MICROFIBRILLATED CELLULOSE, A NEW CELLULOSE PRODUCT: PROPERTIES, USES, AND COMMERCIAL POTENTIAL

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SYNOPSIS

A new form of cellulose, which is expanded to a smooth gel when dispersed in polar liquids, is produced by a unique, rapid, physical treatment of wood cellulose pulps. A 2% suspension of microfibrillated cellulose (MFC) in water has thixotropic viscosity properties and is a stable gel on storage, or when subjected to freeze–thaw cycles. At this concentration, MFC is an excellent suspending medium for other solids and an emulsifying base for organic liquids. In laboratory tests, microfibrillated cellulose has been demonstrated to have wide utility in the preparation of foods such as low-calorie whipped toppings, cake frostings, salad dressings, gravies, and sauces. At 0.3% cellulose concentration in ground meats, MFC helps retain juices during cooking. Tests were also conducted in formulating paints, emulsions, and cosmetics and in the use of MFC as a binder for nonwoven textiles and as a mineral suspending agent. From economic studies, it is estimated that a 2% MFC dispersion can be produced for about 1.5¢/lb, total cost.

INTRODUCTION

Microfibrillated cellulose (MFC) is a low-cost, totally new form of cellulose where wood pulp fibers have been rapidly expanded in surface area and opened into their substructural microfibrils by mechanical action and heat. After repeated homogenization, a dilute dispersion of cellulose has the appearance and properties of a gel. Under high magnification, using an electron microscope, the microfibrils appear like a gossamer web or fabric having a very large surface area and increased accessibility to other materials.

The physical and chemical properties of MFC suggest a wide range of potential commercial uses. Research, reported in this and the preceding article [1], was

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carried out during a five-year period. Additional and different facets of physical and chemical studies are presented in this report, as is a summary of application research on uses in foods, cosmetics, paints, paper and nonwoven textiles, oil field services, and medicine.

EXPERIMENTAL

Preparation of Microfibrillated Cellulose

Cellulose raw materials. A wide variety of purified wood cellulose pulps was subjected to homogenization in this study. The dry analyses of three pulps, typical of ITT Rayonier pulping processes, are listed in Table I. Additional details regarding pulp analyses and dry cutting to reduce fiber length are given in the companion article [1].

Homogenization procedure. A small commercial homogenizer, model 100-KF3-8BS, manufactured by the Gaulin Corporation, was used to prepare 3- to 6-L batches of MFC products and MFC cohomogenized with vegetable oils, food ingredients, or other materials of interest. All wood pulps were precut to reduce fiber length to 0.6–0.7 mm. The homogenizer was provided with an 8-L reservoir and product recycle line so that a given volume of slurry could be passed through the homogenizer valve in a plug-flow manner and the number of passes through the machine could be estimated by measuring flow rate. All homogenization was carried out using a pressure of 55 MPa (8000 psi). Cooling was employed to maintain a product temperature in the range 70–80°C during homogenization, but higher temperatures are not harmful.

Pulp A was used to prepare a 2% MFC 12-pass product for most end-use tests. Pulp B was used in a comparison of the accessibility of MFC products homogenized in water, glycerin, and propylene glycol (Fig. 5). A 4-L batch of 2%, 12-pass product was prepared in each case.

TABLE I
Analysis of Wood Cellulose Raw Materials

	Pulp		
	A	B	C
	Source: Southern Pine		Western Hemlock
	Process: Sulfite	Prehydrolyzed Kraft	Sulfite
Grade	Paper	Rayon	Acetate
R_{10} (cellulose), %	88.5	95.6	95.1
S_{10}, %	11.5	4.4	4.9
S_{18}, %	9.3	2.9	2.9
ELB, %	93.4	89.8	95.0
Cuene Intrinsic Viscosity, dl/g	8.9	6.0	9.1

Preparation of Beaten Pulps for Hydrolysis Tests

Samples of wood cellulose B were used to prepare glassine-type pulps in water, glycerin, and propylene glycol media, employing a PFI mill under standard pulp testing conditions [2]. A 24.5-g sample of dry pulp was slurried in enough liquid to provide 245 g total weight. The mill was run to 10,000 revolutions. A sample of the beaten pulp was used for measuring Canadian Standard Freeness (CSF) [3]. In the case of the pulp slurries in glycerin or propylene glycol, these liquids were carefully exchanged with water prior to CSF measurement.

Physical Properties

Scanning electron micrography (Fig. 3) and determination of the water retention values of various MFC products (Fig. 4) were conducted as described previously [1].

The physical properties of cohomogenized MFC mixtures with other materials were compared in terms of visual observations of smoothness, gel or emulsion stability over a period of days or weeks, and by side-by-side tests using MFC formulations and commercial products.

Chemical Properties

Accessibility of MFC and Beaten Pulps to Mineral Acid Hydrolysis (Fig. 5)

Pulp B was subjected to homogenization and PFI mill beating in water, glycerin, and propylene glycol. Appropriate dry samples of each product were prepared by solvent exchange with acetone followed by vacuum drying. One-gram samples of each dry product were subjected to aqueous hydrolysis in 1 *N* hydrochloric acid at 60°C for 1, 2, 3, and 5 h. The cellulose residue remaining from these standard hydrolysis tests was then recovered by filtration, washing, and drying. The cupriethylenediamine intrinsic viscosity (Cuene I.V.) [1] was then determined. These values were converted to degree of polymerization (DP) by reference to standard tables. The calculation of percent degradation increase (% DI) was made using the equation

$$\% \text{ DI} = 100 \left(\frac{1}{\text{DP}_1} - \frac{1}{\text{DP}_0} \right)$$

where DP_0 is the initial DP of the starting material and DP_1 is the degree of polymerization of the cellulose sample after the HCl hydrolysis treatment. The term "percent degradation increase" [4, 5] represents the number of glucosidic linkages broken per 100 anhydroglucose units in a cellulose polymer. Thus, a value of 1, calculated with reference to pulp B, having an initial Cuene I.V. value of 6.0 dl/g and a DP_w of 1543, means that 15.43 linkages were broken when the MFC-modified polymer was subjected to acid hydrolysis.

Accessibility of MFC and Other Cellulosic Materials to Enzymatic Hydrolysis (Fig. 6)

Samples of never-dried pulp C were homogenized at 1% slurry solids using a Gaulin model 15M-8TA laboratory homogenizer [1]. MFC products receiving 5 and 10 passes through the homogenizer were prepared. A sample of the same pulp at 10% slurry solids was beaten to 12,500 revolutions in a PFI mill. These products were tested in a "never-dried" form in enzymatic hydrolysis.

A *Trichoderma viride* cellulase preparation having an activity of 4000 μ/g (Control No. 5482) was obtained from Nutritional Biochemicals Corporation. MFC and other cellulosic materials, corresponding to 0.5 g dry weight, or 50 mL 1% slurry, were placed in small flasks and buffered with 0.41 g sodium acetate and 0.30 g acetic acid. The cellulase (0.16 g) was then added and all samples were incubated at 37°C for 70 and 170 h. Filtrates were analyzed for glucose by the orcinol method [6].

End-Use Application Research

Fruit creams, dessert sauces, and ices were prepared by blending 2% MFC (12-pass) from pulp A with frozen concentrated fruit juices at a ratio of 3 : 1 on a volume basis. These creams were further converted to gelatin desserts or ices by blending unflavored gelatin (3.6 g) dissolved in 175 mL hot water with about 120 mL of the fruit cream and allowing the mixture to stand. These desserts could also be served as frozen ices.

Cream soups, sauces, and gravies were formulated from 2% MFC by flavoring with meat bouillon concentrates and cooking with, or adding to cooked vegetables, cereals, meats, cheeses, etc. A mild-flavored onion dip or spread was prepared by blending 4 L of 3% MFC with one package (135 g) of onion soup and dip mix. This composition was varied by adding spices, grated cheese, and chopped vegetables.

A pudding base and pudding desserts were prepared by adding 100 g of soybean oil to a 5-L batch of 2.6% MFC and passing the mixture one more time through the homogenizer at a pressure of 27.5 MPa. The product was then sweetened to taste and flavored with a variety of chocolate, vanilla, or fruit concentrates. Nonfat milk solids were also added to such desserts. (Synthetic sweeteners could be substituted for sugar to make low calorie products.)

Samples of the above food products were given taste and mouth-feel tests by a panel of laboratory employees. All were judged to be acceptable in comparison with commercial or home-style foods of the same type.

MFC was tested in many other end-use applications and was generally compatible or could be cohomogenized with a variety of liquid and solid materials to form stable suspensions or emulsions. Some of these applications for MFC are included in the discussion below. While much of the formulation testing was empirical and qualitative in nature, it was considered important in establishing the broad utility of MFC.

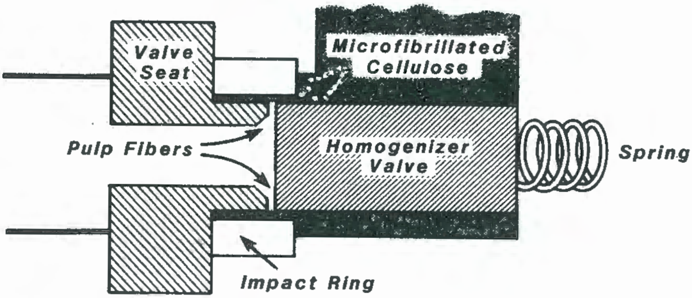

FIG. 1. Schematic representation of homogenizer action.

DISCUSSION

Preparation of Microfibrillated Cellulose

Figure 1 is a schematic representation of the mechanical action of a homogenizer valve on a slurry of pulp fibers. The reciprocating action of the valve, coupled with the high pressure drop and impact with the valve seat, results in cellulose fibrillation. MFC can be envisaged as being a superbeaten pulp, even though no amount of conventional beating results in the open fibril structure and degree of microfibrillation observed in an optimally homogenized product.

While water is the most convenient and cheapest liquid for preparing MFC

FIG. 2. The viscous gel appearance of MFC at 3% in water.

dispersions with exceptionally smooth characteristics (Fig. 2), any polar fluid may be used, and the degree of microfibrillation that is achieved will vary with the polarity and swelling properties of the chosen liquid. Satisfactory MFC dispersions have been prepared in glycerin, propylene glycol, dimethyl sulfoxide, dimethylformamide, and mixtures of these with water.

A wide range of purified wood celluloses may be employed in the MFC process. Pulps from the sulfite, sulfate, and prehydrolyzed kraft pulping processes yielded reasonably good results. However, the best results were obtained using selected pulps such as pulp A (Table I) produced by the sulfite pulping process.

MFC products were prepared routinely in the laboratory as 2% solids dispersions in water. At this solids content, a well-homogenized product had the consistency of mayonnaise and was an opaque, stable hydrogel that did not settle out or separate appreciably from the water phase during 18 months or more when stored at room temperature in a closed container. In trials using larger commercial homogenizers, it was demonstrated that MFC products could be prepared at solids contents as high as 6%. However, homogenization efficiency in terms of the physical properties of the product appears to favor processing in the 2–4% solids range.

Physical Properties

Figure 3 is a scanning electron micrograph of an MFC product from pulp C, after 20 passes of homogenization in a 1% water dispersion at a pressure of 55 MPa (8000 psi). At ×10,000 magnification, the predominant net-like structure of the product, after carbon dioxide critical point drying, contains microfibrils having diameters of 25–100 nm.

The large increase in the surface area of cellulose in MFC products, as illustrated in Figure 3, also leads to dramatic increases in water retention values. Wood pulps, as manufactured, have water retention values in the range of 50–90%.

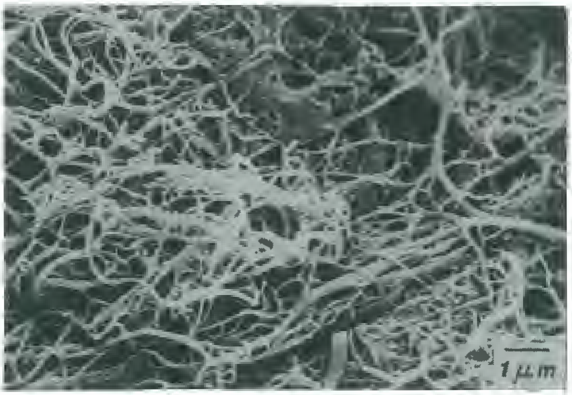

FIG. 3. Scanning electron micrograph of microfibrillated cellulose from pulp C at ×10,000 magnification.

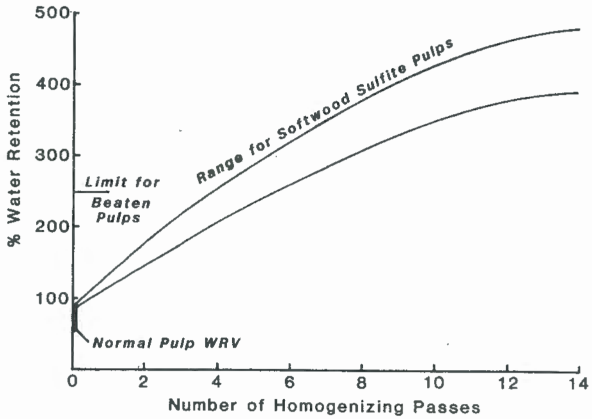

FIG. 4. Water retention of microfibrillated cellulose.

Water retention increases when a cellulose fiber is subjected to mechanical fibrillation as in conventional beating processes. The upper limit of water retention for pulp A, when beaten to a Canadian Standard Freeness (CSF) of 50, was 240%, while the MFC product from this pulp exhibited over 400% water retention under the same conditions of measurement (Fig. 4).

All highly swollen and fibrillated cellulose systems suffer some irretrievable loss of properties on drying, and MFC is no exception. MFC has been spray dried and freeze dried from water to produce a powdered solid product. Such products when redispersed in water to form the hydrogels displayed only 80–85% of their original properties. Careful solvent exchange resulted in dry MFC products that retained useful properties but would be too expensive for commercial consideration.

Chemical Properties

The microfibrillation process using the Gaulin-type homogenizers results in surprisingly minor degradation to the cellulose polymer. For example, a pulp with a starting Cuene I.V. of 8.66 dL/g, corresponding to a DP_w of 2501 may be converted to MFC having an I.V. of 7.86 dL/g or a DP_w of 2202.

The physical expansion of the original cellulose fibers undoubtedly contributes to increased chemical accessibility. This property of MFC was investigated by means of several reactions as described previously [1]. It was of particular interest to determine the comparative accessibility properties of MFC products and highly beaten pulps prepared in different homogenizing liquids, all from the same cellulose raw material. In Figure 5, hydrolysis rates for MFC prepared in water, glycerin, and propylene glycol are compared with rates for highly beaten pulps (PFI mill tests) in these same media. The MFC materials were hydrolyzed from 2 to 3.5 times faster than the beaten pulps, demonstrating that the MFC process yields higher accessibility, regardless of the liquid medium employed.

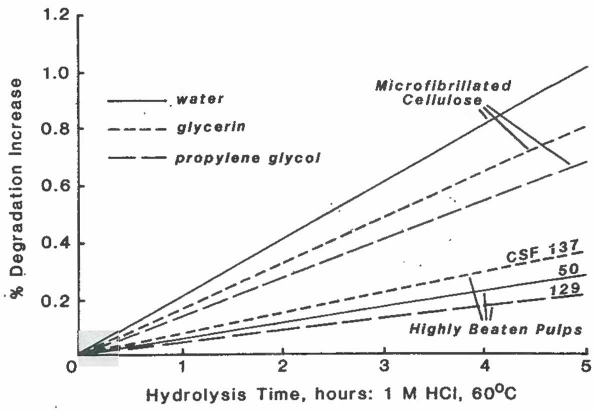

FIG. 5. Relative hydrolysis rates of microfibrillated cellulose and highly beaten pulps.

Figure 6 is an illustration of the increased accessibility of MFC products prepared from pulp C to hydrolysis by cellulase enzymes, compared with the rates of hydrolysis of the unmodified pulp, a highly beaten product from the same pulp and a sample of Avicel. A 10-pass MFC from pulp C when subjected to a standard hydrolysis reaction yielded about 320 mg glucose per gram cellulose substrate, while the yield of glucose from the beaten pulp leveled off at 180 mg/g, or about 56% of the glucose produced from the MFC product. In a previously described experiment [1], a five-pass MFC product prepared from a different western hemlock pulp (for rayon manufacture) yielded 170 mg/g glucose in 216 h, compared with about 218 mg/g in 170 h for the five-pass MFC used in this test.

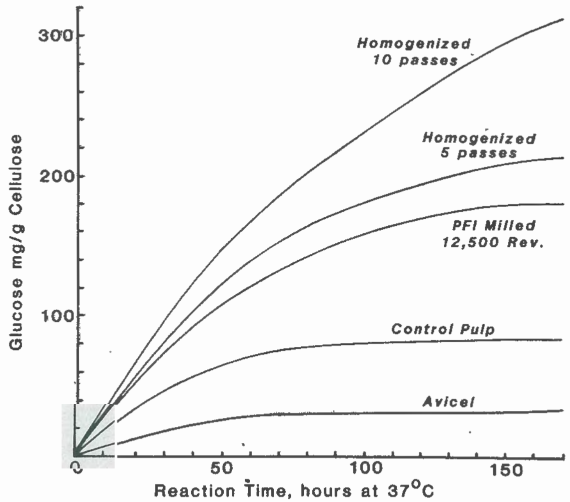

FIG. 6. Cellulase accessibility of a western hemlock sulfite cellulose.

End-Use Applications

Microfibrillated cellulose dispersions are excellent thickeners and yield viscous mixtures that exhibit thixotropic properties. In addition to controlling flow, the high thixotropy is useful in dispersing and suspending other solid materials. MFC preparations also have the unique property of stabilizing emulsions of organic liquids in water without the use of surfactants. At low shear rates, the viscosities of 2% aqueous MFC products are only moderately affected by increased temperature in the range 25–95°C. At high shear rates (1000 s^{-1}), advantageous flow properties and low viscosity are evident as temperature is increased to 90°C [1]. Properly formulated MFC products can also withstand repeated freeze–thaw cycles without damage or separation.

The unique viscosity properties of MFC were emphasized by measurements made at ITT Continental Baking Company during a joint program aimed at developing a low-calorie whipped topping. The prepared material did not "sag" or tend to "puddle" on standing, even at high temperatures. This behavior was measured quantitatively using a Contraves viscometer and found to have a "yield point" of about 14 dyn/cm^2 between 70 and 160°F. The results obtained by Ms. Cheryl Weiss are given in Table II. The property of having a relatively constant yield point over such a wide temperature range is a unique asset of MFC and helps to account for some of its outstanding performance behavior in suspending solids for drilling muds and paint formulations, and in whipped topping, frostings, salad dressings, and other food uses.

Food Products

Since cellulose is not appreciably digested in humans, the thickening properties of MFC were of immediate consideration for preparing noncaloric or low-calorie

TABLE II
Contraves Viscometer Behavior of MFC

2% Sulfite pulp
CONTRAVES VISCOMETER
MEASURING SYSTEM "C"

Temperature (°F.)	Av. Visc. (Casson) (cp)	Yield (Dynes/cm^2)
40	226.9	81.4
50	376.6	37.1
60	459.0	20.1
70	449.8	14.6
80	403.6	13.2
90	336.7	14.7
100	297.7	14.1
110	258.9	14.3
120	226.8	14.4
130	202.2	15.0
140	210.3	12.0
150	206.5	11.0
160	170.7	16.2

FIG. 7. No-calorie salad dressing using 2% MFC.

foods. Salad dressings of this type are easily prepared by adding the flavoring ingredients to a 2% MFC dispersion in water (Fig. 7). Such dressings have excellent organoleptic response and are stable for six months or more. Similarly, 2% MFC mixed with a small amount of vegetable oil and synthetic sweetener provides a tasty low-calorie frosting or topping for desserts (Fig. 8). A number of whipped toppings were prepared and were subjected to repeated freeze–thaw cycles without sagging on standing.

MFC gravy formulations for pouch-packaged stews or meat dinners performed well under hot conditions. MFC was also excellent for thickening hot soups, chowders, and sauces of all types. In these applications, 0.75% cellulose solids (as MFC) in gravies or soups gave good results.

The addition of MFC to ground meats and meat emulsions gave exceptional results. As little as 0.3% cellulose added to hamburger meat prevented excessive

FIG. 8. Cake-frosted with no-calorie vanilla-flavored synthetic sweetened MFC.

FIG. 9. Juice retention in ground beef (burger on the right has 0.3% MFC added).

moisture and fat loss during frying or broiling, resulting in a plumper, juicier, and tastier meat (Fig. 9).

Cosmetics

While much is claimed for special oils and emollients in the preparation of cosmetic skin creams, the main skin softening ingredient is really glycerin, and the expensive oils serve mostly to help form the thick emulsion cream base. By using MFC prepared in glycerin or propylene glycol, it is possible to make a quality cream base with little or no expensive oil which will adequately soften skin at significantly reduced costs. The excellent thickening properties of MFC in water allow it to serve as a bodying agent for shampoos. Aqueous 2% MFC dispersions can also be applied to skin and dried to a film with a hot-air dryer. This film is then peeled from the skin taking with it the deep-seated dirt from the pores. If used in toothpaste formulations, the MFC not only serves as a bodying agent but the dispersed cellulose serves as a cleaning agent.

Paints

There are several properties of MFC that can be advantageously employed in the paint industry. As an inexpensive highly thixotropic thickener, MFC is useful in formulating water-based ceiling and wall paints. In addition to being a thickener, MFC is also a film former and an opacifying agent. A cinder block panel previously finished with blue interior paint was repainted with 2% MFC. On drying, the MFC film adhered tenaciously to the previous paint and could not be removed by wet scrubbing. In laboratory paint formulations, it was possible to replace significant quantities of titanium dioxide pigment with the opacifying effect of cellulose in MFC. MFC was found to be a good suspendng agent for pigments.

Paper and Nonwoven Textiles

When used in a paper-coating formulation, MFC appeared to improve opacity and surface uniformity. MFC was used as a binder for an air-laid rayon fiber nonwoven fabric. Potential use in flushable sanitary products was indicated.

Oil Field Services

The rheological properties of MFC are particularly advantageous for dispersing and suspending solids as required in preparing drilling muds and packer fluids in oil field operations. A suspension of 10% w/w fine sand in 2% MFC was observed for three months and was stable without settling even when heated to 100°C. In another test, a layer of fine sand was placed on top of 2% MFC and after three months had not penetrated the MFC material significantly. Ground coal was also suspended in MFC, suggesting that MFC might be used as an aid in coal slurry or mineral slurry pumping through pipelines over long distances.

Medical

Finally, use of MFC suspensions as carriers for various medications is obvious. One potential use worth mentioning is the use of MFC medicated gel as a barrier coating for burn patients. As the gel dries, it forms a protective medicated film and the numerous cellulose fibrils enhance new skin growth.

Economic Considerations

The shipping of a cellulose product at 2–4% solids would be uneconomical. Therefore, a commercial MFC operation should be carried out on-site where this material is incorporated into a final product. Commercial machinery for production of MFC is already available and of a quality suitable for food grade products. With such equipment, a 2% MFC may be prepared at rates of a few liters to as high as 200 L per min (1.6 to 55 gpm). The total cost of preparing a 2% MFC product, including capital investment, production and pulp costs have been estimated as 1.5¢ per pound. In many applications, all ingredients can be added directly to the MFC product and cohomogenized to provide emulsification or dispersion as desired.

At present, ITT Rayonier is marketing MFC technology and licensing the process to companies interested in various industrial applications. Process and end-use patents have been applied for in the United States and many other countries.

CONCLUSIONS

Microfibrillated cellulose, because of its high surface area, unique yield value behavior, and gel-like properties in dilute aqueous or polar liquid dispersions, is an excellent suspending and emulsification medium and carrier for other solids and organic liquids. It is predicted that wide commercial utility will be found in food, cosmetic, and medicinal products. Industrial uses as a suspending agent, film-forming or fiber-bonding agent, and general thickener are also forecast. Due to the process requirement that MFC be produced in relatively dilute liquid dispersions, it is likely that commercial manufacture will be carried out on-site by companies interested in MFC formulated or compounded products.

Note added in proof: Since this article was submitted in mid-1982 three U.S. patents on MFC have been issued in the name of A. F. Turbak, F. W. Snyder, and K. R. Sandberg; all are assigned to ITT, Rayonier Division. The patents are U.S. 4341807, July 27, 1982; U.S. 4374702, February 22, 1983; and U.S. 4378381, March 29, 1983.

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