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PHYSICO-CHEMICAL AND THERMAL PROPERTY STUDIES OF GG/CMC BLEND THIN FILMS

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ABSTRACT

Physico-chemical, and thermal properties of blend thin films of Guar Gum (GG) and Carboxymethylcellulose (CMC)were studied by Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Differential Scanning Calorimetric (DSC) methods.Based on FTIR, SEM, and DSC-Tgmeasurements, it is found that the polymer blend of Guar Gum/CMC is miscible by forming intermolecular hydrogen bonding only when the GG content is more than 60%. Below this critical GG concentration the blends were found to be immiscible. Hence GG/CMC blend in solid state is semi-miscible in nature.

Keywords:blends, CMC, Guar Gum, FTIR, SEM, DSC

I. INTRODUCTION

Blending is one of the most effective methods of manufacturing new polymeric materials [1, 2]. Blends can be produced that have properties independent of either the original homopolymers or structurally similar copolymerized macromolecules. However, mixing of polymers to produce novel materials is typically possible only if two compounds are miscible [3]. It is important to relate the chemical structure of polymers to their physical properties, as miscibility is often a result of physical interaction between two materials. The advantage of combining polymers within a blend is twofold. First, as the blend is completely miscible, the physical properties of the material will be dependent not only on the constituent polymers but also on their interactions [4]. As such, the material's key physical properties, such as its glass transition temperature and melting/decomposition regions, can be altered, depending on the molecular organization of the two polymers in the blend [5]. Second, the mixing of two polymers adds a second functionality with which the blend can form chemical or physical interactions. A polymer blend can act in similar manner to a mixed surfactant/polymer system, which can be used to enhance the interactions of incompatible compounds or bridge immiscible environments [6].

Guar gum is a natural biocompatible polysaccharide and obtained from the endosperm of *Cyamopsistetragonalobus*[7]. Guar gum and its derivatives are water soluble, hydrophilic polymers, and the solutions are highly viscous in nature. These polymers and their derivatives have commercial applications in fields such as oil recovery and drilling [8, 9],textiles [10, 11], cosmetics [12], foods [13],and pharmaceuticals [14].

Carboxymethylcellulose (CMC) is a white, non-toxic, odorless, biodegradable in nature. It is a water-soluble polymer which will dissolve in hot or cold water [15]. CMC is used for a variety of applications in a various industries such as pharmaceutical, personal care, paper, oilfield, and food industries. It is used as a binding, thickening, and stabilizing agent [16, 17, 18].

In our previous work we extensively investigated about the viscosity, density, ultrasonic velocity, and refractive index of guar gum/carboxymethylcellulose blends in solution state [19]. In this research miscibility of natural polymer guar gum, a synthetic polysaccharide carboxymethylcellulose, and their blend thin films at different compositions were studied by FTIR, SEM, and DSC-Tgmeasurement techniques.

II. EXPERIMENTAL PROCEDURE

The polymers employed in the present study are Guar Gum (Merck, India) and Carboxymethylcellulose(Merck, India).

Thin films of the polymers and their blends were prepared by solution casting method. Separate aqueous solutions of GG and CMC were prepared. A solution of CMC was added to that of GG with constant stirring. The mixture was stirred for 45 minutes at room temperature to ensure complete mixing. The total polymer concentration was kept at 0.1% (w/v). Stock solutions of GG and CMC and their different blend compositions were then casted onto teflon-coated clean glass plate and dried in a dust free atmosphere. The dried thin films were peeled off from the glass plate and were found to be transparent.

SEM photographswere recorded using a JOEL (JSM 6380LA) analyzer. FTIR spectra were recorded using NICOLET AVATAR 530 spectrophotometer. DSC thermograms were produced with a TA Q200 Differential Scanning Calorimeter, under nitrogen environment. The first temperature cycle heated the sample to 100ºC, where it remained isothermal for 15 minutes to remove the remaining water in the samples. The sample was then cooled to -10ºC and immediately reheated to 250ºC. The heating/cooling rate was set at 10ºC/min.

III. RESULTS AND DISCUSSIONS

Fourier transform infra red spectroscopic measurements:

FTIR spectra of GG, CMC and their blend films (80/20, 60/40 and 50/50) were recorded. Fig. 1 shows the FTIR spectra of pure and blend films in the wave length range of 4000-500 cm^{-1}.Guar gum showed the presence of a very strong and broad absorption band at 3347.3cm^{-1} is assigned to –OH bond stretching, while the sharp absorption band located at 2918.2cm^{-1} may be attributed to –CH group stretching. The absorption band appearing at 1628.3cm^{-1} is due the –OH bond belonging to water molecules. $–CH_2$ group bending is assigned to an absorption band located at 1370.9cm^{-1} and the bending of $–CH_2–O–CH_2–$ appears in the 1012.7cm^{-1}frequency region [20]. The FTIR spectra of CMC showed an hydroxyl group (–OH stretching) at 3500cm^{-1}, a hydrocarbon group (C-H stretching of the $–CH_2$ groups) at 2916.7cm^{-1}, a carbonyl group (C=O stretching) at 1593.7cm^{-1}, a $–CH_2$ scissoring around 1412cm^{-1} and ether groups (-O- stretching) at 1026cm^{-1}[21, 22]. It is noticed that the hydroxyl stretching bands became much broader for 80/20 and 60/40 GG/CMC blends compared to CMC. The hydroxyl and carbonyl characteristic bands for 20/80, 40/60 and 50/50 blend compositions are observed at 3336.3cm^{-1}, 3340.4cm^{-1}, 3348.2cm^{-1} and 1591.5cm^{-1}, 1592.2cm^{-1}, 1593.5cm^{-1} respectively. The hydroxyl characteristic bands for 60/40 and 80/20 GG/CMC blends got shifted to lower wave length compared to GG and CMC whereas for 50/50 GG/CMC blend such observations are not found. Similarly the carbonyl characteristic bands for 60/40 and 80/20 blend compositions are shifted towards lower wave numbers compared to that of CMC. These observations confirms the formation of intermolecular hydrogen bonding between the hydroxyl groups of Guar gum and carbonyl groups of carboxymethylcellulose for 60/40 and 80/20 blend compositions. Hence, the FTIR spectroscopic measurement confirms that GG/CMC blend is miscible for higher proportions of GG in the blend and GG/CMC blend is semi-miscible in nature.

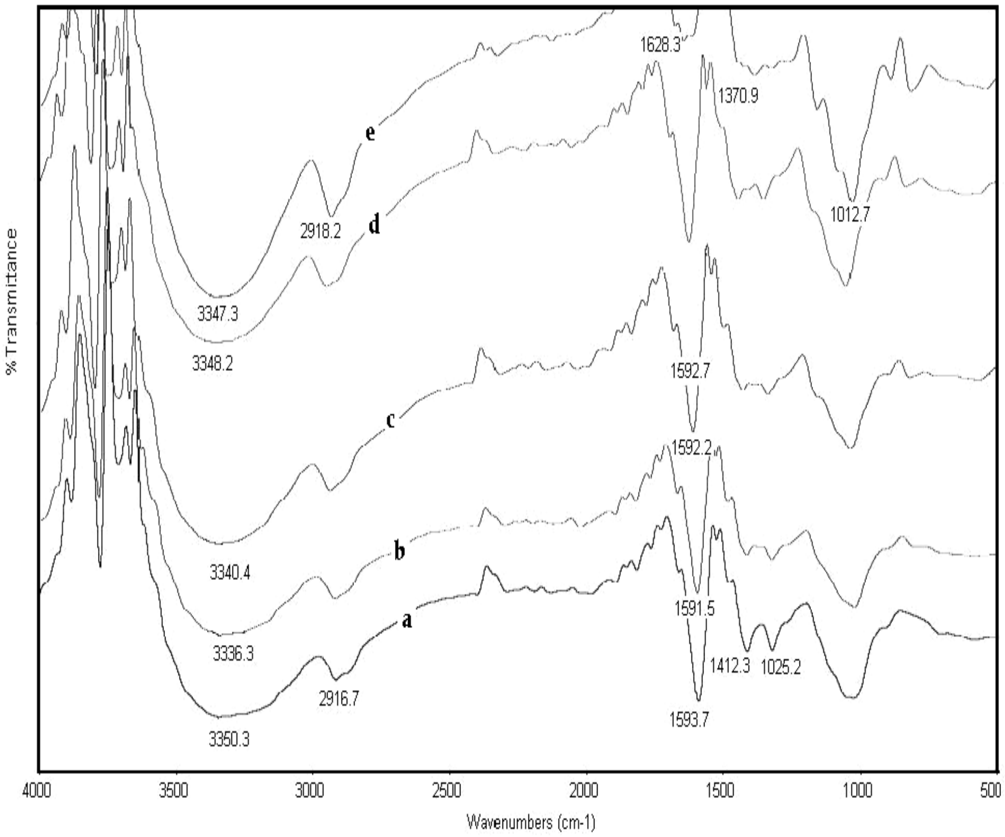

Figure 1: FTIR spectroscopy for (a) CMC, (b) 80/20 GG/CMC blend, (c) 60/40 GG/CMC blend, (d) 50/50 GG/CMC blend and (e) GG

Morphological studies:

All the solution-casted films of GG, CMC and their blends (20/80, 40/60, 50/50, 60/40 and 80/20) were transparent. To check the morphology of the blends SEM was used. The results are given in Fig. 2. GG/CMC blends show aggregated particles for 20/80, 40/60 and 50/50 GG/CMC blend compositions. For 60/40 and 80/20 GG/CMC, it can be observed that the GG granule was well distributed in the CMC matrix, confirming a good interaction between GG and CMC. From the SEM images, measured at high magnification (X 5,000), it was distinctly observed that the blend with 60/40 and 80/20 GG/CMC compositions are homogeneous. The observation suggests that GG/CMC blend is miscible only when the GG content is more than 60 weight percentage. Hence GG/CMC blend is semi-miscible in solid state.

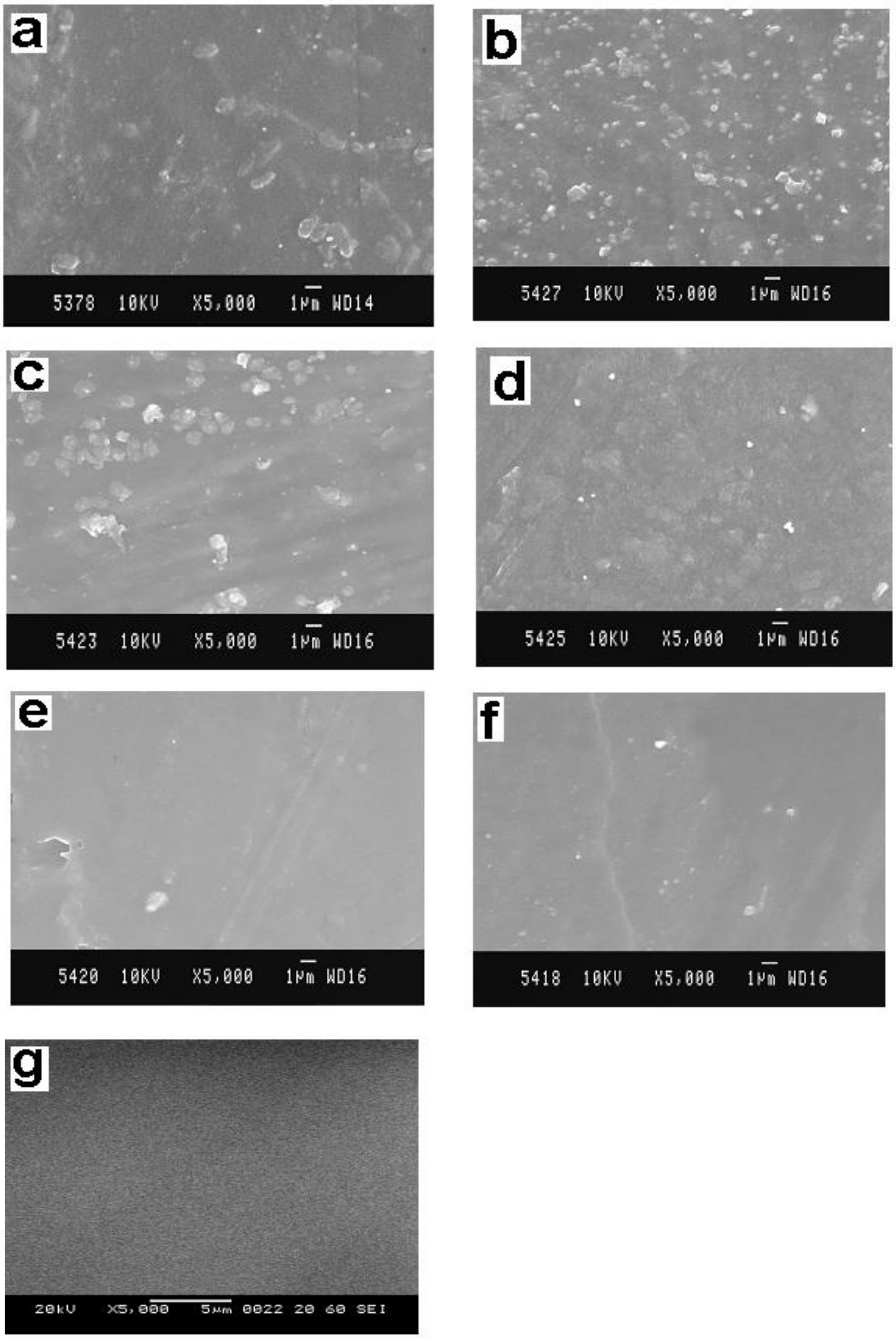

Figure 2: Scanning electron micrographs for (a) GG, (b) 20/80 GG/CMC blend, (c) 40/60 GG/CMC blend, (d) 50/50 GG/CMC blend, (e) 60/40 GG/CMC blend, (f) 80/20 GG/CMC blend and (g) CMC

Glass transition temperature measurements:

The thermal properties of GG, CMC and their blend composition 80/20 were studied by means of DSC-Tg determination and the thermograms are given in Fig. 3. The glass transition temperature was taken as the mid-point of the change of slope in the DSC curves [23, 24, 25].

It is observed in the respective thermograms that all the blends showed single composition-depended glass transition temperature and Tg is in between GG and that of CMC, indicating intermolecular interaction between the polymers [26].

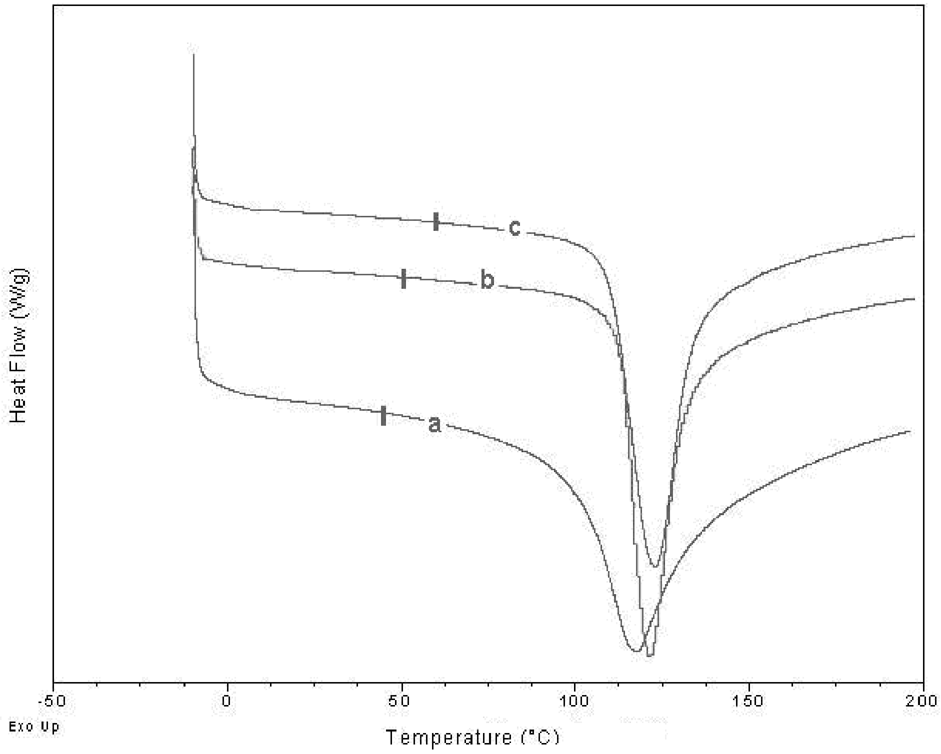

Figure 3: DSC traces of (a) GG, (b) 80/20 GG/CMC blend and (c) CMC

The Tg of miscible blend can calculated using Fox Equation (1) [27], or Wood's Equation (2) [28], or Pochan's Equation (3) [29].

$$1/Tg = w_1/Tg_1 + w_2/Tg_2 \tag{1}$$

$$Tg = w_1 Tg_1 + w_2 Tg_2 \tag{2}$$

$$\ln Tg = w_1 \ln Tg_1 + w_2 \ln Tg_2 \tag{3}$$

where w_1, w_2, $T_{g,1}$ and $T_{g,2}$ are the weight fractions and glass transition temperatures of the corresponding polymer 1 and polymer 2 respectively.

The experimental Tg values compared with theoretical Tg values and are summarized in Table 1. Experimental Tg values for 80/20 GG/CMC blend is in good agreement with the theoretically calculated Tg values indicating an intermolecular interactions of hydrogen bonding type between the polymers [26, 30, 31, 32].

Table 1: Experimental and theoretical glass transition temperature (Tg) of GG/CMC blends

Blend comp. GG/CMC	Experimental Tg values (ºC)	Theoretical Tg values (ºC)		
		Fox equation	Wood equation	Pochan's equation
0/100	57.8	--	--	--
40/60	53.13	51.63	52.48	52.06
100/0	44.5	--	--	--

VI. CONCLUSION

Guar Gum/Carboxymethylcellulose blend thin films were prepared by solution casting method using distilled water as common solvent. The studies confirm that the polymer blend of Guar Gum/CMC is miscible only when the GG content is more than 60%. Below this critical GG concentration the blends were found to be immiscible. Homogeneity of miscible compositions of GG/CMC blends and specific intermolecular interactions of hydrogen bonding type were investigated by SEM, FTIR, and DSC analysis.

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