Determination of structural and mechanical properties, diffractometry, and thermal analysis of chitosan and hydroxypropylmethylcellulose (HPMC) films plasticized with sorbitol

Determinação das propriedades mecânicas e estruturais, difratometria e análises térmicas de filmes de quitosana e hidroxipropilmetilcelulose (HPMC) plastificados com sorbitol

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Abstract

In this work, the structural, mechanical, diffractometric, and thermal parameters of chitosan-hydroxypropylmethylcellulose (HPMC) films plasticized with sorbitol were studied. Solutions of HPMC (2% w/v) in water and chitosan (2% w/v) in 2% acetic acid solution were prepared. The concentration of sorbitol used was 10% (w/w) to both polymers. This solutions were mixed at different proportions (100/0; 70/30; 50/50; 30/70, and 0/100) of chitosan and HPMC, respectively, and 20 mL was cast in Petri dishes for further analysis of dried films. The miscibility of polymers was assessed by X-ray diffraction, scanning electronic microscopy (SEM), differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA). The results obtained indicate that the films are not fully miscible at a dry state despite the weak hydrogen bonding between the polymer functional groups.

Keywords: *films; chitosan; hydroxypropylmethylcellulose; physico-chemical properties.*

Resumo

Neste trabalho, os parâmetros estruturais, mecânicos, difratométricos e térmicos de filmes de quitosana e hidroxipropilmetilcelulose (HPMC), plastificados com sorbitol, foram estudados. Soluções de HPMC (2% m/m) em água, e quitosana (2% m/m) em uma solução de ácido acético 2%, foram preparadas. A concentração de sorbitol usada foi de 10% (m/m) para ambos os polímeros. Estas soluções foram misturadas em diferentes proporções (100/0; 70/30; 50/50; 30/70 e 0/100) de quitosana e HPMC, respectivamente, e 20 mL foram vertidos em placas de Petri de poliestireno, para posterior análise dos filmes prontos. A miscibilidade dos polímeros foi avaliada através da Difração por Raio-X, Microscopia Eletrônica de Varredura, Calorimetria Exploratória Diferencial (DSC) e Análise Termogravimétrica (TGA). Através dos resultados obtidos, os filmes não são totalmente miscíveis no estado seco, embora existam ligações fracas de hidrogênio entre os grupos funcionais dos biopolímeros.

Palavras-chave: *filmes; quitosana; hidroxipropilmetilcelulose; propriedades físico-químicas.*

1 Introduction

Recently, there has been an increasing interest in edible films and coatings. This is partly due to increased interest in renewable resources and in improved food preservation (CANER; VERGANO; WILES, 1998). Materials available for forming films and coating generally fall into the categories of polysaccharides, proteins, lipids, and resins. As mentioned by Yang and Paulson (2000), films made from polysaccharides are expected to be excellent oxygen barriers due to their highly packed and ordered hydrogen-bonded networked structure. However, hygroscopic characteristics of natural polymers such as cellulose derivatives show that swelling by water leads to a loss of the gas and vapor barrier properties. The antimicrobial activity by certain substances is another extremely important factor, and coatings active in this way attracts considerable interest. The final properties of films are determined by the miscibility of polymers, which is greatly favored by the formation of intermolecular hydrogen bonds between component polymers (YANG; PAULSON, 2000).

Chitosan is a biodegradable polysaccharide with active amino groups. Many papers have recently been published on the utilization of chitosan as a functionalized polymer (TERBOJEVICH; MUZZARELLI, 2000; HIRANO et al., 1997). A method of blending chitosan with other polymers is often applied. Such polymers, such as hydroxypropylmethylcellulose (HPMC), are recognized as materials supporting chitosan to obtain material with sufficient mechanical strength of films and fibers prepared (WRZYSZCZYNSKI et al., 1995).

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Cellulose-based biopackagings, due their hydrophilic nature, are poor moisture barriers and are frequently soluble in water thus reducing their potential use at food applications. Pawlak e Mucha (2003) reported that the hydroxypropylmethylcellulose (HPMC) form strong hydrogen bonding interactions between the functional groups of the component with chitosan. Additives (plasticizers), such as sorbitol, glycerol, or poly (ethylene glycol), are in general used to enhance the films flexibility and extensibility (YANG; PAULSON, 2000).

In the present work, we evaluated the mechanical, structural, and thermal parameters of chitosan-hydroxypropylmethylcellulose (HPMC) films plasticized with sorbitol.

2 Materials and methods

2.1 Material

Chitosan, with $2.75.10^5$ g.mol^{-1} of viscosimetric molar mass and deacetylation degree 80.6%, was purchased from Phytomare® Food Suplements located in Governador Celso Ramos – SC; hydroxypropylmethylcellulose (HPMC), with $5.25.10^4$ g.mol^{-1} of viscosimetric molar mass, was purchased from Henrifarma® Chemical and Pharmaceutical Products located in São Paulo – SP; destillated water, acetic acid, and sorbitol, were purchased from Vetec®, Duque de Caxias – RJ, and were used to prepare the solutions.

2.2 Films preparation

Two separate solutions were prepared : a HPMC (2% w/v) solution in water; and a chitosan (2% w/v) solution in 2% acetic acid. The concentration of sorbitol used was 10% (w/w) for both polymers. The chitosan/HPMC films were prepared by casting solutions of polymers in Petri dishes (polytetrafluoroethylene), with 20 mL in each dish, with subsequent drying at room temperature (20 °C ± 2 °C) for 24 hour. Before casting, the solutions of chitosan and HPMC were mixed at different proportions (100/0; 70/30; 50/50; 30/70; 0/100), respectively. All samples were stored in a dessecator.

2.3 Mechanical properties

The mechanical properties of chitosan/HPMC films were assessed by measurements of Tensile Strength (TS), Maximum Elongation (E), and Young Module (YM). The conditions of temperature and relative humidity were 23 °C and 50%, respectively. A mechanical equipment DL1000 model, manufactured by Emic®, São José dos Pinhais – PR, Brazil, with load cell of 50 kgf, was used to determine the Tensile Strength (TS), Maximum Elongation (E), and Young Module (YM) of films. The ASTM D882-95a method includes the determination of this parameters. We made 12 repetitions were performed for each sample with the following dimensions: 10 cm of length and 2.5 cm of width. The thickness of samples was measured with a hand micrometer (MYTUTOYO 102-217) graduated in 0,01 mm increments. The thickness used was an average of six measurements taken randomly. These measurements were performed within an average time of 5 minutes. Hence, the conditions of temperature and relative humidity did not interfere with experimental results.

2.4 Scanning Electronic Microscopy (SEM)

The micrographs were produced at a scanning electron microscopy, model Philips XL 30, manufactured by Mems®, Reston – Virginia, United States. The samples were fractured in liquid nitrogen, and the surface and cross section of chitosan/HPMC films were analyzed.

2.5 X-ray diffractometry

Analysis by X-ray diffractometry were performed using a diffractometer, X'pert model, manufactured by Philips®, Reston – Virginia, United States, with Cu Kα (λ = 1.5418 Å) radiation and 40 kV e 30 mA.

2.6 Thermal Analysis

Differential scanning calorimetry (DSC)

8-10 mg of sample were placed in aluminum pans, not hermetically sealed, in the equipment sample chamber, model DSC-50, manufactured by Shimadzu®, United Kingdom, under nitrogen atmosphere, with a flow of 50 mL/minute and warming rate of 10 °C/minute until 180 °C. In order to eliminate the thermal history of the samples, they were withdrawn from the equipment and were subjected to treatment by thermal shock with liquid nitrogen and, then, analyzed in a second sweep of 25 °C to 250 °C (10 °C/minute). The glass transition temperature (Tg) was obtained at the inflection point between the base lines tyhrough the change in the heat capacity of the sample.

Thermal gravimetric analysis (TGA)

The thermal gravimetric analysis (TGA) was used to measure the thermal stability of chitosan/HPMC films. A thermogravimetric analyzer, TGA-50 model, manufactured by Shimadzu®, United Kingdom, was used. The analyses were made varying the temperature from room temperature until 600 °C in an inert nitrogen atmosphere with flow of 50 ml/minute and rate warming of 10 °C/minute using 2-6 mg of sample.

3 Results and discussion

Table 1 summarizes the results for tensile strength (TS), maximum elongation (E), Young Module (YM), and thickness for chitosan/HPMC films.

The pure chitosan films showed the greatest medium to Tensile Strength. The pure HPMC films showed the highest values to Elongation. The Young Module (YM) is a parameter that characterizes the rigidity of a material. Moreover, it provides information about the hardness or resistance that this material presents to elastic deformation. The higher the Young Module values, the higher the resistance to deformation, and rigidity. With regard to the films made with a mixture of polymers, the Young Module depends on their composition (percentage). The Young Module value of pure chitosan films was 1998.18 ± 40.84 MPa and their maximum elongation were 1.85% ± 0106. The Young Module value of the pure HPMC films was of 808.13 ± 31.14 MPa and their maximum elongation was 5.14 ± 0.68%. The higher the Young Module value, the lower the flexibility of films (CANEVAROLO JUNIOR, 2002; LUCAS; SOARES; MONTEIRO, 2001). Similar behavior was observed by Chiellini et al. (2001) when the concentration of glutaraldehyde increased at the gelatin film. This behavior was also observed by Kolodziejska, Piotrowska (2006) in studies on mechanical propertiefs of gelatin-chitosan films chemically modified with transglutaminase.

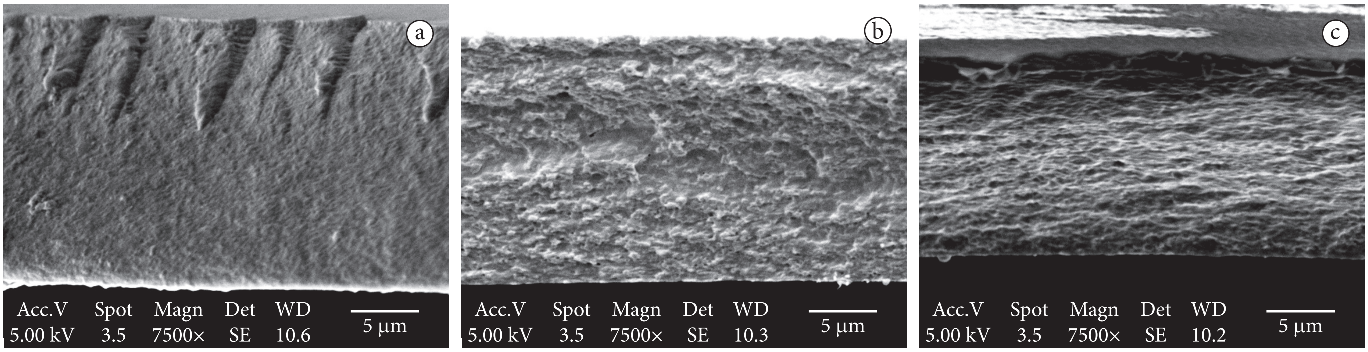
Figure 1 shows the micrographs obtained of cross sections of chitosan/HPMC films. All films had a smooth, compact, and homogeneous surface. The cross section of micrographs b, c, and d (Figure 1) showed some cavities with some tortuosities, which varied depending on the HPMC concentration on the film (the higher the HPMC concentration, the higher the totuosity). These results are consistent with those found by Yin et al. (2006), in which the micrographs of cross section confirm the partial miscibility between polymers

The diffractograms of chitosan/HPMC films are represented in Figure 2. The pure chitosan film had four diffraction peaks ($2\theta = 8.6^{o}$; 11.7^{o}; 15.1^{o}, and 20.6^{o}) thus confirming the presence of crystalline fields in its structure. These values are very similar to those found by Yin et al. (2006), (8.3^{o}; 11.28^{o}; 18.1^{o},

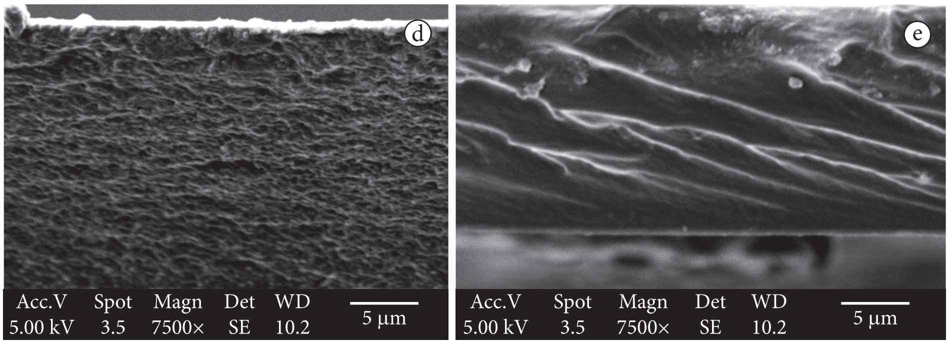
Table 1. Mechanical properties of chitosan/HPMC films at 23 °C and 50% of relative humidity.

	Tensile strength (MPa)	Maximum elongation (%)	Young module (MPa)	Thickness (μm)
Q100/HPMC0	35.2 ± 1,41^{a}	1.85 ± 0,106^{a}	1998.1 ± 40,8^{a}	17.10 ± 1,2^{a}
Q70/HPMC30	30.92 ± 0,81^{b}	4.59 ± 0,44^{b}	1290.6 ± 37,2^{b}	16.80 ± 0,8^{a,b}
Q50/HPMC50	26.26 ± 0,05^{c}	4.39 ± 1,03^{b,c}	1153.45 ± 10,1^{c}	16.48 ± 0,5^{a,b,c}
Q30/HPMC70	23.95 ± 0,021^{d}	2.35 ± 0,5^{d}	1249 ± 62,2^{b,d}	16.14 ± 0,6^{a,b,c,d}
Q0/HPMC100	21.45 ± 3,07^{d,e}	5.14 ± 0,68^{b,c,e}	808.1 ± 31,14^{e}	15.4 ± 1,5^{a,b,c,d,e}

Where: Different letters between cells of same column indicate that the values are significantly different ($p < 0,05$).



Chitosan100/HPMC0 (cross section) Chitosan70/HPMC30 (cross section) Chitosan50/HPMC50 (cross section)



Chitosan30/HPMC70 (cross section) Chitosan0/HPMC100 (cross section)

Figure 1. Scanning Electronic Microscopy (SEM) micrographs of chitosan/HPMC.

and 22.44°). On the other hand, the pure HPMC films had only two diffraction peaks ($2\theta = 11.7^{\circ}$ and 20.18°), which is a similar result to those reported by Sakata, Shiraishi and Otsuka (2006), which were approximately 10° and 20° demonstrating that films made from this polymer are, usually, more amorphous. The diffractograms of chitosan70/HPMC30, chitosan50/HPMC50, and chitosan30/HPMC70 films indicate a shift of diffraction angles and a change in the peaks intensity, which, according to Yin et al. (2006) can be considered an indicative of a partial miscibility between polymers. The development of crystallinity in a polymer is dependent upon its structural regularity, and the factors that affect this crystallinity include polarity, the presence of hydrogen links as well as the ability to pack polymer chains (CANEVAROLO JUNIOR, 2002).

Table 2 shows the glass transition temperature (Tg) of pure chitosan film. Some properties of chitosan, such as crystallinity, molar mass, and degree of deacetilation, may have some variations depending on the source and/or method of extraction. These parameters influence directly the Tg value. Ratto, Hatakeyama and Blumstein (1995) obtained a Tg value of 30 °C for a chitosan sample. Sakurai, Maegawa and Takahashi (2000) found a Tg value of 203 °C, whereas Kittur et al. (2002) and Netto et al. (2005) did not found any evidence of Tg suggesting, therefore, that the Tg of chitosan could be close to the polymer's thermal degradation temperature

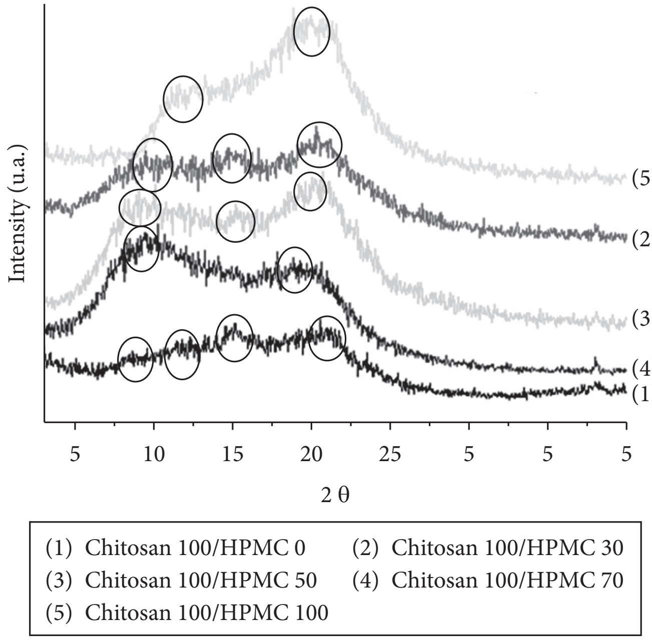


Figure 2. Diffractograms of chitosan/HPMC films.

One of criteria adopted for assessing the miscibility of polymer systems is based on the determination of glass transition temperature (Tg). In order to be considered a miscible polymeric system, it must have a single glass transition located at an intermediate range of temperature for transitions of pure components (BARBANI et al., 2005). Several specific types of interactions are responsible for miscibility, such as hydrogen links and dipole-dipole interactions, among others (LAU; MI, 2002).

The Tg of pure HPMC films is shown in Table 2. The chitosan70/HPMC30 and chitosan30/HPMC70 films had two glass transition temperatures (Tgs), and the first temperature of both films is located between the Tg of pure polymers. This is a sign of a partial miscibility between polymers.

Figure 3 (graphs A and B), in which the blue lines mean residual mass loss and the black lines mean derivative termogravimetric curve, shows that the pure chitosan and pure HPMC filmshave two degradation stages, respectively. The first stage is the water loss of films and the second stage is the depolymerization of chitosan chain, cellulose ethers degradation of HPMC, decomposition (thermal and oxidative), steaming, and disposal of volatile compounds (NETTO et al., 2005). The result obtained for the chitosan films is similar to that found by Netto et al. (2005), which was 60 °C in the first stage (water loss), and in the second stage it started at 240 °C and reached a maximum at 380° With regard to chitosan, C. Zohuriaan and Shokrolahi (2004) reported a first degradation stage with Tmax of 47 °C, and in the second degradation stage the Tmax was 325.5 °C. Yin et al. (2006) found values of 65.5 °C for the first stage and 355 °C for the second stage for films of pure HPMC.

The others films (Q70/HPMC30; Q50/HPMC50, and Q30/HPMC70), graphs C, D, and E in Figure 3, respectively, had three stages of mass loss, in which the first stage refers to water loss. The degradation of these films is in accordance with studies carried out by Khutoryanskiy et al. (2003), in which the degradation profile was typical for films of pure chitosan and pure HPMC. This behavior also confirms the partial miscibility between the polymers. The pure HPMC film proved to be more thermally stable that those derived from cellulose such as carboxymethylcellulose (CMC), hydroxyethylcellulose (HEC), and methylcellulose (MC), which had DTGA maximum for the mass loss at 303.4 °C, 298.9 °C, and 370.4 °C, respectively (LI; HUANG; BAI, 1999).

Table 2. Glass transition temperature (Tg) of chitosan/HPMC films.

	Q100/HPMC0	Q70/HPMC30	Q50/HPMC50	Q30/HPMC70	Q0/HPMC100
Tg (°C)	114.06	124.85 and 169.03	196.23	127.65 and 170.43	164.56

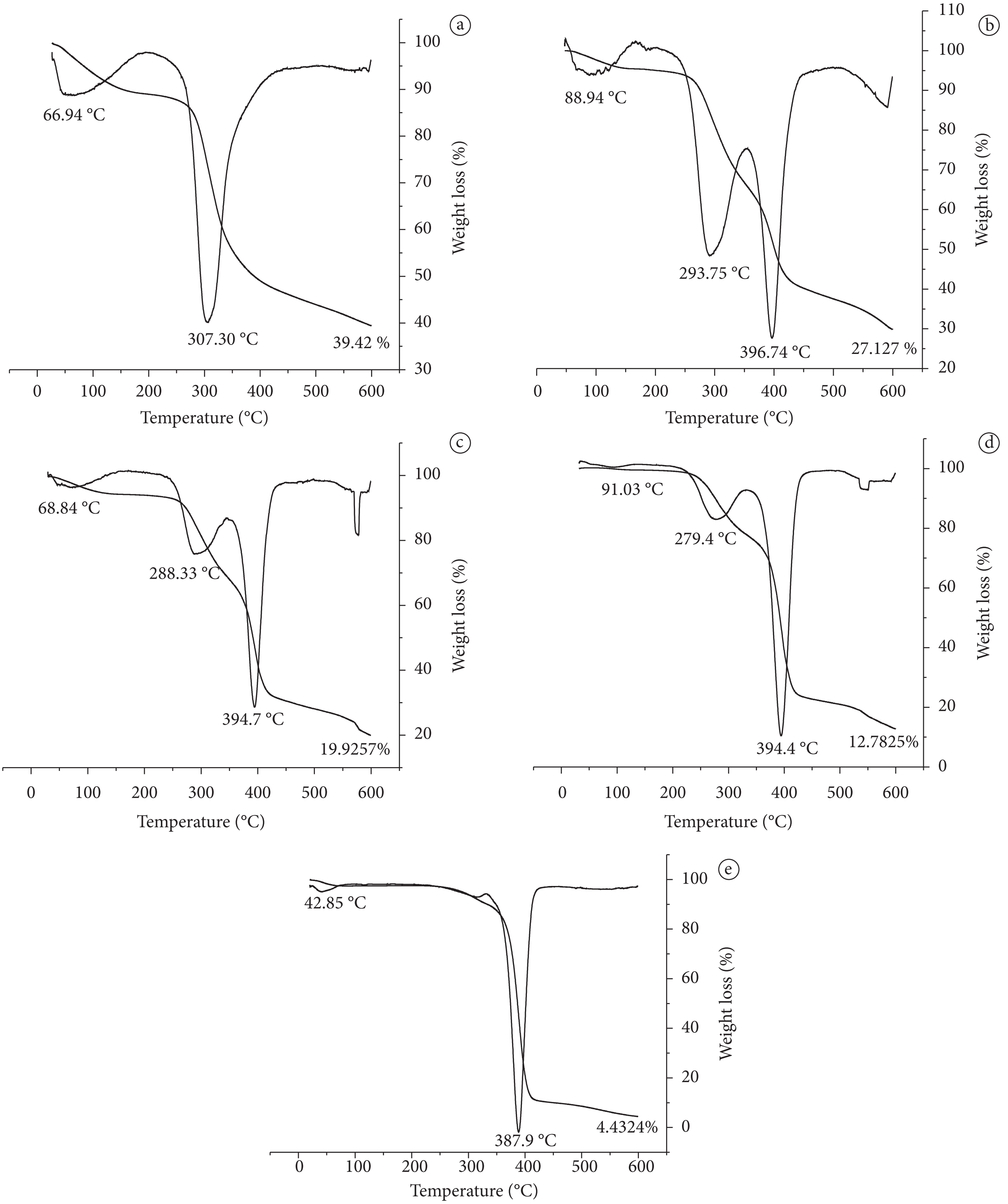


Figure 3. Thermogravimetric analysis of chitosan/HPMC films (A:Q100/HPMC0; B:Q70/HPMC30; C:Q50/HPMC50; D:Q30/HPMC70, and E:Q0/HPMC100).

4 Conclusions

The results obtained revealed that chitosan and hydroxypropylmethycellulose are not fully miscible blends. If hydrogen bondings between polymers are relatively weak, the full miscibility cannot be achieved. The micrographs of surfaces were smooth, compact, and homogeneous. The higher the proportion of HPMC in the samples, the more roughness of the cross section with some cavities. The films of pure chitosan showed the highest averages on Tensile Strength and Young Module and lowest on Elongation.

Despite the differences in the chemical composition of chitosan and HPMC, all prepared films were manageable and had good appearance. The additive (sorbitol) used was compatible with both biopolymers. The crystallinity was highly dependent on the chemical composition of the films, which had a critical influence on the properties of the resulting films.

We can conclude that films made with both polymers, chitosan and hydroxypropylmethylcellulose (HPMC), can have a wide range of industrial applications (packing and coverage), which depends on knowledge of the physical and chemical properties of the materials used. Moreover, the use of biomaterials may reduce the use of non-renewable resource materials (petroleum) and reduce pollution levels.

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