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Research Article

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Characterization of Cellulose Ether Films Containing Tween 20 and Tween 40

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ABSTRACT

In the present study, cellulose ether films containing two kinds of sorbitan based surfactants, namely, polyoxyethylenesorbitan monolaurate (Tween 20) and polyoxyethylenesorbitan monopalmitate (Tween 40) were prepared by casting from aqueous solutions. Three cellulose ethers were used hydroxyethylcellulose (HEC), hydroxypropylcellulose (HPC), and carboxymethylcellulose (CMC). The obtained films were characterized by means of attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), optical properties, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). ATR-FTIR spectra of cellulose ether/tween films showed that OH band shifted towards higher wavenumber values when compared to pristidine cellulose ethers. The transparency of cellulose ether films was reduced after the addition of Tween 20 and 40. The thermal stability of CMC and HPC films increased in the presence of Tween 20 and 40. For HEC film, the thermal stability depends on the Tween used. DSC measurements indicated that Tween 20 and 40 act as plasticizers for CMC, HEC and HPC.

Keywords: CMC; HPC; HEC; Tween; Miscibility

INTRODUCTION

Non-ionic cellulose ethers such as hydroxyethylcellulose (HEC), hydroxypropylcellulose (HPC), and carboxymethylcellulose (CMC) are water-soluble derivatives of cellulose that have been widely used as food additive, coatings, pharmaceutical excipients, encapsulations, plastics, and food packaging [1-3]. Among the various additives incorporated in the polymer films, plasticizers are widely used to improve processability, flexibility, and durability [4]. In general, plasticizers are small, non- volatile molecules which promote a higher separation among polymer chains leading to lower glass transition and melting temperatures [4]. Moreover, their use can also bring health risks, especially when used in its composition, plasticizers such as di(2-ethylhexyl) phthalate (DEHP) [5-7].

Non- toxic surfactants based on sugar, such as sorbitan derivatives, like polyoxyethylenesorbitan monolaurate (Tween 20) and polyoxyethylenesorbitan monopalmitate (Tween 40) appear as an alternative to the replacement of DEHP and other plasticizers sparingly toxic and traditionally used such as polyethylene glycol (PEG), glycerin and propylene glycol [8].

The aim of this work was to characterize films prepared by mixing of carboxymethylcellulose (CMC), hydroxypropylcellulose (HPC) and 2-hydroxyethylcellulose (HEC) with two different types of sorbitan-based surfactants, Tween 20 and Tween 40. The effect of addition of surfactants on the thermal, spectroscopy and optical properties of cellulose ether films were evaluated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), fourier transform infrared spectroscopy (FTIR), and UV–vis absorbance spectra.

EXPERIMENTAL MATERIALS

For this present study, carboxymethylcellulose, CMC, ($\overline{M_w}$=90,000 g.mol, DS_{cm}=0.9), hydroxypropylcellulose, HPC, ($\overline{M_w}$=80,000 g.mol), 2-hydroxyethylcellulose (HEC) with viscosity average molar mass of 90,000, and the surfactants: polyoxyethylenesorbitan monolaurate (Tween 20) and polyoxyethylenesorbitan monopalmitate (Tween 40) were purchased from Sigma- Aldrich. Both polymers and surfactants were used as received. The chemical structures of polymers and surfactants are schematically represented in Figure 1.

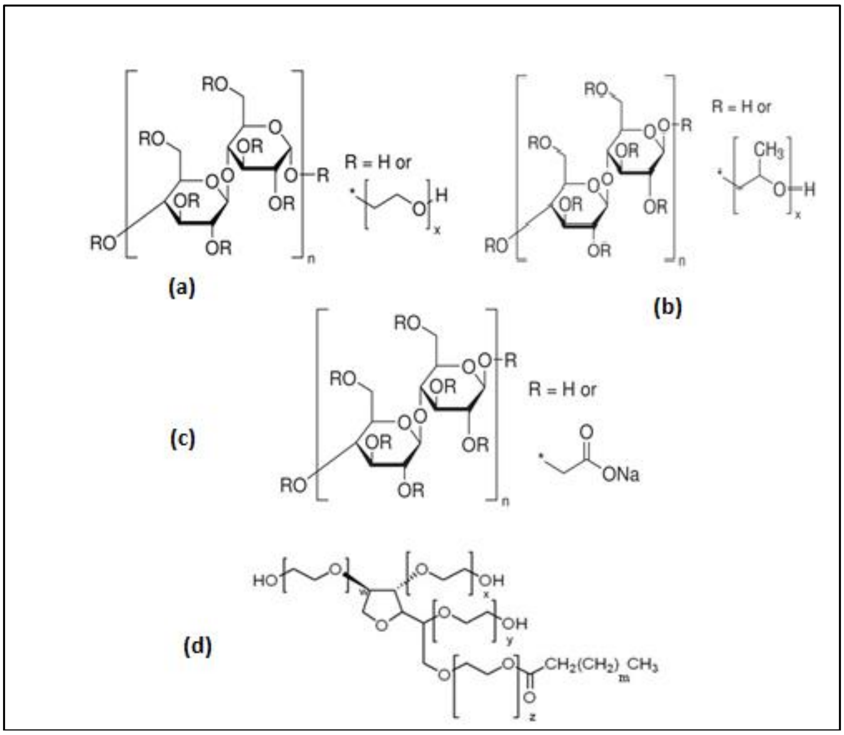


Figure 1: Schematic representation of chemical structures of (a) 2-hydroxyethylcellulose (HEC), (b) hydroxypropylcellulose (HPC), (c) carboxymethylcellulose (CMC), and (d) surfactants: Tween 20 and Tween 40. These surfactants possess 12 and 16 carbons in alkyl chain, respectively [9]. Where: x + y + z + w = 20.

METHOD

Sample preparation

Films of CMC, HPC and HEC with Tween 20 and 40 were obtained by casting method from aqueous solutions at 60ºC. The samples were dried until constant mass. The content of surfactants (as weight fraction, W) in the dried mixture with the polymers ranged from 0.1 to 0.30.

Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR)

ATR-FTIR spectra of Tween 20 and 40, cellulose ethers and cellulose ether/Tween films were obtained using a Shimadzu IRAffinity-1 spectrometer equipped with a single-reflection attenuated total reflectance (ATR) accessory. A ZnSe crystal mounted in tungsten carbide was used. The analysis was carried out in the frequency range between 700-4000 cm^{-1}.

Optical properties of the films

Transmittance spectra of cellulose ethers and their films with the surfactants (Tween 20 and 40) were obtained on quartz substrate using UV-Visible spectrophotometer (Shimadzu, UV2600).

Thermogravimetric Analysis (TGA)

Thermal stability of the pristidine cellulose ethers and cellulose ether/Tween films were performed using a Shimadzu thermogravimetric analyzer (Model DTG-60) under dynamic N_2 atmosphere (gas flow of 50 mL/min). The samples were heated in an alumina crucible at a rate of 10°C/min over a temperature range of 30–500°C.

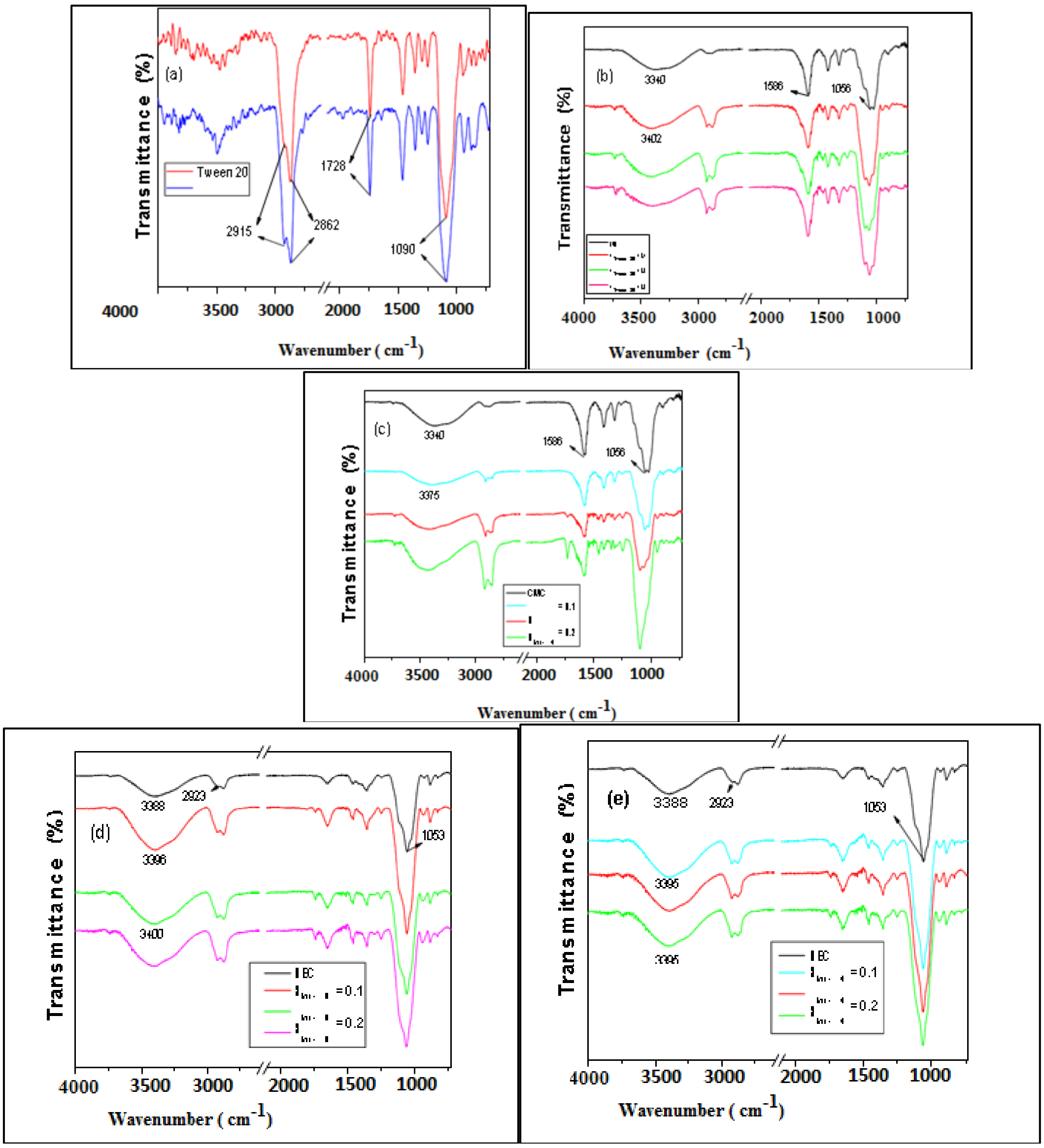
Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) curves were obtained in a TA-DSC Q10V9.0 equipment. Closed Al crucibles loaded with 3 mg of each sample under a dynamic N_2 atmosphere (50 mL/min) were heated and cooled down at rates of 10°C/min, in the temperature range from -80°C to 200°C. Empty pans were used as reference. The second heating was considered for the determination of the glass transition temperature (T_g), melting temperature (T_m) and $\Delta_{fus}H$ of the samples. The DSC cell was calibrated with In (T_m = 157°C; □*H*fus = 28.54 J g^{-1}) and Zn (T_m = 420°C). One should notice that typically the standard deviation determined for triplicates was 1^{O}C.

RESULTS AND DISCUSSION

Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy

ATR-FTIR spectroscopy analysis was performed to better understand the effects of Tween 20 and 40 molecules on the structure of the cellulose ether films. Figure 2 shows ATR-FTIR spectra for the surfactants (Tween 20 and 40) and HEC, HPC, and CMC films containing different contents of Tween 20 and 40. ATR-FTIR spectra for pristine cellulose ethers were showed in the Figure 2 (b-g) for comparison. All plots were shifted for clarity.



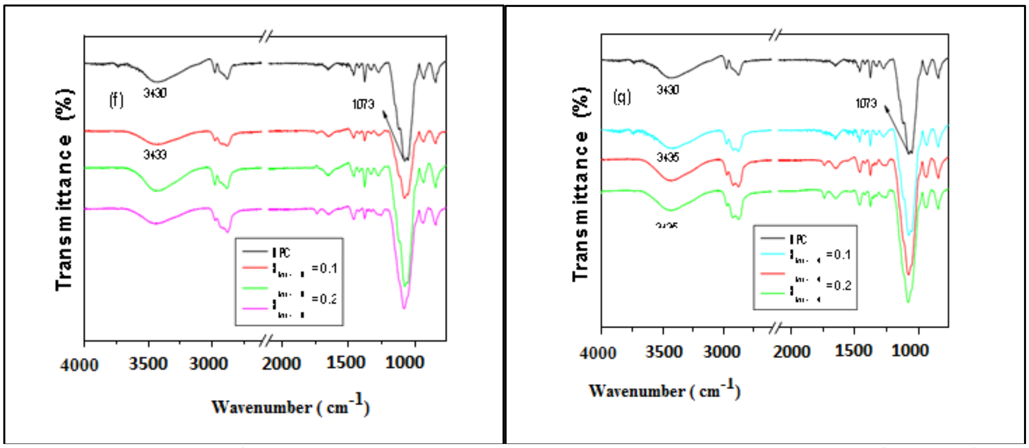


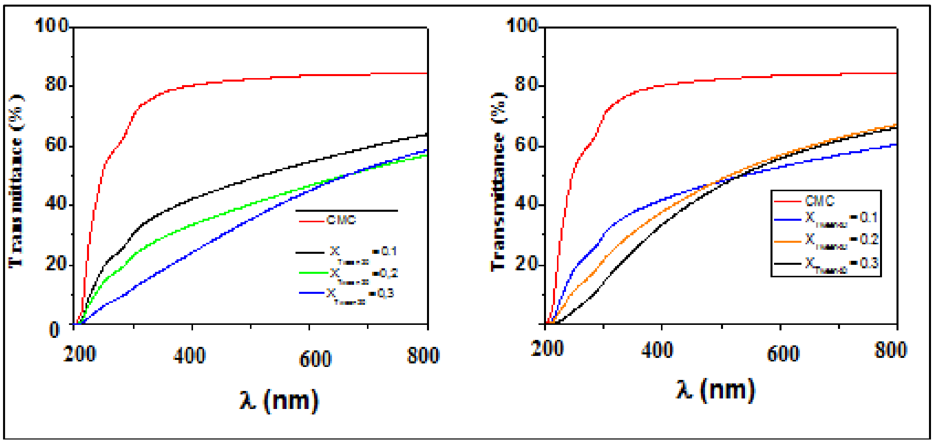
Figure 2: ATR-FTIR spectra of (a) Tween 20 and 40, (b-g) cellulose ethers and cellulose ether/Tween films as a function of surfactant content (Tween 20 (b,d and f) or Tween 40 (c,e and g)).

The ATR-FTIR spectra for pure Tween 20 and 40 (Figure 2a) showed characteristic bands. The strong broad band in the range of 3200-3700 cm^{-1} was assigned to OH stretching. Bands at 2915, 2862, 1728, and 1090 cm^{-1} were assigned as CH3 stretching, CH$_2$ stretching, C=O, and C-O-C stretching, respectively [10, 11]. ATR-FTIR spectrum of CMC (Figure 2 b and c) exhibited bands at 3340, 1586, 1056 cm^{-1}that can be attributed to the stretching of the hydroxyl group (OH), COO$^-$ group, and C-O-C stretching, respectively [12,13]. From Figure 2 d and e, ATR-FTIR spectrum of HEC showed bands at 3388, 2923, and 1053 cm^{-1} that are assigned to OH stretching, CH stretching, and stretching vibration of C-O group [14]. In the case of HPC, ATR-FTIR spectrum (Figure 2 f and g) presented typical bands at 3430 and 1073 cm^{-1} that are attributed to the stretching of the OH and C-O-C groups [15].

The ATR-FTIR spectra of cellulose ether films containing various surfactant proportions are depicted in Figure 2 b-g. As can be observed in Figure 2 b-g, for all the composition of cellulose ether/Tween studied, the OH band shifted to higher wavenumber when compared with the pure cellulose ethers, suggesting the formation of the inter and intra-molecular hydrogen bonding between surfactants (Tween 20 and 40) and cellulose ethers.

Optical properties of the films

As can be observed in Figure 3, regardless of the type of Tween used in the preparation of the films, the transmittance of cellulose ether films decreased in comparison with the pure cellulose ether films. Furthermore, the extent of reduction of the transmittance is dependent on the surfactant content in the films. These results indicate that the incorporation of the Tweens into HPC, HEC and CMC films alter their physical structure making them more opaque. Moreover, the cellulose ether/Tween films can inhibit the light-induced deterioration of packaged foods due to the higher absorption of ultraviolet radiation than pure cellulose ethers. This property is fundamental to the development of packaged foods [16].



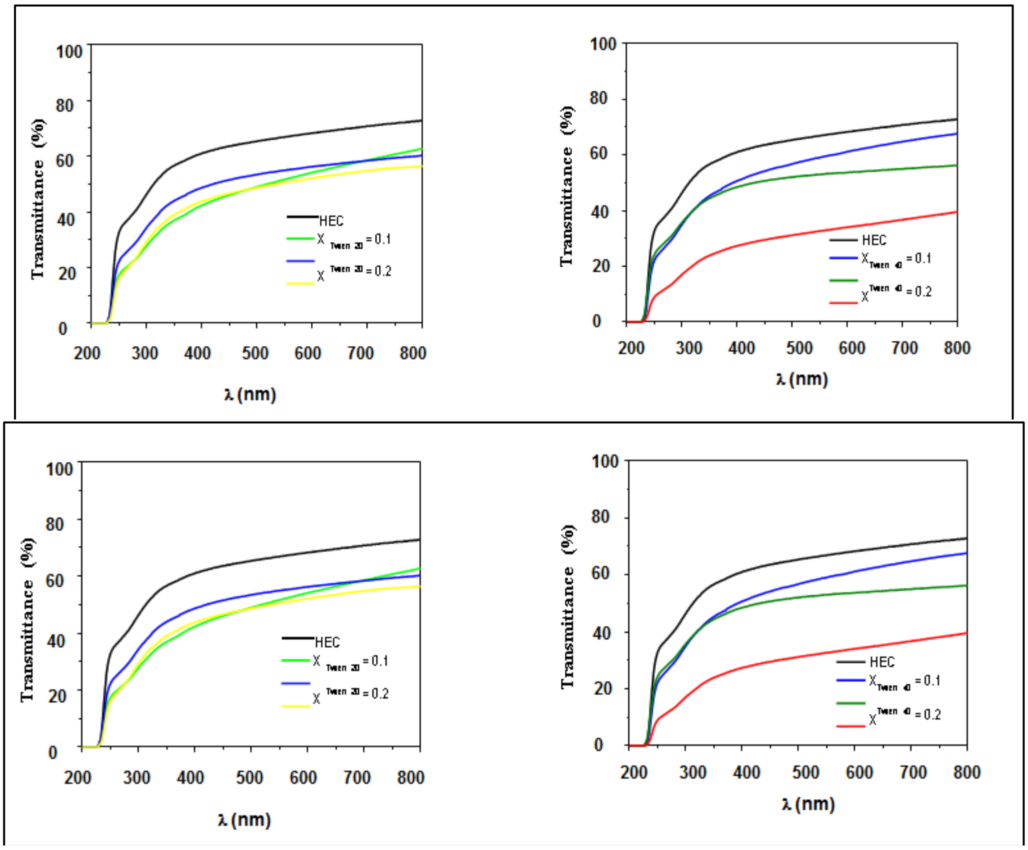
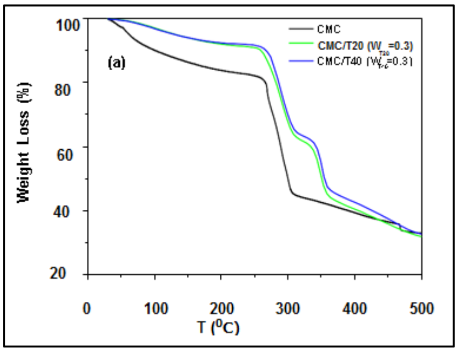


Fig.3 Transmittance spectra of cellulose ethers and cellulose ether/Tween films as a function of surfactant content (Tween 20 or Tween 40).

Thermogravimetric Analysis (TGA)

Figure 4 illustrates the thermogravimetric analysis of pristine cellulose ethers and their mixtures with the Tween 20 and 40 (W_{Tween} = 0.3) in the temperature range of 30-500°C. In general, the major weight losses occurred in the range 250-400°C and can be attributed to the decomposition of the cellulose ethers and surfactant molecules. Table 1 shows the onset thermal decomposition temperature (T_{onset}) obtained from TGA for pristidine cellulose ether films and cellulose ether/Tween films. As can be observed in Table 1, T_{onset} values of CMC and HPC films enhanced with the addition of Tween 20 or 40, suggesting an increasing in the thermal stability. In the case of HEC/Tween films, T_{onset} was dependent on the type of surfactant used to prepare the films, where T_{onset} decreased with the incorporation of Tween 20 and increased with the Tween 40. Furthermore, the obtained results showed that the T_{onset} values are higher for HPC/Tween films, indicating that the presence of the hidroxypropyl group of HPC contributed to a higher interaction with the Tween 20 and Tween 40 than hydroxyethyl and carboxymethyl groups of the HEC and CMC, respectively.



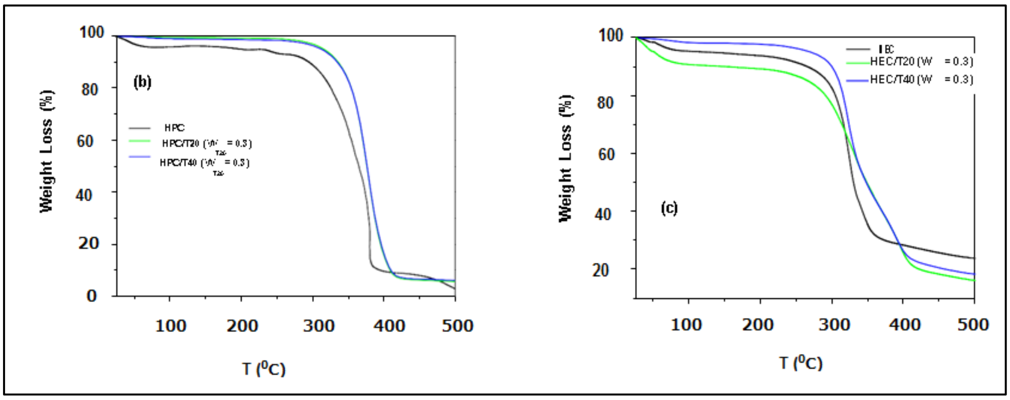


Figure 4: TG curves for pure cellulose ethers and cellulose ether/Tween films.

Table 1: T_{onset} values obtained from TGA for pristidine cellulose ether films and cellulose ether/Tween films (W_{Tween} = 0.3)

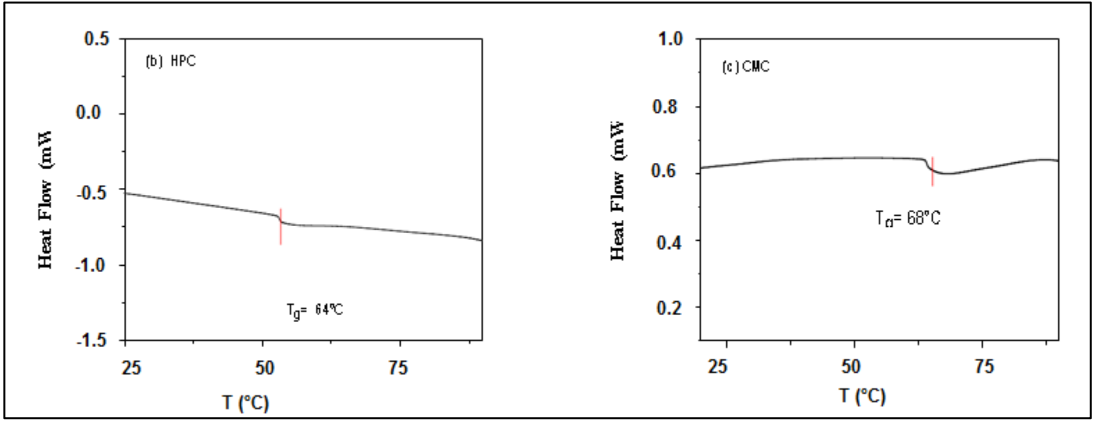
Cellulose Ethers	Tonset (°C)		
	Pritidine Cellulose Ether	**Cellulose Ether/ Tween 20**	**Cellulose Ether/ Tween 40**
CMC	262	264	269
HEC	300	280	304
HPC	318	352	352

Differential Scanning Calorimetry (DSC)

To properly understand the miscibility between cellulose esters and the Tween 20 and 40, DSC measurements were performed for pristine polymers and for the formed films. DSC curves

Recorded for pristine cellulose ethers are shown in Figure 5. The T_g values for HEC, HPC and CMC were determined as 63ºC, 64ºC and 68ºC, respectively. Tween 20 and Tween 40 possess T_g at -61°C [17].

Figure 5: DSC curves for HEC, HPC, and CMC films



All films of HEC, HPC and CMC with Tween 20 and 40 presented only one T_g in the DSC curves (not shown), suggesting a compatibility between the components of the mixtures. Experimental values of T_g obtained for cellulose ethers in the presence of Tweens (W_{T20} and W_{T40} = 0.3) are showed in Figure 6.

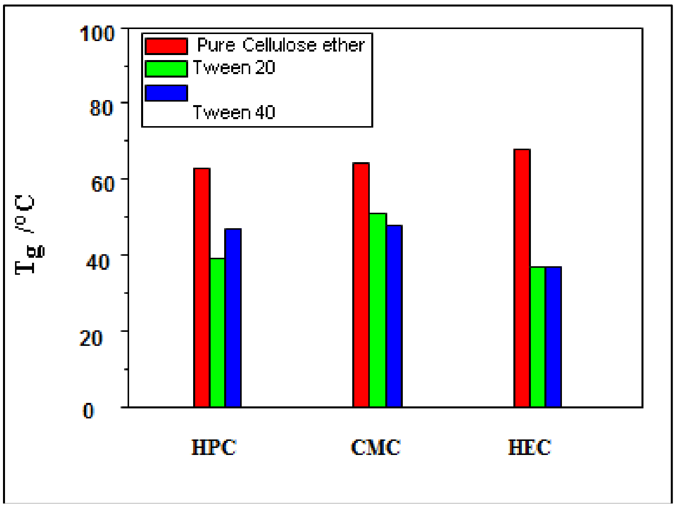


Figure 6: Tg values for pure cellulose ethers and cellulose ether/Tween films obtained with W_{Tween} = 0.3.

Figure 6 shows that Tg values of pure cellulose esters decreased upon addition of Tween 20 and 40. This effect can be associated to an increase in polymer chain mobility and flexibility when the surfactants were incorporated in the free volume of polymer. Similar behavior was observed for mixtures of Tween 20, 40 and 60 with cellulose esters [17]. Furthermore, the effect of alkyl chain length of surfactants on the Tg values of HEC, HPC, and CMC can be analyzed through Figure 6. Tween 20 and 40 possess 12 and 16 carbon atoms in the alkyl chains, respectively [9]. Figure 6 shows that the surfactants alkyl chain length has practically no effect on the Tg values of CMC. However, for mixtures of HEC with Tween 20 and 40, Tg values enhanced with the increasing surfactant alkyl chain length. In the case of HPC, higher reduction of Tg value occurred in the presence of the surfactant of longest alkyl chain, Tween 40.

CONCLUSIONS

In this work, cast films of CMC, HEC, and HPC were obtained in the presence of two types of non-ionic surfactants, Tween 20 and 40. ATR-FTIR spectra of cellulose ether films showed that the hydrogen bonds of these polymers were altered upon addition of Tween 20 and 40. The experimental results suggest that these surfactants have significant influence on the thermal and optical properties of cellulose ether films. The DSC results demonstrated that Tween 20 and 40 can be used as plasticizers for CMC, HEC and HPC at W_{Tween} = 0.3.

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