

## PREPARATION OF SELF-REINFORCED CELLULOSE COMPOSITE USING MICROCRYSTALLINE CELLULOSE

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### ABSTRACT

**Application of natural fibres in self-reinforced composite is increasing tremendously due to their specific mechanical properties, biodegradability, environment benefits, and renewability. In this study, microcrystalline cellulose (MCC) of size 13  $\mu\text{m}$  was dissolved in a LiCl/DMAc solution (DMCC). This solution was used to form self-reinforced cellulose films (SRC) using MCC having 200 $\mu\text{m}$  (MCC-200 $\mu\text{m}$ ) size as a reinforcement. The MCC and SRCs were characterized for thickness measurement, tensile strength, FTIR, XRD and SEM technique. Higher tensile strength and decrease in % extension of SRC was attributed to the partial dissolution of MCC-200 $\mu\text{m}$  fibres in DMCC matrix. These biodegradable SRC films can find applications in variety of fields like medical, packaging etc.**

**Keywords:** Biodegradability, LiCl/DMAc, Microcrystalline cellulose, Self-reinforced composite

Nowadays with the development of modern society, there are growing demands for renewable and biodegradable composites. At the same time usage of petroleum based material increased day by day which is non-biodegradable, and regarded as non-sustainable. Because there is too much attention on environmental problems such as white pollution [1], [2], researchers take more effort on the exploitation of new materials from biomass resources [3].

Cellulose is the most abundant natural polymers on the earth which is renewable, biodegradable, biocompatible, have several other advantages including ubiquitous availability, recyclability, low cost and low density [4], [5]. Cellulose is insoluble in most common organic and inorganic solvents. Most of the investigations carried out in recent years have concentrated on dissolution of cellulose in solvent systems such as NaOH/Urea and LiOH/Urea aqueous solution [6], 1-ethyl-3-methylimidazolium acetate (EmimAc) [3], LiCl /DMAc solvent System [7], [BMIM]Cl solvent [2]. Recently wide research is going on to find out the pathway to convert cellulose into bio fuels [8].

Self-reinforced composite (SRC) are compounds in which, both matrix and reinforced materials are of same chemical nature. Advantages of this SRC are excellent interfacial adhesion between matrix and reinforced materials, pure chemical functionality, recyclability due to their relative homogeneity compared to composites composed of different chemical nature of components [9], [8]. In biomaterials applications, any additive materials composed of different chemicals could affect its biocompatibility and biodegradation therefore single-polymer composites are particularly important.

In this study, the aim was to obtain high-strength random-oriented bio based, easily recyclable and biodegradable SRC. For preparation of SRC, partially surface dissolution of MCC-200 $\mu\text{m}$  as a reinforcement in DMCC matrix was done. The composite films were tested for their mechanical properties along with FTIR, XRD and SEM.

### **MATERIALS AND METHODS**

MCC of 13  $\mu\text{m}$  and 200  $\mu\text{m}$  were purchased from Rettenmaier India Pvt Ltd., Mumbai, India. Lithium chloride (LiCl) and N-dimethylacetamide (DMAc) AR grade were purchased from S.D. Fine

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chemicals, Mumbai.

#### **Pre-treatment of MCC**

Both the MCC were pre-treated with 100 ml of solvents serially in deionised water, methanol and DMAc for 6 hours at room temperature. Treated samples were vacuumed filtered and dried in hot air oven at 100°C. Treated MCC was used as a matrix, after dissolution in LiCl/DMAc solvent and MCC-200μm as filler.

#### **Preparation of DMCC Matrix**

8 gm LiCl was dissolved in 100 ml DMAc in three necked flasks in a dry nitrogen atmosphere having provision for thermometer and stirrer. 3.5 gm of pre-treated MCC was introduced after the temperature was reached to 80°C. The reaction was continued under anitrogen atmosphere at 80°C for 4 hours. This dissolved MCC was designated as DMCC.

#### **Preparation of Composite**

Different quantities (2.5 gm, 5.0 gm and 10.0 gm, designated as MCC-200μm\_2.5, MCC-200μm\_5, MCC-200μm\_10 respectively) of MCC-200μm samples were mixed with 66 ml of DMCC solution using over head stirrer. This mixture was then poured onto the three A4 size glass mould as well as one empty mould (without MCC-200μm). After a while the composite started gelatinizing due to absorption of moisture present in surrounding air. All the composite samples were kept at room temperature for 24 hours for drying. For extraction of LiCl/DMAc solvent, the composite was immersed in methanol for 12 hours and exchanged with fresh methanol after 1 and 6 hours of the time interval. The samples were then dried at room temperature for 12 hours, then vacuum dried at 60°C for 24 hours.

### **CHARACTERIZATION**

#### **Thickness Measurements**

The thickness of the sample was measured using Digital Vernier Caliper by Mitutoyo Corporation, Japan. Total 30 readings were taken for each sample and average was reported.

#### **Tensile Strength Testing**

Tensile tests were performed as per ASTM D 5035; 1995, using strips of composite film with a

width of 25mm and length of 150 mm. A grip distance and load range of 20mm and 300 kgf respectively was maintained on tensile strength tester (Model H5KS, Tinius Olsen Inc., Horsham, PA, USA) at a speed of 200 mm/minute.

#### **Fourier Transform Infrared Spectra Analysis**

The structural changes of composite samples were analyzed by FTIR spectroscopy (Shimadzu Corporation, Japan). Before testing all composite samples were dried at 55°C for 2 hours. FTIR spectrum was recorded between 4000 cm<sup>-1</sup> and 650 cm<sup>-1</sup>, 4.0 resolution and 36 scans per sample [5], [10].

#### **X-Ray Diffraction**

The crystallinity of samples was examined by XRD using powder X-ray diffractometer, XRD-6100 (Shimadzu Corporation, Japan). The operation voltage and current were maintained at 40 kV and 30 mA, respectively. The diffraction spectra were collected using θ-2θ method. Samples were scanned from 2θ range of 5-35° in steps of 0.020° using continuous mode of scanning, at the rate of 2°/minute, symmetrical reflection mode with Cu Kα radiation ( $\lambda = 1.5405 \text{ \AA}$ ). Crystallinity index of the samples was calculated using Segal method [11].

$$\%ICr = \left[ 1 - \left( \frac{I_{am}}{I_{002}} \right) \right] \times 100 \quad (1)$$

Where,

ICr is the crystalline index,  $I_{am}$  is the intensity of the background scatter measured at 2θ angle range between 16° to 22°, when the intensity is minimal, and  $I_{002}$  is the maximum intensity of diffraction from the 002 plan at a 2θ angle between 22° to 24° [12].

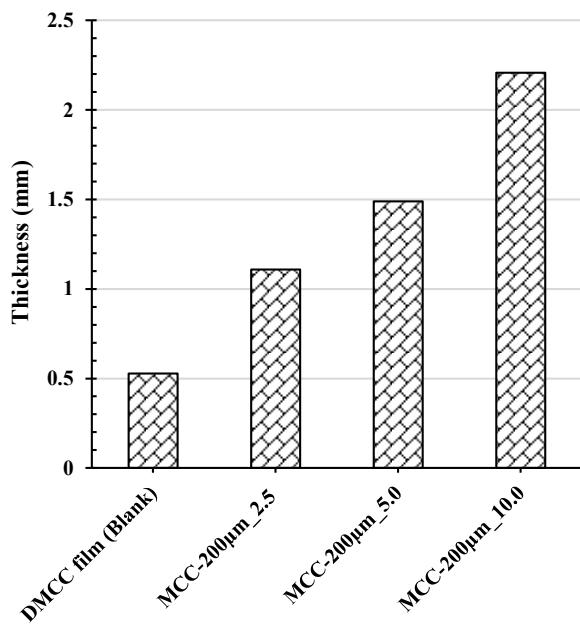
#### **Scanning Electron Microscopy Analysis**

Surface morphology of the samples was studied using scanning electron microscope JSM 680LA (JEOL ltd., Japan) with accelerated electrons having 10kv energy. Samples were prepared onto adhesive carbon tape on an aluminum stub followed by gold sputter coating for 3 to 4 minutes using sputter coater to dissipate the static charges occurring due to electron bombardment.

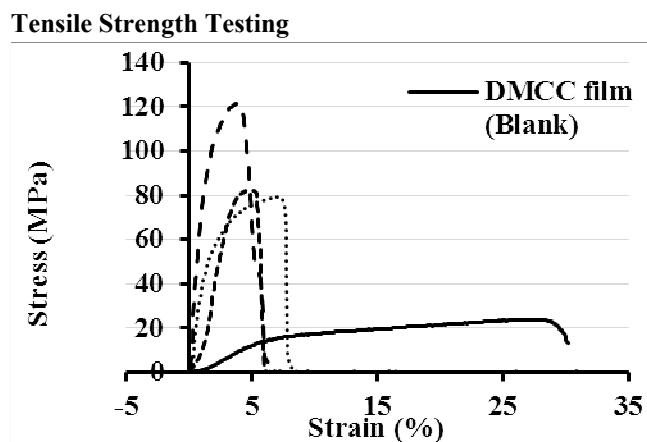
## RESULT AND DISCUSSION

### Thickness Measurements

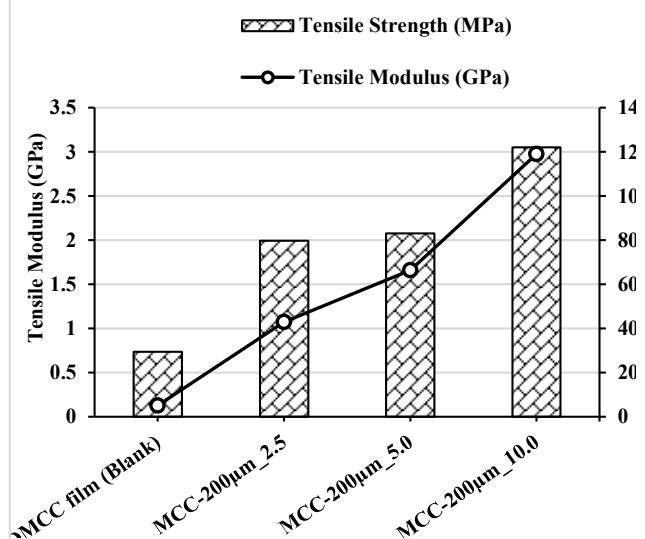
Fig. 1 shows the thickness of composite samples along with the DMCC film (Blank). Thickness of composite film increased due to increasing loading of MCC-200 $\mu$ m as expected.



**Fig. 1:** Thickness of composite samples for different loadings of MCC-200 $\mu$ m



**Fig. 2a:** Stress - strain curves of composite samples for different loadings of MCC-200 $\mu$ m



**Fig. 2b:** Relationship between tensile modulus and tensile strength of composite samples for different loadings of MCC-200 $\mu$ m

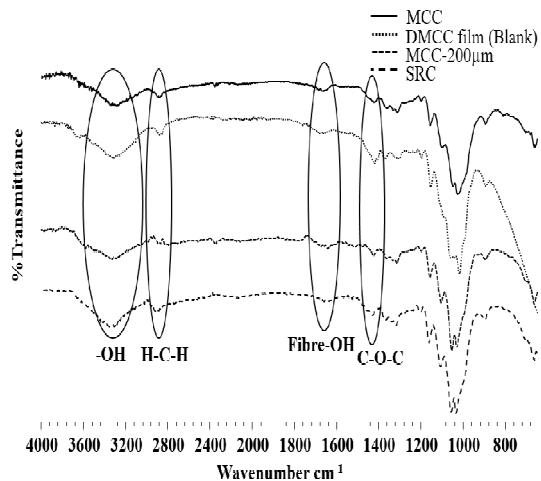
Stress - strain curves of composite films and blank film are shown in Fig. 2a. SRC composite samples exhibited higher strength as compared to DMCC film (Blank). Elongation-at-break of the SRC composite samples decreased as compared to that of DMCC film (Blank) which indicates that addition of MCC-200 $\mu$ m in DMCC matrix increases its brittleness.

Tensile modulus and tensile strength of DMCC film (Blank) and SRC composite samples are shown in Figure 2b. Addition of MCC-200 $\mu$ m significantly enhanced the tensile modulus and strength of the SRC as compared to DMCC film (Blank). The better phase adhesion between the MCC-200 $\mu$ m and DMCC matrix may be accountable for enhanced tensile properties of the SRC. The strong interfacial bond in these SRC can be ascribed to the presence of strong hydrogen bonding within the MCC, DMCC matrix phase and interphasial region [13, 14, 15, 16] (SEM and FTIR section).

### Fourier Transform Infrared Spectra Analysis

Fig. 3 shows the FTIR spectra for MCC, DMCC film (Blank), MCC-200 $\mu$ m and SRC for 10% loading. The appearance of peaks at wave numbers of 1430 cm $^{-1}$ , 1640 cm $^{-1}$ , 2950 cm $^{-1}$  and 3450 cm $^{-1}$  are due to C-O-C, fibre-OH (moisture or water), H-C-H (alkyl-aliphatic) and -OH (or methanol) functional

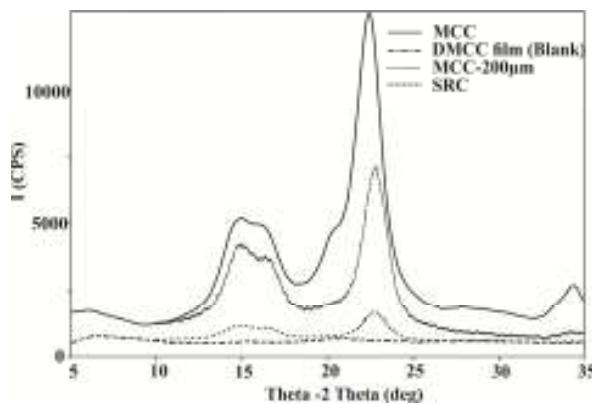
group respectively, which is typical of cellulose molecule [4]. The similarity of MCC, DMCC film (Blank) and SRC shows that there was no chemical modification by LiCl/DMAc solvent. At the same time, no peak was observed at  $1620\text{ cm}^{-1}$ , corresponding to amide I (C-O stretching vibrations). This confirmed the complete removal of LiCl/DMAc during the after treatment with methanol [7].



**Fig.3: FTIR Spectra for the MCC, MCC-200μm, SRC and DMCC film (Blank)**

#### X-Ray Diffraction

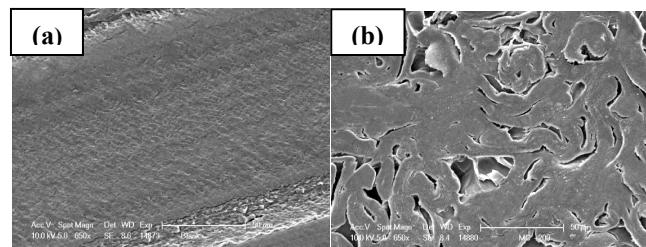
Fig. 4 shows the X-ray curves of MCC, DMCC film (Blank), MCC-200 $\mu\text{m}$  and SRC (MCC-200 $\mu\text{m}_10.0$ ). The crystallinity values of MCC (83%) were higher than MCC-200 $\mu\text{m}$  (68%) followed by SRC (45%) and DMCC (18%). This was due to the partial or incomplete surface dissolution of MCC-200 $\mu\text{m}$  fibres while preparation of SRC which is confirmed in the SEM analysis. DMCC film had very low crystallinity as its crystalline structure was destroyed during complete dissolution of MCC in LiCl/DMAc solvent [9].



**Fig. 4 :XRD spectra for the MCC, MCC-200 $\mu\text{m}$ , SRC and DMCC film (Blank)**

#### Scanning Electron Microscopy Analysis

The morphology of samples was examined using SEM analysis. Fig. 5 shows the cross-sectional views of DMCC film (Blank) and SRC (MCC-200 $\mu\text{m}_10.0$ ). A uniformly distributed rough matrix structure of DMCC is observed in Fig. 5 (a), whereas in the cross section of SRC, the boundary of the MCC-200 $\mu\text{m}$  seems to have been dissolved in the DMCC giving an impression as if it is merged with the matrix (Fig. 5 (b)). This was accompanied by few cracks and voids appearing in between the fibres over the cross-sectional area. The DMCC acted as a glue to join partly dissolved MCC-200 $\mu\text{m}$  fibres forming a strong bonding between them which reflected in excellent mechanical properties of the composites.



**Fig. 5: Scanning Electron Micrograph of (a) DMCC film (Blank) and (b) SRC composite sample**

#### CONCLUSION

Self-reinforced cellulose bio-composites were successfully prepared by partial dissolution or selective surface dissolution method. As amount of the filler (MCC-200 $\mu\text{m}$ ) is increased, thickness of SRC also increased with rise in stiffness and mechanical strength. Better interfacial adhesion between MCC-200 $\mu\text{m}$  fibre and matrix was created which allows for a good stress transfer capability in the composite. The FTIR results showed complete removal of LiCl/DMAc from SRC by using methanol washing. These biodegradable SRC films can find applications in variety of fields like medical, packaging etc.

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