Synthesis and characterization of carboxymethyl cellulose/polyethylene glycol/montmorillonite clay blends

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Abstract
The present study deals with the synthesis and characterization of the ternary blends of carboxymethyl cellulose, polyethylene glycol and montmorillonite clay of ratio 1:1:1 in the presence and the absence of the crosslinker glutaraldehyde. The prepared blends were characterized using the analytical tools such as FTIR, TGA, DSC, XRD and SEM. The effective formation of the ternary blend was confirmed using FTIR studies. The thermal stability of the blends was determined from the TGA and DSC results. XRD and SEM results confirm that the degree of crystallinity was altered during blending and crosslinking and the prepared blend is suitable for adsorption and also as an excipient material in pharmaceutical industries.

Keywords: ternary blend, crosslinking, characterization

INTRODUCTION
Biopolymers are renewable, biodegradable, biocompatible diverse and versatile class of materials that have potential applications virtually in all sectors of the economy. Hence for the present work, carboxymethyl cellulose the biopolymer derivative was selected. Cellulose is a naturally occurring polymer, and it is the most abundant and renewable polymer in the world. It is a linear polysaccharide with long chains which consists of β-D-glucopyranose units joined by β-1, 4- glycosidic linkages [1-3]. Cellulose lacks some properties such as poor solubility in common solvents, poor crease resistance, poor dimensional stability. The presence of three reactive hydroxyl groups on each glucan unit of cellulose makes it relatively easy to modify. Carboxymethyl cellulose (CMC) is one of the most important derivatives of cellulose and it is the sodium salt of carboxymethyl cellulose. It is formed by the carboxymethylation of the hydroxyl group in cellulose [4]. Carboxymethyl cellulose (CMC) is the most important water soluble derivative, with many applications in the food, cosmetics, pharmaceutical and detergents industries and so on [5]. Since CMC have wide range of applications, its solubility restricts its application on the water treatment field. Thus to improvise its property CMC was blended and crosslinked with PEG, MMT and glutaraldehyde. An important property of a polymer blend is the miscibility of its components, because it affects the mechanical properties, the morphology, its permeability and degradation [6]. Polyethylene glycol (PEG) is the most popular and best synthetic non-fouling materials, which have the ability to resist protein adsorption and used in various industrial membranes [7]. The unique property of PEG is its high level of hydrophilicity, vigorous chain mobility and a high extent of coordination with surrounding water molecules [8]. Montmorillonite, which is the best-known member of a group of clay minerals, called “smectites” or “smectite clays”, is the most widely used layered. Montmorillonite (MMT) clay is a naturally occurring 2:1 phyllosilicate with other layered and crystalline clays such as talc and mica. The general formula of montmorillonite clay is Mx (Al4-xMgx) Si8O20 (OH) 4, where M is a monovalent cation and x is the degree of isomorphous substitution [9]. Clays themselves possess the high adsorption capabilities, the modification of their structure can successfully improve their capabilities [10]. In the present investigation ternary polymeric blends of CMC/PEG/MMT of ratio 1:1:1 in the...
presence and absence of glutaraldehyde were synthesized and characterized using FTIR, TGA, DSC, XRD and SEM. The results were discussed.

MATERIALS AND METHODS
Materials
Carboxymethyl cellulose, Polyethylene glycol and Montmorillonite clay were purchased from Sigma Aldrich, Bangalore and all the other chemicals were of analytical grade and used as received without further purification.

Preparation of carboxymethyl cellulose/polyethylene glycol/montmorillonite clay ternary blend with and without glutaraldehyde (1:1:1)
1gm of Carboxymethyl cellulose and 1gm of polyethylene glycol were dissolved in minimum amount of water. 1gm of montmorillonite clay mixed in water was also added. The three were mixed and stirred for 20 minutes and poured in the petri dish for drying.
1gm of Carboxymethyl cellulose and 1gm of polyethylene glycol were dissolved in minimum amount of water. 1gm of montmorillonite clay mixed in water was also added. The three were mixed and stirred for 20 minutes. 5ml of the cross linking agent glutaraldehyde was added to the above mixture and stirred for 30 minutes. The solution was cast on plastic weighing boats and dried in vacuum for 10 h.

Characterization of the polymer blends
FTIR studies
Fourier Transform Infra-Red spectra of the ternary blend of carboxymethyl cellulose were recorded in the frequency range of 400–4000 cm⁻¹ using Thermo Nicolet AVATAR 330 spectrophotometer. The sample was pressed into pellets with KBr.

Thermo gravimetric analysis
Thermo gravimetric analysis of the ternary blend of carboxymethyl cellulose was conducted by SOT Q600. V8.0 Build 95 to measure the weight loss at different temperatures with the heating range 20-850°C and rate 20°C per minute.

Differential scanning calorimetric analysis
The thermal behavior of the blend was studied using NET 2 SCH DSC thermal analyzer. The sample was inserted into the Al pan and DSC scan was made from 30 – 300°C in nitrogen atmosphere at a heating rate of 20°C min⁻¹. The results were recorded and analyzed.

X-ray diffraction studies
X – ray diffractograms of powdered samples were obtained using an X - ray powder diffractometer (XRD – SHIMADZU XD – D1) with Ni – filter, Cu Kα, radiation source. The relative intensity was recorded in the scattering range 2θ of 10 – 90°.

Scanning Electron Microscopy (SEM)
The surface morphology and cross section morphology of binary and ternary blends of carboxymethyl cellulose were observed with scanning electron microscopy to verify the compatibility of the mixtures of polymers. To analyze the blends, films were cut into pieces of various size and wiped with a thin gold – palladium layer by a sputter coater unit (UG – microtech, UCK field, UK) and the cross section topography was analyzed with Cambridge stereoscan 440 Scanning Electron Microscope (SEM, Leica, Cambridge UK).

RESULTS
FTIR studies
FTIR Spectroscopy is a technique based on the determination of the interaction between an IR radiation and a sample. It measures the frequencies at which the sample absorbs, and also the intensities of these absorptions. Figure-1 and 2 shows the FT-IR spectrum of the ternary blend (Carboxymethyl cellulose/polyethylene glycol/Montmorillonite clay blend) prepared in the 1:1:1 ratio with and without glutaraldehyde. The main characteristic band at 3741.80 cm⁻¹ are ascribed to O-H stretching vibration with sharp intense peak due to O-H group from montmorillonite clay [11]. A broad peak at 3426.0cm⁻¹ indicated the presence of O-H stretching vibration with sharp intense peak due to O-H group from montmorillonite clay [11]. The presence of a strong band at 2922.5cm⁻¹ can be assigned to C-H asymmetric stretching of methylene group. The peak at 1403 cm⁻¹ is for Al-O stretching vibration with sharp intense peak due to O-H group from montmorillonite clay [11]. The presence of Al-O stretching and CH2 bending, confirms the presence of the kaolin clay in the prepared composite [12]. The presence of a strong band at 1604.9 cm⁻¹ confirms the presence of COO- group and also the H-O-H deformation. The peak at 1105.9 cm⁻¹ was characteristic of the C-O stretching on polysaccharide skeleton and also Si-O-Si stretching [13].
P. Sathiyanarayanan et al., Synthesis and characterization of carboxymethyl cellulose/polyethylene glycol/montmorillonite clay blends

TGA studies
TGA Thermogram of CMC/PEG/MMC-1:1:1 prepared in the absence of glutaraldehyde was represented in Figure –3. From the thermogram it is evident that 60% of the sample disintegrated within 680°C. There was steady increase in the weight loss from 200 to 400°C showing slow decomposition of the – CH2 – linkages, H–bonding and other interactions between the polymers. The second degradation around 450°C -750°C in which the maximum weight loss was occurred, and it may be due to the degradation of organic molecules.[14] At the end of the experiment around 40 % weight of the residue was left. 

Figure – 4 represents the TGA thermogram of CMC/PEG/MMC-1:1:1 with GLU. About 25% of the sample disintegrated in the temperature range of 210°C. From 210°C there is only a gradual decrease in weight with increase in temperature. At the end of the experiment around 40% of the sample remained as residue. The residual temperature of the sample is 870°C. It was found that the CMC/PEG/MMT blend prepared in the presence of glutaraldehyde exhibited a higher thermal decomposition temperature compared to ternary blends prepared in the absence of glutaraldehyde. This increase in the thermal stability can be attributed to the interaction between the clay particles and other polymers through crosslinker.[15]

Differential Scanning Calorimetry
DSC thermal analysis helps us to find out the miscibility of the two polymers which are involved in blending. Figure –5 represents the DSC thermogram of CMC/PEG/MMC-1:1:1 blend. The glass transition temperature of the blend is observed at 185°C. An endothermic peak was observed at 118.4°C and no exothermic peak was observed. From the thermogram it was evident that the melting temperature of the blend would be greater than 300°C.

Figure - 6 shows the DSC thermogram of CMC/PEG/MMC-1:1:1 with GLU having the glass transition temperature at 210°C and the crystallization temperature at 112.4°C. The single glass transition indicated attractive molecular interactions and high degree of compatibility of all the materials. As the crosslinking agent glutaraldehyde was added the crystallization temperature was changed.

X-ray diffraction (XRD) has long been successfully used to study various aspects of these structures in semicrystalline polymers, which includes thermoplastics, thermoplastic elastomers and liquid crystalline polymers. Figure 7 shows the XRD pattern of CMC/PEG/MMC blend of ratio 1:1:1 prepared in the absence of glutaraldehyde. It illustrates the existence of the interaction between the polymers through hydrogen bonding. The number of peaks reveals that there are different crystalline forms and the blends are semi-crystalline in nature. In addition, the percentage of crystallinity was found to be 27%.

Scanning Electron Microscopy (SEM)
The surface morphology and cross sectional morphology (Figure 7a and 7b) of CMC/PEG/MMT ternary blend prepared in the presence of glutaraldehyde crosslinker was characterized by SEM. Scanning electron microscopy is an extremely useful method for visual confirmation of surface morphology and the physical state of the surface.

DISCUSSION
The FTIR spectrum of carboxymethyl cellulose/polyethylene glycol/montmorillonite clay (1:1:1) blend in the presence and absence of glutaraldehyde as the crosslinking agent. The XRD spectrum showed two to four at 2θ in the range of 18° to 45°. Compared with the XRD pattern of the blends in the absence of crosslinker the peak reduction and the increased amorphous nature was seen when crosslinker was used. The degree of crystallinity was found to be reduced to 25% during the addition of crosslinker.
The TGA thermogram showed the improved thermal stability on comparing the blends in the presence and absence of crosslinker.

Fig 1. FTIR spectrum of Carboxymethyl Cellulose/ Polyethylene Glycol/ Montmorillonite clay blend (1:1:1)

Fig 2. FTIR spectral details of Carboxymethyl Cellulose/ Polyethylene Glycol/ Montmorillonite clay blend (1:1:1) + Glutaraldehyde

Fig 3. TGA thermogram of Carboxymethyl Cellulose/ Polyethylene Glycol/ Montmorillonite clay blend (1:1:1)

Fig 4. TGA thermogram of Carboxymethyl Cellulose/ Polyethylene Glycol/ Montmorillonite clay blend (1:1:1) + Glutaraldehyde

Fig 5. DSC thermogram of Carboxymethyl Cellulose/ Polyethylene Glycol/ Montmorillonite clay blend (1:1:1)

Fig 6. DSC thermogram of Carboxymethyl Cellulose/ Polyethylene Glycol/ Montmorillonite clay blend (1:1:1) + Glutaraldehyde
The crosslinker increases the initial decomposition temperature and decreases the decomposition rate resulting in leaving the maximum residue at the end of the experiment confirming the higher thermal stability. The changes in the thermal behavior were due to the participation of all the polymers and also the crosslinker. The crosslinker increases the thermal stability of the blend. The DSC thermogram of the samples showed the single glass transition temperature which indicated the miscibility and compatibility of the polymers.

From the XRD patterns of the prepared ternary blends, the percentage crystallinity values are calculated and were found that the blends prepared using crosslinker showed lesser value when compared with blends without crosslinker. Thus it was concluded that crosslinking increased the amorphous nature by inducing effective blending. This tells us that amorphous nature is suitable and also favors the adsorption process, which is an efficient method for wastewater treatment. Also the scanning electron micrograph of CMC/PEG/MMT ternary blend prepared in the presence of glutaraldehyde crosslinker shows improved porosity and fractured structure, which can be responsible for adsorption of molecules due to blending. The surface area of ternary blend films is highly rough in comparison with binary blend. This obviously accounts that ternary blend (1:1:1) has good adsorbing property which is useful for wastewater treatment.

**CONCLUSION**

The formation of ternary blends was confirmed by FT-IR Spectroscopy. The transformation from semi-crystalline to amorphous nature by the addition was confirmed by XRD. Thermogravimetric analysis showed that the prepared blends were thermally...
more stable. The SEM images confirmed that the prepared blend in the presence of glutaraldehyde have more number of porous, which can be used as the good adsorbent and also as an excipient material in pharmaceutical industries.

REFERENCES