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Agricultural residues in plastics

Part I. Agricultural residue flours*

by T. F. CLARK[1], R. V. WILLIAMSON[2] and E. C. LATHROP[3] 1885- Elbert Clyde

THE utilization of agricultural residues or farm wastes in the manufacture of plastics has been the subject of inquiries referred with increasing frequency to the Bureau of Agricultural and Industrial Chemistry. Work on this problem at the Bureau's Agricultural Byproducts Laboratory, formerly at Ames, Iowa, was directed to the preparation of thermoplastic lignin molding powders produced by the acid or aniline hydrolysis of such materials as bagasse or cornstalks, followed by compounding with plasticizers such as furfural or aniline.[4-7] One company in Louisiana[8] extended these studies through pilot-plant operations and development work, and is manufacturing thermosetting plastic molding powders from sugar cane bagasse. The thermoplastic compositions produced at Ames required rather long molding cycles, were somewhat deficient in strength properties, and have not proved generally attractive to commercial molders.

The Regional Laboratory program provided for a broad and concentrated attack on the problem of the industrial utilization of agricultural residues at the Northern Laboratory, Peoria, Ill., to which the work at Ames was transferred July 1, 1941. A completely equipped pilot plant for the study of plastics was provided, and the personnel assigned to the plastics problem was increased.

Research was directed first to the use of finely ground residues as a component of thermosetting molding powders. It was recognized that the powders must be capable of use under present commercial molding practices to produce products whose physical properties are at least equivalent to general-purpose powders. If this use were developed, the agricultural residues would require only simple low-cost processing, comparable with the processing of woodflour, and would find a potentially large-volume market, particularly if used with phenol-formaldehyde resins. At the same time, use of the residues in this manner would benefit the plastics industry by making available a greater range of raw materials, many of them of wide geographic distribution. It was also possible that improved molding powders might result from the work. Our entry into the war emphasized the importance of this approach.

For years woodflour has been the standard lignocellulose material which is used with phenol-formaldehyde resins in the production of molding compositions. The present state of perfection of these compositions is the result of extensive research by several large organizations—research work directed toward the perfection of both the woodflour and the phenol-formaldehyde resins in order to produce the best possible physical properties in the final combination of these materials into finished molded articles.

Experiments made in the past to determine the properties of various agricultural residues in phenolic molding compositions led to the general conclusion that agricultural residues were inferior to woodflour in such compositions.[9] The usual experimental procedure was to substitute a ground residue in place of a perfected woodflour in a composition that was known to give good properties. The results with agricultural residues were unfavorable, and no special effort was made to trace or overcome the difficulties.

In this study of the conditions favorable to the use of agricultural residues, it has been shown that agricultural residue compositions can be produced that have molding and physical properties comparable with those made with woodflour. The term "composition" as used in this paper denotes a finished powder ready for molding.

Experimental procedures

When the experimental work on this project was started, the decision was made to use commercial phenol-formaldehyde resins. Therefore, several different commercial resins, both liquid and powdered, were obtained. Compositions were prepared from these various resins with six different agricultural residues including corncobs, corn stover, wheat straw, flax shives, hemp hurds and peanut shells.

The flours derived from the residues were prepared by grinding the whole residue in a hammer mill using a screen with holes 1/2 in. in diameter, the comminution being completed in a ceramic-lined ball mill (24 by 30 in.). A ball-mill charge consisted of 30 lb. of the residue to 300 lb. of assorted-size porox balls, and a period of approximately 16 hr. or overnight was needed for the grinding of a dry residue. The product, essentially finer than 80 mesh, was air-separated to remove particles of unground fiber and foreign material. Ball-mill grinding produced a granular flour which gave somewhat lower impact values than a more fibrous type of flour, as was shown by a few experiments in which specially ground fibers were used. Ball-mill ground material was used in the major portion of the experiments since practically the entire residue could be conveniently ground to pass a No. 80 U. S. standard sieve. However, it is feasible to grind agricultural residues in the equipment commonly used for producing woodflour and at approximately the same power cost. This has been shown in grinding studies which were conducted with commercial equipment.

The general procedure used in the preparation of the molding compositions consisted in a) mixing or compounding all ingredients in a Banbury mixer at 150° F., b) milling on heated differential rolls to advance the resin and to control the curing time of the product, and c) grinding in a burr mill to pass a

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[1] Chemical engineer, Plastics and Building Materials Section, Agricultural Residues Division.

[2] In Charge, Plastics and Building Materials Section, Agricultural Residues Division.

[3] Head, Agricultural Residues Division.

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[7] T. R. McElhinney, T. F. Clark and D. F. J. Lynch, "Low-Cost Molding Material from Agricultural Wastes," MODERN PLASTICS *16*, 42–44, 70, 72, 74, 76 (Mar. 1939).

[8] T. R. McElhinney, "Bagasse Molding Compounds," MODERN PLASTICS, *20*, 64–5, 136 (Nov. 1942).

[9] "Fillers for Molding Compounds," Plastics Catalog 1944, Plastics Catalogue Corp., New York, N. Y., p. 286.

No. 35 U. S. standard sieve. Compounding in a dough mixer may be substituted for mixing in a Banbury, with some modification in the subsequent milling. The conditions of milling varied somewhat with the particular resin, flour or resin-flour combination.

Of the commercial resins used, liquid resins produced strength properties superior to those that were obtained with either one- or two-stage types of powdered resins. The addition of hexamethylenetetramine to the molding compositions showed no improvement. Neither available liquid nor powdered commercial resins imparted to the compositions the water-resistant properties equal to those of commercial molding compositions. Inferior water resistance manifested itself by the tendency of molded specimens to crack when subjected to alternate soaking in water and drying, rather than by the actual amount of water absorbed. Some compositions showed better resistance to cracking than others which absorbed much less water. The method for correction of this defect will be described below.

Standard methods for determining resistance to cracking were too slow and the man-hours required for making the tests were too great to be used for control purposes. For example, compositions ready for molding could be produced within 30 min., but hours or days were required to make the test by standard methods. Therefore, the following rapid control method was developed. Short-skirt 28-mm. bottle caps, molded for periods of 1/2, 1, 2, 2 1/2 and 5 min., were weighed accurately and immersed in individual beakers of boiling distilled water. At the end of 15 min. the caps were removed from the boiling water, immersed 15 sec. in distilled water at room temperature, dried superficially with a blast of air saturated with water vapor, reweighed immediately and allowed to dry at room temperature. (Drying at 105° C. will not accelerate this test as caps which crack at room temperatures will not necessarily crack at the elevated temperature.)

Observations for detection of cracks were made through 2-power binocular spectacles immediately after the test, 24 hr. later and, finally, after 4 weeks. The behavior of a prewar bottle-cap molding composition when subjected to the test was used as the standard of quality. Molded caps of this composition showed no cracking immediately after the test. The cap that was molded for 1/2 min. showed slight cracks after drying for 24 hours. The cap that was molded for 1 min. showed no cracks for several days, but failure occurred some time previous to the end of a drying time of 4 weeks. After the 4-weeks' drying period no cracks had developed in the cap that was molded for 2 minutes.

This method of testing permitted a tentative classification of molding compositions with respect to rate of cure, resistance to water absorption and resistance to cracking within 30 min. from the time that specimens had cooled to room temperature.

Cause of instability of molded products to water

Using the boiling-water test as a measure of relative resistance to water absorption and cracking, a series of experiments was conducted for the purpose of determining the cause of cracking of molded specimens. Agricultural residues *per se* were eliminated as the cause as a result of comparisons with woodflour compositions, which were no better. Water-soluble materials in the finished molding composition were shown to be primarily responsible for cracking. A molding composition which had been prepared with a liquid resin was extracted with water and air-dried. Specimens molded from the extracted composition satisfactorily met the boiling water test, whereas specimens molded from the original composition had poor resistance.

To determine whether water-soluble components of the residue or of the resin were responsible for poor resistance, molded specimens from compositions of (a) water-extracted flax-shive flour and unextracted dry resin, (b) unextracted flax-shive flour and water-extracted dry resin, and (c) unextracted flax shives and unextracted resin were subjected to the boiling-water test. The extracted flour composition (a) showed decreased resistance to cracking, but improved resistance to water absorption. The extracted resin composition (b) showed improved resistance to both water absorption and to cracking. This indicated that the water-soluble materials in the resin were important factors in connection with resistance both to water absorption and to cracking, evidence which was corroborated by the fact that liquid resin compositions showed poorer resistance than dry-resin compositions to the action of water. However, compositions containing liquid resins produced molded specimens of superior strength properties as compared with those of the available dry resins. Therefore, experiments were directed toward the improvement of the water-resistant properties of liquid resins.

Extracted resins in compositions of normal resin content

Liquid resins in alcoholic solution could be precipitated readily at room temperature by the addition of excess water, while liquid resins in water solution could be precipitated in the presence of excess water by the application of heat. The advancement of the resins was controlled by the temperature and time of heating, while soluble materials were removed by washing with water. Based on these facts, 20 lb. of precipitated resin were prepared in a dough mixer by adding excess water to a commercial liquid resin in alcoholic solution. The precipitated resin was washed with cold water, dried at 50° C. and ground to a powder in a ball mill. This resin was then compounded with several agricultural residues.

The resistance to water absorption and to cracking of specimens molded from these compositions was uniformly good. Table I shows water absorption values and strength characteristics as determined by A.S.T.M. methods. The formulation of these compositions was as follows: agricultural residue flour, 50 percent; water-precipitated resin, 47.2 percent; black dye, 2.0 percent; zinc stearate, 0.5 percent; calcium oxide, 0.3 percent. Test specimens were molded at a temperature of 320° F. and a pressure of 3000 p.s.i. The

TABLE I.—PROPERTIES OF COMPOSITIONS WITH A PHENOL-FORMALDEHYDE RESIN CONTENT OF 47.2 PERCENT AND A FIBER CONTENT OF 50 PERCENT

Composition	*Flexural strength*	*Tensile strength*	*Impact strength, notched Izod*	*Water absorbed (24 hr. immersion at 70° F.)*[a]
	p.s.i.	*p.s.i.*	*ft-lb./in. of notch*	*percent*
A.S.T.M. specifications for general-purpose wood-flour phenolics	9,500	7,000	0.24	0.80
Corncob	11,990	10,240	0.20	0.49
Wheat straw	10,450	9,080	0.20	0.42
Peanut shell	10,200	9,320	0.21	0.35
Hemp hurd	9,680	7,460	0.21	0.37
Corn stover	9,570	7,600	0.20	0.69
Flax shive	9,530	8,730	0.20	0.36
Woodflour[b]	11,220	8,650	0.20	0.39

[a] Values are for 2-in. diameter disks, 1/8-in. thick, molded for 2 1/2 minutes.
[b] Made from equal parts of knot-free Ponderosa and Lambertiana pines.

molding powder was ground to pass a No. 35 U. S. standard sieve and was preformed previous to molding.

The results in Table I show that with the exception of impact strength, all of the compositions met A.S.T.M. specifications. The compositions made from corncob flour were outstanding in strength properties. Previous tests on corncob compositions using entirely different liquid or dry resins had shown very poor strength properties. This improvement in the strength properties of the corncob compositions showed that the resin must fit the residue in order to obtain the best results. This fact should be borne in mind in connection with the data presented, because proper changes in composition might change the order of merit of the several residues that have been investigated.

That the slightly low impact strength is not a special characteristic of agricultural-residue compositions is shown by the fact that the woodflour composition was also low in impact strength. After these results were obtained, it was found that the low impact strength of these compositions was the result of the granular character of the flours, both corncob and wood, which were produced by ball-mill grinding. By grinding corncobs so that a more fibrous flour was produced, the impact value of the specimens from the corncob compositions met A.S.T.M. specifications for general-purpose woodflour phenolic molding compositions.

Table III gives a comparison of the physical characteristics of compositions from commercial woodflour and from corncobs ground in the following two ways: 1) Granular corncob flour produced in the ball mill and 2) a fibrous flour prepared by milling coarsely ground moist cobs on heated differential rolls. Both the dry resin and woodflour used in these experiments were commercial products which were obtained during the later stages of this research. In all three cases, the same technique of compounding was used. The formulation of each was as follows:

	Percent
Lignocellulose material	50.0
Phenol-formaldehyde resin	47.5
Black dye	2.0
Zinc stearate	0.5

Compositions were molded at 350° F. and 3000 p.s.i. pressure from powders ground to pass No. 35 U. S. standard sieve.

The results in Table III show that the composition prepared with fibrous corncob flour was the only one which met fully the A.S.T.M. specifications for general-purpose phenolic molding compositions. Both of the corncob compositions showed flexural and tensile strengths superior to those of the woodflour phenolic. The results in Table III also show that commercial dry resins are available which produce excellent results when combined with agricultural residue flours.

The results shown in Tables I and III indicate that the first objective of this investigation has been successfully accomplished, i.e., that excellent molding compositions can be made by formulating agricultural residues with the normal concentration of phenol-formaldehyde resin (47 percent), if the proper type of resin is used

Molding compositions of reduced resin content

In this study, a series of compositions was made from the same agricultural residue flours and the same resin as used

Table II.—Properties of Compositions with a Phenolic Resin Content of 35 Percent and a Fiber Content of 62.25 Percent

Composition	*Flexural strength*	*Tensile strength*	*Impact strength, notched Izod*	*Water absorbed (24 hr. Immersion at 70° F.)*[a]
	p.si.	*p.s.i.*	*ft.-lb./in. of notch*	*percent*
A.S.T.M. specifications for general-purpose woodflour phenolics	9,500	7,000	0.24	0.80
Corncob	10,000	10,210	0.24	1.03
Wheat straw	9,390	8,710	0.21	0.95
Hemp hurd	8,680	7,240	..	0.56
Corn stover	8,350	7,890	0.20	1.68
Flax shive	8,340	7,410	0.18	0.76
Peanut shell	8,200	6,590	0.21	0.56
Woodflour[b]	9,440	8,650	0.21	0.65

[a] Values are for 2-in. diameter disks, 1/8 in. thick, molded for 2 1/2 minutes.
[b] Prepared from equal parts of knot-free Ponderosa and Lambertiana pines.

Table III.—Properties of Phenolic Molding Compositions Made with Commercial Woodflour and Experimental Corncob Flours

Composition	*Flexural strength*	*Tensile strength*	*Impact strength, notched Izod*	*Water absorbed (24 hr. immersion at 70° F.)*[a]
	p.s.i.	*p.s.i.*	*ft.-lb./in. of notch*	*percent*
Woodflour, commercial	11,490	7380	0.22	0.33
Granular corncob flour	12,085	8900	0.20	0.59
Fibrous corncob flour	11,990	8490	0.25	0.66

[a] Values are for 2-in. diameter disks, 1/8 in. thick, molded for 2 1/2 minutes

Table IV.—Properties of Flax Shive Compositions with Varied Resin Content

Composition		*Flexural strength*[a]	*Tensile strength*[a]	*Impact strength, notched Izod*[a]	*Water absorbed (24 hr. immersion at 70 °F.)*[b]	*Resistance to cracking*[c, d]
Resin	*Fiber*					
percent	*percent*	*p.s.i.*	*p.s.i.*	*ft.-lb./in. of notch*	*percent*	*min.*
55	42.1	10,487	7853	0.19	0.27	1
47.2	50	9,530	7470[e]	0.20	0.36	2 1/2
35	62.3	8,250	7410	0.18	0.76	2
30	67.3	7,663	7730	0.25	0.82	2 1/2
25	72.3	7,384	7038	0.22	1.04	[f]

[a] Molding time, 7 minutes.
[b] Values are for 2-in. diameter disks, 1/8 in. thick, molded for 2 1/2 minutes.
[c] Time shown is the molding period required to obtain 28-mm. bottle caps that withstood cracking following 15-min. immersion in boiling water, and drying at room temperature for 4 weeks.
[d] Specimens which do not crack after 2 min. molding are equal to prewar commercial compositions.
[e] Preheating molding powder previous to molding gave tensile strength of 9360 p.s.i. Other compositions in the table were not improved by preheating.
[f] Cracked after 5-min. molding.

in the compositions shown in Table I. The resin content, however, was reduced from 47.2 percent to 35 percent, and the fiber content was increased from 50 to 62.25 percent. Molding conditions were the same as those for the compositions shown in Table I; i.e., a temperature of 320° F. and a pressure of 3000 p.s.i. were used. The results of physical tests on specimens molded from these compositions are given in Table II.

The results in Table II indicate the superior strength properties of the corncob composition. From a practical point of view, the properties of the wheat straw composition were equal to those of the woodflour composition. Water absorption of the corncob and wheat-straw compositions was above that of the woodflour product. However, none of the compositions including that of woodflour met fully the A.S.T.M. specifications for general-purpose phenolics. All met some of the specifications and were only slightly deficient in those respects in which they failed to meet general-purpose specifications. The molding properties of these compositions were good, but conditions of compounding and molding were more critical than for compositions with higher resin content. Completeness of cure of standard water absorption test disks $^1/_8$ in. thick, as estimated by resistance to water absorption and to cracking, was attained at about 2-min. molding under the temperature and pressure conditions used, i.e., 320° F. and 3000 p.s.i., which are conditions commonly used in commercial practice.

Molding compositions of varied resin content

A series of compositions was prepared with flax-shive flour as the fibrous component and with resin contents of 55, 47, 35, 30 and 25 percent. The same resin was used as in the compositions shown in Tables I and II. The physical properties of specimens molded from these compositions are shown in Table IV. The temperature of molding of these specimens was 320° F. and the pressure was 3000 p.s.i.

The following general relationships may be deduced from the results in Table IV Under constant conditions of molding, flexural and tensile strengths decreased roughly in proportion to the reduction in resin content between 55 and 25 percent. However, the rate of decrease for flexural strength was greater than for tensile strength. Impact strength did not change appreciably with change in resin concentration, but the results show slightly higher values for resin concentrations below 35 percent. Milling and molding conditions became more critical when the resin concentration was reduced below 35 percent. The percent of water absorbed was found to be proportional to the product of the percent fiber and the reciprocal of the percent resin in the compositions.

Summary

1. Excellent molding compositions were prepared from agricultural-residue flours with the proper types of phenol-formaldehyde resin. Several residue compositions yielded molded products which had flexural and tensile properties not only well above A.S.T.M. specifications for general-purpose phenolics but also superior to those of woodflour compositions made with the same resin. The selection of the proper types of resin appears to be essential for optimum results with a given residue. A corncob composition prepared with a commercial dry resin gave outstanding flexural and tensile strengths.

2. Resistance to water absorption within A.S.T.M. limits was readily attainable with residue compositions of normal resin content. Several compositions containing less resin (35 percent) also developed resistances which were well within the specifications.

3. The method of fiber grinding affected the impact strength of the compositions.

4. The cause of cracking on alternate wetting and drying of the compositions containing lignocellulose has been traced as due mainly to the water-soluble compounds in the resin constituents. Removal of these water solubles by washing of dry resins or by precipitation of liquid resins followed by washing, was shown to increase resistance to cracking greatly.

5. The agricultural-residue compositions were prepared by the usual techniques and equipment used by industry and possessed flow and molding characteristics which adapt them to commercial use.

6. Compositions prepared with 35 percent resin and with 62.5 percent fiber showed molding and physical properties satisfactory for many uses.

7. Compositions containing 25 percent resin and 72.5 percent residue flour could be molded. However, the physical properties of the products were inferior and molding conditions were probably too critical for industrial use.