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Extruded Cellulose/Ionic Liquid Carbon Scaffolds

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Abstract. Monolithic carbon scaffolds were obtained by pyrolysis of regenerated cellulose. First, microcrystalline cellulose was compounded, at a 1:1 mass ratio, with 1-ethyl-3-methylimidazolium acetate, choline chloride or a mixture of the two ionic liquids. Test bars were extrusion-molded and the ionic liquid removed by leaching with water. The porous cellulose bars were carbonized at 800 °C in a nitrogen atmosphere. The Raman I_D/I_G peak intensity ratios ranged from 0.74 to unity confirming the formation of amorphous carbon. Scanning electron microscopy revealed a highly porous structure consisting of both micro- and nanopores.

Keywords: Microcrystalline Cellulose, Ionic liquid, 1-Ethyl-3-methylimidazolium acetate, Choline chloride, Extrusion-molded, Scaffolds, Carbon

INTRODUCTION

Cellulose is an almost inexhaustible, renewable polymeric raw material. The structure, properties, and abundant availability of cellulose in plants makes it a promising alternative to petroleum-derived resources[1]. However, cellulose cannot be melt processed or dissolved in common organic solvents. This is due to the chain stereoregularity and the abundance of hydroxyl groups present that engage in inter- and intramolecular hydrogen bonding [1, 2, 3, 4, 5, 6]. Therefore, economical and environmentally friendly chemical processing of cellulose has proven to be extremely difficult [7].

Solvents for cellulose exist, but most have limitations such as toxicity, cost, difficulty in solvent recovery, or instability during processing [2, 4, 7, 8, 9]. Thus, despite the vast production volume and renewable nature of cellulose, it remains underutilized [3]. A new class of novel cellulose solvents, ionic liquids (ILs), could lead to greater use of this resource [3, 6, 8, 10, 11, 12, 13]. ILs offer many distinct advantages over traditional solvents. These include high thermal stability, low volatility, outstanding solvation ability, ease of tailoring to meet specific requirements, and a wide electrochemical window [2, 3, 9, 11, 13]. Cellulose can be regenerated from ionic liquid/cellulose solutions by the addition of an anti-solvent. Typically, water is used, but ethanol, methanol and compressed CO_2 are also suitable. The spent IL can be recovered and reused. Several technologies are used to recover and purify ILs including distillation, extraction, adsorption, membrane separation, aqueous two-phase extraction, crystallization and external force field separation [14]. For common anti-solvents like water, organic solvents, and supercritical CO_2 extraction is typically used.

Unfortunately, even the most effective ILs dissolve less than 30 wt-% cellulose, and typical values are much lower. Raut et al. [4] reported that N-allyl-N-methylmorpholinium acetate ([AMMorp][OAc]) dissolved just 28 wt-% micro crystalline cellulose (MCC) at 100 °C. The acetate and chloride salts of 1-ethyl-3-methylimidazole, i.e. [Emim][OAc] and [Emim][Cl] and 1-buthyl-3-methylimidazolium chloride ([Bmim][Cl]) dissolve, at 100 °C, only 18.7 wt-%, 10.7 wt-% and 22.5 wt-% MCC respectively. Interestingly, mixtures of ILs dissolve more cellulose than pure ILs [12]. At 100 °C, a 30:70 molar ratio of [Emim][Cl] and [Emim][OAc] dissolves 28.6 wt-% MCC while the eutectic mixture of [Emim][Cl] and [Bmim][Cl] dissolves up to 25.9 wt-% [12].

Most common cellulose-dissolving ionic liquids are expensive. Choline chloride, a substituted quaternary ammonium salt [15] is actually used as an animal feed supplement and thus relatively inexpensive. It has been used with

several substances, e.g. carboxylic acids [16], to produce deep eutectic solvents (DES). Some choline chloride-based DES dissolve small amounts of cellulose [17, 18]. According to Ren et al. [17], imidazole-choline chloride DES dissolve the most cellulose (2.48 wt-%).

The aim of this work was to prepare monolithic carbon scaffolds from MCC via an extrusion-compounding process. MCC was plasticized with ILs (choline chloride and/or [Emim][OAc]) in a 1:1 by mass ratio. Samples were compounded using an extrusion-molding process in a co-rotating, twin-screw Thermo Scientific HAAKE MiniLab II micro compounder. The ILs were removed by leaching with water. The dried cellulose extrudates were converted into carbon by pyrolysis.

EXPERIMENTAL SECTION

Materials

MCC powder (20 μm) and EmimOAc (> 95 %) were obtained from Sigma-Aldrich Co. Choline chloride (98 %) was supplied by Shaanxi Yuan Tai Biological Technology Co., Ltd.

Scaffold preparation

Table 1 lists the compositions of the cellulose-ILs mixtures studied presently. These were mixed in a co-rotating, twin-screw Thermo Scientific HAAKE MiniLab II micro compounder. The temperature was set at 120 °C, the screw speed was 80 rpm and the cycle time was 4 min. Test samples, as shown in Fig. 1, were extrusion-molded in the shape of rectangular bars.

Just like cellulose, choline chloride decomposes at about 300 °C without melting. This made it necessary to add a small amount of water in order to obtain a feedable mixture. After compounding, the test samples were immersed in water acting as the anti-solvent. This regenerated the cellulose solids and allowed removal of the IL. The washed samples were air-dried and pyrolyzed at 800 °C for 10 min in a N_2 atmosphere.

Scaffold characterization

The phase structure of the carbon scaffolds was determined by Raman spectroscopy. Raman analysis was recorded with a HORIBA Scientific, Jobin Yvon Technology T64000 series II triple spectrometer system using a 514 nm laser line of a coherent Innova® 70C series Ar+ laser (spot size ∼2 μm) with a resolution of 2 cm^{-1} in the range of 200 cm^{-1} – 1800 cm^{-1}. The measurements were obtained in a backscattering configuration with an Olympus microscope attached to the instrument (using an LWD 50× objective). The laser power was set at 1.7 mW. An integrated triple spectrometer was used in the double subtractive mode to reject Rayleigh scattering and dispersed the light onto a liquid nitrogen cooled Symphony CCD detector.

The physical morphology was investigated with a scanning electron microscope. Fractured samples were mounted on metal stubs with double-sided carbon tape. Each sample was cleaned using compressed air to remove loose particles and other contaminants. The samples were placed in a charge-reduction sample holder and viewed with a Phenom PRO-X SEM (Phenom, The Netherlands) at a working distance of 3 mm and an acceleration voltage of 10 kV.

RESULTS AND DISCUSSION

It proved possible to extrusion-compound and mold all the MCC/IL combinations into homogeneous test bars. This implies that cellulose can be rendered flowable by less IL than is required for solubilization of cellulose. In fact, a 1:1 mass ratio of [Emim][OAc] and choline chloride was sufficient for this purpose.
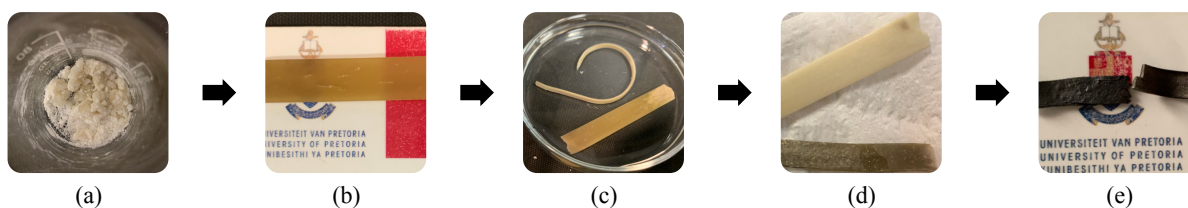
FIGURE 1. Key stages in process of producing carbon scaffold: (a) pre-compounding mixture of MCC and [Emim][OAc], (b) extruded profile, (c) removing [Emim][OAc] with water, (d) leached cellulose scaffolds, (e) monolithic carbon scaffold.

Therefore, it was demonstrated that, when plasticized with ILs, cellulose can be compounded into a fluid state using conventional polymer processing equipment. The fact that choline chloride was as effective as [Emim][OAc] to turn MCC into an extrudable fluid phase opens up new opportunities for affordable cellulose-based materials. It is even possible that the MCC can be extruded using a lower IL content than is reported here.

Fig. 1 shows Sample 1 in all its different states following processing. Some discoloration is evident after extrusion for samples containing [Emim][OAc]. However, this disappeared when the IL was removed. As ILs discolor from exposure to heat, it is suspected that the discoloration was due to the degradation of the IL rather than the cellulose. Fig. 1(d) reveals that the dried cellulose profiles did discolor after prolonged exposure to ambient air. This could have been due to the presence of residual amounts of IL.

Pyrolysis in the furnace in a N_2 environment produced monolithic carbon scaffolds in yields of $12 - 15$ % as shown in Table 1.

**TABLE 1.** Carbon yield of cellulose extrudates after pyrolysis.

Sample	MCC (wt-%)	[Emim][OAc] (wt-%)	Choline chloride (wt-%)	Mass carbon yield (%)	I_D/I_G
1	50	50	0	15.14	0.871
2	55	45	0	12.50	0.843
3	45	55	0	12.16	1.043
4	50	25	25	12.75	0.919
5	50	0	50	13.21	0.740

The structure of the carbonized samples was determined by Raman spectroscopy. The recorded spectra are presented in Fig. 2 It shows the disorder induced defect 'D' band, located at approximately 1370 cm⁻¹, and the structural order induced Graphite 'G' band at approximately 1590 cm⁻¹. The degree of structural order was quantified by the I_D/I_G peak intensity ratio and is reported in Table 1. The lower the ratio, the higher the degree of structural ordering in the carbon material. Pure crystalline graphite has an intensity ratio close to zero, as the D-peak has very low intensity [19] [20]. This confirms that primarily amorphous carbon was formed by pyrolyzing the cellulose.

The SEM images in Fig. 3 clearly show an increase in porosity after pyrolysis. A hierarchy of micro- and nanopores is observed. Further analysis, including BET, is required to determine pore size and overall porosity. Nevertheless, the SEM images do suggest that the materials are highly porous.
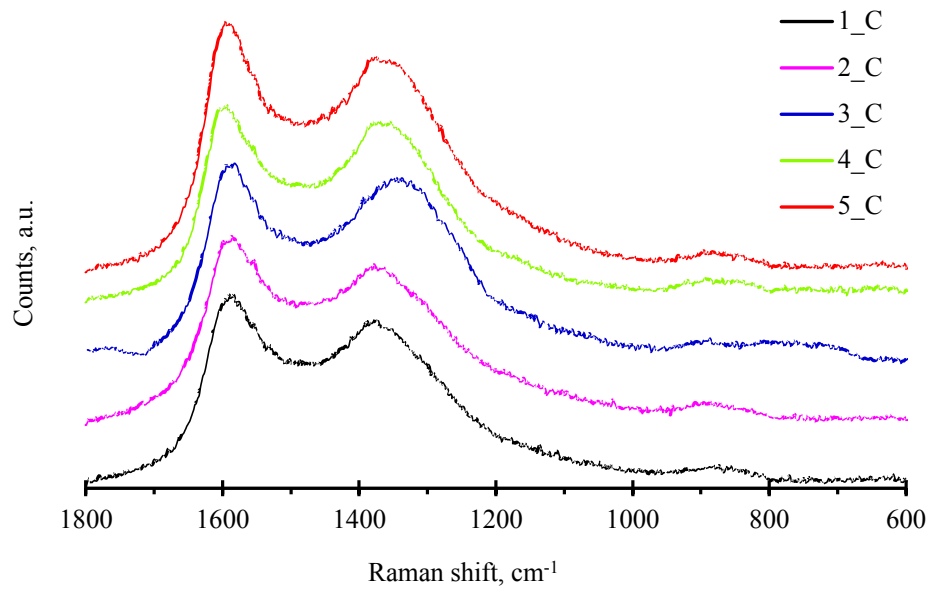
FIGURE 2: Raman spectroscopy absorption curves for samples 1 – 5 after pyrolysis.
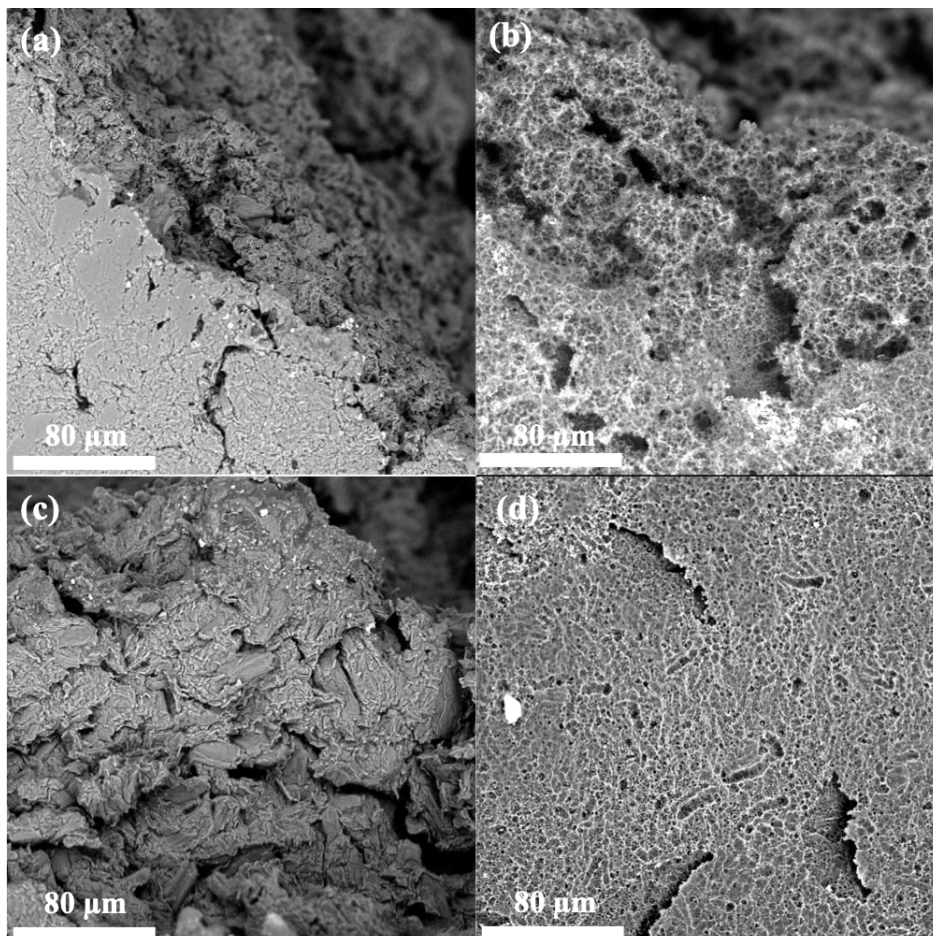
FIGURE 3: SEM images of cellulose sample made with (a) 50 wt-% choline chloride before and (b) after pyrolysis, and sample made with (c) 50 wt-% [Emim][OAc] before and (d) after pyrolysis.

CONCLUSIONS

Cellulose was successfully extruded in a fluid state using a conventional compounder. This was done by plasticizing the MCC with an IL, rather than fully dissolving it. A 1:1 mass ratio of cellulose and IL was sufficient to process the cellulose. Both [Emim][OAc] and choline chloride were effective. The relatively inexpensive nature of choline chloride, coupled with the fact that conventional polymer processing equipment was used introduces new, economically viable, cellulose processing avenues that deserve further study.

The extruded cellulose profiles were successfully pyrolysed to form porous, amorphous carbon scaffolds. Raman spectroscopy as well as SEM imaging confirmed this. The ability to render the cellulose flowable, allows one to produce monolithic carbon scaffolds of any desired shape that might be required.

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