat starch

TABLE 11. Effect of nature of dyes on the K/S and fastness properties of wool fabric printed using maize starch

Nature of thickener	Concentration of thickener	Nature of dye	Storing	K/S	Washing fastness		Rubbing fastness		Perspiration fastness			
					St.	Alt.	Dry	Wet	Acidic		Alkali	
									St.	Alt.	St.	Alt.
Meypro-gum	3%	Nylosan Red	F	14.88	4	4	4-5	4-5	4-5	4	4-5	4
		F-2B	S	10.24	4	4	4	4	4-5	4	4-5	4
		Isolan Bo-deayx 2S-B	F	6.11	4	4	4	4	3-4	4	4	4
		S	5.43	4	4	4	3	4	4	4	4	
Maize	12%	Nylosan Red	F	15.13	4	4	4	4	4-5	4	4-5	4
		F-2B	S	14.49	4	4	4	4	4-5	4	4-5	4
		Isolan Bo-deayx 2S-B	F	8.72	4	4	4-5	4	4	4	4	4
		S	6.38	4	4	4-5	4	4	4	4	4	
	15%	Nylosan Red	F	12.34	4	4	4	4	4-5	4	4-5	4-5
		F-2B	S	11	4	4	4	4	4-5	4	4-5	4
		Isolan Bo-deayx 2S-B	F	7.18	4	4	4-5	4	4	4	4	4
		S	4.71	4	4	4-5	3-4	4	4	4	4	

St.: Staining Alt.: Alteration

F: Fresh S: Storing 3 days

## Conclusion

The present work is undertaken with a view to discover the effect of enzymatic hydrolysis using  $\alpha$ -amylase enzyme on different kinds of starches. This was done while starch was in the gelatinized form under the action of urea.

The modified starches were evaluated via measuring the solubility and the apparent viscosity at various rates of shear. The modified starches were evaluated as thickeners in printing wool fabrics with acid dye and polyester using disperse dye. The results of these investigations demonstrated that the concentration of starch increases from 30 to 40 to 50g%, the apparent viscosity increases regularly irrespective of the rate of shear. The apparent viscosity increases by increasing the amount of urea. Increasing of  $\alpha$ -amylase enzyme concentration is accompanied by a decrease in the apparent viscosity at any specific rate of shear. The most suitable pH for starch modification by enzyme was found at pH 7. The temperature highly influences the apparent viscosity of maize starch at any specific rate of shear. However 80 °C can be considered as the optimum temperature in enzymatic modification of maize starch to obtain soluble starch which acquire a suitable viscosity. Generally speaking enzymatic treated starches give better results in direct printing when compared with Daico-thic or mypro gum.

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## تأثير المعالجة بالانزيمات على النشا المحور في الصورة الجيلاتينية باستخدام اليوريا

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يهدف العمل في هذا الفصل الى دراسة تأثير انزيم الفا اميليز في تحلل النشا. تم ذلك بعد تحويل النشا الى الصورة الجيلاتينية (gelatinized) باستخدام اليوريا.

ولتحقيق هذا الهدف تم تحويل نشا الذرة للصورة الجيلاتينية (gelatinized) باستخدام اليوريا على البارد تحت ظروف مختلفة اشتملت هذه الظروف على دراسة تأثير كل من تركيز النشا، تركيز اليوريا، الأس الهيدروجيني للخليط، الزمن، درجة حرارة المعالجة بالإضافة الى دراسة تأثير تركيز انزيم الفا اميليز وتم تقييم نتائج تلك المعالجة الحيوية بالانزيم عن طريق قياس الذوبان في الماء البارد وكذلك تقدير قيم اللزوجة الظاهرية عند معدلات القص المختلفة.

هذا وقد اشتملت الدراسة على دراسة امكانية استخدام النشويات المحضرة كمتخانات في طباعة اقمشة الصوف باستخدام صبغتين من صبغات الفصيلة الحامضية وكذلك طباعة اقمشة البوليستر باستخدام صبغتين من صبغات الفصيلة المشتتة.

ويمكن تلخيص اهم النتائج التي تم التوصل اليها في هذا الفصل فيما يلي:-

- 1- كلما زاد تركيز النشا ٤٠:٥٠:٣٠٪ تزداد اللزوجة الظاهرية بانتظام بغض النظر عن قيم معدل القص.
- 2- تزداد اللزوجة الظاهرية بزيادة كمية اليوريا المستخدمة في عملية تحويل النشا الى الصورة الجيلاتينية.
- 3- زيادة تركيز انزيم الفا اميليز يكون مصحوبا بنقص في اللزوجة الظاهرية عند ثبوت معدل القص.
- 4- انسب اس هيدروجيني لتحويل النشا بالانزيم كان عند اس هيدروجيني ٧.
- 5- تلعب درجة الحرارة دورا كبيرا على اللزوجة الظاهرية عند اى معدل قص وعلى اى حال فإن درجة ٨٠ درجة مئوية يمكن اعتبارها الدرجة المثلى في تحويل نشا الذرة بانزيم الاميليز للحصول على نشا قابل للذوبان في الماء البارد ولزوجة مناسبة للطباعة.
- 6- كلما زاد زمن المعالجة قلت درجة اللزوجة.
- 7- بغض النظر عن نوع وطبيعة النشا المستخدم فإن الظروف المثلى لتحويله بهذا الاسلوب للحصول على منتج قابل للذوبان في الماء ويتميز بلزوجة مناسبة هي عندما يكون تركيز النشا ٤٠ جرام وكمية الماء ١٠٠ مللى واليوريا ٧٠ جرام مع اضافة ٢,٥ مللى انزيم الفا اميليز وضبط الاس الهيدروجيني عند ٧ وتقليب الخليط جيدا مع رفع درجة الحرارة الى ٨٠ درجة مئوية وتركه عند هذه الدرجة لمدة ١٠ دقائق.
- 8- تتميز عجائن النشويات المعالجة بالانزيم بهذه الطريقة بخواص ريولوجية غير نيوتينية من النوع البيسيدوبلاستيك.
- 9- عند طباعة اقمشة البوليستر باستخدام الصبغة المشتتة (Dianix Classic Blue BG) فإن شدة اللون للإقمشة المطبوعة باستخدام النشويات المحورة اعلى من مثيلتها المطبوعة باستخدام المتخن التجارى (Daico thickener) بينما تتماثل شدة اللون عند تخزين العجائن لمدة ثلاثة ايام.
- 10- بالإضافة الى ذلك فإن درجات الثبات المختلفة سواء قبل او بعد تخزين العجائن لمدة ثلاثة ايام قبل الطباعة تكون متماثلة باستخدام النشويات المحورة والمتخن التجارى.
- 11- وعند طباعة الاقمشة الصوفية باستخدام الصبغة الحامضية (Ys-B Isolan Bordeayx) فإن شدة اللون للإقمشة المطبوعة باستخدام النشا المحور كانت اعلى من الاقمشة المطبوعة باستخدام المتخن التجارى (mypro gum) كما ان شدة اللون للإقمشة المطبوعة باستخدام نشا الارز المحور اعلى من تلك المطبوعة بنشويات الذره والقمح.
- 12- كما ان درجات الثبات المختلفة للاقمشة الصوفية المطبوعة باستخدام النشويات المحورة سواء قبل او بعد التخزين لمدة ثلاثة ايام متماثلة مع الاقمشة المطبوعة بالصمغ التجارى.
- 13- بصفة عامة فإن النشويات المعدلة تعطى نتائج افضل عن استخدام المتخانات التجارية في حالة الطباعة المباشرة.