



*Dedicated to Professor Ionel Haiduc  
on the occasion of his 75<sup>th</sup> anniversary*

## STRUCTURAL AND PROPERTIES CHANGES INVESTIGATION UPON ORGANIC ACID MODIFIED STARCH-BASED FILMS

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Influence of organic acid treatment of corn starch upon structural properties of modified starch microparticles/plasticized starch based films was investigated. X-ray diffraction curves showed a disruption of the  $V_H$ -style crystalline structure of starch due to reaction with the organic acid. Chemical modification of starch microparticles by treatment with organic acid was evidenced through FTIR spectroscopy. The organic acid modified starch microparticles/plasticized starch films were characterized through diminution their water uptake. Due to their outstanding properties, these chemically modified starch-based films may have potential applications in medical, agriculture, drug release, and packaging fields such as edible films, or food packaging.

### INTRODUCTION

Starch is an inexpensive and natural renewable polysaccharide, which was widely investigated as matrix for biomaterials.<sup>1</sup> Use of starch in the plastics industry would reduce dependence on synthetic polymers. Native starch commonly existed in granule structure with about 15-45% crystallinity. During the thermoplastic process, the strong action between hydroxyl groups of starch molecules was substituted by hydrogen bonds formed between plasticizers and starch, thus the starch was plasticized. Traditional plasticizers were polyols (such as sorbitol, glycerol, glycol).<sup>2-4</sup>

Plasticizers can be defined as low molecular weight substances that are incorporated into the polymer matrix to increase the film flexibility and processing. They increase the free volume or molecular mobility of polymers by reducing the H-bonding between the polymer chains. The main drawbacks to the more extensive use of starch as a thermoplastic are the sensitivity of its mechanical properties to fluctuations in water content and its

aging through crystallization. Both aspects are affected by the choice of the plasticizer.

In the present study, thermoplastic starch-based films were prepared from chemically modified corn starch microparticles dispersed within a glycerol (30%) plasticized starch matrix.<sup>5</sup> Different organic acids (adipic, malic, tartaric) were used for chemical modification of corn starch microparticles. After casting and water evaporation, the starch-based films were investigated by X-ray diffraction and FTIR spectroscopy. Opacity and water uptake of starch based films were also evaluated.

### RESULTS

#### X-ray diffraction

Fig. 1 shows X-ray diffractograms for components (S, SM, ASM, MSM, and TSM) of starch-based films.

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### FTIR spectroscopy analysis

The FTIR spectra of the starch based films are represented in Fig. 2-a,c. FTIR spectra for their individual components are shown in Fig. 2-b,d.

The chemical modification of starch (Fig. 2-d) and the hydrogen bond interaction between components of the starch based films can be observed.

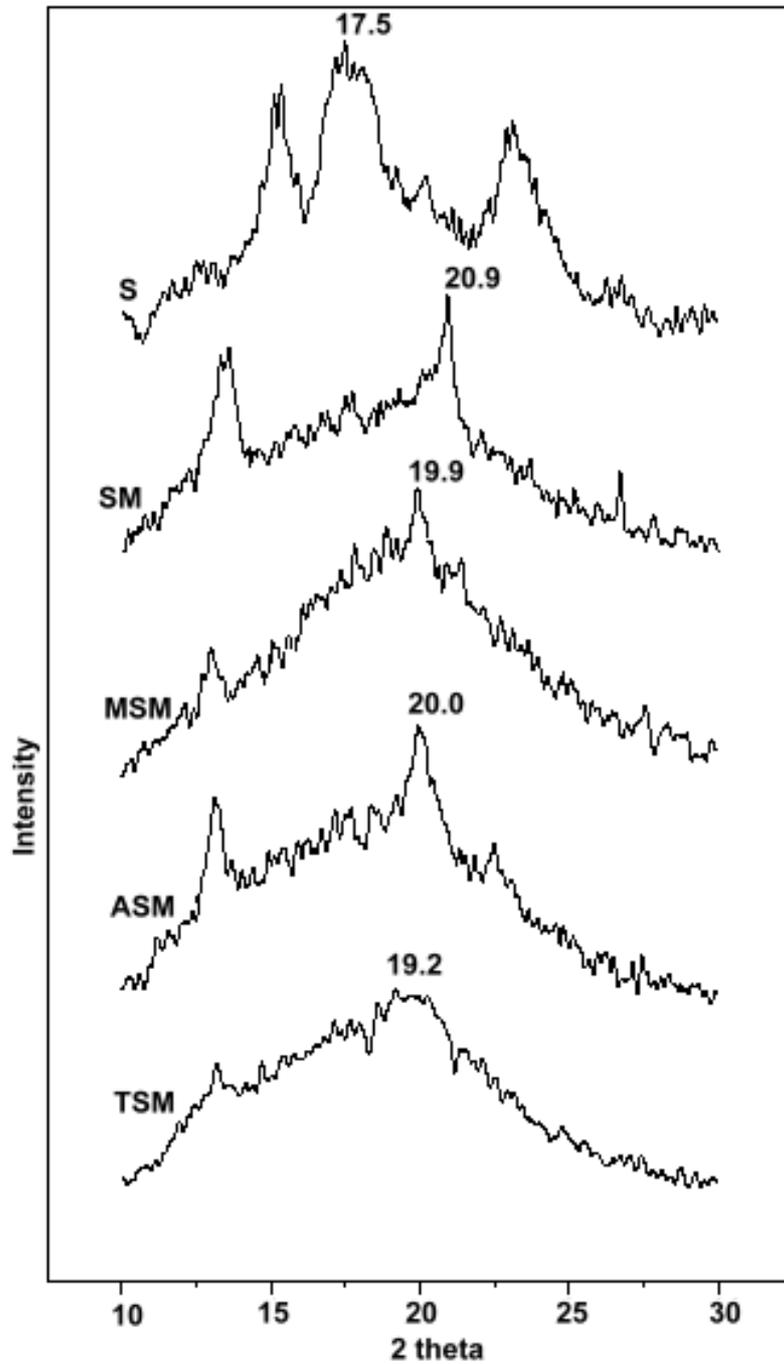


Fig. 1 – X-ray diffraction of corn starch (S), starch microparticles (SM) and chemically modified starch microparticles with malic acid (MSM), adipic acid (ASM), and tartaric acid (TSM).

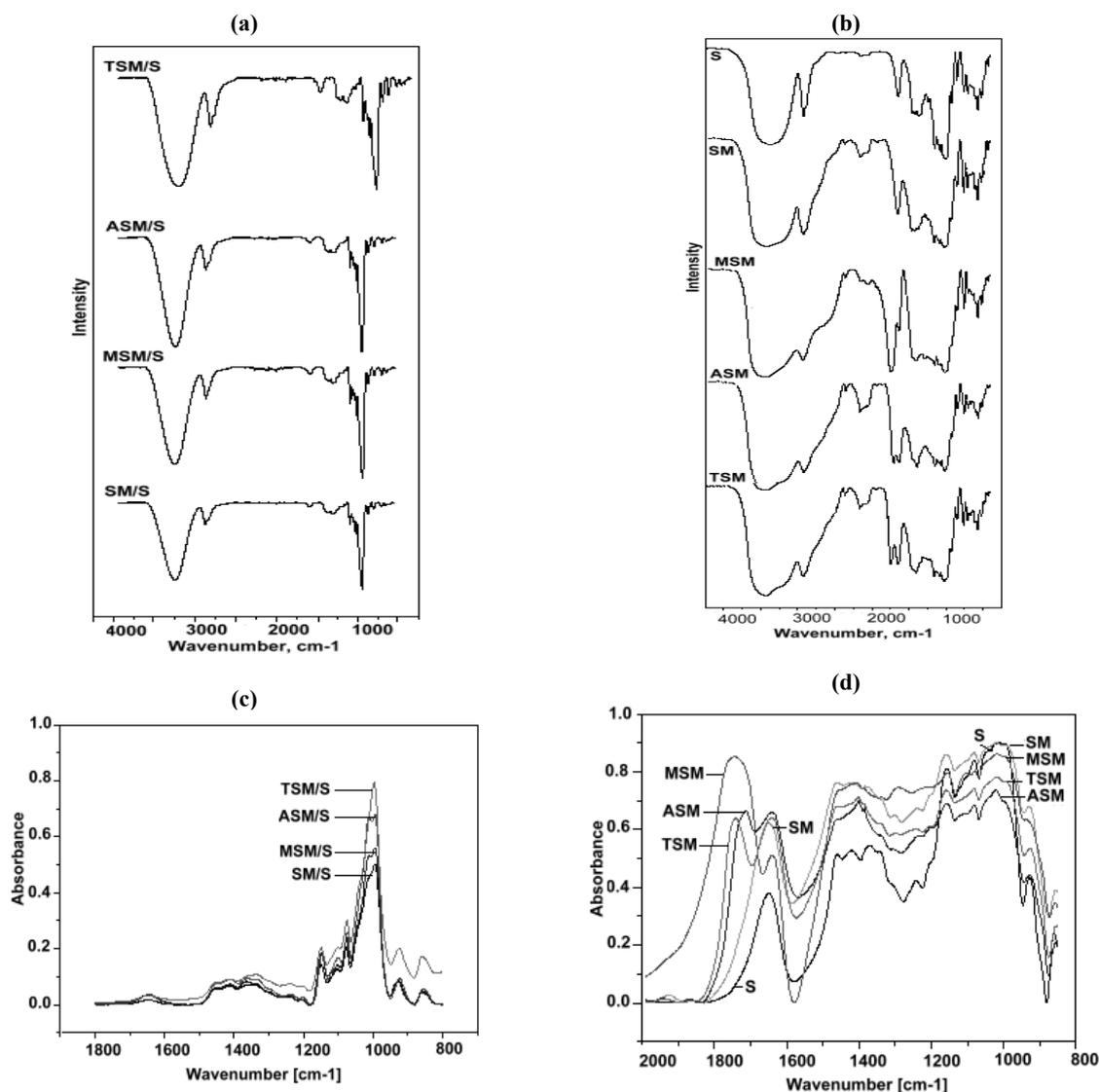


Fig. 2 – FTIR spectra of starch based films (a, c) and their components (b, d).

### Film opacity

The starch-based films opacity varied with organic acid type used for chemical modification of corn starch (Fig. 3).

### Water uptake

The water uptake of starch based films decreases in films with chemically modified starch comparatively with SM/S (Fig. 4).

## DISCUSSION

The starch microparticles (SM) were obtained by delivering ethanol into starch paste solution

dropwise. SM was further treated with malic acid (M), adipic acid (A) and tartaric acid (T). The organic acid modified SM could not be gelatinized in hot water even at the high temperature (90 °C). SM/S film was obtained by incorporation of SM within a glycerol-plasticized starch matrix. Organic acid modified starch microparticles/plasticized starch films were also obtained by casting.

MSM/S, ASM/S, TSM/S films can be considered in accordance with the principles of green chemistry,<sup>6</sup> because organic acid modified starch microparticles represent a granular resistant starch with many health benefits such as no toxic and reduced caloric potential. These starch-based films can be used in several medical and industrial purposes (packaging fields such as edible films, food packaging, agriculture, and drug release). In

addition, starch derivatives could be also applied as the filler for the matrix of other natural polysaccharides (chitin, alginate, cellulose, and cellulose derivatives).

### X-ray diffraction

According to the literature,<sup>7</sup> it was a typical A-style crystallinity in the native corn starch as it is shown in Fig 1. A-style crystallinity type disappeared and  $V_H$ -style crystallinity (the crystallinity between plasticizer and starch) was formed by the inductive of the thermal process. During the thermoplastic process, the strong interaction between hydroxyl groups of starch molecules was substituted by hydrogen bonds formed between plasticizer and starch.

The thermal treatment caused starch gelatinization by disruption of its double helix conformations. When organic acid penetrated the SM granule, it could disrupt the  $V_H$ -style crystalline structure of starch due to a concentrated solution of organic acid. The reaction should occur

both in the amorphous phase and crystalline phase.<sup>8</sup> According to these X-ray diffraction analysis, organic acid modified SM presented an amorphous characteristic, but some crystalline peaks at  $2\theta \cong 20^\circ$  were evidenced for MSM, ASM, TSM.

### FTIR spectroscopy analysis

Corn starch and SM exhibited similar FTIR spectra. Some differences in terms of band shape and intensity can be observed in the fingerprint of starch-based films in the FTIR spectra (Fig. 2a, c), as a result of organic acid used for chemical modification. The characteristic peak occurred at  $1650\text{ cm}^{-1}$ , which Fang<sup>9</sup> believed to be a feature of tightly bound water present in the starch. The characteristic peak  $1081\text{ cm}^{-1}$  and  $1157\text{ cm}^{-1}$  (Fig. 2 b) was ascribed to C-O bond stretching of C-O-H group.

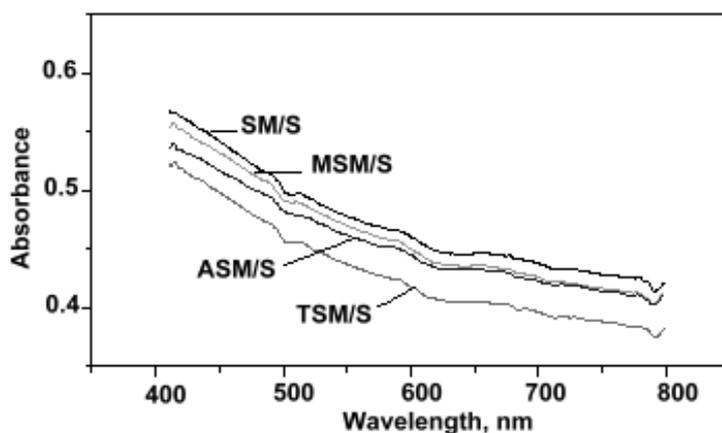


Fig. 3 – Starch based films opacity.

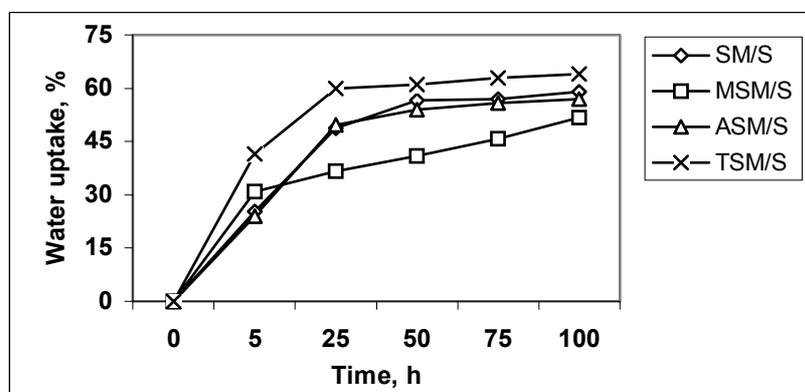


Fig. 4 – Water uptake of starch based films.

Another two peaks at  $1013\text{ cm}^{-1}$  and  $1020\text{ cm}^{-1}$  attributed to C-O bond stretching of C-O-C group in the anhydro-glucose ring<sup>9</sup> shifted from  $1013\text{ cm}^{-1}$  for starch at  $1018\text{-}1022\text{ cm}^{-1}$  for MSM. The absorption bands between  $1000$  and  $1200\text{ cm}^{-1}$  were characteristic of the -C-O- stretching on polysaccharide skeleton.

As it is shown in Scheme 1, when organic acid was heated, it dehydrated to yield an anhydride, which could react with starch to form a starch-organic acid derivative. Further heating resulted in additional dehydration with cross-linking.<sup>10</sup> For organic acid-SM powders, a new peak at  $1744\text{ cm}^{-1}$  (MSM),  $1712\text{ cm}^{-1}$  (ASM) and  $1708\text{ cm}^{-1}$  (TSM) respectively was characteristic of an ester group. In corn starch and SM, the oxygen of the C-O-C group could form the hydrogen-bond interaction with the hydrogen of hydroxyl groups, while the ester bonds in ASM, MSM, and TSM as the cross-linking of starch sterically hindered this hydrogen-bond interaction.

The analysis of FTIR spectra of the films enabled the hydrogen bond interaction to be identified.<sup>11</sup> The peak observed at  $1011\text{ cm}^{-1}$  that appeared as a shoulder in starch became more prominent and presented a shift to  $1020$ ,  $1018$ ,  $1022$ , and  $1020\text{ cm}^{-1}$  for SM, MSM, ASM, and TSM, respectively. These peaks can be associated with both vibration / solvation of C-OH bond, and changing from amorphous to a semi-crystalline state.<sup>12, 13</sup> The shift of the peak observed at  $996\text{ cm}^{-1}$  for SM/S to  $998\text{ cm}^{-1}$  for organic acid modified starch-SM/S film can be associated to the amorphous-crystalline transition in these films. The absorbance values at  $995\text{-}1014\text{ cm}^{-1}$  for organic acid modified SM/S films were different as organic acid used for chemical modification and higher comparatively untreated SM/S film.

## Film opacity and water uptake

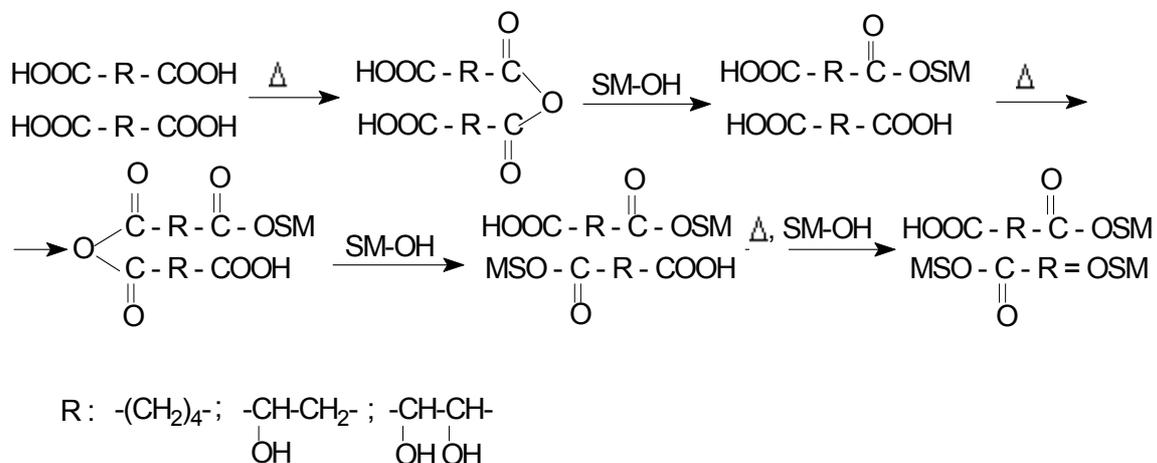
In Figs. 3 and 4 the opacity values and water uptake of starch-based films respectively are presented. Film opacity is a critical property if the film is used as a surface food coating. Transparent films are characterized by low values of the area below the absorption curve. The obtained values showed that films with addition of organic acid modified SM were more transparent than film without chemically modified filler. Besides, the opacity of films decreased due to addition of organic acid modified SM, this tendency being more noticeable in TSM/S film. Film opacity decreased in order: TSM/S < MSM/S < ASM/S < SM/S. After drying, the films without organic acid modified SM exhibited the highest equilibrium moisture content while the lowest values were observed when organic acid modified SM was added due to their hydrophobic properties.

## EXPERIMENTAL

### Materials

A commercial corn starch (S) constituted the continuous matrix of films. Starch microparticles (SM) were obtained from corn starch according to a previous work.<sup>5</sup> Glycerol was purchased from Fluka (98% purity, Fluka Chemical, Germany) and used as plasticizer. Malic acid (M), adipic acid (A), and tartaric acid (T) of 98% purity were purchased from Fluka, Germany, being used for chemical modification of SM.

In our work there were obtained films with a concentration of 4 g/100g of organic acid modified SM and 30% glycerol related to the corn starch amount, being coded as MSM/S, ASM/S, TSM/S, respectively. A possible reaction of organic acid with starch microparticles is presented in Scheme 1:



Scheme 1 – Possible reaction of organic acid with SM for preparing chemically modified SM.

### X-ray diffraction

Corn starch (S), SM, and MSM, ASM, TSM powders were tightly packed into the sample holder. X-ray diffraction patterns were recorded in the reflection mode in angular range  $3^{\circ}$ - $30^{\circ}$  ( $2\theta$ ) at a speed of  $2^{\circ} \text{ min}^{-1}$  and at ambient temperature by means of Bruker AD8 ADVANCE X-ray diffractometer equipment with Cu  $K\alpha$  radiation operating at 40 KV and 35mA.

### FTIR spectroscopy

FTIR spectra of starch-based films were recorded on a Bruker Vertex 70 spectrophotometer. The spectral resolution was  $4 \text{ cm}^{-1}$  and the scanning range varied from 400 to  $4000 \text{ cm}^{-1}$ .

### Film opacity

The starch-based films opacity was measured by a JENWAY 6405 UV-VIS spectrophotometer and defined as the area under the absorbance spectrum between 400 and 800 nm according to the ASTM D 1003-00 method (ASTM D 1003-00 Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics, 2000a). The film samples were cut into a rectangular piece ( $1 \times 2.5 \text{ cm}$ ), fixed on the inner side of 1cm spectrophotometer cell and the absorbance spectrum recorded. The film opacity determinations were repeated three times.

### Water uptake

To determine the water absorption,<sup>7, 14</sup> the films used were thin rectangular strips with dimensions of  $10 \text{ mm} \times 10 \text{ mm} \times 0.2 \text{ mm}$ . The films were supposed to be thin enough so that the molecular diffusion was considered to be one-dimensional and were vacuum-dried at  $90^{\circ}\text{C}$  overnight. After weighing, they were conditioned at  $25^{\circ}\text{C}$  in a desiccator containing sodium sulfate in order to ensure a relative humidity (RH) of 95%. They were then removed at specific intervals and gently blotted with tissue paper to remove the excess of water on the surface, and the water uptake was calculated with Eq. 1, as follows:

$$\text{water uptake (\%)} = [(W_t - W_0)/W_0] \times 100 \quad (1)$$

where:  $W_t$  and  $W_0$  represents the weight at time  $t$  and before exposure to 95% RH, respectively. The determinations were performed in triplicate.

## CONCLUSIONS

Starch microparticles were obtained from corn starch and further subjected to chemical modification with different organic acids (malic, adipic, tartaric). The structural and properties changes of starch, starch microparticles, organic

acid modified starch microparticles (MSM, ASM, TSM) and their films obtained by addition within a glycerol plasticized starch matrix were investigated.

X-ray diffraction curves showed a disruption of the  $V_H$ -style crystalline structure of the corn starch after reaction with organic acids. Structural changes were also evidenced through FTIR spectroscopy analysis. For organic acid modified-SM powders, a new peak characteristic of an ester group was noticed at  $1744 \text{ cm}^{-1}$  (MSM),  $1712 \text{ cm}^{-1}$  (ASM) and  $1708 \text{ cm}^{-1}$  (TSM) respectively.

The organic acid modified starch microparticles/plasticized starch films were characterized through diminution their water uptake. The opacity of films decreased due to addition of organic acid modified SM, this tendency being more noticeable in TSM/S film.

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