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Application of Multi-function thickener from Chitosan/ Starch blend in textile Pigment Printing

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Abstract : Multi-functional finishing of textiles using chitosan is gaining more and more interest contributes to its antimicrobial properties and enhancement of fabric colour strength. This paper aims to produce a multi-functional thickener via adding of chitosan to gelatinous starch that it act as antibacterial agent, binder, and improve the pigment printing properties of different fabrics. The used chitosan was extracted from Egyptian marine shrimp shell and characterized by IR,[1]H-NMRand X-ray powder diffraction. The blends were prepared by adding fixed ratios of Chitosan to all the gelatinized starch samples. Different fabrics (natural, blend and synthetic) were printed by screen printing technique. For the comparison another samples were printed using the traditional printing paste which contain commercial binder .Generally, the data showed that the printed samples using starch /chitosan blends either in a ratio of 5% or 6% achieved improvement in the colour strength and related colour parameters are higher than those printed using the traditional pigment printing paste with good to excellent fastness properties.
Keywords: pigment printing, multifunctional thickener , chitosan /starch blend.

Introduction

Pigment printing on textile has grown all over the world due its numerous advantages[(1-6)]. The main constituents of the pigment printing paste are binder, thickener and the used pigment. The used binders are polymers based on styrene-butadiene, styrene-acrylate orvinyl acetate-acrylate copolymers. Binder must be used to bound physically the pigment to the fabric by forming adhesive film as pigments have little or no chemical affinity to the fibers. Both mechanical and fastness properties (washing and perspiration) of pigment prints depend on the formed film. The development of new polymers using natural materials has become an area of great interest, mainly due to producing environmental friendly materials that could replace, totally or partially, the currently used ones[(6-9)].Chitosan (biopolymer) is extracted from by-product (crab shell)[(10-13)]and has numerous applications in textile industries[(14-17)]. Recently, there was an attempt to used Chitosan as a binder and thickener for the pigment printing of both polyester and polyester/cotton blends [(18)]. The results showed that the pigment printing with chitosan printing paste gave prints of satisfactory colour fastness but the noticeably problem were the poor colour value and the stiffness of the printed fabrics. Many studies about the preparation and identification of starch -chitosan films as green composite have been published in food preservation and packaging technology[(19-21)]but fewer in their application in textile. This work exam the using of chitosan –starch

composite as multifunction thickener in textile printing that could overcome the disadvantages of the only using of chitosan.

Experimental

Materials: Soluble starch obtained fromFluka Chemical Company, alcoprint (synthetic thicknere), commercial binder.

Fabrics: Cotton: Mill desized, bleached and mercerized cotton fabrics (130 g/m^2) produced by Misr/ Helwan for Spinning and Weaving Company, Egypt.

- Nylon: Nylon-6 fabric produced by El-Shourbagy Co.Cairo, Egypt.
- Polyester: Polyester (PE) knitted fabric of 150g/m2, supplied by a private sector company which was treated with a solution containing 1g/l non-ionic detergent at 70 ^{o}C for 1/2 h., thoroughly washed, and air dried at room temperature.
- Blend fabrics: different kinds of blended fabrics comprise Viscose/ Polyester (80/20) and Cotton / Polyester (60/40) were also used.

Methods

Preparation of the thickener(Chitosan /Starch blend)

The extracted chitosan was mixed with different percent of gelatinous starch to form the required thickener.

Characterization of Chitosan blends with starch

The extracted Chitosan from marine shrimp shells and its blends with starch were characterized using Fourier Transform Infrared (FTIR) Spectroscopy, X-ray powder diffraction and thermal gravimetric analysis .

Preparation of printing pastes

The printing pastes were prepared as the formulation state in Table 1. Ammonia, urea, diammonium phosphate and binder were mixed with water then the synthetic thickener PTP was introduced and the paste was stirred using a high shear mixer for 10 minutes to allow full viscosity to develop. The pigment was then added to the mixture with stirring using a high shear mixer for 15 minutes. Prints were dried at room temperature, and then fixed at 160^{o}C. for 4 min in an automatic thermostatic oven (Wemer Mathis Co., Switzerland). The printed fabrics were washed and rinsed thoroughly with cold water, before being treated with hot water to remove the residual unfixed dye.

Preparation of starch-chitosan blends printing paste

Different printing pastes using the new prepared thickener (kitosan/starch) were prepared according to the recipe given in Table2.

Printing procedure

The printing pastes either using (chitosan/starch blend or alcoprint) were applied to the fabric using screen printing technique. The printed fabric samples were fixed by thermo fixation for 3 min at 160◦C.

Washing**:** the fixed printed goods were subjected to washing to remove the unfixed colour through five stages as follows. Rinsing thoroughly with cold water, Treatment with hot water, Treatment nears boiling temperate with a solution containing 2g/l aspkon 1030, Washing with hot water, Rinsing with cold water. At the end, the samples were dried and assessed for colour strength (K/S)and related parameters.

Measurement

Rheological properties

Rheological properties of blends were studied using Brookfield Digital Rheometer, model HA DVIII Ultra (Brookfield Engineering Laboratories INC.), with spindle No. SC4-21.

Determination of colour strength and related parameters

The colour strength of the printed samples was evaluated by Hunter Lab Ultrascan PRO.at λ_{max} .The colour difference and relative colour strength % between the control samples and the examined one chitosan were calculated by using the following relationships.

$$\text{Relative colour strength \%} = \frac{\text{K/S of chitosan /starch blend}}{\text{K/S of control sample}} \times 100$$

$\Delta E = \sqrt{(\Delta L)2+(\Delta a)^2+(\Delta b)^2}$ where $\Delta L = L \_ L^*.; \Delta a = a \_ a^*.; \Delta b = b \_ b^*.$

ΔE= total colour difference, 'L' describes lightness; 'a' measures redness or greenness and 'b' measures yellowness or blueness.L^* , a^* and $b^*$are colour parameter of control sample.

Determination of fastness properties and roughness

The treated samples were washed as per the conditions specified in the test AATCC test method [22].The color fastness to rubbing, perspiration and light were determined according to the AATCC test methods [(23-25)]. The surface roughness of printed fabric was measured by using surface roughness instrument SE 1700α.

Antibacterial activity

The Antibacterial activity was assayed in the Micro Analytical Centre of Cairo University using Kirby-bauer disc diffusion method [26].

Results and discussion

Fourier Transform Infrared Spectrometry

The starch /chitosan interaction is characterized using FTIR spectra where, Figure 1 represent the IR spectra of chitosan where, the peak at 3435.7 cm^{-1} is the OH stretching, which overlaps the NH stretching in the same region. The peak at 2923.3 cm-1 represents C-H stretch. C=O appears at 1633 cm-1.spectrum for starch (Figure 2),OH groups are represented by a broad band around 3400 cm^{-1}. In Figure 3, The FTIR spectrum chitosan / starch shows a broad band around 3650-3200 cm^{-1}, indicating enhanced hydrogen bonding compared to that of chitosan or starch alone, the NH_2 peak of chitosan shifted from 1650 to 1672 cm-1. This attributed to interaction between the hydroxyl group of starch and the amino group of chitosan [27]

X- Ray Diffraction:

X-ray diffraction patterns of the obtained chitosan and its starch blend is shown in Figures (4, 5**)**. The chitosan blend film is formed all identifying crystalline peaks of chitosan have been disappeared given broad amorphous x-ray. This could be revealed to the formation of hydrogen connection between the OH group of starch which has been appeared by depolymerization of starch by gelatination and protonated NH_2 group of chitosan.

DSC-TGA analysis

The thermogravimetric of the two main component of prepared thickener chitosan and modified starch in Fig. 6. show that chitosan loss its weight in two stages the first at 64.83 ºC about 9.05 % while the dramatic loss was at 304 ºC as it loss 91.01 % of its weight whilst the modified starch decompose on three stages the maximum loss in weight 69.32% was in the second stage at 295.15 ºC. As for the four tested thickeners they are all decompose in two stages but the mainly loss in weight percent was in the second stage at temperature near 290ºC but with different percent. For the first blend with ratio 3% of starch it loss 51% of its weight at 290.44 while for the 4,5,6 % starch the loss was 68.68,60.26,69.06 % at 289.34,291.75 and 292.74 ºC respectively.

Rheological Properties

Figure 7, 8 show the Rheograms of different concentrations of starch / chitosan thickener. The investigation blend pastes are non-Newtonian pseudoplastic behavior.

color strength and related parameters

Table 3 shows the K/S values and relative color strength for all the pigment printed fabrics using the traditional and examined thickener pigment paste. The values show that although the chitosan ratio is fixed in all the chitosan starch blends but the results are differ depending on both (1-the nature of fiber used and (2- the starch percent in the thickener. The film is formed by intermolecular hydrogen bond between the NH_3^+ of the chitosan backbone and OH^- of starch. Gelatinous starch has disorder crystalline structure which leaves the OH^- group exposed to link with the $NH_3^+$of chitosan. The increasing in the starch percent increases the OH^-groups which could react with NH_3^+ of chitosan . For instant the thickener formed from 3% starch has lowest K/S and negative relative K/S values than the control sample in all the pigment printed samples. By increasing the starch percent (4%) in the prepared thickener the K/S and relative K/S values has increased than the control sample by 12.11and 18.4 respectively for the polyamide pigment printed sample only this could be attributed to the nature of the polyamide as its light weight than the other fabrics used. Further increase in the starch ratio to5 and 6 % in the blend samples give highest K/S in all the pigment printed samples. The increasing in the K/S varies depending on the nature of fiber wher, the polyamide pigment printed samples posses highest K/S by 79.9% while for the blend fibers (viscose/polyester, cotton/polyester)were 41.9 and 59.5respectively.

These results illustrate that the most successful chitosan/starch blend were 5% and 6 % starch this may be due to the nature of the fabrics and the thickener viscosity. It can be seen from Table 4 that the L values decrease in all the printed samples indicating that the sample becomes darker compared to that of the control sample. This is confirm by color difference (ΔE) values it can be clearly seen that there is a colour difference between the samples and the control samples though the dye concentration is constant.

Determination of fastness properties

Table 5 shows the roughness and overall fastness properties of printed fabrics using Starch/ Chitosan blends with 5% and/or 6% starch as well as the commercial binder. The data listed in Table 5 shows that the roughness and overall properties depend on the type of fabric. The rubbing, washing and perspiration fastness ranged from good to excellent in the case of prepared blends, while it ranged from poor to good in the case of commercial binder. In addition, roughness results show soft handle for all samples, except in commercial binder where the handle is harsh.

Antimicrobial activity of treated fabrics

Table 6 represents the antibacterial activity of 100% cotton printed fabrics using kitosan /starch blend at 6% starch concentration. The sample showed inhibition zones that reveal the antibacterial activity. Generally, recent data in literature describe the mechanism between chitosan and microbial cell as the interaction between positively charged chitosan molecules and negatively charged microbial cell membranes[28]. The result confirms that the cotton printed fabrics using chitosan-starch blend exhibit antimicrobial characteristics.

Conclusion

The chitosan starch blends has been successfully formed and applied in textile pigment printing. Chitosan was extracted from Egyptian marine shrimp shell and characterized by IR, ^{1}H-NMRand X-ray powder diffraction. Its blends were prepared by adding fixed ratios of Chitosan to different gelatinized starch samples. the prints using starch /chitosan blends in a ratio of 5% or 6% achieved improvement in the colour strength and related colour parameters with good to excellent fastness properties. roughness results show soft handle for all samples, except in commercial binder where the handle is harsh.

Acknowledgement

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Table 1: recipe of The printing paste

Pigment	40 **g**
Urea	25 g
alcoprint Thickener	25 g
Binder	50 g
Sodium dihydrogen phosphate	50 g
Water	X g
	1000 g

Table 2*:* recipe of The printing paste *using Chitosan/starch blends*

Chitosan -starch blends	50
Urea	25
Pigment (Green 3GL)	40
Water	Y
Total	1000g

Table 3: the K/S and relative colour strength % of printed samples

Kind of fabric used:										Thickener Used
Cotton		**Cotton /Polyester**		**Polyester**		**Viscose/Polyester**		**Polyamide**		
%K/S	**K/S**	**%K/S**	**K/S**	**%K/S**	**K/S**	**%K/S**	**K/S**	**%K/S**	**K/S**	
100	12.58	100	7.83	100	8.15	100	10.05	100	10.23	Alcoprint PTP
-7.7	11.68	-4.5	7.47	-42.2	4.71	-30	7.04	-4.1	9.81	3%Starch/ Chitosan
-1.9	12.33	-3.6	7.55	-39.1	4.96	-7.3	9.32	18.4	12.11	4% Starch/ Chitosan
6.4	13.39	33.1	10.42	16.3	9.48	41.9	14.26	79.9	18.4	5% Starch/ Chitosan
10.8	13.94	59.5	12.49	44.4	11.77	40.3	14.1	76.1	18.01	6% Starch/ Chitosan

Table 4:colour parameters and the colour difference of the highest K/S printed Fabrics

ΔE	ΔL	Δb	Δa	L*	b*	a*	L	B	A	Printed Sample
13.90	-10.89	-4.87	7.14	47.72	25.90	-42.36	36.83	21.03	-35.22	Cotton
7.79	-3.82	4.71	-4.89	41.9	16.79	-30.38	38.08	21.5	-35.27	Cotton /Polyester
5.88	-5.64	-0.75	1.49	46.12	25.24	-38.73	40.48	24.49	-37.24	Polyester
3.90	-3.71	1.12	0.47	40.36	19.06	-33.81	36.65	20.18	-33.34	Viscose/ Polyester
7.70	-5.4	4.64	-2.94	36.82	16.12	-29.14	31.42	20.76	-32.08	Polyamide

Table 5: Roughness and overall fastness properties of printed fabrics using prepared Starch/ Chitosan and commercial binders.

Printing paste	Rubbing fastness		Washing fastness		Perspiration fastness					Roughness
					Acid		Alkaline			
	Dry	Wet	Alt.	St.	Alt.	St.	Alt	St.		
Cotton fabric (100%)										
Commercial paste	3-4	2	2	2-3	2-3	2	2	2	6-7	16.26
5% Starch/ Chitosan	3	3	4-5	4-5	4-5	4-5	4-5	4-5	6	12.63
Cotton/polyester blend fabric (35/65)										
Commercial paste	2-3	3	4	4	2	2	2-3	2-3	6-7	21.28
6% Starch/ Chitosan	3-4	3	4-5	4-5	4-5	4-5	4-5	4-5	6-7	15.77
Viscose/Polyester (80/20).										
Commercial paste	3	3 – 4	4-5	4-5	4-5	4-5	4-5	4-5	7	15.8
5% Starch/ Chitosan	3-4	3	4-5	4-5	4-5	4-5	4-5	4-5	6-7	10.33
Polyester										
Commercial paste	3	3 – 4	4-5	4-5	4-5	4-5	4-5	4-5	7	22.4
6% Starch/ Chitosan	3-4	3	4-5	4-5	4-5	4-5	4-5	4-5	6-7	16.7
Polyamide										
Commercial paste	3	3 – 4	4-5	4-5	4-5	4-5	4-5	4-5		13.77
6% Starch/ Chitosan	3-4	3	4-5	4-5	4-5	4-5	4-5	4-5		9.87

Table6 : antibacterial activity of 100% cotton printed fabrics

Sample	Inhibition zone diameter (mm/mg sample)			
	Bacillus *Subtilis* *(G+)*	**Esherichia Coli *(G-)***	**Staphylococcus Aureus *(G+)***	**Pseudomonea Aeuruginous *(G-)***
Control	22	22	23	22
Cotton	23	22	24	23

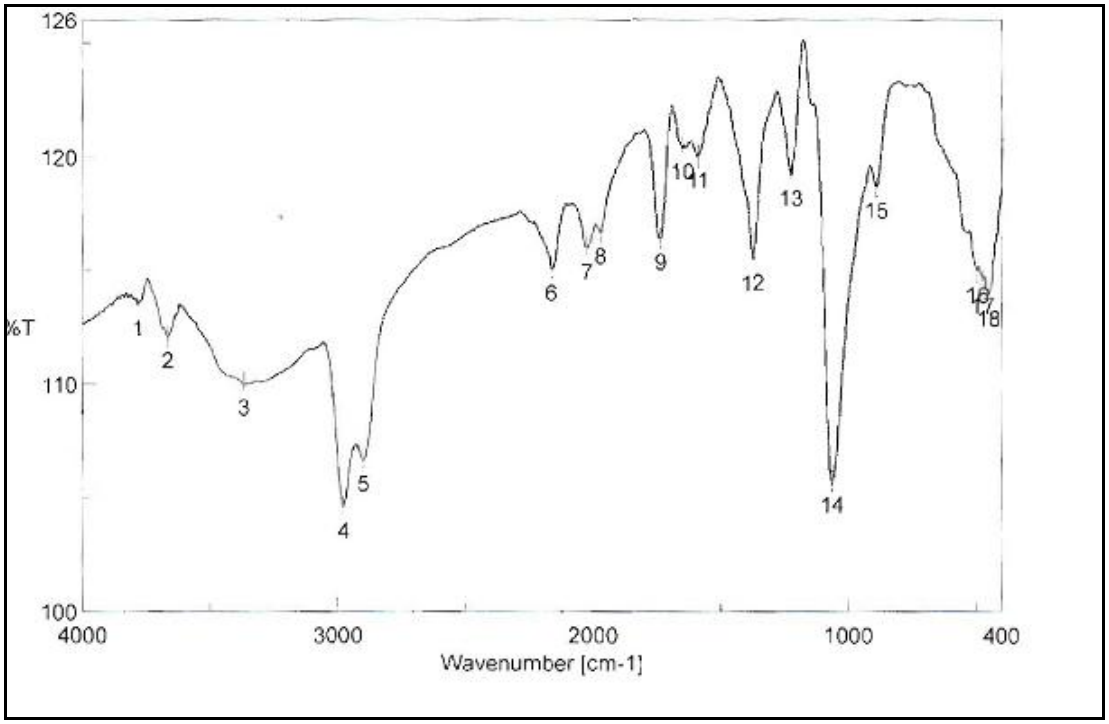

Figure (1) FTIR spectra of chitosan

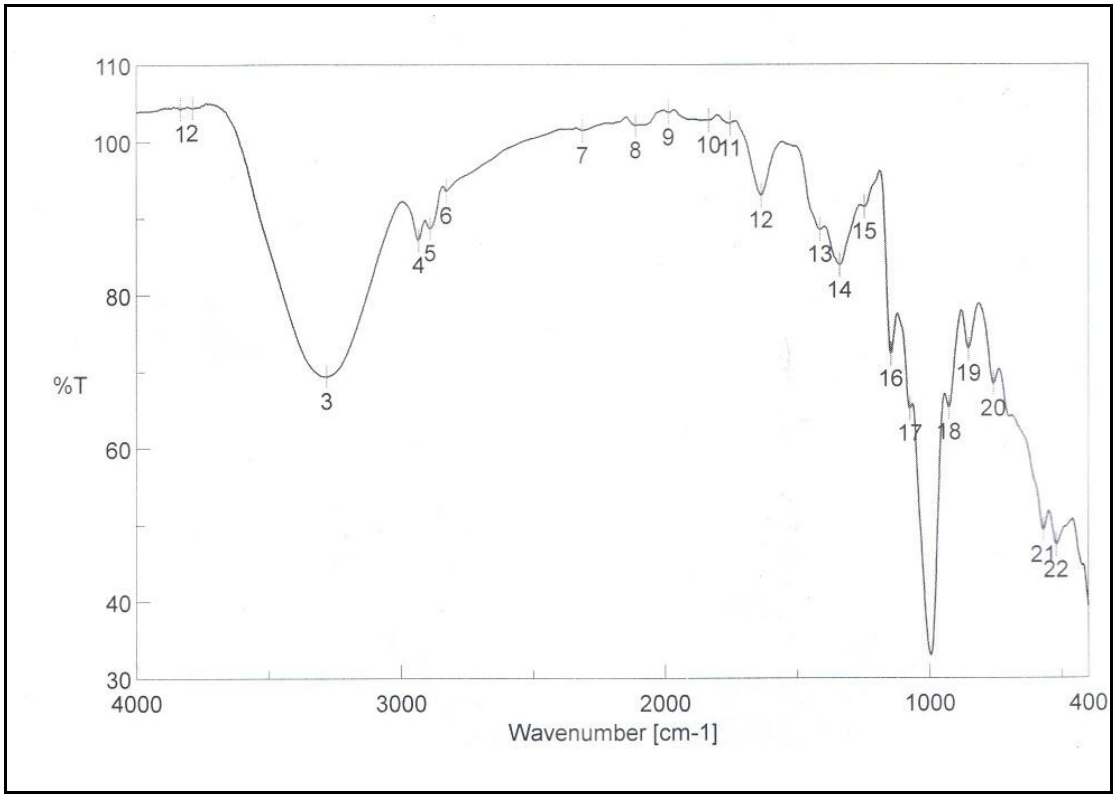

Figure (2) FTIR spectra of starch

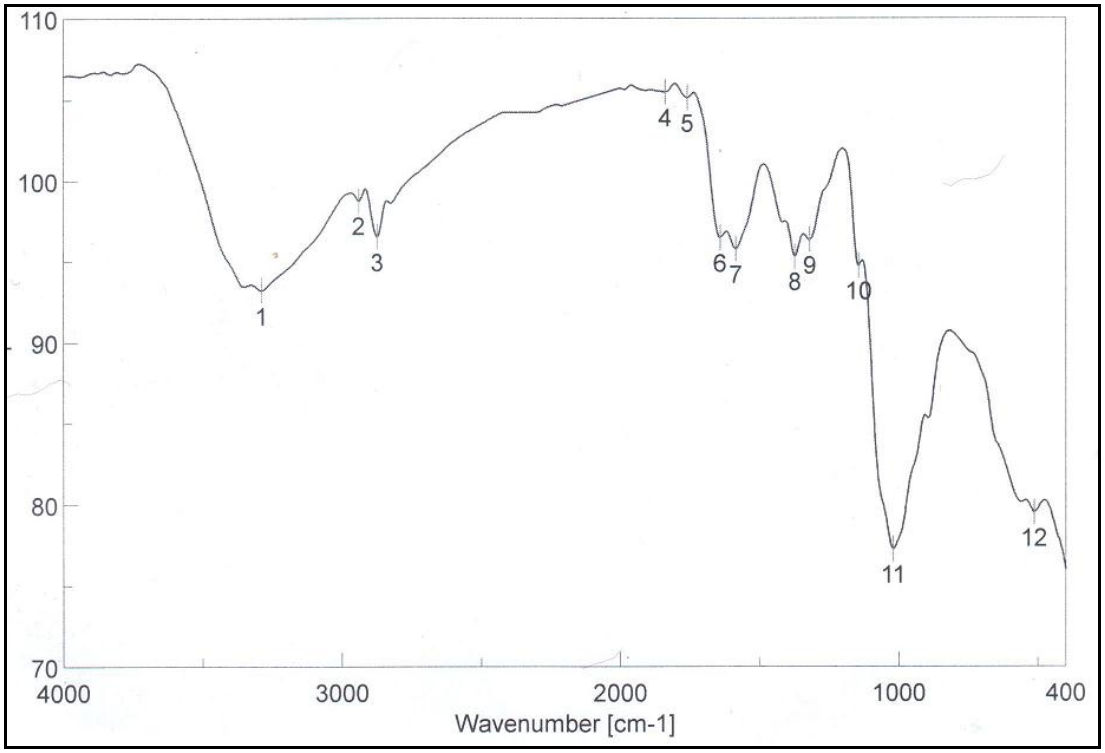

Figure (3) FTIR spectra of Chitosan/starch blend

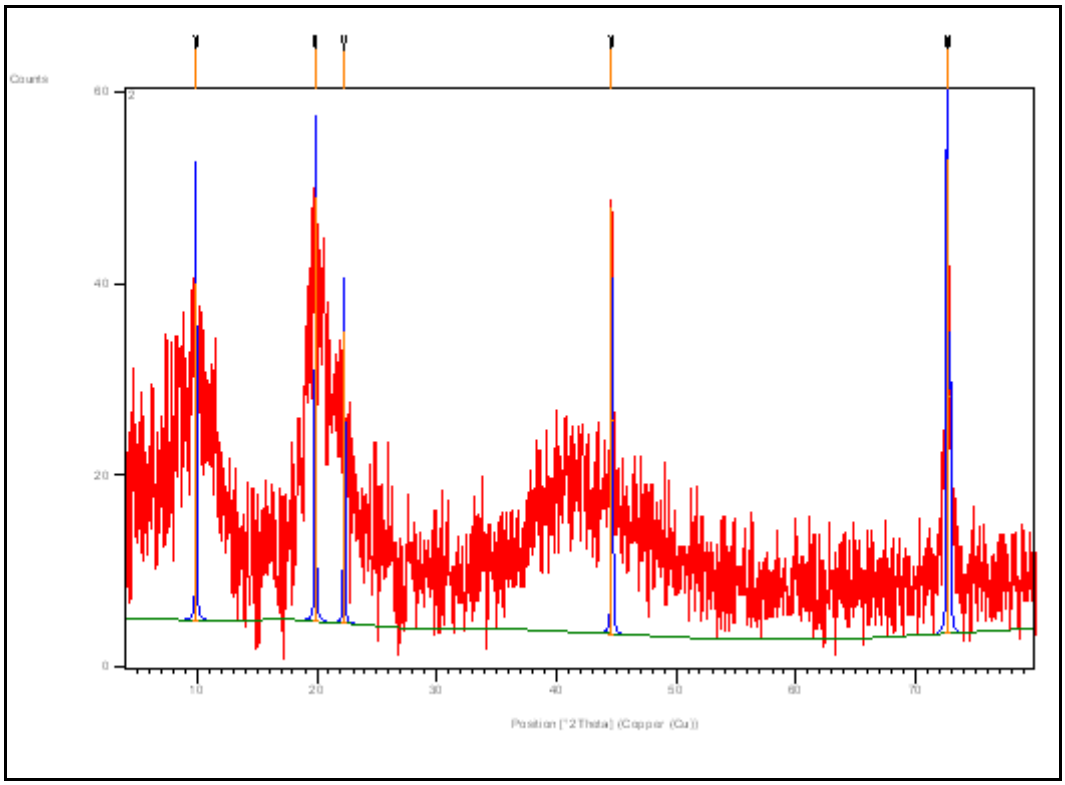

Fig.(4) X-ray diffraction of chitosan

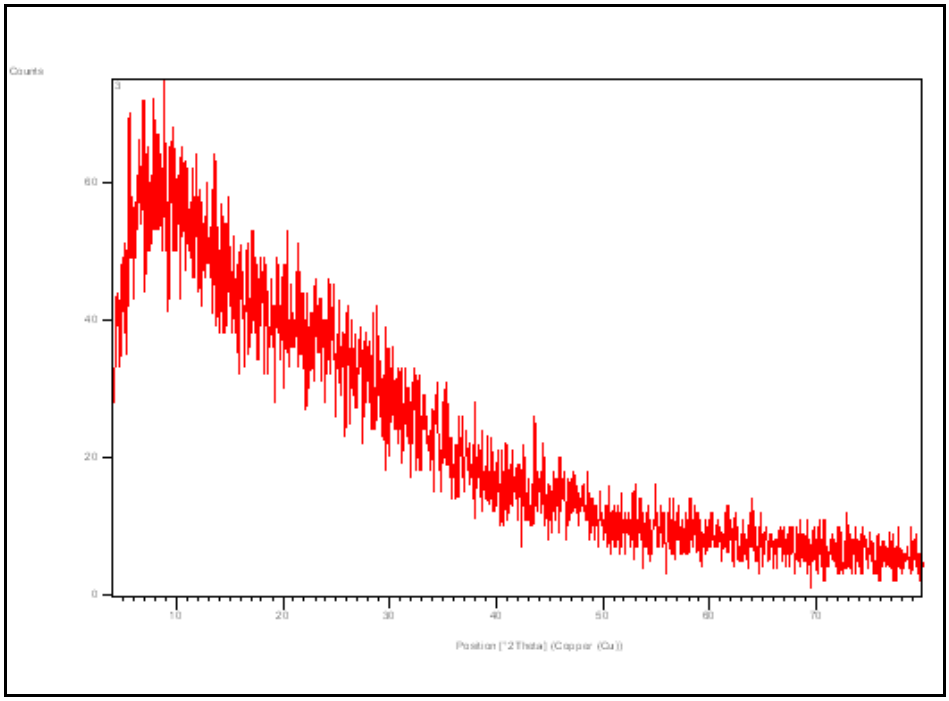

Fig. (5) X-ray diffraction of 3 % chitosan – starch blend

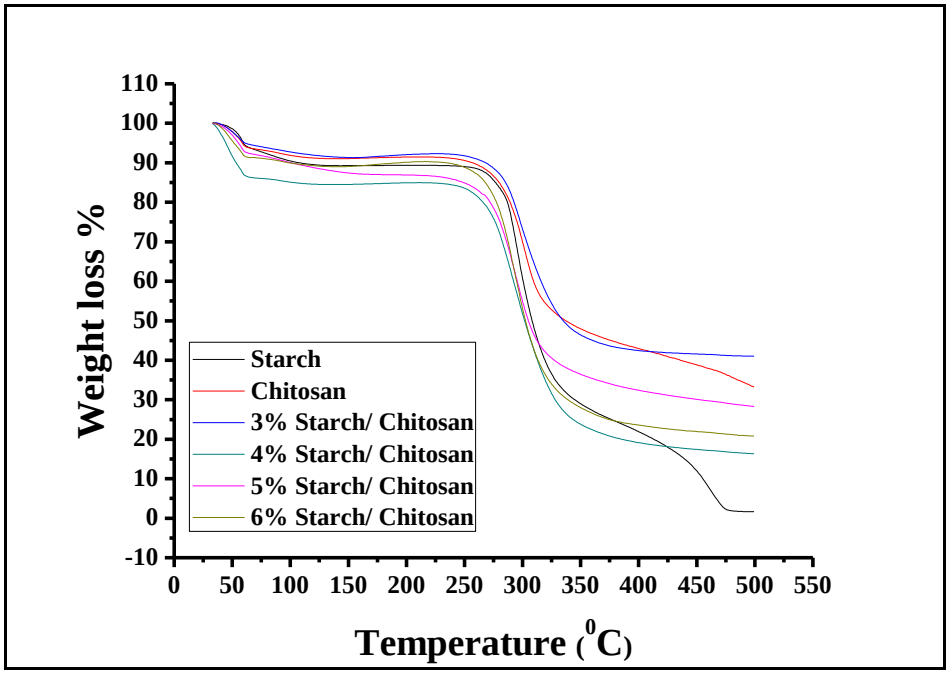

Fig. 6 The thermogravimetriccurvesof chitosan, starch, and chitosan/starch blends.

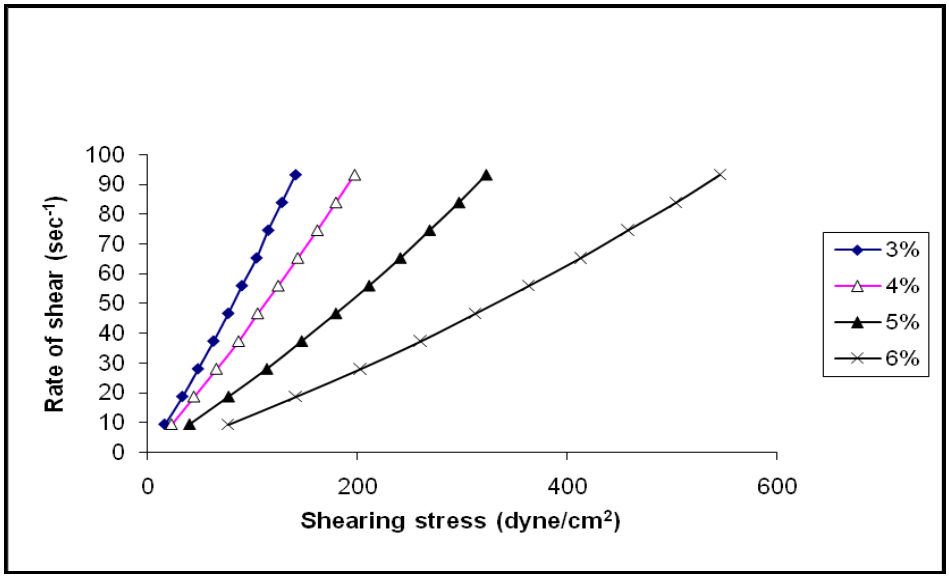

Figure 7: Rheograms of different concentrations of fresh preparedstarch / chitosan thickener

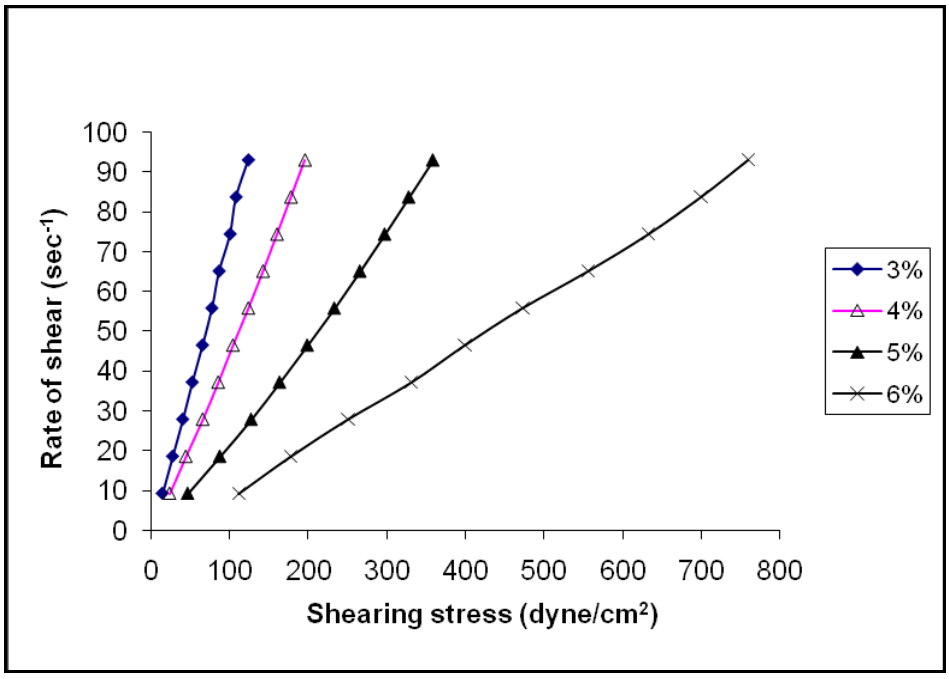

Figure 8 Rheograms of different concentrations starch / chitosan thickener after storing for 24 hours

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