Synthesis and Application of Methylcellulose Extracted from Waste Newspaper in CPV-ARI Portland Cement Mortars

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ABSTRACT: Cellulose extracted from waste newspaper was methylated using dimethylsulfate to produce methylcellulose with degree of substitution of 1.46 ± 0.06. This material was characterized by FTIR and DSC. An aqueous dispersion of methylcellulose was used to produce mortars of Portland cement (CPV-ARI). The results showed an increase on the consistency index with the production of a system that presented good workability, homogeneity, and high viscosity, which was corroborated by the tacky aspect of the produced mixture. Hardened mortar presented an increase in the potential resistance to traction adherence when compared to the reference mortar. Those characteristics indicate that this material could be used in situations that need good workability, increasing on viscosity and adhesive properties, such as in tile installation, covering, and finishing. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1380–1385, 2010

Key words: additives; water-soluble polymers; renewable resources; recycling; biodegradable

INTRODUCTION

Brazilian paper and cellulose industry aggregates about 220 companies that produce around 12.8 million metric tons of cellulose and 9.2 million metric tons of paper each year. This production corresponds to 1.4% of Brazilian gross domestic product and makes Brazil the seventh major producer of cellulose–leader in the production of short fiber cellulose and 11th in the production of paper.[1] Brazilian paper and cellulose products are manufactured exclusively from wood of forests planted on degraded areas, what reduces the cut of native trees. The forestal base of this country, with 1.7 million hectares of planted area (75% eucalyptus, 24% pine, and 1% of other woods),[1,2] constitutes one of the major comparative advantages for the local companies against their global competitors.

Brazilian consumption of recyclable paper in 2007 was around 3.6 million metric tons, 160 thousand metric tons of which corresponds to newsprint. Brazilian newsprint recycling rate is 44.5%. Nowadays, the search for alternatives, such as polymer recycling for producing new materials, for preserving the environment and aggregating value to industrial and urban residues is increasing significantly. In this way, the Group of Polymer Recycling of the Universidade Federal de Uberlândia (GRP-UFU) has been demonstrating the viability of chemically recycling cellulose from renewable sources, e.g., sugarcane bagasse, for producing derivatives such as cellulose acetate and methylcellulose.[3–11]

Methylcellulose (MC) is usually synthesized through heterogeneous route in alkaline medium since cellulose is insoluble in water and in most of the common organic solvents due to its high crystallinity and great number of hydrogen bonds.[7,11,12] Therefore, MC is a heterogeneous polymer, consisting on hydrophobic high substituted regions and hydrophilic low substituted regions. Commercial MC with degree of substitution (D.S.) between 1.2 and 2.4 is water soluble and exhibits thermo-reversible sol–gel transition in aqueous solutions.[3,6,7,12–14] Water-soluble MC is used in applications such as auxiliary agent on oil recovery, alternative matrices for drug delivery systems, in blends with chitosan to produce films and as admixture for mortars and concrete.[6,11,13,15–17]

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Cellulose ethers are semi-synthetic cellulose derivatives, which are commercially used in civil construction as cellulose ethers mixtures (some products are powdered mixtures of MC and hydroxypropylmethylcellulose) known as Methocel®. Several other products based in cellulose derivatives can be found in liquid based formulations.[18] Commercial MC is produced from wood cellulose. The Group of Polymer Recycling (GRP-UFU) has been studying the use of MC on civil engineering[6] for replacing commercial admixtures by alternative raw materials such as sugarcane bagasse and waste newspaper. Some water-soluble polymers, such as cellulose ethers, polyvinyl alcohol, and polyethylene oxides are used as viscosity-enhancing admixtures (VEA).[18,19] The use of this kind of polymer increases water viscosity enhancing the cohesion and stability of cement based systems, improving properties of fresh mixtures.[18,20]

Those admixtures reduce the separation of concrete heterogeneous compounds during transport and storage, making them stable while fresh. For resulting in high viscosity systems, with good adherence, and water retention, cellulose derivatives are frequently used to produce concrete for underwater repair of marine and hydraulic structures, special mortars for cement grouts, repair, and adhesive mortars for tile settlement.[18,21,22]

Mortars that are commercially available for tile setting consist on a binder and mineral fillers and are usually modified with cellulose ethers (CE) and redispersible polymer powder (RP). These additives fulfill different tasks during the transition from fresh to hardened mortar, e.g., thickening, air entrainment, and water retention to establish the proper workability properties.[18,21,23–25] The most typical binder is ordinary Portland cement used in combination with different types of mineral fillers. The simultaneous existence of binder and polymers causes the interaction of two fundamental processes: polymer film formation and cement hydration.[23–25]

Cellulose ethers act by avoiding excessive water loss to the substrate, what can cause failure on the adherence mechanism. CE have also been used to produce self-compacting mortars[19,20,22] since they avoid the segregation of compounds in the mixture. As the lubrication of the cementitious system increases, there is less friction of the aggregate what improves the homogeneity and fluidity of the system.

In this work, MC from waste newspaper (NMC) was used on mortar production, what has not been previously described in the literature. Cellulose was extracted from waste newspaper and dimethyl sulfate was used as methylating agent. NMC had its degree of substitution determined through the chemical route and was also characterized by Fourier Transformed Infrared spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC). The application of NMC on civil engineering was evaluated by the measurement of the consistency index of fresh mortars and by the determination of the bond tensile strength after 28 days cure.

EXPERIMENTAL

Delignification of newspaper

The delignification was carried out as previously described[3,7,8,11]: 4 g of shredded newspaper was mixed with 76.00 mL water. After 24 h, the mixture was filtered and 76.00 mL NaOH (0.25 mol L^{-1}) was added to the newspaper. After 18 h, the mixture was filtered again, and the newspaper was put into reflux with three successive portions of a 20% v/v mixture of nitric acid and ethanol, which was changed after each hour. After the reflux, the mixture was filtered and then washed with distilled water until the filtrate became uncolored. The newspaper was dried at 105°C for 180 min and then ground.

Synthesis of methylcellulose

Extracted cellulose (1.0 g) was mercerized using NaOH solution (50%) for 1 h at room temperature. The excess of NaOH solution was removed and acetone (9.0 mL) was added as solvent. Dimethyl sulfate (3.0 mL) was added drop-wise, and the reaction was carried out at 50°C. After each 1 h reaction, the system was filtered and fresh reagents were added, keeping the same proportion. The same procedure was repeated for 5 h of reaction. At the end, the material was neutralized using acetic acid (10%), filtered, washed with acetone, and finally oven dried at 50°C for 6 h.

Determination of the degree of substitution (DS)

The determination of the methoxyl group content was made through the modified procedure of Viebock and Schawappach, described by Saliba et al.[26] Figure 1 shows a scheme of the system used in this determination. A mixture containing 0.10 g of phenol, 1.20 g of potassium iodide, 2.00 mL of orthophosphoric acid, and 50.00 mg NMC was added to the reaction flask [Fig. 1(A)].

The washing tube [Fig. 1(B)] was filled with a saturated solution of sodium bicarbonate (3.00 mL). A solution containing 20% sodium acetate in acetic acid (1.50 mL) was added to the first absorption tube [Fig. 1(C)]. Ten drops of bromine were added to this solution under light stirring, and then this tube was filled up with the 20% sodium acetate solution. This solution was then distributed among the three absorption tubes by inclining the system. The reaction was maintained at 150°C for 1 h in an inert atmosphere produced by nitrogen flow, which drags the formed

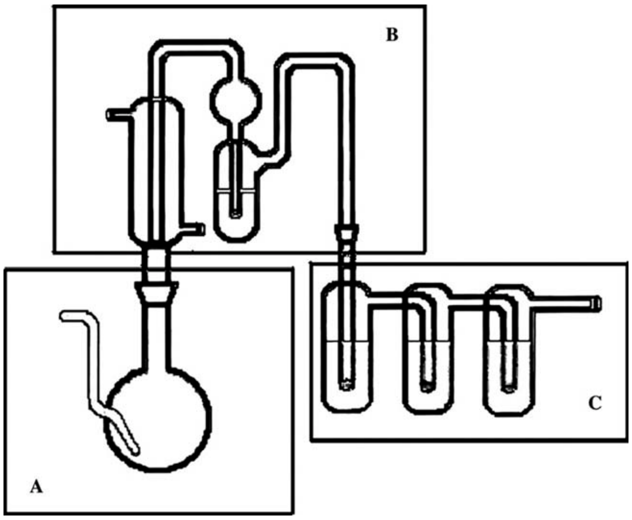

Figure 1 System used in methoxyl groups determination (A: Reaction flask; B: Washing tube; C: Absorption tube).

methyl iodide. After this period, the content of the absorption flasks was transferred to an Erlenmeyer containing sodium acetate (1.50 g) and distilled water (60.00 mL). To remove the excess of bromine of the absorption solution, five drops of formic acid were added to the solution, under stirring. Soon after, a solution of 10% sulfuric acid (5 mL) and potassium iodine (0.1 g) was added; it was mixed and kept still for 10 min, in the dark. Finally, the formed iodine is titrated by a standard solution of sodium thiosulphate using a starch solution as indicator.

Preparation of methylcellulose suspension

Due to the unusual behavior of MC water solutions, the suspension used in the preparation of the mortar was produced in two stages: (i) mixing of MC with water at 80°C to accelerate the process of water accessibility to the polymer; and (ii) the temperature of the solution was cooled down to 4°C to increase the solubility of the polymer, since in this temperature the water molecules are organized in enclosed structures that surround the hydrophobic groups on the polymeric chains, weakening the association between them.[27] The procedure was summarized below: A system containing methylcellulose (3.00 g) and water (100.00 mL) was heated for 1 h at 80°C under stirring. Then the suspension was cooled down to room temperature and then put on a refrigerator for 24 h at 4°C. This amount of the polymer was used to maintain the polymer/cement ratio in 0.60% (w/w).

Characterization of the cellulose extracted and methylcellulose by FTIR

The experiments were carried out using a Shimadzu IRPrestige-21 equipment with step size of 4 cm^{-1}. Twenty scans were collected using KBr pellets [1/100 (w/w)].

Differential scanning calorimetry

Differential scanning calorimetry (DSC) experiments were carried out using a Rheometric Scientific DSC-SP equipment. The tests performed at a heating rate of 20°C min^{-1}, under nitrogen flow (20 cm^3 min^{-1}), from 25 to 400°C.

Mortar preparation

Commercial Portland cement (CPV-ARI, Brazilian norm NBR 5733) and medium sand were used for mortar preparation. Polymer/cement ratio (p/c) was 0.60%, water/cement ratio (w/c) was 0.70, and sand/cement ratio (s/c) was 3.93. An aqueous suspension of the polymer was previously prepared and added to the cement/sand/water mixture. A reference mortar was prepared without polymer addition.

Consistency index and adherence essays

The consistency of fresh mortar was evaluated using a slump table, according to Brazilian norm NBR 7215.

The fresh mortar is placed on a slump table, which is spun thirty times, then two orthogonal diameters are collected and the consistency index value is given by the arithmetic average.

The bond tensile strength test was carried out according to the Brazilian norm NBR 15,258, which specifies that the mortar must be placed onto a substrate and after normal cure (28 days), the test is carried out by measuring the strength applied to take the mortar off the substrate.

RESULTS AND DISCUSSION

Synthesis and characterization

NMC was produced from the reaction between alkali-cellulose and dimethyl sulfate. The obtained material was a white powder with good dispersion in water and D.S. of 1.46 $\pm$ 0.06. Properties of MC solutions are consequence of both of the interactions between the methoxyl groups and the strong hydrogen bonds between the hydroxyl groups.[7,11,14] In spite of the D.S. being in the range for water solubility, the produced polymer was not completely water-soluble. That is due to the physicochemical properties of the polymer not being dependent only on its degree of substitution, but also on the distribution of methoxyl groups on the anhydroglucose units (AGU) and along the polymeric chain.[14] Therefore, NMC described in this work probably presents a nonuniform substitution.

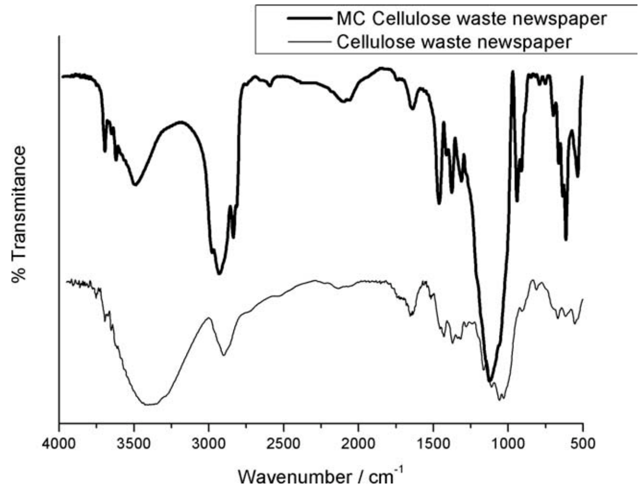

Figure 2 FTIR spectra of methylcellulose and cellulose from newspaper.

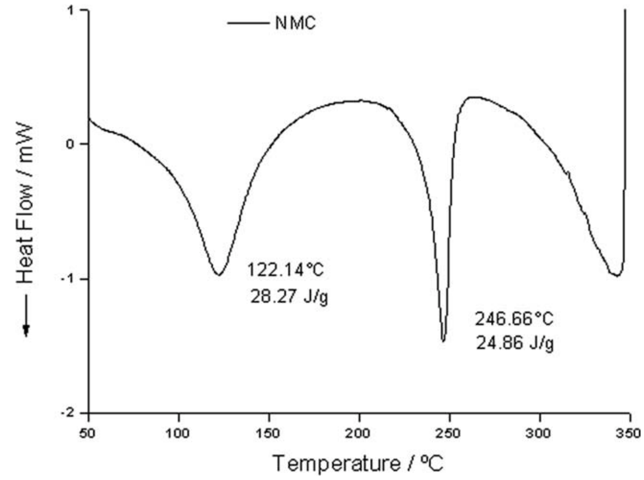

Figure 3 DSC thermogram, first scan, of methylcellulose produced from waste newspaper.

Figure 2 shows the infrared spectra of methylcellulose and cellulose extracted from newspaper. The substitution of the methoxyl groups is confirmed by the inversion of the bands around 3500 cm^{-1} (O—H) and 2900 cm^{-1} (C—H). The presence of an intense band around 1100 cm^{-1} indicates the presence of C—O—C bonds, characteristics of cellulosic ethers.[7]

MC spectra usually present bands at 1460, 1380, and 1320 cm^{-1} attributed to C—H stretching of CH_2 and CH_3 groups. In some methylated derivatives, the region between 1500 and 1200 cm^{-1} is not well defined, what is characteristic of a more amorphous pattern and of a possible heterogeneous distribution of the substituent groups on the polymeric chains.[7,28] As the mentioned region is well defined in the infrared spectrum shown in Figure 2, this indicates a more crystalline pattern than other methylated derivatives.[7,11]

DSC thermogram of methylcellulose, Figure 3, shows an endotherm around 122°C, attributed to the dehydration of the material. This behavior is typical of cellulosic materials, due to the interactions between water and the nonsubstituted hydroxyl groups. It is also observed an endotherm around 250°C due to the fusion of the material. As nonmodified cellulose degrades before melting, the endotherm of fusion shown in Figure 3 is another confirmation of the chemical modification of cellulose. It is also noteworthy that: (i) the endotherm of fusion is relatively narrow, what indicates the homogeneity on the crystal size distribution and (ii) the value of the enthalpy of fusion (24.86 J/g) is the highest ever registered for this derivative when produced from alternative sources.[7,11]

Application in civil engineering

Cellulose ethers are typically used as additives in special mortars for tile setting, coverings, and finishing.[18,19,22,29] These additives are hydroxyalquilated and methylated cellulose derivatives.[29]

These products present properties that improve the lubrication between the disperse cement particles, resulting in a fluid, homogeneous mortar. The addition of aqueous suspension of methylcelluloses improves the lubrication of the system due to interactions of polymer with water molecules, improving the dispersion of the components of the mortar and facilitating settlement,[18] which can be observed by an increasing on the Consistency Index (CI). It also allows an increase in the viscosity of the fresh mortar when at rest, improving the adhesion to the substrate. That is due to the substitution of some hydroxyl groups by methoxyl groups in the production of MC, what increases the capacity of the residual hydroxyl groups to make hydrogen bonds with water molecules,[7,11,12] it also changes the rheological properties of the suspension since the presence of the methoxyl groups also increase the viscosity of this kind of mixture.

The methycellulose was added to the mortar with a polymer/cement (p/c) dosage of 0.6%. As reported by Chung and coworkers,[30–32] methylcellulose was used with (p/c) ratio between 0.2 and 0.8%, as an admixture to improve the adhesive properties of cementitious matrices with carbon fibers and steel. It was observed an increase of adherence of matrix and fibers for (p/c) dosage of 0.4%. In another study, Chung and coworkers[13] observed an

TABLE I
Results of the Consistency Index and Bond Tensile Strength

Samples	CI (mm)	Resistance (MPa)
R	241.15 ± 2.43	0.65 ± 0.16
NMC	309.40 ± 3.26	1.08 ± 0.06

Figure 4 (A) Mortar without polymer (reference) and (B) mortar containing polymer (NMC).

increase in the values of tensile strength by increasing p/c dosage, however, an opposite effect was observed for compressive strength. Considering these aspects, the adequate dosage of methylcellulose to be applied should allow an improvement in a desired property (as adhesion and consistency index) without hampering other important properties (tensile strength, compressive strength) of the system. In this case, the 0.6% dosage was chosen for being in the range (0.4–0.8%) where the best results of application were observed by Fu and Chung.[13]

The consistency index (CI) of fresh mortars prepared with NMC was measured to evaluate their workability. The adhesive capacity of these mortars was evaluated by essays of bond tensile strength. Results are shown in Table I for the reference mortar (R) and for the mortar containing NMC.

It is observed an increase of 22.06% on CI for the MC mortar in relation to the reference. This modification is expected since the polymer increases the lubrication of the cement system. This is confirmed during the mixture of the mortar components where a fluid, homogeneous mixture is observed. The visual differences between the two mortars (R and NMC) after the mixture can be observed in Figure 4.

It can also be observed that after the CI essay the mortar presents a tacky, cohesive, and homogeneous aspect when MC is added to it (Fig. 5). The observed behavior is typical of cement systems with polymers that increase viscosity, such as cellulose ethers that present thixotropic nature. This tacky aspect presented by the mixture is an important property for tile setting, since one of the key properties for tacky mortars is its open time, which is defined as the time during which tiles may be applied to the mortar surface and achieve adequate adhesion (i.e., the time during which the mortar surface remains "tacky" to the touch).[20]

The mortar with NMC presented an increase on bond tensile strength of 39.81% in relation to the reference. This result shows the alteration of the characteristics of the mortar modified with polymer also in the hardened state. These modifications, also observed in the fresh state, are the result of the improving in the dispersion and homogenization process of the mixture what frequently leads to an improve in the mechanical properties.

The bond tensile strength value obtained for the mortar modified with polymer was 1.08 MPa and is higher than the values found for the classification of

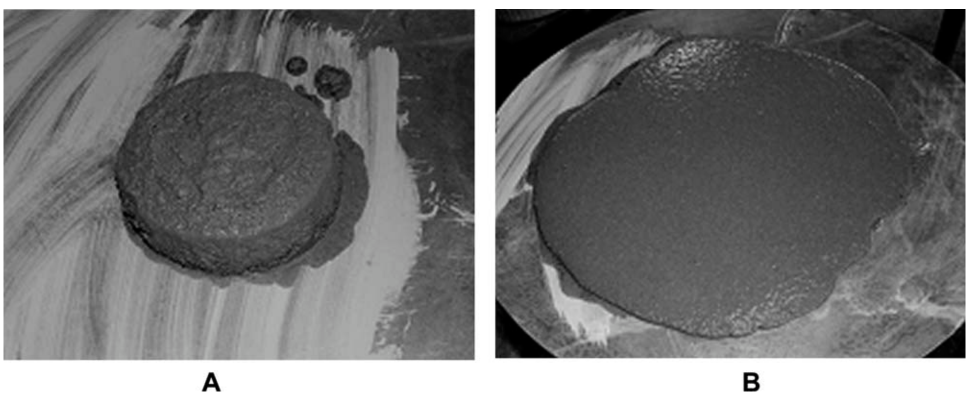

Figure 5 Mortar with polymer (A) before essay and (B) after essay.

mortars for tile setting and covering. Among those, the mortar with best performance presents resistance of adherence higher or equal to 0.3 MPa; and presents performance similar to tacky mortars of high resistance, whose values of bond tensile strength are higher or equal to 1.0 MPa.

The dosage of cellulosic derivatives used on the mortar and concrete preparation depends on the kind of polymer, commercial formulation of the product, and desired application. Values found on the literature vary from 0.05 to 1.2% in relation to the cement weight. It is important to emphasize that the polymer dosage used in this work was 0.6%, presenting performance equal or superior to the predicted to some commercial materials such as Super Cimentcola® Quartzolit for which the bond tensile strength after normal cure is 0.8 MPa. That shows that the derivative produced from the heterogeneous methylation using DMS as methylating agent (more accessible than methyl chloride or methyl iodine) and newspaper cellulose as cellulosic source is a promising additive for applications in civil engineering.

CONCLUSIONS

It was possible to produce methylcellulose from recycled newspaper, aggregating value to this important urban residue. Based on the results of the essays of plastic consistency and bond tensile strength, the produced polymer presented favorable properties for being used in civil construction as VEA. Results indicated improving, not only on the consistency index, but also on the bond tensile strength, for normal cure, in relation to the mortar without methylcellulose. These properties are important on using this system, particularly considering its use in special mortars for tile setting and coverings.

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