

# Comparative Analysis of Desizability and Retrogradation Behavior of Various Sizing Materials

B. K. Behera, R. Gupta

Department of Textile Technology, Indian Institute of Technology, Delhi 110016, India

Received 28 June 2007; accepted 27 November 2007

DOI 10.1002/app.28184

Published online 15 April 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The advent of high-speed shuttleless looms has increased the importance of sizing. Starch has been the most popular and economic size material. Synthetic binders are also being blended with starch to improve weaving loom efficiency. Some synthetic size materials have restrictions in use mainly because of ecological reasons. In the recent years, many modifications have come up in the starch as a sizing agent. Different modifications can give different properties, which can suit to particular application. In this study, different varieties of natural starch, modified starch, and synthetic size materials are evaluated,

and properties like retrogradation and desizability were studied to investigate their potential for modern weaving conditions. Comparison is made between various materials and it is observed that paste characteristics and film properties of certain modified starches are better than the natural starch. The experiment was also designed to check the properties of blend constitution. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1076–1082, 2008

**Key words:** desizability; modified starch; moisture regain; natural starch; retrogradation; synthetic size; viscosity

## INTRODUCTION

Desizing is the process of removing the size material from the warp yarns in woven fabrics. The nature of this process depends upon the type of size applied. Water soluble size may simply be washed out, whereas water insoluble size must first be subjected to chemical or enzymatic degradation. This prevents size recovery and therefore a large burden is placed on waste water streams.<sup>1</sup> Insufficient, nonuniform removal of size, which protects the warp during weaving, produces a fabric with a hard papery handle, or causes stains compromising its appearance and subsequent use.<sup>2</sup> Easy desizability is one of the greatest requirements of sizing agent. Higher the water solubility of sizing agents, lesser will be the energy consumption. This leads to more economic process. Highly efficient desizing process leads to lower energy consumption.<sup>3–5</sup> Efficient desizing also helps in the smooth running of further processes like bleaching, dyeing, finishing, etc. Desizability of sizing agents depends on factors like viscosity of size paste, moisture regain of size film, and solubility of size film in water. All these factors are directly or indirectly dependent on the chemical structure of the size material. The starch paste remains fluid as long as it is stirred and kept hot.<sup>6</sup> However, if the solution becomes concentrated by evaporation of water, and/or

by cooling the solution, an irreversible gel is formed, which will not redisperse, no matter how long it is heated or stirred. Retrogradation is the process in which the viscosity is gradually increased again when the solution is chilled down, and continuous chilling makes the solution cloudy and less clear.<sup>7,8</sup> Leaving the solution to stand, it shows more whiteness; in the case of higher concentration of starch, it gels, and in the case of low concentration, syneresis and precipitation will be caused. This behavior depends on the molecular structure of the size material.<sup>9–11</sup> In the case of starch, the linear amylose molecules align themselves, and through hydrogen bonding, form three-dimensional arrays that are difficult to break apart. This peculiarity in starch is the reason that specific processing conditions are needed to economically remove it during desizing. Whereas modified starch shows lower retrogradation of paste because modification process causes depolymerization of structure leading to lower retrogradation. For sizing process the size material with lower retrogradation behavior is preferred.<sup>12–14</sup> In this study, different varieties of natural starch, modified starch, and synthetic size materials are evaluated and properties like retrogradation and desizability were studied to investigate their potential for modern weaving conditions.

## EXPERIMENTAL

### Materials

For experimental purpose, natural and modified starches, synthetic size materials, and their blends

Correspondence to: B. K. Behera (behera@textile.iitd.ernet.in).

**TABLE I**  
**Different Constitution Size Materials**

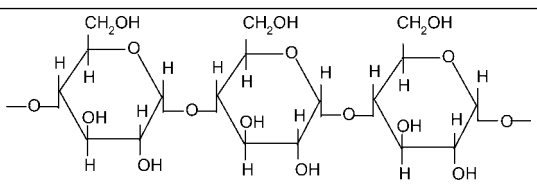
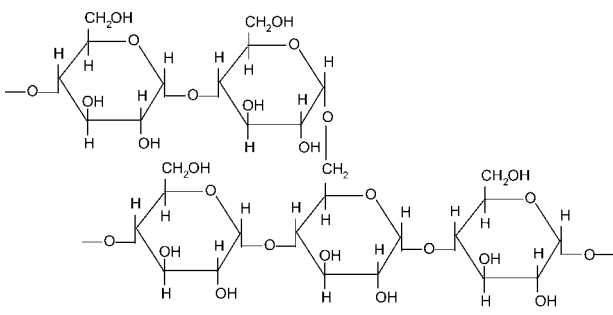
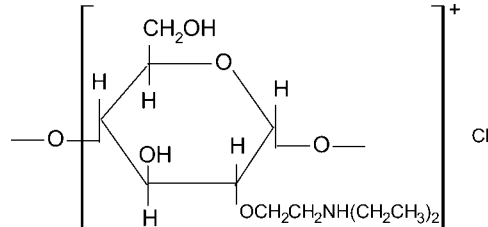
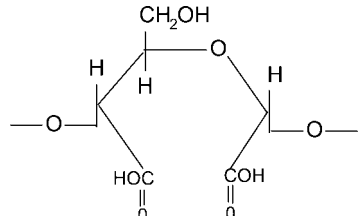
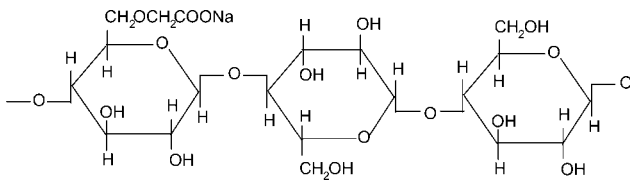
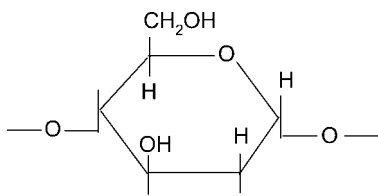
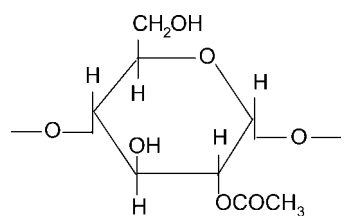
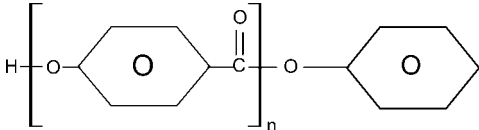
Sample	Type	Chemical structure
S1	Unmodified starch	 <p>Amylose</p>  <p>Amylopectin</p>
S2	Acid modified starch	
S3	Oxidized starch	
S4	Carboxymethyl cellulose	
S5	Hydroxy ethyl starch	
S6	Starch ester	

TABLE I Continued

Sample	Type	Chemical structure
S7	Polyvinyl alcohol (polysizer)	$\text{--- CH}_2\text{--- CH --- CH}_2\text{--- CH --- CH}_2\text{--- CH ---}$ $\begin{array}{c}   \quad   \quad   \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$
S8	Acrylic polymer emulsion 25 %	$\left[ \text{CH}_2\text{--- CH} \right]_n$ $\begin{array}{c}   \\ \text{CONH}_2 \end{array}$
S9	Polyester resin 30 %	

were used. The objective to use different material is to analyze the effect of chemical structure on the properties of corresponding material. The materials used are shown in the Tables I and II.

## Methods

### Preparation of size mix

Required quantity of size material listed in the tables is mixed with water to prepare 5% size slurry. Initially, the mixture was stirred for about 10 min when it is cool, then cooked at about 100°C temperatures for about 45 min for complete cooking of the size slurry. In case of synthetic sizes, these materials are cooked for 25–30 min, and in case of blends, synthetic components were added after half cooking of the starch. In the case of size with lubricants, the lubricant is added to cooked size slurry just 5 min before transfer of the size slurry to sow box.

### Preparation of size film

Size film is prepared using a flat surface over which acrylic plate is placed. The cooked size mix is spread over the acrylic plate. Now the doctor knife is used

TABLE II  
Different Blends Size Materials

Sample	Type
B1	S6 + PVA (75 : 25)
B2	S2 + PVA (75 : 25)
B3	S6 + Acrylic (75 : 25)
B4	S2 + Acrylic (75 : 25)
B5	S6 + PR (75 : 25)
B6	S2 + PR (75 : 25)

to even out the surface of size film. The film so formed is allowed to get dried in atmospheric conditions. The dried film is the required film for testing.

### Testing of moisture regain of size film

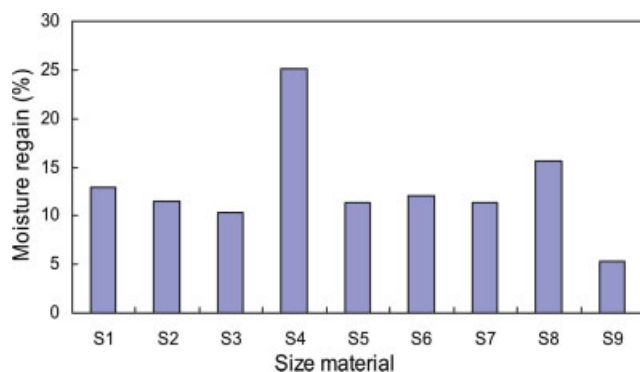
Different size films were kept in desiccators with P<sub>2</sub>O<sub>5</sub> for 24 h at 0% RH. After weighting, films were conditioned in desiccators with 65% RH. The oven dry weight of the film was measured. Moisture regain of film was calculated by the following formula:

$$\text{Moisture regain(\%)} = \frac{W - D}{D} \times 100$$

where *W* is the weight of size film at 65% RH and *D* is the oven dry weight of size film at 0% RH.

TABLE III  
Moisture Regain, Viscosity, and Solubility Results for Different Constitution Size Materials

Sample	Moisture regain (%)	Viscosity at 90°C (cSt)	Solubility in terms of time to break (s)
S1	12.86	410.06	6000.0
S2	11.54	117.46	166.7
S3	10.34	13.51	Film too brittle to handle
S4	25.12	—	20.0
S5	11.34	213.71	1157.9
S6	12.02	252.21	92.0
S7	11.32	21.21	Not broken, stretched up to base
S8	15.67	21.21	83.2
S9	5.32	17.36	Film too brittle to handle



**Figure 1** Moisture regain of size films with various compositions. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

#### Viscosity measurement of size paste

The viscosity of size paste so formed was measured using viscosity cup. Here, in this experiment, the cup so used is B4 viscosity cup. The size paste was filled in the viscosity cup and time to flow out the paste from the cup was noted. The time to flow was directly used to compare the viscosity of various size compositions. For getting the exact value of viscosity in terms of centistokes the conversion factor is used based on ASTM standards. Viscosity cSt =  $3.85(t - 4.49)$ .

#### Solubility test of size films

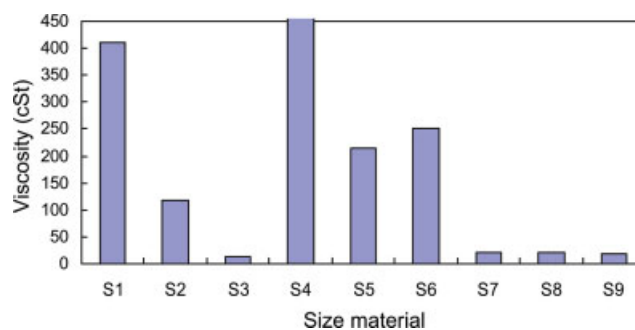
To test the solubility of various size films, the size films were cut in rectangular shape of 2 cm × 5 cm dimension. At one end of the films was attached a dead weight. Now these films with dead weight at one end were hanged in glass beakers with water at room temperature. The time to break the film in the beaker was noted and used to compare the solubility of various size compositions. The solubility of size films determines their desizability.

## RESULTS AND DISCUSSION

In Table III, the viscosity of size paste at 90°C, moisture regain, and solubility of size film are shown. These results can also be explained more clearly from the figures shown at the end.

#### Moisture regain of size film

Moisture regain plays a major role in determining the performance of sized yarn at the time of weaving. When size film absorbs moisture, it becomes pliable and the ability to sustain weaving stresses is increased. Figure 1 shows the moisture regain of various constituent size films. It is clear from the figure that carboxyl methyl cellulose (CMC) has highest moisture regain at 65% RH, which is due to more OH

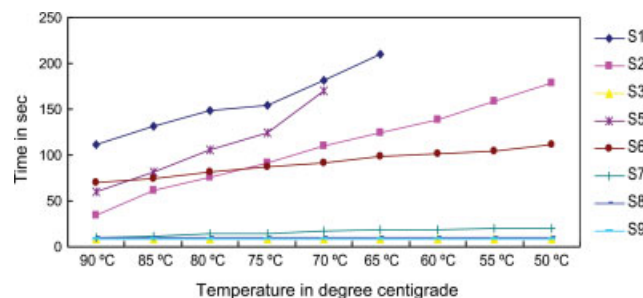


**Figure 2** Viscosity of size pastes with various compositions. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

group in the structure. Moreover, sodium carboxymethyl cellulose is a water-soluble cellulose based on wood. Next to CMC, acrylic polymer solution shows high moisture regain because of presence of amide group in the structure. Polyester resin shows least moisture regain because of the absence of hydroxyl group in structure. Modified starch shows lower moisture regain when compared with native starch, as a modification process causes removal or substitution of OH group in the structure.

#### Viscosity of size paste

Figure 2 shows the viscosity of various size materials. For sizing, less viscosity of the size paste is advantageous because less viscous paste will penetrate easily into the yarn and give a good cover with penetration which will not be removed easily during the abrasion of warp yarn on loom. Less viscosity also offers high concentration and so high add-on % is only possible with less-viscosity paste. So less viscous solution is preferable over the highly viscous paste. The viscosity of a material mainly depends on the degree of polymerization of the material. Higher degree of polymerization leads to higher molecular weight. From the above results it is clear that CMC has maximum molecular weight followed by natural starch and starch ester. Acid-modified starch and



**Figure 3** Retrogradation behavior of size pastes with various compositions. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE IV**  
Time to Flow of Size Paste in Viscosity Cup (in seconds)

Sample	90°C	85°C	80°C	75°C	70°C	65°C	60°C	55°C	50°C
S1	111	132	148	155	182	210	Fluid not flown completely		
S2	35	62	76	92	110	125	138	159	178
S3	8	8	8	8	8	8	8	8	8
S4	Fluid not flown completely								
S5	60	82	106	125	170	Fluid not flown completely			
S6	70	74	82	87	92	98	101	105	112
S7	10	12	14	15	17	19	19	20	20
S8	10	10	10	10	10	10	10	10	10
S9	9	9	9	9	9	9	9	9	9

oxidized starch have lower degree of polymerization leading to low viscosity of the paste. Oxidized starches have lower viscosity than the acid-modified starches, and oxidation causes depolymerization, which results in a lower viscosity. Natural starch shows higher viscosity because of the bulky structure of amylose and amylopectin. Other materials also have lower molecular weight which results in lower viscosity.

#### Solubility of size films

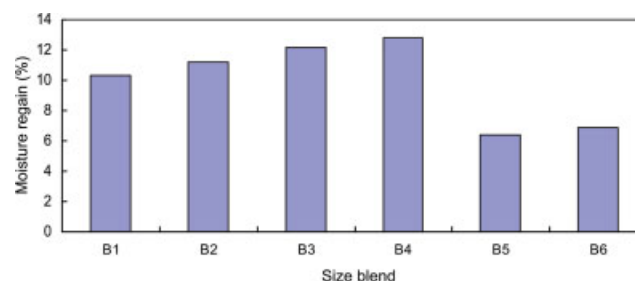
The solubility of size films mainly depends on the hygroscopic nature of material and also on the molecular weight of the material. From Table I it can be seen that CMC has maximum solubility in water because of the presence of hygroscopic group. Acrylic polymer has linear structure with amide group leading to high solubility of the film. Poly vinyl alcohol (PVA) molecule is linear along with the presence of OH group, which when dissolved in water becomes soft and extended and does not break. Natural starch is highly bulky leading to lower solubility of the structure. In the case of starch, the linear amylose molecules align themselves, and through hydrogen bonding, form three-dimensional arrays that are difficult to break apart. This peculiarity in starch is the reason for using specific processing conditions to economically remove it during desizing.

**TABLE V**  
Moisture Regain, Viscosity, and Solubility Results for Different Blends Size Materials

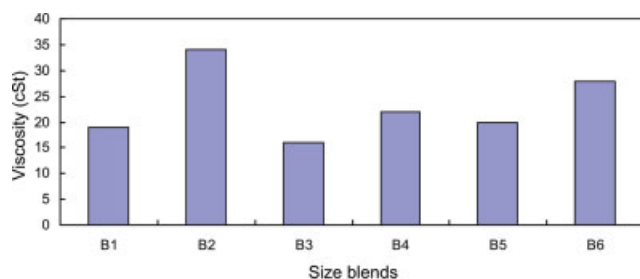
Sample	Moisture regain (%)	Viscosity at 90°C (cSt)	Solubility in terms of time to break (s)
B1	10.3	55.86	Film not broken
B2	11.2	113.61	Film not broken
B3	12.2	44.31	2600.0
B4	12.8	67.41	173.3
B5	6.40	59.71	Film too brittle to handle
B6	6.92	90.51	Film too brittle to handle

#### Retrogradation behavior of size paste

Retrogradation is the change in viscosity with change in temperature of the solution. The lower change is preferable from the sizing point of view, because as the size box is open, the atmospheric temperature will cause gel formation in the case of high change in viscosity at reducing temperature which in turn will affect the penetration and take up of size paste by the yarn passed for sizing. As penetration and take up affects the weaving performance of the yarn, comparison of retrogradation behavior of various size pastes is also important. The retrogradation behavior of various size materials is shown in Figure 3. The time to flow (in seconds) is shown in Table IV. In native starch, single helical amylose has hydrogen-bonding O and OH atoms on outside surface of the helix with only the ring oxygen pointing inwards. Hydrogen bonding between aligned chains causes retrogradation. The oxidation causes depolymerization, which results in a lower viscosity dispersion, and introduces carbonyl and carboxyl groups, which minimizes the retrogradation of amylose, thus giving viscosity stability of the oxidized starch. PVA, acrylic polymer, and polyester resin do not show any significant change in viscosity during cooling. This means that the natural starch is highly unstable, whereas modified starch has a stable viscosity over



**Figure 4** Moisture regain of size films with various blends. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 5** Viscosity of various size blends. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

the temperature range from 100 to 50°C. In the case of synthetic size material once it is dissolved in water the viscosity is almost constant and it will not change with change in temperature. Overall, all synthetic size materials show very slow change in their viscosity with reducing temperature compared with starch. At the same time, some modified starches also give better performance.

#### Properties of blends

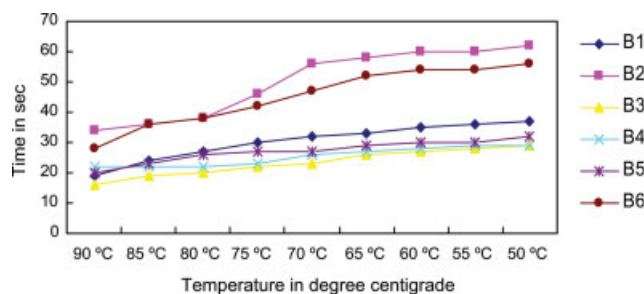
In Table V, the viscosity of size paste at 90°C, moisture regain, and solubility of size film for different blends are shown.

#### Moisture regain of size films

From Figure 4, from B1 to B4, it can be seen that the moisture regain of the size film of blends with acrylic polymer shows higher moisture regain because of higher moisture regain of acrylic polymer. Blend with polyester resin shows significantly lower values of moisture regain because of the presence of hydrophobic polyester resin molecules.

#### Viscosity of size paste

From the results in Figure 5, it is clear that the blend of acid-modified starch shows higher viscosity than starch ester blend with synthetic size materials. This can be explained that esterification is a severe treat-



**Figure 6** Retrogradation behavior of size pastes. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

ment leading to breaking of structure because of which starch ester has lower molecular weight.

#### Solubility of size films

The solubility of films of various blends shows that because of the presence of PVA, the film does not break and remains intact, but the film with acrylic polymer breaks down.

#### Retrogradation behavior of size paste

Table VI and Figure 6 shows the retrogradation behavior of different blends, from the figure it is analyzed that the blends show lower retrogradation behavior as compared to native starch. There is no significant difference between different blends except blends with PVA which shows comparatively higher retrogradation than other blends.

### CONCLUSIONS

The structure of the size material plays a major role in determining various properties of size material. The solubility is mainly influenced by the presence of hygroscopic group, whereas the viscosity depends on the molecular weight depending on degree of polymerization of the molecule. It is seen that modified starch shows significantly different results when compared with the native starch, as modification causes significant change in the structure. Blending leads to change in availability of the reactive group,

**TABLE VI**  
Time to Flow in Viscosity Cup (in seconds)

Sample	90°C	85°C	80°C	75°C	70°C	65°C	60°C	55°C	50°C
B1	19	24	27	30	32	33	35	36	37
B2	34	36	38	46	56	58	60	60	62
B3	16	19	20	22	23	26	27	28	29
B4	22	22	22	23	26	27	28	29	29
B5	20	23	26	27	27	29	30	30	32
B6	28	36	38	42	47	52	54	54	56

which causes the change in the properties of the blend so formed.

### References

1. Walters, A.; Santillo, D.; Johnston, P. Textiles processing and related environmental concerns, Greenpeace Research Laboratories, University of Exeter, UK, 2005.
2. [www.kotonline.com/english\\_pages/ana\\_basliklar/bozetto.asp](http://www.kotonline.com/english_pages/ana_basliklar/bozetto.asp)
3. <http://www.answers.com/topic/desizing>
4. Kerr, R. W. Chemistry and Industry of Starch; Academic Press: New York, 1950; p 571.
5. Behera, B. K. Presented at the Workshop on the Process Control in Sizing, NITRA-86, Sept. 26–27, 1986.
6. Whistler, R. L.; Paschall, E. F.; Bemiller, J. N. Starch—Chemistry and Technology, 2nd ed.; Academic Press: New York, 1984; p 153.
7. Redley, J. A. Starch and Its Derivatives, 4th ed.; Chapman and Hall Ltd.: London, 1968.
8. Garg, S. Ph.D Thesis, Department of Textile Technology, IIT-Delhi, India, 1988.
9. Abdel-Hafiz, S. A. Polym Degrad Stab 1995, 47, 275.
10. Modi, J. J. Text Ind 1983, 147, 58.
11. Behera, B. K. Ph.D. Thesis, Department of Textile Technology, IIT Delhi, India, 1989.
12. Mostafa, Kh. M. Polym Degrad Stab 1997, 55, 125.
13. Athar, T. Text Res J 1983, 53, 791.
14. Joshi, V. K. Ph.D. Thesis, Department of Textile Technology, IIT Delhi, India, 2003.