Supporting information: *RSC Advances*

Cellulose-based spreadable new thixo gels: Synthesis and their characterization

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ESI1. Materials and Methods

Materials

Isopropyl alcohol, methanol, sodium hydroxide and mono-chloroacetic acid (MCA) were of LR grade and were purchased from S. D. Fine Chemicals Ltd. Mumbai, India. *m*-Aminobenzoic acid (MABA; AR grade) and *p*-aminobenzoic acid (PABA; AR grade) were purchased from M/s Sisco Research Laboratories Pvt. Ltd., Mumbai. 1-ethyl-[3-(dimethylamino) propyl]-3-ethylcarbodiimide hydrochloride (EDC) was purchased from Spectrochem Pvt. Ltd, Mumbai, India. *N*-Hydroxysuccinimide (NHS), 2-[*N*-morpholino]-ethanesulfonic acid (MES) buffer and 2,4,6-trinitrobenzene sulfonic acid (TNBS), 1,1-diphenyl-2-picryl hydrazyl (DPPH) were purchased from M/s. Sigma-Aldrich, USA.

Synthesis of Carboxymethyl cellulose(CMC)

The α-cellulose was converted to CMC in two steps, alkalization and etherification of cellulose under heterogeneous conditions-. In alkalization pre-treatment, 1g of cellulose (6 mmol AGU – anhydroglucose unit) was added to 30 ml of isopropyl alcohol (IPA) to which a 20% aqueous sodium hydroxide (3.24 mol/AGU) was added drop-wise with stirring at 30ºC. After alkali treatment, etherification reaction was carried out by adding monochloroacetic acid (2.05 mol/AGU; 20% in IPA) in the reaction mixture was heated up to 55ºC under microwave irradiation for 15 min. The resultant slurry was cooled down to room temperature, 70% methanol was added to the mixture followed by neutralization with 90% of acetic acid, and then it was filtered. CMC was purified by washing with 70% ethanol (10 v/w × 5) to remove the undesired by-product. Then the CMC was filtered and dried at 60ºC in an oven for 24 h.

The degree of substitution for CMC was determined by the standard method (ASTM, 2005). CMC sample (0.25 g) was dissolved in a mixture of 25 ml of water and 25 ml of 0.1M NaOH solution. The mixture was titrated with 0.1N HCl using phenolphthalein as an indicator until the color changed from dark pink to colorless. To calculate the degree of substitution, the equation (1) was used.

$$DS_{CMC} = 0.162 \times A / 1-(0.058 \times A) \qquad \ldots\ldots\ldots (1)$$

Where, A = milli-equivalents of consumed acid per gram of specimen, 162 is the molecular weight of the anhydrous glucose unit and 58 is the net increment in the anhydrous glucose unit for every substituted carboxymethyl group.

Synthesis of CMC-aminobenzoic acids conjugate

In optimization studies 68-205 mg (0.5–1.5 mmol) of each of MABA and PABA were added to a 1 % (w/v) solution of CMC (20 ml, 162 mg (1.00 mmol)) in 0.1 M MES buffer at pH 6.0, in separate experiments. The reaction mixture was stirred at room temperature for 10 min to facilitate formation of a homogeneous dispersion of the aminobenzoic acid in the reaction mixture. This was followed by the addition of 288 mg (2.5 mmol) of NHS and 790 mg (4.12 mmol) of EDC, having calculated the ratios of reagents considering an estimated 80% molar modification of the number of carboxylic groups of CMC repeating unit would occur. After 12 h of stirring at room temperature, the resulting mixture was dialyzed against distilled water (Mw cutoff ~1200), which was replaced thrice a day with fresh water for 2 days. Finally, the modified CMC was obtained by lyophilization of the dialyzate.

ESI2. Characterizations

^{13}C NMR spectra were recorded on a Bruker Avance-II 500 (Ultra shield) Spectrometer, Switzerland, at 125 MHz. Samples were dissolved in D_2O (50 mg/ml), and the spectra were recorded with 2000 accumulations, a pulse duration of 9.40 μs, an acquisition time of 1.048 s, and a relaxation delay of 6 μs using DMSO-d_6 (ca. δ 39.4) as

internal standards. FTIR spectra were recorded on a Perkin-Elmer GX FTIR (USA) machine using KBr pellets (2.0 mg sample per 200 mg of KBr). The molar mass distribution (average molecular mass, Mz; number-average molecular mass, Mn and polydispersity index, PDI of 500 ppm solution in water at 45°C) were determined by size exclusion chromatography or gel permeable chromatography (SEC/GPC, Waters Alliance HPLC, on Waters 2695 separation modules and a Waters 2414 refractive index detector, USA) using 0.1M $NaNO_3$ as a mobile phase (ionic strength 0.1; spH~7.0). The UV-vis absorption spectra of the samples were recorded on a Varian CARY 500 UV-VIS-NIR spectrophotometer. Thermal behavior of cellulose samples was carried out by thermogravimetric analysis on a Mettler Toledo TGA system (Switzerland), using a temperature program from 30°C to 750°C at a heating rate of 10°C/min in a nitrogen atmosphere. Differential scanning calorimetric (DSC) measurements were done on a Mettler Toledo DSC822 equipment (Switzerland), using a heating rate 2°C/min in the temperature range −20°C to 25°C, and 10°C/min in the temperature range 30°C to 500°C in separate experiments. X-ray diffraction patterns were recorded on a Philips X'pert MPD X-ray powder diffractometer. The Cu Kα radiation was used (λ = 1.54 Å) generated at a voltage of 40 kV and current of 30 mA, with a scan speed of 3°/min having set the angle 2ϑ between 2° and 60°. Scanning electron micrograph (SEM) of each sample was recorded on a Carl-Zeiss Leo VP 1430 operating at an accelerating voltage 20 kV and magnification 252X 286X to 306X and 8 kX, the powdered samples were mounted on aluminum stubs and coated with gold under vacuum.

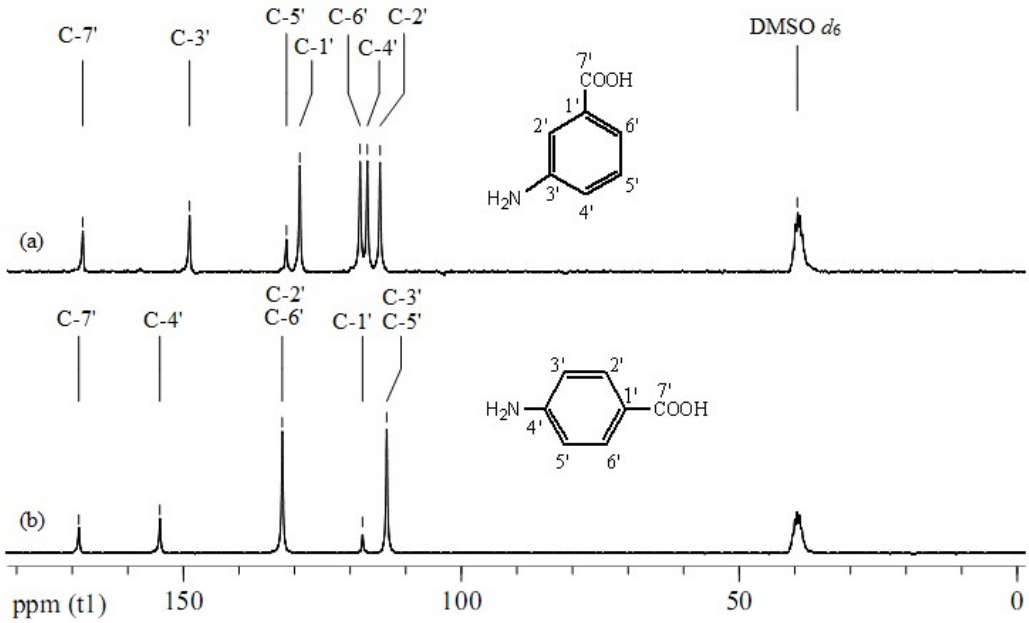

Fig. S1 ^{13}C NMR spectra of (a) MABA and (b) PABA

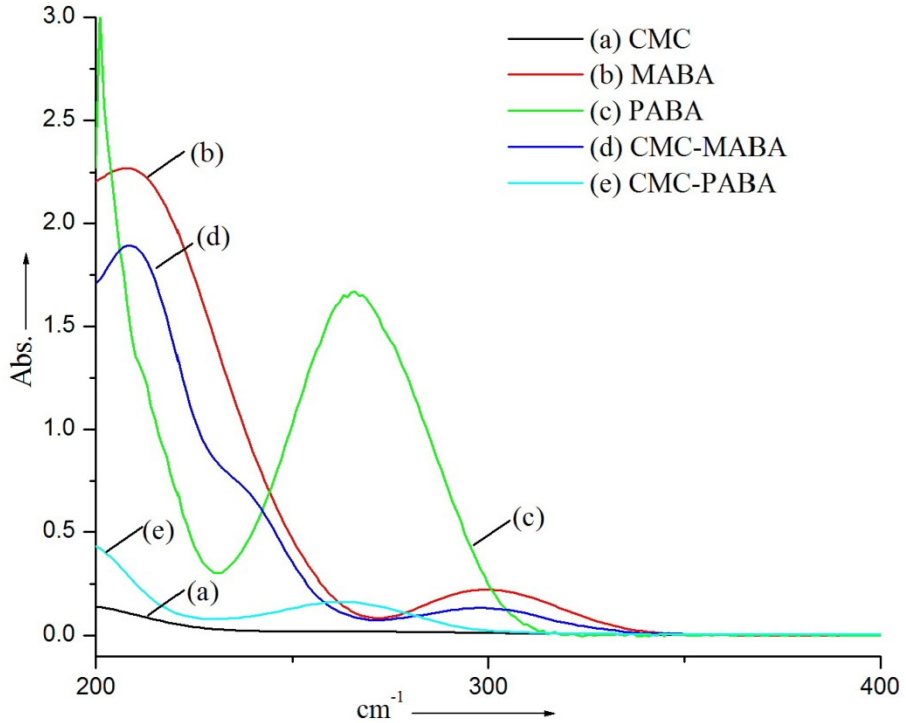

Fig. S2 UV spectra of (a) CMC, (b)MABA, (c) PABA, (d) CMC-MABA and (e) CMC-PABA

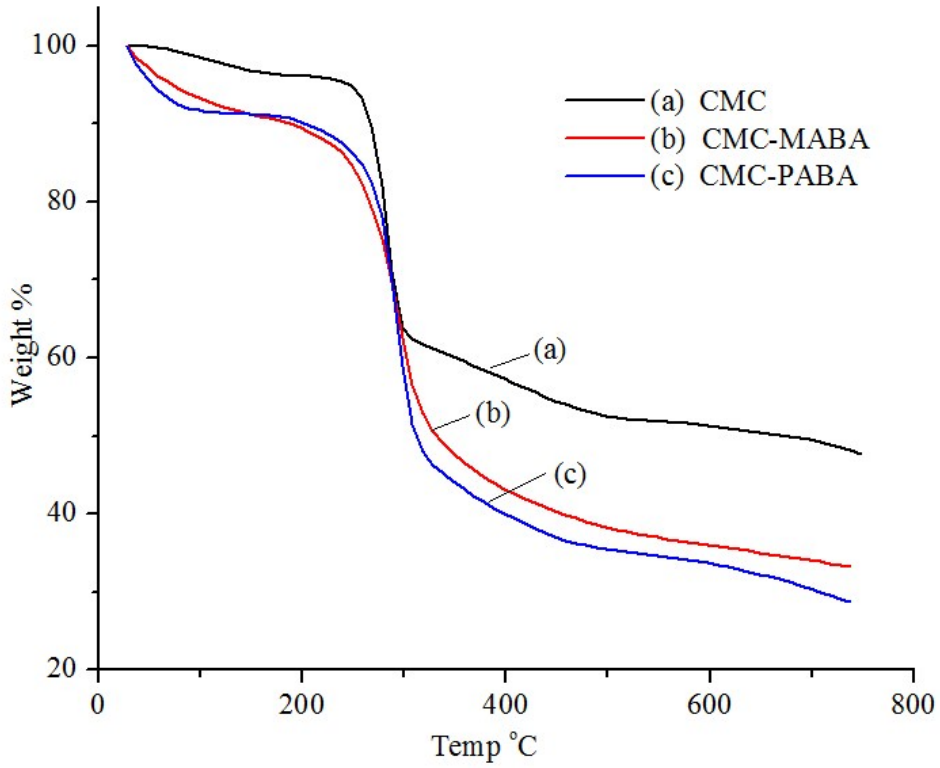

Fig. S3 Thermogravimetric analysis of (a) CMC, (b) CMC-MABA and (c) CMC-PABA

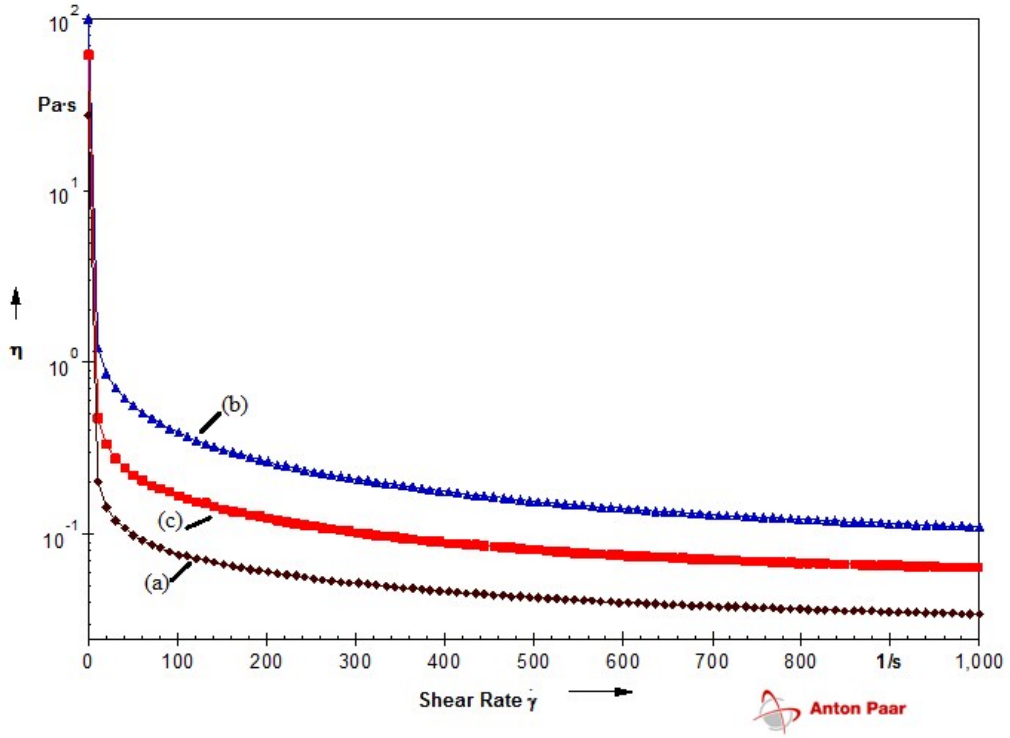

Fig.S4 Shear viscosity measurement with increasing shear rate of 4% solution (a) CMC, (b) CMC-MABA and (c) CMC-PABA