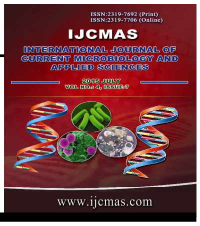

International Journal of Current Microbiology and Applied Sciences
ISSN: 2319-7706 **Volume 4 Number 7 (2015) pp. 43-53**
http://www.ijcmas.com

Original Research Article

Chemical Modification of Tapioca Starch via Simultaneous Oxidation and Vinyl Graft Copolymerization and its Onset on Size Ability of Cotton Based Yarns

Ali Hebeish[1], M.H.El-Rafie[1], Ali Sayed[1], Emad Drag[2] and M.A.Ramadan[1]*

[1]National Research Centre, Textile Research Division, Egypt
[2]Misr Company for Spinning and Weaving, Egypt

**Corresponding author*

ABSTRACT

Keywords

Starch, Vinyl monomer, Sizing formulation, Size warp yarns and Weaving efficiency

In this work the oxidation of Tapioca starch via simultaneous oxidation and vinyl graft copolymerization and its onset on size ability of cotton based yarns will done. Preparation of tapioca starch size carried out via incorporation of a proper amount of ammonium persulphate (APS) during cooking of starch in presence Acrylic acid monomer. This innovative size based formulation is applied a beginning by trials and applied different cotton and blends warp yarns. The so sized yarn were woven using fast looms, namely sulzer, rapier and air jet and compared with those of the conventional sizing formulation with respect to technical properties of the sized yarns, efficiency of the looms, quality and reduction in the production cost. The results indicate that (a) higher abrasion resistance and tensile strength with innovative size - based formulation as compared with conventional sizing formulation, (b) the weaving efficiency observed with warps sized with innovative formulation is equal to or in some cases higher than the weaving efficiency found with warp sized using conventional formulation (c) omitting of CMC along with complete replacement of PVA by vinyl monomers this leads to production cost saving exceeds 37%; That is the latter could be achieved with the innovative formulation as a result of complete imitation of CMC and PVA by oxidizing starch with vinyl monomer graft polymerization.

Introduction

Sizing is generally defined as the application of a protective polymeric material (warp size) to warp yarns prior to weaving. Warp size binds together the individual fibers in yarn bundle and coat the surface of the yarn to smooth down protruding fibers (reduce hairiness). Development in production of weaving looms reflects the need for continuous development in sizing formulation (Conway and Sohns, 1975) Starch is the most important component in sizing formulations for cellulosic based warp yarns. Warp yarns with high count number need high concentration of sizing agent 15–18%. Cooked native starch with concentration higher than 10% suffer from serious detects, the most outstanding of which are (a) unstability of viscous solution of starch particularly when there is fluctuation of temperature during cooking and sizing operation, (b) the very high molecular size of starch limits the penetration in the bulk of textile threads, (c) rigidity of starch film particularly in the absence of good lubricant and (d) susceptibility of starch to rot and degradation by microorganisms (Dekking, 1969)

Most of the aforementioned shortcomings could be overcome through chemical modification of starch (Hebeish *et al.*, 1996).Of these mention is made of the following: oxidation (Hebeish *et al.*, 1996; Hebeish *et al.*, 2008; El-Sheikh *et al.*, 2010; Muhrbeck *et al.*, 1991) hydrolysis (Muhrbeck and Tellier, 1991; Jarowenko, 1987; Maroza and Tomasik, 1991) etherification and esterification (Agboola *et al.*, 1991; Forrest, 1992; Hellwlg *et al.*, 1992; Nachergaele, 1989), cross linking (Kulicke *et al.*, 1990; Hebeish *et al.*, 1996; Hebeish *et al.*, 1992) and dextrinization. Such reaction process cause significant change in physical as well as chemical structure of starch which, in turn, are reflected on solubility, viscosity performance and resistance to ageing and solutions of pastes prepared thereof.

Oxidation of starch is one of the most promising techniques for modification of starch to achieve suitable sizing agent for textile industry. Oxidation of starch could be achieved via chemical oxidation in several media such as hypochlorite, hydrogen peroxide (El-Rafie *et al.*, 1995; Hebeish *et al.*, 1996; Ali and Kempf, 1986) and air oxidation (Hebeish *et al.*, 1996). It is a common practice to add polyvinyl alcohol (PVA) to starch based sizing formulation to attain the proper viscosity.

In current work we present an industrial innovation which provides cleaner, safer and cheaper practice for sizing of cotton and cotton/ polyester blend warp yarns. The innovation is based on conducting concurrent oxidation and vinyl grafting of starch during the sizing operation in a textile mill. The experimental development involves incorporation of a proper amount of ammonium persulphate during cooking the starch in the presence of vinyl monomer. Thus obtained innovative chemically modified size-based is formulation applied in many trials on industrial scale to different cotton and blends warp yarns using the available facilities at Misr Company for Spinning and Weaving, Mehalla El-Kubra. Weaving of the so sized yarns as well as their mate yarns sized using the conventional sizing formulation are performed using fast looms namely sulzer projectile, Rapier and Air jet looms. The efficiency of weaving is calculated in both cases along with the cost of sizing using the innovative size – based formulation vis-a-vis cost of conventional sizing.

Materials and Methods

Tapioca starch supplied by Emanz Co. for Starch., El-Obour city, Industrial Zone. Producer name: Intimex Import Export, Joint—stock Company Hanol Branch, Origin/ Vietnam.

Harprax and ammonium persulphate, vinyl monomer, its name is acrylic acid monomer and supplied from Egypt British Co.,El-Obour city, Industrial Zone, were purchased by Misr Company for Spinning and Weaving, Mehalla El-Kubra, Egypt as technical grade chemicals. Other chemicals were of laboratory grades. Misr company for spinning and weaving will be abbreviated to Misr-Mehalla Company hence forth.

The Tapioca starch was chemically modificated via oxidation with ammonium persulphate (APS) by incorporation of proper amount of (APS) to the sizing formulation.

The oxidation reaction and vinyl graft polymerization were simultaneously carried out during the cooking process in weaving sector at Misr-Mehalla Company using the available equipment and instrument in the sizing sector.

An aqueous dispersion of native Tapioca starch was prepared at the concentration range of 8-18% solid content followed by the addition of a calculated amount of ammonium persulphate (2.5gm APS/1kg Tapioca starch). At this end, the reactants were kept under continuous stirring at 40 °C for 15 minute followed by addition of other components of the sizing formulation (vinyl monomer and softener).

The reaction temperature was gradually raised to 95°C for 30 minutes for cooking under continuous stirring and complete consumption of APS. The so prepared formulation is referred to as the innovative size-based formulation.

Cotton and cotton/ polyester blended warp with different count and ends were sized using the innovative size-based formulation and the conventional size formulation.

Characterization

The sized and unsized 100% cotton and polyester/ cotton blended warp yarns were evaluated via determining the abrasion resistance using kzweiyl (Hellwlg *et al.,* 1992) tester (Chaudhari *et al.,* 1989) and the tensile strength and elongation at break using uster tensamat tester (Maroza and Tomasik, 1991). The efficiency of looms during production was evaluated by the quality control sector and the sizing process cost was evaluated by the production sector in Misr, Mehalla Company.

Results and Discussion

Sizing agent usually used in textile warp sizing is film-forming materials of one or more polymeric products. In essence, it is applied to the warp yarns in order to bind together the individual fibers in the yarn bundle and coat the surface of the yarn to smooth down protruding fibers (reduce hairiness) of the yarn bundle. The ultimate mate aim of this is to increase weaving efficiency and minimize the numbers of ends downs.

In a very recent study, we have carried out a thorough through investigation into oxidation of starch with APS during the initial slurry step as well as during addition of the vinyl monomer during the cooking step there by effecting concurrent oxidation and grafting of starch and brought into focus the newly synthesized chemically modified starch-based innovative size. The latter exhibits salient features which advocate this innovative size for industrial trials. Such innovative size could be prepared in one-stage process during preparation of the sizing formulation. Hence it can substitutes starch vinyl (polymer) composites and oxidized starch-vinyl (polymer) composite which were prepared independently them as used as the polymeric ingredients in the sizing recipe. As evident the one stage preparation of the innovative chemically modified starch-based size seems more pliable it cleaner production in the area of warp sizing.

The validity of the above is confirmed in current work through practicing the application of the innovative size-based formulation vis-a-vis the conventional size-based formulation on full industrial scale.

Needless to say that the innovative size-based formulation is exerts by better environmental and economical impact as compared with the conventional size-based formulation-omitting PVA incorporated in the conventional sizing formulation. From the innovative size-based formulation may account for this.

Technical and economical evaluations of the sizing process using the innovative size-based formulation and conventional sizing formulation were performed by monitoring technical properties of the sized yarns, efficiency of the looms and reduction in the production cost.

Factors affecting oxidation of tapioca starch by ammonium persulphate

Dependence of the extent of oxidation, expressed as meg. COOH/ 100g tapioca starch, on reaction time and temperature as well as on concentration of ammonium persulphate is shown in table 1. It is clear that the extent of oxidation increases by increasing any of these variables as evidenced by the significant increments in the carboxyl groups. It is logical that raising the temperature would enhance decomposition of the persulphate along with increasing the degrees of mobility, miscibility, compatibility and molecular collision of reactants; meanwhile the time would provide better contact opportunities among the reactants. The ultimate effect of all this is increased oxidation. Similarly, the extent of oxidation, expressed carboxyl content increases considerably by increasing ammonium persulphate concentration within the range studied. Higher concentration of the persulphate would certainly lead to higher amounts in the reaction medium of the oxidizing species which, in turn attack the starch molecules thereby creating more carboxyl groups.

It is seen (Table 1) that the carboxyl contents increases with increasing concentration of ammonium persulphate. In addition, the carboxyl percent was increased with both the time and temperature required for cooking process. The cooking process was carried at 600 rpm.

Effect of oxidizing agent concentration as well as duration and temperature of size preparation on apparent viscosity and carboxyl content of Tapioca starch

Table 2 shows the effect of the conditions of APS oxidation treatment on the apparent viscosity of the oxidized Tapioca starches prepared there under. It is seen that the apparent viscosity decreases significantly by increasing the amount of ammonium persulphate (APS) incorporated in the treating medium. This is observed irrespective of the reaction temperature. Nevertheless, the apparent viscosity is lower the higher the temperature; a point which could be associated with structural changes in the chemical composition of Tapioca starch under different Temperatures. Such changes encompass:

(a) oxidation of reducing groups to carboxyl groups, (b) oxidation of the starch hydroxyls to aldehyde groups, (c) oxidation of the newly introduced aldehyde groups to carboxylic groups and (d) breaking down the glucosidic bond of the starch chains. It is further noted that the apparent viscosity in step A is measured after filtration whereas the apparent viscosity in step B is measured directly after cooking without

The apparent viscosity of 8% tapioca starch samples oxidized using different concentrations of ammonium per sulfate (0.15%, 0.20%, 0.25%) at different temperatures (40 °C – 50 °C – 60 °C), for fixed time (30 min.) was measured. This was done with respect to step A and step B samples, results of table 2 exhibit that direct cooking (step B) displays much lower apparent viscosity than (step A), samples. Results of table 2 make it evident that the apparent viscosity of step A samples displays much higher values than those of step B samples. This implies that the oxidizing agent (ABS) which is not filtrated in case of step B samples stands as a reason for the exceedingly lower viscosity values abet and with step B samples. Absence of APS by filtration in case of sample A would not logically exert negative effect on apparent viscosity. Meanwhile the values of carboxyl content of step B samples (direct cooking process) are higher than the corresponding values of step A samples (indirect cooking process). This again is a manifestation of the absence of APS through filtration in case of step A samples.

Factors affecting graft polymerization of acrylic acid with tapioca starch the effect of tapioca starch concentration on the grafting process

Concentration tapioca starch under the industrial condition adapted in Misr-Mehalla Co.

Graft polymerization of acrylic acid onto tapioca starch was carried out as follows; APS was used as chemical initiation for inducing the polymerization of acrylic acid with tapioca starch. Hence this initiation was added to soluble tapioca starch at room temperature and stirred for 15 min. to yield oxidized starch. Acrylic acid was then added slowly to the so oxidized starch while stirring for another 15 min. after which cooking process started by gradually injecting steam (95 °C) under vigorous stirring for 30 min. At this end, the modified tapioca starch obtained was evaluated via monitoring carboxyl content and percentage add-on (increase in weight of the starch due to the modification) at different concentration of tapioca starch. Results obtained are set out in table 3.

It is obvious (Table 3) that increasing the tapioca starch concentration and consequently decreasing the acrylic acid concentration are accompanied by significant decrease in the extent of starch modification expressed as carboxyl content and add-on. The adverse effect of tapioca starch concentration on the extent of its modification is unequivocally due to the dement in acrylic acid concentration upon using higher concentration of tapioca starch. It is understandable that availability of acrylic acid monomer molecules in the vicinity of the starch is a prerequisite of propagation of the growing acrylic acid chains. Lowering the acrylic acid concentration decreases the add-on and, in turn, the carboxylic content.

APS initiator concentration

Table 4 shows the effect of APS initiator on the extent of modification of tapioca starch, given in terms of carboxyl content and add-on percent. Apparently, both carboxyl content and add-on decrease by decreasing the APS and acrylic acid concentration through increasing the tapioca starch concentration. That is, taking the APS as a fixed amount then relating it to acrylic acid at fixed concentration which is related to increasing concentration of tapioca starch would account for this since we are, indeed, dealing with decreased concentration of APS and acrylic acid. Graft polymerization onto starch needs reasonable concentration of APS and acrylic acid.

Concentration of acrylic acid monomer

Table 5 depicts the effect of acrylic acid concentration on the extent of starch modification, expressed as carboxyl content and add-on percent. Obviously, the extent of starch modification is greater upon using higher concentrations of acrylic acid. Greater availability of acrylic acid monomer molecules in the proximity of starch hydroxyls at higher acrylic acid concentration accounts for this.

Temperature of polymerization

Table 6 illustrates the effect of polymerization temperature on the extent of tapioca starch modification, given in terms of carboxyl content and add-on percent the extent of modification is exceedingly higher at temperature above 70 °C as compared at 60 °C as below. The add-on at 40 °C-60 °C is very low as so does the carboxyl content. This means that temperature range (40-60 °C) has little or no effect on the extent of starch modification. On the contrary, cooking temperature (95 °C) induces the heights effect as evidenced by the higher values of carboxyl content and add-on percent of tapioca starch modified through polymerization with acrylic acid and APS at 95 °C.

Experimental development output

With the above ends in view, it is clear that a system containing tapioca starch, acrylic acid, APS and water yields oxidized tapioca starch, tapioca starch grafted with poly acrylic acid, oxidized tapioca starch grafted with poly acrylic acid, homo poly acrylic acid and intact tapioca starch. These resultant components are intimately association in as such to for tapioca starch – poly acrylic acid composite. Stated in other words, polymerization of tapioca starch under acrylic acid using APS as initiation results in innovative composite the contrition of which relies on conditions of polymerization which indeed are characterized in comment was by being true industrial conditions. In the next paragraph the application of the innovatively synthetic sized composites in warp sizing of cotton and polyester/cotton blend yarns along with technical properties of the sized warps are reported.

Technical properties of cotton and polyester (cotton blend yarns) sized with innovation size

Sizing operation was carried out on an industrial scale

Table 7 shows the effect of sizing using determined innovation size on mechanical properties of different cotton as poly ester/cotton blended yarns. Properties, measured include abrasion resistance, tensile strength, and elongation at break.

Table 7 illustrates that the physical properties of yarns sized with composite formed from tapioca oxidized starch reacted with acrylic monomer (Abrasion, tensile strength, elongation) and poly vinyl alcohol, it was observed that the physical properties of sized yarns by acrylic acid –starch composite better (recipe 1) than in case sizing by PVA- starch composite (recipe 2). It also observed that by increasing size concentration (solid content) the physical properties of sized yarns decrease regardless type of the size materials, i.e. physical properties of sized yarns were improved in case of recipe 1 &3 compared with that of recipe 2 &4 respectively. This due to the penetration of size material in case less solid content more than in case high solid content and in this time the viscosity decrease.

The data obtained from table 8 illustrate that: 1) Increasing the technical and physical properties (abrasion, tensile strength and elongation) of the sized yarns, 2) Increasing the concentration of sizing agent depending on the concentration of acrylic acid monomer leads to improving the physical and technical properties of the sized yarns, 3) The recipe number 4 (sizing mixture) is more favored than obtained with 1, 2 and 3 recipes as a result elasticity of size film formation around yarns increased by increasing monomer (AA) concentration.

Table.1 Variations of the extent of oxidation, expressed as carboxylic content of the oxidized tapioca starches with change in temperature, duration and ammonium per sulphat (APS) concentration

[APS] % (ows)	Carboxylic content											
	Reaction temperature											
	40 °C				50 °C				60 °C			
	Duration time (min)											
	15	30	60	90	15	30	60	90	15	30	60	90
0.15	5.5	6.0	7.0	9.0	6.5	7.5	9.0	11.0	8.5	10.0	11.5	13.0
0.20	6.0	6.5	8.0	10.5	7.5	8.5	10.	11.5	9.0	10.5	12.0	14.0
0.25	7.5	8.0	8.5	10.5	8.0	9.0	10.5	12.0	10.0	11.5	13.0	15.0
0.30	8.5	9.0	10	11.0	10.	10.0	11.5	13.5	11.0	12.5	14.5	17.0

Table.2 Impact of direct cooking process and indirect cooking process on the apparent viscosity and carboxyl content of tapioca starch oxidized under different APS concentration and temperature

[APS] (%) (OWS)	**Temp. (°C)**	**Indirect cooking (Washed and filtrated) (Step A)**		**Direct cooking (Step B)**	
		Ap-viscosity (c.p) After filterate	**carboxyl content meq/100g st**	**Ap-viscosity (c.p) direct cooking**	**carboxyl content meq/100g st**
0.15	40	3600	6.0	440	15.0
0.20	40	3200	6.5	420	16.6
0.25	40	2200	8.0	335	18.8
0.30	40	2000	9.0	330	20.0
0.15	50	3100	7.5	375	10.5
0.20	50	2600	8.5	245	18.9
0.25	50	2000	9.0	220	20.5
0.30	50	1600	10.0	200	25.5
0.15	60	2400	10.0	300	17.2
0.20	60	1800	10.5	240	19.4
0.25	60	1200	11.0	190	22.2
0.30	60	800	12.5	150	30.5

Condition used: concentration of tapioca starch, 8%; time of cooking, 30 min.

Table.3 Effect of tapioca starch concentration on its graft polymerization of acrylic acid process

[Tapioca starch] g /L	[Acrylic acid] % (OWS)	Carboxyl content (meq/ 100 g st)	Add-on (%)
50	50	84.5	6.478
100	25	68.0	5.148
150	16.6	67.0	5.0
200	12.0	47.0	3.5

Reaction conditions: [APS], 0.3% (OWS); Temp, 95 °C; time, 30 min, OWS : based on weight of starch.

Table.4 Effect of oxidizing agent concentration (APS) on the grafting process and its adverse on carboxyl content and add-on percent

[Tapioca starch] g/L	**]APS] %**	**]Acrylic acid] %(OWS)**	**COOH meq/100g st**	**Add-on %**
50	2.28	50	281.5	25.420
100	1.14	25	217.5	18.567
150	0.76	16.6	170.5	13.993
200	0.57	12.5	123.5	9.759

Reaction conditions: Temp, 95 °C; Time, 30 min.; OWS: based on weight of starch.

Table.5 Effect of acrylic acid monomer concentration on the extent of modification of tapioca starch, expressed as carboxyl content and add-on percent

[Tapioca starch] (g/L)	**]Acrylic acid] (OWS)**	**COOH meq/100 g starch**	**Add-on** (%)
50	50	281.50	25.420
50	70	377.0	37.257
50	90	429.0	44.692
50	100	431.5	45.070
50	110	462.0	49.840

Reaction conditions: [APS], 2.28% (OWS); Temp, 95 °C; time, 30 min., OWS: based on weight of starch

Table.6 Effect of temperature on the extent of modification of tapioca starch expressed as carboxyl content and add-on percent

Temperature (°C)	**COOH (meq/100g st)**	**Add-on (%)**
40	11.0	0.798
50	13.0	0.945
60	14.0	1.018
70	91.5	7.05
80	185.0	15.4
95	431.5	45.07

Condition used [st], 50 g/L; [APS], 2.28% (OWS) g/ starch; [AA], 100 (g/st), time, 30 min., OWS : based on weight of starch.

Table.7 Properties of the Abrasion resistance, tensile strength and the elongation of the yarns which sized by different recipes of the composite

recipe No.	The count yarn No	The analysis properties			
		Abrasion resistance	+ Δ %	tensile strength	Elongation %
1	40/1 PES 65%	581.4	+ 750%	330	4.04%
	40/1 combed COTT- 100%	232.1	+530%	412	2.92%
	36/1 PES 45%	264.0	+331.5	332	4.0%
2	40/1 PES 65%	397.1	+480.5%	306	4.16%
	40/1 combed COTT- 100%	201.3	+447.0	418	3.32%
	36/1 PES 45%	260.8	+326.0	328	3.76%
3	40/1 PES 65%	168.6	+146.5	316	4.04%
	40/1 combed COTT- 100%	158.0	+329.3	394	3.36%
	36/1 PES 45%	89.0	+45.4	326	4.36%
4	40/1 PES 65%	152.4	+122.8	286	4.28%
	40/1 combed COTT- 100%	154.8	+320.6	384	3.72%
	36/1 PES 45%	94.2	+53.9	330	4.0%
grey	40/1 PES 65%	68.4	-	274	4.04%
grey	40/1 combed COTT- 100%	36.8	-	284	3.08%
grey	36/1 PES 45%	61.2	-	240	4.2%

Condition used : [APS]; 2.28% (OWS), 500 ml of water.

The recipes numbers:

1- [5% oxidize tapioca starch +5% AA] = 10%. 2- [5% oxidize tapioca starch +5% PVA] = 10%

3- [10% oxidize tapioca starch +5% AA] = 15%. 4- [10% oxidize tapioca starch +5% PVA] = 15%

Table.8 Evaluation of the mechanical properties of the yarns which sized by different recipes concentrate of the composite (graft of oxidize starch with AA)

recipe No.	The count yarn No	The analysis properties			
		Abrasion resistible	+ Δ %	tensile strength	Elongation %
1	40/1 PES 65%	168.6	+148.5%	316	4.04
	40/1 combed COTT- 100%	158.0	+329.3%	394	3.36
	36/1 PES 45%	89.0	+45.4	326	4.36
2	40/1 PES 65%	169.2	+147.3%	318	4.64
	40/1 combed COTT- 100%.	170.2	+362.5	396	3.16
	36/1 PES 45%	173.0	+182.6	324	3.76
3	40/1 PES 65%	189.0	+176.3%	332	4.4
	40/1 combed COTT-100%	173.0	+370.1	410	2.6
	36/1 PES 45%	186.8	+205.2	349	4.32
4	40/1 PES 65%	234.5	+242.8%	342	6.48
	40.1 combed COTT- 100%	191.4	+420.0	376	3.84
	36/1 PES 45%	262.8	+329.9	394	4.48
grey	40/1 PES 65%	68.4	-	274	4.04%
grey	40/1 combed COTT- 100%	36.8	-	284	3.08%
gery	36/1 PES 45%	61.2	-	240	4.2%

Condition used : [APS], 2.28% (OWS), 1000 ml of water.

1 = [5% oxidize tapioca starch +2.5% AA] = 7.5%, 2 = [5% oxidize Tapioca starch +3.5% AA] = 8.5%

3 = [5% oxidize tapioca starch +4.5% AA] = 9.5% 4 = [5% oxidize tapioca starch +5.5% AA] =10.5%

Table.9 Properties of the yarns

The Article/wide-cm	Type of the loom	total No of ends	Yarn count cotton 100%		ends/inch picks/inch		Type of weave
			W	F	W	F	
4002/178 cm	Rapier	5220	24	24	75	68	Plain $^1/_1$

Table.10 Properties of the yarns grey, sized and the efficiency of weaving mill

Article	Type	The analysis properties						Efficiency (%)
		add on	Abrasion resistance	+Δ%	E. (%)	T. St. (kg)	Hum %	
4002/178 cm	Grey	-	57	+ 208%	3.08%	460	2.9	94%
	Size	14.5	176		3.12%	662	4.1	

Condition used Recipe [6% oxidize starch+ 6% AA], [APS], 0.25% (OWS); Temp, 95 □C; time, 30 min; speed of loom, 400 picks/min

The application of the trials in sizing department by using the oxidize tapioca starch - AA Composite and determine the analysis properties of the yarns grey, sized and the efficiency of weaving mill (Table 9 & 10).

It was observed from the above tables 9 & 10 that the sizing recipe is well when it was used in large and industrial scale. Moreover the data shows improved in abrasion for sized yarns when it compared with grey yarns.

The oxidation of tapioca starch dependence on the extent of oxidation, expressed as m.eq of COOH/ 100g tapioca starch, reaction time and temperature and concentration of APS. The obtained results show that the apparent viscosity decreases significantly by increasing the amount of APS. This is observed irrespective of the reaction temperature. Tapioca starch – acrylic acid composite carried out under the following conditions: [APS], 2.28% (ows); Temp, 95°C; time, 30 min at different concentrations of AA. The effect of acrylic acid (AA) concentration on the extent of starch modification, expressed as carboxyl content and add-on percent. Obviously, the extent of starch modification is greater upon using higher concentrations of acrylic acid. The physical properties of yarns (abrasion resistance, tensile strength, and elongation at break) sized with composite formed from tapioca oxidized starch reacted with acrylic monomer and poly vinyl alcohol, it was observed that the physical properties of sized yarns by acrylic acid –starch composite better (recipe 1) than in case sizing by PVA- starch composite (recipe 2) as shown in table 7. It also observed that by increasing size concentration (solid content) the physical properties of sized yarns decrease regardless type of the size materials, i.e. physical properties of sized yarns were improved in case of recipe 1 &3 compared with that of recipe 2 &4 respectively as shown in table 8. This due to the penetration of size material in case less solid content more than in case high solid content and in this time the viscosity decrease.

References

Agboola, S.O., Akingbala, J.O., Oguntimein, G.B. 1991. Production of low substituted cassava starch acetates and citrates. *Starch / Starke,* 43: 13–15.

Ali, S.Z., Kempf, W. On the degradation of potato starch during acid modification and hypochlorite oxidation. *Starch / Starke,* 38: 83–86.

Chaudhari, M.R., Kamath, N.D., Bhide, S.V., Kale, N.R. 1989. Preparation of crosslinked starch beads as a medium for gel filtration. *Starch / Starke,* 41: 415–416.

Conway, H.F., Sohns, V.E. 1975. Starch-encased powdered rubber: Pilot-plant production. *J. Elast. Plast.,* 7: 365.

Dekking, H.G.G. 1969. Preparation and properties of some polyrner—clay compounds. U.S. Patent, 3, 455, 853.

El-Rafie, M.H., Zahran, M.K., El-Tahlawy, Kh.F., Hebeish, A.A. 1995. Polymer & polymer stability. *Starch / Starke,* 47: 73–85.

El-Sheikh, M.A., Ramadan, M.A., El-Shafie, A 2010. Photo oxidation of rice starch II: Using a water soluble photo initiator. *Carbohydr. Polymers,* 78(2): 235–239.

Forrest, B. 1992. Identification and quantitation of hydroxypropylation of starch by FTIR. *Starch / Starke,* 44: 179–183.

Hebeish, A., El-Rafie, M.H., Higazy, A., Ramadan, M. 1996. Synthesis, characterization and properties of polyacrylamide-starch composites. Starch-Stärke, 48(5): 175–179.

Hebeish, A., El-Rafie, M.H., Higazy, A., Ramadan, M.A. 1992. Poly (acrylic acid)-starch composites. A key for improving sizeability and desizeability of starch from cotton textiles. *Starch / Stärke,* 44(3): 101–107.

Hebeish, A., El-Rafie, M.H., Higazy, A., Ramadan, M.A. 1996. Synthesis, characterization and properties of polyacrylamide-starch composites. *Starch / Stärke,* 48(5): 175–179.

Hebeish, A.A., Aly, A.S., Darag, E., El-Rafie, M.H., *Egypt. J. Text. Polym. Sci. Technol.,* 12, No. 1, pp. 77-99(2008)

Hebeish, A.A., Zahran, M.K., El-Rafie, M.H., El-Tahlawy, Kh.F. Polymer & polymer composites. *Starch / Starke,* 4: 129–141.

Hellwlg, G., Bishoff, D., Rubo, A. 1992. Production of cationic starch ethers using an improved dry process. *Starch / Starke,* 44: 6974.

Hellwlg, G., Bishoff, D., Rubo, A. 1992. *Starch / Starke,* 44: 69–74.

Jarowenko, W. 1987. In modified starches: properties and uses. O.B.Wurzburg (Ed.), CRC Boca Raton, Fla. Pp. 55–77.

Kulicke, W.-M., Aggour, Y.A., Elsabee, M.Z. 1990. Behaviour of starch-sodium trimetaphosphate hydrogels. *Starch /Starke,* 42: 134–141.

Maroza, K., Tomasik, P. 1991. *Starch / Starke,* 43: 66–69.

Maroza, K., Tomasik, P. *Starch / Starke,* 43: 66–69.

Muhrbeck, P., Svensoon, E., Eliasson, A.C. 1991. Effect of the degree of phosphorylation on the crystallinity of native potato starch. *Starch / Starke,* 43: 466–468.

Muhrbeck, P., Tellier, C. 1991. Determination of the phosphorylation of starch from native potato varieties by 3'P NMR. *Starch /Starke,* 43: 25.

Muhrbeck, P., Tellier, C. 1991. Determination of the phosphorylation of starch from native potato varieties by 3'P NMR. *Starch / Starke,* 43: 25.

Nachergaele, W. 1989. *Starch / Starke,* 41: 27–31.