Studies in the Preparation of Adhesives from Hemicelluloses of Zea Mays Stem Pith

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For isolation of acid-alcohol insoluble hemicelluloses, the conventional method is to prepare from the plant material first the holocellulose and then subject it to 17.5% alkali extraction. On acidification of the alkali extract and addition of ethanol (95%) the hemicelluloses is precipitated.

By direct alkali extraction of the plant material, at suitable concentration and temperature as much as 80% of the acid-alcohol insoluble hemicelluloses is reported to be isolated. About 89% of the acid-alcohol insoluble hemicelluloses could be isolated from the stem pith of Zeamays.

By borating of the hemicelluloses, adhesives could be prepared which compared favourably with market adhesives and gum acacia solution, for adhesion of papers.

Substances capable of holding together materials by surface attachment are termed as adhesives. The essential qualities of adhesives are that they should be capable of easy dissolution, (preferably in water), and applicability on surfaces intended for adhesion, which is effected on drying of the solution by the cohesion and adhesion mechanism. Polysachharide gums, mucilages, plant latex, etc., have been used as adhesives. The use of cooked starch paste for adhesion is too well known. Jaretzky and coworkers[1, 2] consider that starch granules in the cells are responsible for gum formation, under conditions known as gumosis. However, Lyod[3] is of the opinion that cellulose and hydrocellulose are responsible for the production of gum.

The possibilities of using cellulose mucilage as adhesive were observed by Minor[4]. The decomposition of cellulose into insoluble hydrocellulose and oxycellulose with properties similar to hemicelluloses was studied by Schwalbe and Becker[5], who concluded that the decomposition of hydrocellulose and/or oxycellulose, as well as hemicellulose led to the formation of mucilage with cementing properties and that under severe conditions of decomposition may lead to the formation of sugars or even acids (*loc. cit.*). Naryanamurti and Rao[6] have studied the formation of an adhesive from the hemicelluloses of exhausted myrobalan pulp. Lodh and Rao[7] have prepared a paper adhesive from the hemicellulose fraction of Ekra (*Erianthus ravennac*) reeds.

The effect of boric acid (in absence of water) on high molecular weight polymers was studied earlier by Irany[8,9] and later by Deuel *et al*[10] pointing towards the adhesion properties of the borated complex. The use of borax and boric acid is based on the fact that both form complexes with hemicelluloses[6]. The process of borax-complex formation is reversible as the product hydrolyses. In presence of water or alcohol and the adhesive obtained will not yield water-resistant bonds. Neverthless, both Naryanmurti and Rao[6] and later Lodh and Rao[7] have shown that the borated hemicellulose could be used for satisfactory adhesion of papers.

Isolation of Hemicelluloses

The normal procedure of isolation of hemicellulose is to prepare and isolate first the holocellulose from the extractive free plant material by treatment with sodium chlorite solution on a boiling

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water bath. The holocellulose is then extracted with caustic soda (17.5%) solution at a temperature not exceeding 20°C. The alkali extract on acidification and addition of ethanol (95% or more) precipitates the hemicelluloses, which is filtered, washed with alcohol and dried in vacuum over suitable dehydrating agents.

During delignification of the plant material some alterations and losses of the carbohydrate fraction take place causing degradation and depolymerisation of the hemicelluloses[11]. Many attempts for direct extraction of hemicelluloses from plant material (wood) have, therefore, been made and about 80% of the hemicelluloses in hardwoods are capable of being isolated at room or lower temperatures by extraction with aquous alkali of suitable concentration (*loc. cit.*).

It was reported earlier[12] that the pith of Zea mays stem contains 30.25% (calculated) hemicelluloses, on ash and lignin free basis and that 18.22% hemicelluloses, ash and lignin-free, could be isolated as acid-alcohol insoluble precipitate.

Experimental

Powdered and sieved (40 mesh) *Zea mays* stem pith (50 g. moisture free) was used in each experiment and treated for 48 hours at 20°±2°C with aquous sodium hydroxide solutions of various concentrations. The pith-liquor ratio was maintained in each case as 1 : 30 and the solution stirred occasionally. The alkali extract was filtered and acidified with acetic acid, when a portion of the hemicelluloses was precipitated. The precipitation was completed by addition of 95% ethanol in excess. The precipitated hemicelluloses was chilled (4°C) overnight and filtered, washed successively with increasing concentrations of ethanol (70%, 85%, 95% and absolute) and dried under vacuum over sulphuric acid. The results are given in table I.

A perusal of the figures in table I will show that on extraction with 10 percent aqueous alkali, 17.6% acid–alcohol insoluble hemicelluloses (on pith) could be isolated as compared to 18.22% hemicelluloses (on pith) isolated by first preparing the holocellulose and then extracting the hollocellulose with 17.5 percent alkali at a temperature below 20°C and then precipitating the hemicellulose from the alkali exract by acidification and addition of absolute alcohol. Thus, about 96.7% of the total acid-alcohol insoluble hemicelluloses could be precipitated by direct alkali extraction of the pith with 10 percent alkali solution.

Other conditions remaining unchanged, an increase in the concentration of alkali solution from 1 to 4 percent, increases the yield of acid-alcohol insoluble hemicelluloses (on pith) from 9.6% to 16.2%, that is, an increase of 6.6%. As compared to this, under similar conditions of treatment, increase in the concentration of the alkali solution from 5 to 10 per cent will increase the yield of acid-alcohol insolutble hemicellulose (on pith) from 16.4%, to 17.6% that is, an increase of only 1.2%. Therefore, from the practical stand point, the use of a lower concentration of alkali, (say, around 4 to 5 percent), for extraction

Table I

Yield of Hemicelluloses from Zea Mays Stem Pith by Direct Alkali Treatment

(Figures expressed on 100 g. oven dry basis)

Sl. No.	Conc. of NaOH solution %	Yield of hemicellulose* on pith
1.	1.0	9.6
2.	1.5	10.5
3.	2.0	11.7
4.	3.0	14.5
5.	4.0	16.2
6.	5.0	16.4
7.	6.0	16.8
8.	7.0	17.1
9.	8.0	17.36
10.	9.0	17.4
11.	10.0	17.6

*Acid-alcohol insoluble, incorrect for ash and lignin.

Pith-liquor ratio 1 : 30, Temperature 20°C±2°C Time 48 hours.

is preferable.

The yield of acid-alcohol insoluble hemicelluloses on pith, by direct extraction of pith with alkali solutions of various concentrations has been graphically plotted. The nature of the curve confirms the foregoing observation. The yield of hemicelluloses increases rapidly upto an alkali concentration of 4 percent and thereafter the yield of hemicelluloses increases but slowly with increasing concentration of the alkali solution and the curve tends to become asymptotic. With a concentration of 4 percent alkali solution, the yield of acid-alcohol insoluble hemicelluloses on pith was 16.2% as compared to 18.2% hemicelluloses on pith by using an alkali solution of 17.5 per cent concentration[12]. This will work out to about 89% of acid–alcohol insoluble hemicelluloses which could be isolated via the formation and separation of holocellulose and subjecting the same to extraction with 17.5 per cent alkali solution. It is significant to note that about 80% of hemicelluloses in hardwoods is reported to be removable "by direct extraction with aqueous alkali of suitable alkali concentration and temperature"[11].

Having established that from a practical stand point of isolation of acid-alcohol insoluble hemicellulose, direct extraction of powdered pith with 4 percent alkali is preferable, the following procedure was followed.

Zea mays stem pith powdered and sieved was treated with 4 percent sodium hydroxide solution (pith–liquor ratio 1:30) at 20°C ± 2°C for 48 hours with occasional stirring. The extract was filtered over a Buckner funnel under suction, using folds of muslin instead of filter paper. The filtrate was acidified with acetic acid to a pH of 4.5, when a portion of the hemicelluloses was precipitated. The precipitation was completed by adding 95% ethanol in excess. The precipitate was chilled overnight and the supernatant liquor decanted out. The precipitate was filtered over a Buckner funnel under suction and washed successively with increasing strengths of (70%, 85%, 95% and absolute) alcohols and dried over sulphuric acid under vacuum.

The hemicelluloses was of a light cream coloured amorphous powder and very hygroscopic in nature. It was neither free from ash nor from residual lignin. It was, however, not considered necessary to purify the hemicelluloses for preparation of the adhesives.

Preparation of Adhesives

Weighed quantities (4 g in each case) of hemicelluloses well heated with different concentrations of aqueous boric acid on water bath for one hour in each case, with constant stirring. The light brown viscous fluid formed was tested for adhesion of papers.

Boric acid in aqueous solution is a weak acid, having a dissociation constant of 6.4×10^{-10}. Other chemicals like phenol and hydroquinone having a similar dissociation constant as boric acid were also used to react with hemicelluloses isolated from *Zea mays* stem pith. The effect of glycerol with boric acid has also been studied.

Determination of Strength of Adhesives

The mechanism of paper adhesion is not fully understood. It is, however, believed that adhesion is achieved due to the porous nature of the paper, which permits considerable penetration of adhesive solution and its solidification around the fibres, producing on drying, strong bonds mostly of mechanical nature. It is generally agreed that papers with too high or too low porosity will impair the mechanism of adhesion. In the same way both hard sized and soft sized papers are equally detrimental for adhesion. In the case of very hard sized papers, the penetration of the adhesive solution, within the given time, is restricted and the setting is affected resulting in weak bonding. In the case of soft sized papers, the penetration of adhesive solution is too deep, resulting in loss of adhesions; and little adhesive is left at the surface for sticking together of the two surfaces.

Kraft paper sheets purchased from the market were used for determining the strength of the adhesives prepared. The paper sheets were cut to the size of the plate (20" x 20") of a hand screw press. The adhesive was uniformly applied on the glazed side of one paper and the unglazed side of the other paper. The two sheets were brought in union in such a way that the adhesive treated surfaces come in intimate contact with each other, care being taken that no air space was left in-between the adhesive coated surfaces and that the machine direction of one sheet of the pair being at right angle to the machine direction of the other (that is, in each two coated papers forming a pair, the machine direction of one sheet was in parallel to the cross direction of the other sheet). A number of such pairs of adhesive treated papers were made by application of different adhesives prepared. A blank pair was prepared using distilled water. A pair was also prepared by using gum acacia (gum-water ratio 1:3). Two paper adhesives available in the market, under different trade names. were also used. for adhesion of two different pairs of papers, for comparison.

The pairs of papers were pressed in the screw press for 48 hours and allowed to stick and dry. The pair of paper to which distilled water was applied, had no adhesion, and as the sheets easily separated, they could not be used for evaluation of adhesive strength. One inch border from each pair of paper was trimmed and the trimmings discarded. The rest of the paper sheet pair was cut to size and tested for adhesion strength in Peel Load Tester, M/s. Mc low Smith, U.K. at a rate of traverse of 5 cm per minute and the distance between the grips being 15 cm. The results are given in table II.

The results in table II will show that adhesives prepared by using 4 and 5 percent Boric acid solutions (hemicellulose-boric acid ratio 1 : 6) has good sticking properties, having peeling strengths of 7.5 and 8.0 Kg./Sq. in. respectively and compare favourably with the sticking property of gum acacia solution (gum-water ratio 1 : 3) having a peeling strength of 8.5 Kg/Sq.in. The two market samples have also more or less similar peeling strength.

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TABLE II

Strength of Adhlsive Samples Estimated by Peel Load Tester

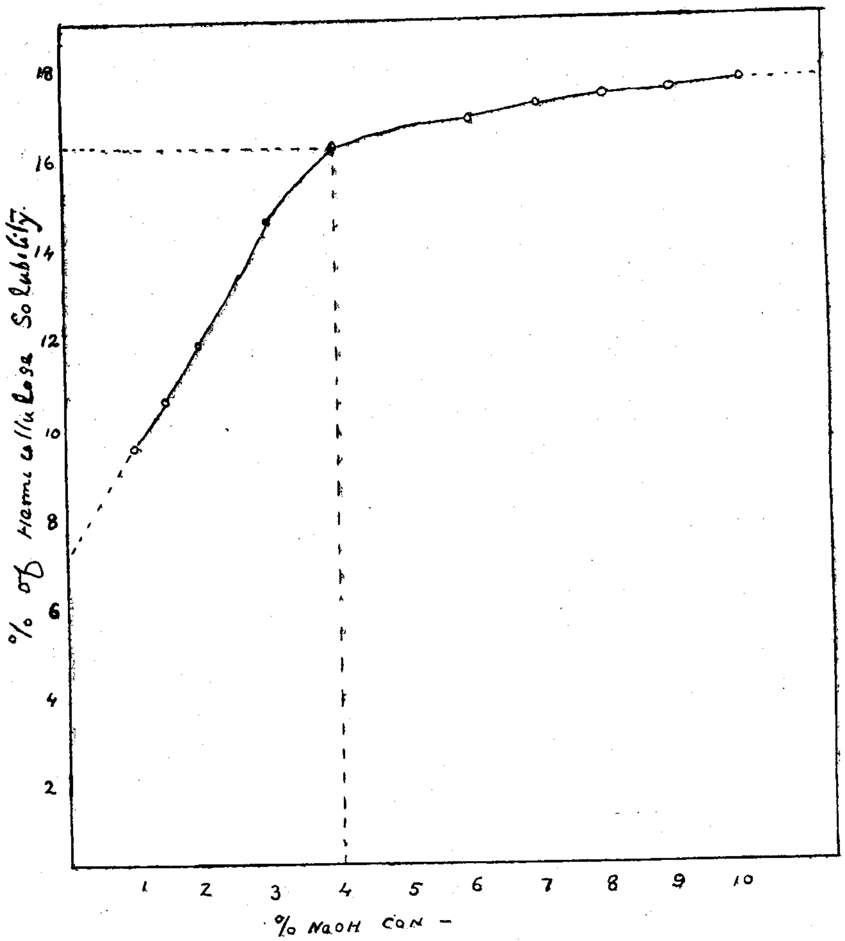
Adhesive	Kg/Sq. m. Strength
1. Prepared by treating (4 g) hemicellulose with 1% Boric acid (25 ml).	5.5
2. Prepared by treating (4 g) hemicellulose with 2% Boric acid (25 ml).	6.0
3. Prepared by treating (4 g) hemicellulose with 3% Boric acid (25 ml).	7.0
4. Prepared by treating (4 g) hemicellulose with 4% Boric acid (25 ml).	7.5
5. Prepared by treating (4 g) hemicellulose with 5% Boric acid (25 ml).	8.0
6. Prepared by treating gum acacia with water/ (gum-water ratio 1:3)	8.5
7. Market Sample 1. Ready made adhesive solution Code-CM.	7.8
8. Market Sample 2. Ready made adhesive solution Code-CDL.	8.2
9. Prepared by treating (4 g) hemicellulose with 5% Boric acid (25 ml) and 5% glycerol (25 ml).	5.5
10. Prepared by treating (4 g) hemicellulose with 5% phenol (25 ml).	6.0
11. Prepared by treating (4 g) hemicellulose with 5% hydroquninone (25 ml).	6.0

* Average of ten observations.

Graph Showing % Yield of Hemicellulose

Vs

Concentration of Sodium Hydroxide



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