MODIFICATION AND CHARACTERIZATION OF STARCH AS AN ADHESIVE

Pradip V.Tekade, Bhagyashri U.Tale, Nakul Barwat, Sakshi Kawale, Harshada Chikhalkar, Manoranjan Patnaik

1Associate Professor, 2, 3 Assistant Professor, 4, 5 P.G.Students, 6 Dy. Director

1-5 Department of Chemistry, Bajaj College of Science (Previously known as Jankidevi Bajaj College of Science), Jamanalal Bajaj Marg, Civil lines, Wardha, Maharashtra, India

6 Chemical based industries division, Mahatma Gandhi Institute for Rural Industrialization (MGIRI), Wardha, Maharashtra, India

Abstract: Increasing demand of energy globally and scarcity of petroleum resources has shifted focus of chemical industries to look for alternative raw material resources. Bio-based adhesive are attracting more and more attention in various fields due to their improved environmental footprint and independence from petroleum resources. Though synthetic chemical based resins have better bonding properties, it shows some drawbacks, which are harmful to humans as well as environment. Starch is produced by plants as a way to store the chemical energy that they produce during photosynthesis. The main goal of this study was to use cornstarch and arrowroot starch in the production of environmentally sound adhesives. Arrowroot & corn starch are environmentally friendly products, they can be modified as adhesive. Starch is considered as an ideal material for manufacturing of wood-composite adhesives because of its low cost, high free hydroxyl content, easy processing and treatment.

I. INTRODUCTION AND LITERATURE SURVEY:

Adhesives play a fundamental role in many modern technologies and adhesive failure have catastrophic consequence. It is necessary to understand the factors responsible for the production of a good durable adhesive bond. Starch is produced from wheat, corn, sweet potato, rice etc. But the corn starch is having a good adhesive and film forming properties. Since starch is renewable, cheap, non-toxic, easily available, biodegradable and hence it has more demand in adhesive industry.

Pure starch powder has white colour with no taste and odour which is insoluble in cold water or alcohol. It is a polymeric carbohydrate, consists a large number of glucose units joined by glycosidic bonds. It consists of two types of molecules; the linear and helical amylose or the branched amylopectin. Depending on a source, starch contains 20 to 25% amylose and 75 to 80% amylopectin [1].

Starch derivatives are used in various industries as thickeners, gelling agents and encapsulating agents for papermaking, as wet-end additives for dry strength, surface sizes and binders, as adhesives (bag, bottle labeling, laminating, envelopes etc.), for warp sizing in textiles, and for glass fiber sizing [2]. Arrowroot becomes thick at a lower temperature than flour & not affected by acidic ingredients as well as freezing [3].

The most commonly available industrial starches are waxy cornstarch, regular corn starch, high-amylose corn starch type V, and high-amylose corn starch type VII, with amylose concentrations of 0, 28, 55, and 70% respectively [4].

Adhesives are substances that are able to make things adhere or stick together without deformation or failure through a process called adhesion. Renewable and biodegradable starch adhesives are topic of interest for research because of its environmental freindliness. Adhesives prepared from starch are most extensively used in corrugated board industry because of its abundant supply, low cost, renewability, biodegradability, and ease of chemical modifications [5].

Properties of good adhesives:

An adhesive is considered to be good if it is able to give complete bonding with good drying rate in presence of adequate heating [6-15]. To realize this, an adhesive needs to have following properties:

1. Appropriate viscosity
2. High initial tack
3. Solids in range of 20-33%
4. Consistency in batch glue properties
5. Fast setting
Experimental:

Materials

Arrowroot starch and corn starch in the powder form was obtained from M/s Deepak Handicrafts, Jaipur, Rajasthan, Sodium hydroxide from M/s Merck Specialties Private Limited, Mumbai commercial grade hydrochloric acid, borax and urea from M/s Maharashtra Scientific, Wardha and Epichlorohydrin from M/s Loba Chemie Pvt. Ltd, Mumbai, distilled water from internal laboratory distillation process.

Preparation of adhesive from Arrowroot Starch

Starch acetate (Sample B) was prepared by slight alteration in conventional method described by Sodhi and Singh [7]. Arrowroot starch (Sample A) was dispersed in distilled water and stirred for 1 h at 30°C. The pH of the slurry was adjusted to 8.0. Acetic anhydride was added drop-wise to the stirred slurry, while maintaining the pH within the range 8.0–8.4 using 3% NaOH solution. This reaction was allowed to proceed for 10 minute after the completion of acetic anhydride addition. The slurry was then adjusted to pH 4.5 with 0.5 M HCl. Set up for experiment has been shown in Fig. 1.

To this arrowroot acetate sample, the additives like borax, urea and sodium hydroxide is added in proper amount. It helps to increases the adhesive property of starch sample.

For the preparation of adhesive (Sample C), 1 g borax and 2.5 g urea, 0.1N sodium hydroxide solution (50 g), raw arrowroot starch (10 g) were mixed together and then added to arrowroot acetate modified solution (200 g) and stirred for half an hour till uniform mixing was obtained. Then it is filtered with 120 micron nylon cloth and stored.

Preparation of adhesive from Corn Starch

Cross linked starch (Sample E) was prepared by the modified method of Wurzburg (1986). Slurry of starch was prepared in 0.5% NaOH. Epichlorohydrin (0.5% v/w) was slowly added with agitation using magnetic agitator. After agitating for 5 h at room temperature, reaction was terminated by adjustment of pH of suspension to 5.0 with 1 M HCl [6]. The slurry was washed with distilled water, filtered, and dried in the oven at 40°C. The experimental diagram is shown in Fig. 1.

The best results with good thickening, transparency and drying properties was obtained with 2 g borax, 1 g urea, 10 g raw corn powder when mixed with the 0.1N Sodium hydroxide solution. And then this mixture was added to crosslinked corn sample E to obtain modified corn adhesive sample F. The adhesive was filtered with 120 micron nylon cloth and stored.
Characterization:

Film properties: Film was made with 90µ film applicator and visually observed after the film is dried.

Drying properties: Arrowroot starch acetate adhesive was applied on a glass plate by using a film applicator (spreader) of 60 µ at a temperature 33˚C and humidity is 22%.

Specific gravity: It was measured using 100 ml capacity specific gravity cup at 25˚C temperature.

Specific gravity = \[
\frac{\text{Density of synthesized compound}}{\text{Density of water}}
\]  

pH: pH was measured with Toshniwal pH meter at 25˚C.

Moisture content: Material is dried in the oven at a temperature of 105 ± 5˚C for two hours and cooled to room temperature. Moisture content of the test sample is determined as follows:

\[
\text{Percent moisture} = \frac{\text{Mass of water in sample}}{\text{Mass of dry sample}} \times 100
\]

Solid content: The oven-drying method was used to test the solid content of adhesive. About 2 g (weight α) of the adhesive was dried in an oven at 100 ± 2 °C until to get a constant weight (weight β). The solid content was calculated from average of three samples as follows

\[
\text{Solid content (\%)} = \frac{\beta (\text{g})}{\alpha (\text{g})} \times 100
\]

Percent of Starch Content

It was determined using following formulae

\[
\text{Percent of Starch} = \frac{W \times V_1 \times 0.93}{w \times V_2} \times 100
\]

Where W = weight of sample in mg
w = dextrose factor (0.93 = 1g reduced starch factor)
V1 = volume made up for hydrolyzing starch
V2 = burette reading

Viscosity: The viscosity of given adhesive was determined by using flow cup B-4 viscometer by the BIS standard IS-3944.

\[
V = 1.37t - 200/t
\]

Where V = kinematic viscosity \( t = \) time flow in seconds

Differential Scanning Calorimetry (DSC): DSC equipment of TA Instruments, model no. DSC Q20 was used to measure DSC traces of samples at a heating rate of 20 °C per minute.

Thermogravimetry analysis (TGA): TGA equipment of TA instrument, model no. TGA Q-20 was used to measure TGA traces of samples at a heating rate of 20 °C per minute.
FT-IR Spectroscopy: PerkinElmer FT-IR Spectrometer, model Spectrum-2 was used to measure FT-IR spectra of samples. Powder sample was taken and FT-IR was measured by ATR system. Scan was done from 650 cm\(^{-1}\) to 4000 cm\(^{-1}\). Data were recorded.

Shear strength: To study the performance properties of adhesive, five samples of card board of 0.2mm thickness and five samples of polyester film of 3 micron sample of size 2.5 cm (width) x 20 cm (length) were prepared and bonded with only 2.5 cm x 10 cm area. The sample was kept for 24 h in a chamber of 25 °C and 50% RH and then tested by tensile testing machine.

Results and Discussion:

Part A: Adhesive based on Arrowroot Starch

(a) Physical properties

<table>
<thead>
<tr>
<th>S. N.</th>
<th>Properties</th>
<th>Pure Arrowroot Starch (Sample – A)</th>
<th>Arrowroot Acetate (Sample-B)</th>
<th>Arrowroot adhesive (Sample-C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Appearance</td>
<td>White solid powder</td>
<td>White viscous dispersion liquid</td>
<td>White viscous dispersion liquid</td>
</tr>
<tr>
<td>2</td>
<td>Film property</td>
<td>-</td>
<td>-</td>
<td>Smooth, translucent</td>
</tr>
<tr>
<td>3</td>
<td>Drying property</td>
<td>-</td>
<td>-</td>
<td>4 – 5 minutes</td>
</tr>
<tr>
<td>4</td>
<td>Specific gravity</td>
<td>135.2</td>
<td>-</td>
<td>1.047</td>
</tr>
<tr>
<td>5</td>
<td>pH</td>
<td>5.5</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>6</td>
<td>Moisture content (%)</td>
<td>15.2%</td>
<td>-</td>
<td>2.31%</td>
</tr>
<tr>
<td>7</td>
<td>Solid content (%)</td>
<td>12-15%</td>
<td>14.5%</td>
<td>16.88%</td>
</tr>
<tr>
<td>8</td>
<td>Starch content (%)</td>
<td>95.06%</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Appearance of final adhesive was white. Drying and film property was as per standard norms of the market adhesive and other properties are also found to be good.
Fig. 5: Film of adhesive Sample – C on a glass plate

(b) **Thermal properties**: In the Fig. 6, the differential scanning calorimetry trace of Sample – A is shown. Exothermic peak is obtained which shows that heat is given up to a temperature of 120 ºC. This indicates that some phase change has occurred which indicates that the material has transformed to crystalline phase.

![DSC of pure arrowroot starch](image)

The Fig.7 shows thermogravimetric (TG) curves of pure arrowroot starch sample A. There is a 10% loss of material at 50 - 100°C, in the first stage, which is attributed to the loss of moisture and some highly unstable product. In second stage, from 260°C to 378°C, almost 74% weight loss occurred. It means sample is stable up to 260°C. The third stage weight loss occurred between 378°C to 482°C at which 9% remaining compound degraded. This shows that some highly stable starch structure is present.

Fig. 7: TGA of pure arrowroot starch

Fig.8 shows the TG trace of sample B which is arrowroot starch acetate adhesive. First stage weight loss occurs between 50 °C to 170°C which is 10 %. In the second stage, 170°C to 378°C, the weight loss is 73 %. In the third stage, 378°C – 422°C, the weight loss is 17%. Thus acetate modified sample B is more stable than pure...
arrowroot starch sample A. Hence after addition of additives resultant adhesive (modified) arrowroot acetate sample are having better thermal stability.

![TGA of arrowroot acetate](image)

**Fig. 8 : TGA of arrowroot acetate**

(c) **Spectral properties** : Fig. 9 shows the FT-IR spectra of pure arrowroot starch sample A. In the given spectra, a peak at 3289 cm\(^{-1}\) broad band may be assigned to the -OH group and the second band at 1336 cm\(^{-1}\) sharp resolution with strong intensity. At 1077 cm\(^{-1}\) the C-O (esteric) group formed and at 998 cm\(^{-1}\) the sharp band obtained showing the (=C-H) group is obtained with strong intensity.

![FTIR of pure arrowroot starch](image)

**Fig. 9 : FTIR of pure arrowroot starch**

In the Fig. 10, arrowroot starch acetate starch (sample B), C-O (esteric) group is obtained at 1148 cm\(^{-1}\) (sharp one) and at 1079 cm\(^{-1}\) ether group is obtained (sharp peak) and with 997 cm\(^{-1}\) (=C-H) group is seen.
(c) **Performance properties**: The performance of adhesive was measured by bonding cardboard with PET film. The sample was prepared and was torn by hand pulling both the loose end apart for tear strength. There is a failure of substrate i.e. de-lamination. This indicates that the adhesive is working well.

(ii) **Part B: Adhesive based on Corn Starch**
(a) **Physical properties**: Physical properties of adhesive samples are shown in Table 2. In case of pure corn starch, the moisture content is approximately 8 % and starch content 90 %. The pH of adhesive found to be neutral, it is shown as 6.5 while crosslinked corn starch was 4.0. The appearance of adhesive is quite good.

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Properties</th>
<th>Pure corn starch (Sample -D)</th>
<th>Cross-linked corn starch (Sample –E)</th>
<th>Corn starch Adhesive (Sample-F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Appearance</td>
<td>White viscous Dispersion liquid</td>
<td>White viscous Dispersion liquid</td>
<td>Colourless transparent viscous dispersion</td>
</tr>
<tr>
<td>2</td>
<td>Moisture content</td>
<td>8.3 %</td>
<td>-</td>
<td>78.18%</td>
</tr>
<tr>
<td>3</td>
<td>Solid content</td>
<td>8.2-9.0%</td>
<td>-</td>
<td>19.59 %</td>
</tr>
<tr>
<td>4</td>
<td>Specific gravity</td>
<td>135.2</td>
<td>-</td>
<td>1.076</td>
</tr>
<tr>
<td>5</td>
<td>Viscosity</td>
<td>13.55 Centipoise</td>
<td>-</td>
<td>110.181 Centipoise</td>
</tr>
<tr>
<td>6</td>
<td>Starch content</td>
<td>90.06 %</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>pH</td>
<td>5.5</td>
<td>4.0</td>
<td>6.5</td>
</tr>
</tbody>
</table>

(b) **Thermal properties**: Fig 11 and 12 shows the DSC traces of sample E & F respectively. When epichlorohydrin crosslinker is mixed with pure corn starch it gives exothermic peak at 105 °C. It indicates that the reaction is completed between corn starch and epichlorohydrin crosslinker in sample E and F. This shows that the given adhesive is cross-linked.
Fig 12: DSC trace of sample F crosslinked corn adhesive

Fig. 13 shows the thermo-gravimetric (TG) curve of pure corn starch sample D. There is a weight loss of 7.6% up to a temperature of 100 °C. This may be attributed to loss of moisture. The compound is stable up to 257 °C. In second stage from 257.71 °C to 392.25 °C, almost 75.99% adhesive degraded. It means our sample E is stable up to 257 °C. After that rapid degradation occurred. In the third stage 392.25 °C to 500 °C, 11.03% weight loss occurred. This shows that some highly stable starch structure is present which are degrading at high temperature.

Fig. 14 shows the thermal degradation of F is crosslinked starch adhesive sample. It is more stable than pure corn starch (Sample D). Cross linked corn starch sample E, which is modified with additives after addition of additives, resultant (modified) cross linked corn adhesive F sample, is having better thermal stability.

(c) Spectral properties: In the Fig. 15, the FT-IR spectrum of pure corn starch is shown. O-H stretch occurs at 3291 cm⁻¹, C-O stretch at 1076 cm⁻¹ and C-O bend at 999.81 cm⁻¹.

Fig. 16 is the spectrum of cross linked starch sample E. Prominent peak are obtained at 3276 cm⁻¹, 1078 cm⁻¹, 1038 and 999 cm⁻¹. This may be explained as O-H stretch, C-O stretch and C-O bend respectively.

Fig 17 is the spectra of crosslinked starch adhesive sample F. Since additives have been added, the additional peak at 1422 cm⁻¹ may be due to C=O stretch.
Performance properties: The performance of adhesive was measured by bonding cardboard of 20 micron thickness with Al foil 2 micron. The sample prepared and was torn by hand pulling both the loose end apart for tear strength. There is a failure of substrate i.e. de-lamination. This indicates that the adhesive is working well.

Effect of cross-linking

Cross-linking affects the physical properties as well as thermal transition characteristics of starch. The effectiveness of cross-linking depends on the source of the starch and the nature of cross-linking agent. In this experiments, it was observed that cross linking effect is not very significant.

Presence of crosslinking agents creates either ester or ether inter-molecular linkages between hydroxyl groups on starch molecules. A small amount of multifunctional reagent is enough to interconnect starch molecules by crosslinking reactions.

Conclusion:

Preparation of arrowroot starch based adhesive and corn starch based adhesive is easy. Arrowroot starch & Corn Starch are an environmentally friendly product, they can be modified as adhesive. Starch is commonly used for manufacturing of wood-composite adhesives because of their low cost, high free hydroxyl content, easy processing and treatment.

Significant improvement in the thermal property of adhesive is observed after modification of Arrowroot starch and Corn starch. Starch based adhesives shows a limited water resistance, which can be improved by
cross-linking of starch. The optimal viscosity values of the adhesives is found to be good i.e. less than 10,000 cps.

The chemical modification of starch with acetylation and cross-linking significantly affected the physicochemical properties of starch. It makes desirable changes in the functional properties with transformation in crystalline phase, increase in thermal stability, good bonding and failure of delamination.

The extent of change in the functional properties after the modification of Arrowroot & corn starch was different possibly due to the differences in the amylose content, molecular structure of amylopectin, granular swelling, degree of substitution, and location of substituent groups.

REFERENCES