

# Compatibility of Polysaccharide/Maleic Copolymer Blends. IV. Thermal Behavior of Hydroxypropyl Cellulose-Containing Blends

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**ABSTRACT:** The compatibility of the hydroxypropyl cellulose (HPC) with maleic acid–vinyl acetate copolymer in the solid state was studied by thermogravimetry, thermo-optical analysis, differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), and optical microscopy. It was established that physical interactions are prevalent in blends with a high content of HPC, whereas chemical interactions predominate in blends with a medium

and low content of HPC. By increasing the temperature, the thermochemical reactions are favored. Thermal properties are dependent on the mixing ratio of the components. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2585–2597, 2003

**Key words:** blends; compatibility; thermal properties; morphology

## INTRODUCTION

Properties of individual synthetic or natural polymers alone are often inadequate to produce materials with good chemical, mechanical, thermal, and biological performance properties. Blends of synthetic polymers with biological macromolecules have been prepared to obtain polymeric biomaterials<sup>1</sup> with special enhanced properties for certain applications. The blends were produced in different forms, like films, sponges, or hydrogels, and were evaluated as dialysis membranes,<sup>1</sup> wound dressings,<sup>2</sup> drug delivery systems,<sup>3,4</sup> etc.

Hydroxypropyl cellulose (HPC) is a cellulose derivative employed as coatings, excipients, encapsulations, binding materials, foaming agents, protection colloids, flocculants, etc., for a wide variety of applications in food, drugs, paper, ceramics, plastics, etc.<sup>3</sup> Cellulose ether–ester films are flexible and transparent, and exhibit a moderate strength, resistance to oil, and fat migration.<sup>6</sup> They act as acceptable barriers to moisture and oxygen.<sup>7,8</sup>

Blends based on HPC with natural or synthetic polymers were proposed to design new materials with enhanced properties and with a wide range of applications. For example, the membrane manufactured from thermally crosslinked poly(1-vinyl-2-pyrrolidone-*co*-acrylic acid)–HPC blends by injection of the

blend with a microsyringe on a C/Al<sub>2</sub>O<sub>3</sub> electrode can be used as an on/off switching sensor at the dew point and as a humidity-sensitive membrane. The impedance of the membrane changes with carbon concentration, blend ratio, and membrane thickness.<sup>9</sup>

HPC in a mixture with a homo- or copolymer of acrylic acid or a pharmaceutically acceptable salt has appropriate oral mucosal adhesion properties and controlled drug-release features and is therefore used as a major excipient for drug tablets intended for bucal and sublingual administration.<sup>10</sup> In Japan, tablets named "Aftach," based on the aforementioned formulations for applications in the treatment of aphtha,<sup>11</sup> are now commercially available.

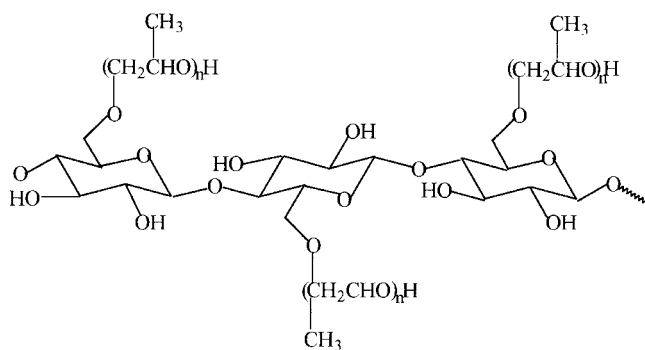
The study of the compatibility of HPC/maleic acid (MAc)–vinyl acetate (VA) copolymer blends in solid state is the focus of this article. The following investigation methods were used: thermogravimetry (TG), thermo-optical analysis, Fourier transform infrared spectroscopy (FTIR), and optical microscopy.

## EXPERIMENTAL

### Polymers

Hydroxypropyl cellulose LF (HPC), Klucel™, a gift of Aqualon, has an intrinsic viscosity at 25°C in aqueous solution of  $[\eta] = 179 \text{ mL/g}^{12}$  and 3.4 mol of substitution. The main chain of HPC consists of glucopyranosyl units linked in the (1→4)  $\beta$  position (see Scheme 1). It is possible that the hydroxypropyl substituents exist as a unit or as short side chains containing one to six hydroxypropyl units.<sup>13</sup>

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Scheme 1

The alternating maleic anhydride–vinyl acetate (MA–VA) copolymer, with  $M_n = 101,300$  g/mol, was synthesized by radical copolymerization in benzene, at 80°C, to high conversion<sup>14</sup> and was purified by extraction with chloroform (for details see ref. 15).<sup>15</sup> The fully water-soluble maleic acid–vinyl acetate copolymer (MAc–VA) was obtained by hydrolysis of MA–VA copolymer at room temperature for 24 h.<sup>16</sup>

### Blends preparation

The blends of HPC with MAc–VA copolymer were obtained as follows: The 10 wt % aqueous solutions (twice-distilled water) of each component were mixed in different ratios varying from 95 to 25 vol % HPC and 5 to 75 vol % MAc–VA. The mixtures were stirred for 10 min at room temperature and then for an additional 30 min at 40°C. The films were obtained by casting from these solutions on glass plates. To prepare a hydrophobic glass surface, the plates were rinsed with 10 wt % solution of trichloromethylsilane in acetone and then dried in air at room temperature before use. The advanced drying of the samples was performed in desiccators in the presence of phosphorous pentoxide. To avoid the degradation of the polymers, no drying by heating was used. The film moisture was checked by TG analysis. The sample film thickness varied between 0.02 and 0.07 mm. The powdered sample was obtained by a spray-drying process with a BÜCHI 190 mini spray dryer.

### Methods of investigation

The TG and derivative thermogravimetric (DTG) curves were recorded on a Paulik–Paulik–Erdey-type derivatograph (MOM-Budapest) under the following operational conditions: film samples; heating rate ( $\beta$ ), 12°C min<sup>-1</sup>; temperature range, 25–600°C; sample mass, 50 mg; in platinum crucibles; and air flow, 30 cm<sup>3</sup> min<sup>-1</sup>. Kinetic analysis of the TG data was carried out on a single curve using the integral Coats–Redfern<sup>17</sup> (CR) method. The determined overall kinetic parameters, activation energy ( $E$ ), pre-exponential factor ( $A$ ), and reaction order ( $n$ ), allow comparison of the

samples, knowing that they do not have a defined physical meaning.

Thermo-optic curves were recorded with a laboratory-made device, using samples as films, in a temperature range 30–170°C, with a heating rate of 7°C min<sup>-1</sup>. The physically absorbed water was totally eliminated by several heating runs in the measuring device under the aforementioned conditions. Reproducible values were obtained after the second, third, or even fourth run. Because of the melting transition of HPC, the determinations were made under an optical microscope. The birefringence disappears when melting takes place, so it is possible to correctly assign the involved transition and differentiation between melting and glass transition. Because this melting of HPC takes place at ~200°C, no interference of transitions is possible, even if a depression of melting temperature appears due to blending. We also recorded the DSC curves for several samples to assess the transitions. The results obtained by both methods are in a good correlation.

Differential scanning calorimetry (DSC) measurements were performed with a Mettler DSC12 instrument under the following conditions: heating rate, 10°C min<sup>-1</sup>; nitrogen flow, 50 mL min<sup>-1</sup>; sample mass, 6.7–13.5 mg; temperature range, 20–250°C. Before recording the DSC curves, the samples were either dried in high vacuum at 25°C for at least 48 h or several runs were performed for each sample.

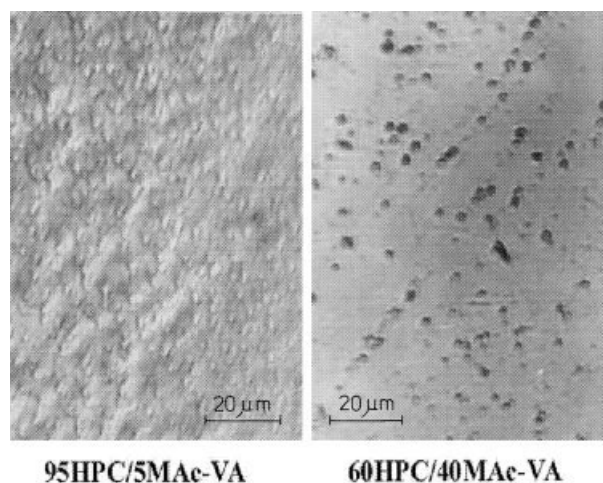
The FTIR spectra of the blends were recorded both on film and in KBr tablets using a FTIR spectrophotometer (BOMEM MB-104, Canada) with a spectral resolution of 4 cm<sup>-1</sup>. The concentration of the sample in the tablets was constant at 1 mg/100 mg KBr. No differences are evident between the FTIR spectra of the thin film obtained by solution casting followed by drying at room temperature and that recorded with powdered samples prepared by spray-drying from the mixed solutions of the partners. The samples were heated at a rate of 1°C min<sup>-1</sup> to 100°C in one experiment and to 200°C in another experiment and then cooled at room temperature. The FTIR spectra were recorded at every 2 min during both heating and cooling. A FTIR spectrum of the cooled tablets at room temperature was recorded on the second day to check the reversibility of some processes like the rebuilt of the H-bonds by cooling. The fitting of the overlapped bands was realized with a Grams/32 program (Galactic Industry Corporation).

Optical examination of the film samples was performed with a microscope (IOR, Bucharest, Romania) in phase contrast at a magnification of 300×.

## RESULTS AND DISCUSSION

### Phase behavior

The solutions of the blends show different phase behavior depending on the mixing ratio of the compo-



**Figure 1** Optical microscopy of (a) 95 wt % HPC/5 wt % MAc-VA and (b) 60 wt % HPC/40 wt % MAc-VA blends (magnification 300 $\times$ ).

nents. The solutions of 95 vol HPC/5 vol MAc-VA and 90 vol HPC/10 vol MAc-VA are homogenous but slightly cloud. The 85 vol HPC/15 vol MAc-VA and 80 vol HPC/20 vol MAc-VA solutions present a phase separation after 1 day, with a transparent phase at the bottom and a cloudy phase on the top (the volume ratios of the phases were 4:1 and 6:1, respectively). The 60–25 vol HPC/40–75 vol MAc-VA blends exhibit a different phase separation, with a significant amount of a white precipitate on the bottom and a cloudy phase on the top. This result could mean the existence of strong interactions between partners in the middle composition range and a high percent of MAc-VA copolymer in blends. The attractive or repulsive nature of these interactions in solution will be demonstrated.

The films were prepared from the fresh stirred solutions as already described. All films of the blends are transparent, independent of the mixing ratio between partners. The transparency is the first proof of the compatibility of the components.

Optical microscopy reveals that the blends with a high content of MAc-VA copolymer have a homogeneous appearance and their films are transparent. Blends with a high content of HPC (90, 95 wt %) appear as a fine and evenly distribution of minor component in the major component (Figure 1).

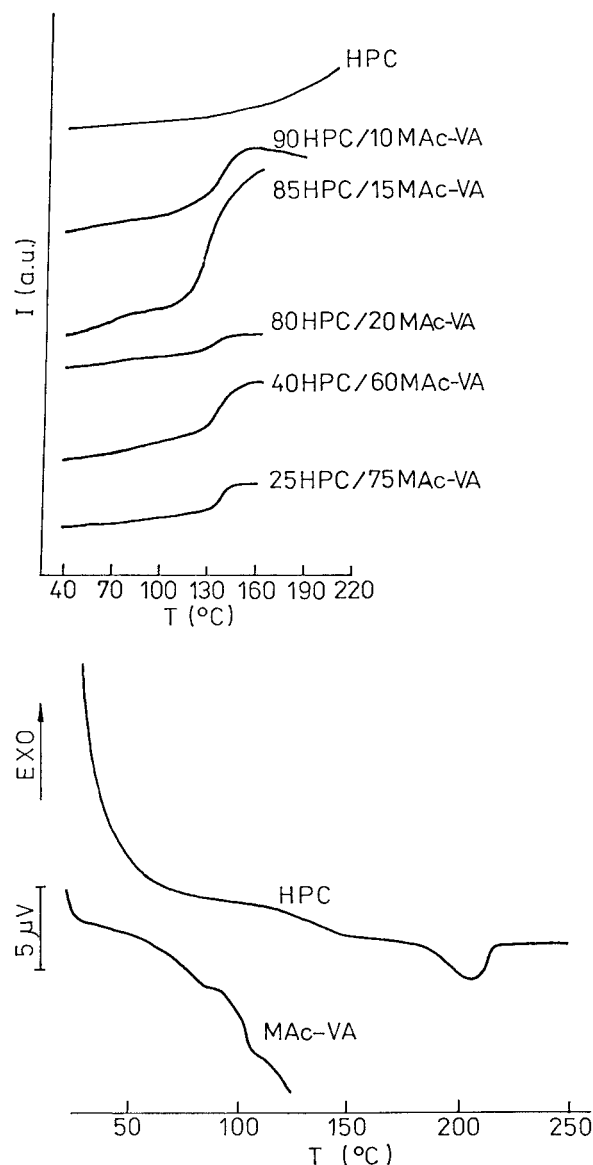
### Thermal properties

The literature data on the glass transition of HPC are very contradictory. An experimental glass transition ( $T_g$ ) of 30 $^{\circ}$ C for the amorphous phase and one at 85 $^{\circ}$ C due to the liquid crystalline mesophase, measured by DSC, were reported by Glasser et al.,<sup>18</sup> whereas Narasimhan and Peppas, using the free volume theory, calculated a  $T_g$  of 124 $^{\circ}$ C.<sup>19</sup> From the thermo-

optical curve, a  $T_g$  of  $\sim$ 137–139 $^{\circ}$ C for HPC (Figure 2a) was determined. This value is very close to the values obtained by DSC measurement (Figure 2b).

For the MAc-VA copolymer we determined a  $T_g$  of 97–99 $^{\circ}$ C from the thermo-optical curve. This value is close to that of  $\sim$ 100 $^{\circ}$ C obtained by DSC.<sup>15</sup>

Films of the 90–70 MAc-VA/10–30 HPC and 10–30 MAc-VA/90–70 HPC blends exhibit single  $T_g$  values varying from 120 to 138 $^{\circ}$ C as the MAc-VA content of the blends is increased. The existence of a single  $T_g$  in a blend and the transparency of a blend are well-recognized criteria of the compatibility of the components; therefore, we can conclude that the components are compatible at these mixing ratios. The films of 60 wt % HPC/40 wt % MAc-VA blend do not present any glass transition. At the 50 wt % HPC/50 wt % MAc-VA mixing ratio, phase separation occurred



**Figure 2** (a) Thermo-optic curves of the HPC and MAc-VA and their blends. (b) DSC curves of HPC and MAc-VA.

**TABLE I**  
**Characteristic Temperatures and Kinetic Data of the First Thermogravimetric Stage of HPC/MAC-VA Mixtures**

Sample	Characteristic temperature <sup>a</sup>			$\Delta w^b$ (%)	$E_a$ (kJ/mol)	$n$
	$T_I$ (°C)	$T_M$ (°C)	$T_F$ (°C)			
HPC	—	—	—	—	—	—
90HPC/10MAC-VA	138	182	236	3.2	—	—
80HPC/20MAC-VA	127	185	242	4.4	—	—
60HPC/40MAC-VA	112	170	240	19.3	97	2.2
50HPC/50MAC-VA	111	172	244	24.7	87	1.8
40HPC/60MAC-VA	109	177	248	28.9	86	2.1
25HPC/75MAC-VA	115	187	260	35.3	76	2.0
MAC-VA	112	194	300	47	—	—

<sup>a</sup>  $T_I$ ,  $T_M$ , and  $T_F$  are the temperatures corresponding to the onset, the maximum rate of the weight loss, and the final temperature, respectively.

<sup>b</sup> Weight loss.

suddenly during the mixing of solutions so the film was not prepared.

For each TG stage, the following thermal characteristics were determined and are listed in Tables I and II: onset temperature ( $T_I$ ); temperature corresponding to the maximum mass loss ( $T_M$ ); temperature corresponding to the end of stage ( $T_F$ ) (errors in temperature determination,  $\pm 2^\circ\text{C}$ ); mass loss ( $\Delta w$ ; error,  $\pm 1\%$ ); and overall kinetic parameters such as activation energy,  $E_a$  (error of determination,  $\pm 10$ – $15$  kJ/mol); pre-exponential factor ( $A$ ), and reaction order ( $n$ ).

In the 20– $120^\circ\text{C}$  temperature range, a TG stage due to the physically absorbed water is recorded for all samples. Obviously, this stage is not considered in thermal characterization of the blends.

In the 110– $450^\circ\text{C}$  studied temperature range, the DTG/TG curves of the MAC-VA copolymer exhibit only one TG stage, but the process of decomposition seems to be very complex (Figure 3). This first degradation lies in the 112– $300^\circ\text{C}$  temperature range, with a  $T_M$  of  $194^\circ\text{C}$ , a shoulder at  $159^\circ\text{C}$ , an inflexion at  $218^\circ\text{C}$ , and a total weight loss of 47 wt % (Table I). We have shown in our previous papers<sup>15,20</sup> that this DTG peak is due to two overlapped processes: recyclization

of MAC units MA and the loss of acetic acid from VA units. Due to the complexity of process, it was not possible to evaluate even its overall kinetic parameters.

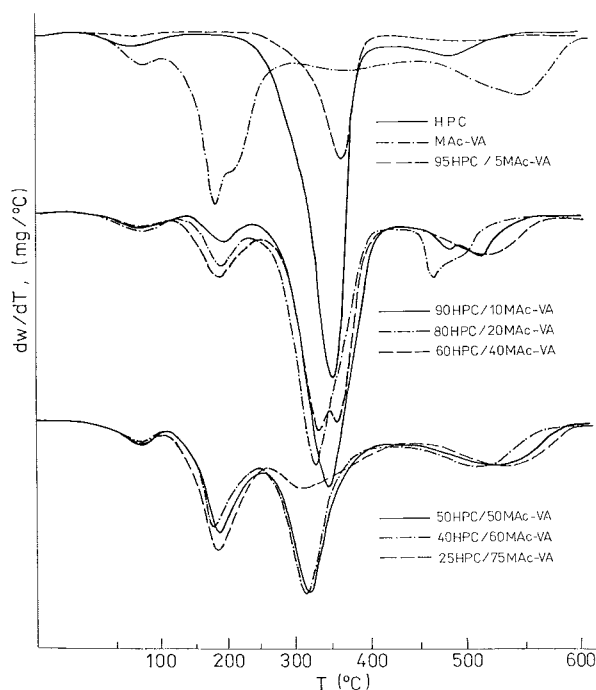
The main TG stage of HPC occurs in the 184– $407^\circ\text{C}$  temperature range, with a  $T_M$  of  $356^\circ\text{C}$ , a weight loss of 83 wt %, and an overall activation energy,  $E_a$ , of 83 kJ/mol (Figure 3 and Table II).<sup>21</sup> This main stage of thermo-oxidative decomposition could be ascribed to the scission of the backbone of the polysaccharide.<sup>21</sup>

It was noted that the components of the blend decompose in different temperature ranges. In the studied temperature range (20– $450^\circ\text{C}$ ), the films of HPC/MAC-VA copolymer blends present two separate TG stages in addition to the process of physical absorbed water loss (Figure 3). The first TG stage of the blends lies in the 120– $260^\circ\text{C}$  temperature domain, which is the same temperature range as the first TG stage of MAC-VA copolymer decomposition. The second one, occurring in the range 225– $447^\circ\text{C}$ , overlapped with the decomposition temperature range of the HPC.

The experimental DTG curves of the blends have different shapes compared with those calculated by the additivity rule, supposing no interaction be-

**TABLE II**  
**Characteristic Temperatures and Kinetic Data of the Second Thermogravimetric Stage of HPC/MAC-VA Mixtures**

Sample	Characteristic temperature			$\Delta w$ (%)	$E_{a,CR}$ (kJ/mol)	$n_{CR}$
	$T_I$ (°C)	$T_M$ (°C)	$T_F$ (°C)			
HPC	184	356	407	83	83	0.6
90HPC/10 MAC-VA	225	370	428	79.8	110	1.3
85HPC/15 MAC-VA	236	360	426	74.5	128	1.4
80P/20MAC-VA	240	335	420	77.5	132	1.5
60HPC/40MAC-VA	240	322	414	53.8	100	2.2
50HPC/50MAC-VA	243	315	426	44.9	100	1.7
40HPC/60MAC-VA	248	320	447	42.6	136	2.4
25HPC/75MAC-VA	260	313	437	29.3	93	2.0
MAC-VA	—	—	—	—	—	—



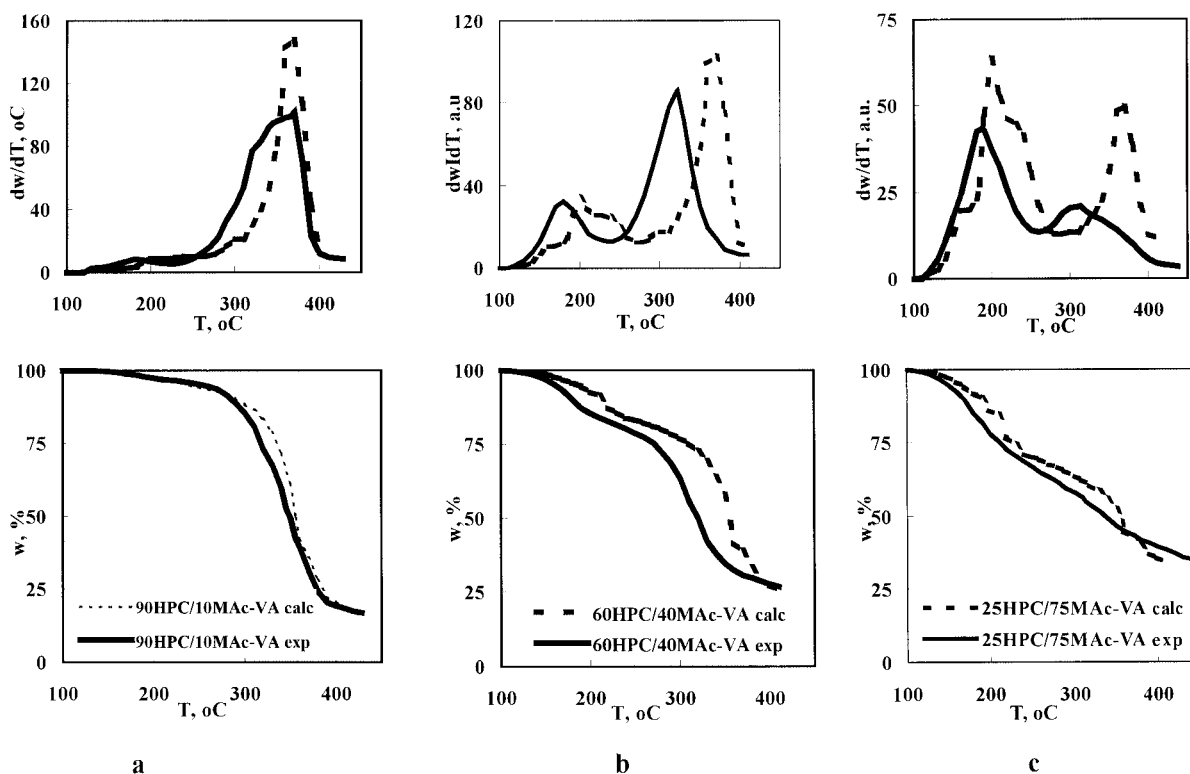
**Figure 3** TG curves of (I) individual polymers; (II) 90–80 wt % HPC/10–20 wt % MAc-VA; and (III) 60–25 wt % HPC/40–75 wt % MAc-VA blends.

tween partners (Figure 4). The difference between experimental and calculated DTG curves could be a good proof of the existence of some interactions

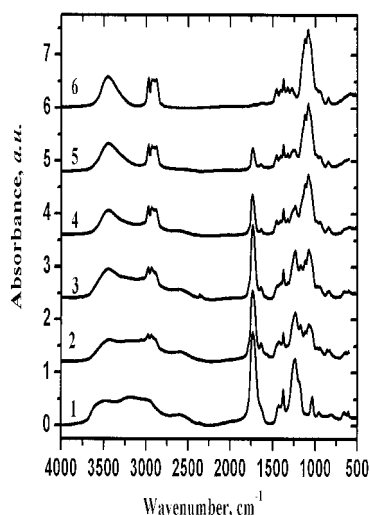
between components. In the 100–230°C range, the calculated DTG curves of the blends exhibit many shoulders or inflexions like the processes corresponding to the MAc-VA copolymer decomposition, whereas the experimental DTG curves are simpler. The calculated DTG curves are shifted to the lower temperatures compared with the experimental DTG curves. This shift is very prominent for the 60–25 wt % HPC/40–75 wt % MAc-VA (Figures 4b and 4c).

Depending on the mixing ratio of the partners, two distinct thermal behaviors of the blends are noted. In blends with an HPC content of 85 and 90 wt %, the first DTG peak is shifted to lower temperature and the experimental weight loss is close to that calculated by the additivity rule (Figure 4 a). For the second TG stage, the experimental  $T_I$  is 30–40°C lower than that calculated, but the  $T_M$  of the process is approximately the same in both DTG curves.

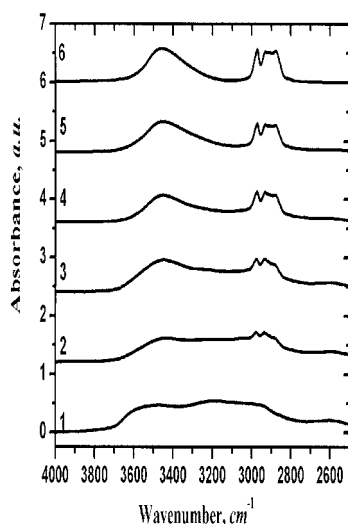
For the blends with a medium and low HPC content (60–25 wt % HPC), both the experimental TG and DTG curves are shifted to lower temperatures than those calculated (Figures 4b and 4c). The experimental  $T_I$  of the first DTG peak is close to that determined by the additivity rule. In contrast,  $T_M$  increased by increasing the MAc-VA content (Table I), but the values are lower than those calculated. The experimental weight loss of the blends is 4–9 wt % higher than that determined by the additivity rule.



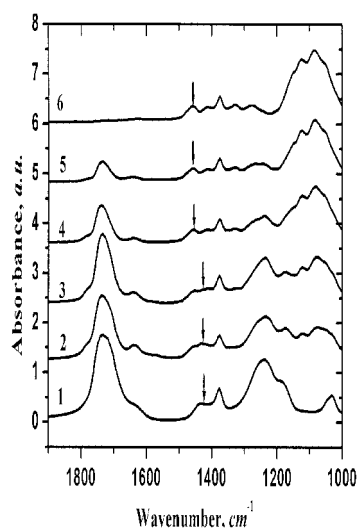
**Figure 4** Experimental and calculated TG/DTG curves of (a) 90 wt % HPC/10 wt % MAc-VA; (b) 60 wt % HPC/40 wt % MAc-VA and 40 wt % HPC/60 wt % MAc-VA; and (d) 25 wt % HPC/75 wt % MAc-VA blends.



a.



b.



c.

The experimental  $T_1$  of the second TG stage of the blends is shifted 23–40°C to lower temperatures than those calculated.

Taking into account all the aforementioned differences between experimental and calculated values of thermal characteristics, we ascribe the first TG process to that of MAC-VA copolymer decomposition only for the blends with a high content of MAC-VA (>85 wt %). In the case of the other blends, if the second process could be ascribed to polysaccharide decomposition, the first TG stage takes place in a different temperature range and has a completely different shape comparatively with that of the copolymer. In this case, we can presume the existence of physical or chemical interactions between components that strongly influenced their thermal behavior.

The overall activation energies of the first stage of degradation of the blends decrease with increasing MAC-VA content, whereas those corresponding to the second stage take higher values than that of HPC. The decomposition process of this polymer in the blends, therefore, is different than that occurring in pure polymer; that is, the influence of the second component is evident.

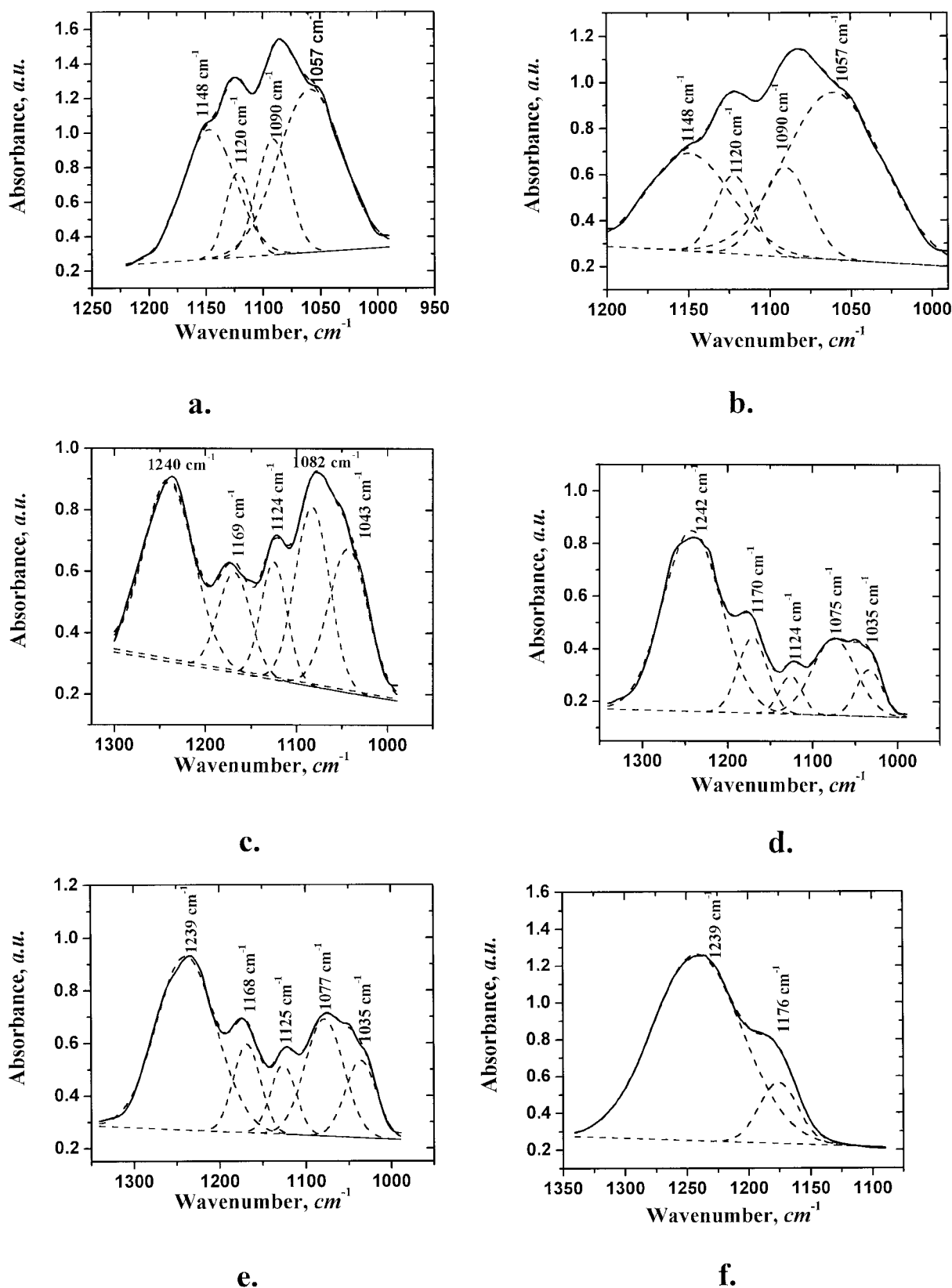
Generally, all blends are more unstable than was expected from the behavior of the individual components. A particular thermal behavior is evidenced depending on the composition of the blends.

### IR spectroscopy

The IR spectra of HPC, MAC-VA, and their blends in different mixing ratios are shown in Figure 5. All characteristic bands of the components are present in the IR spectra of the blends<sup>23</sup> and the intensity of the bands varies in the same way with the mixing ratio of the components, with many of them overlapping. The differences in the IR spectra of the blends can be mainly evidenced in the 1000–1800 and 2600–4000  $\text{cm}^{-1}$  wave number regions (Figures 5b and 5c, respectively).

In the 1000–1850  $\text{cm}^{-1}$  range (Figure 5c), the IR spectra of the blends have specific shapes depending on the mixing ratio of the partners. The peaks at 1464 and 1340  $\text{cm}^{-1}$  (arrow on spectra 4–6), assigned to the OH, CH<sub>3</sub>, and CH<sub>2</sub> groups of HPC,<sup>23</sup> are either shifted to lower wave numbers or disappear for the blends with a low content of HPC (<60 wt %). The modified shape of the IR spectra of the blends in this region could be due to the physical

**Figure 5** The IR spectra of HPC and MAC-VA copolymer and their blends in various ratios [(6) HPC, (5) 90HPC/10MAC-VA, (4) 80HPC/20MAC-VA, (3) 60HPC/40MAC-VA, (2) 25HPC/75MAC-VA, and (1) MAC-VA] shown at (a) 500–4000  $\text{cm}^{-1}$  (b) 2600–4600  $\text{cm}^{-1}$  and (c) 1000–1800  $\text{cm}^{-1}$ .



**Figure 6** Deconvoluted 1000–1350  $\text{cm}^{-1}$  region of HPC, MAC-VA, and their blends: (a) HPC, (b) 80 wt % HPC/20 wt % MAC-VA, (c) 60 wt % HPC/40 wt % MAC-VA, (d) 40 wt % HPC/60 wt % MAC-VA, (e) 25 wt % HPC/75 wt % MAC-VA, and (f) MAC-VA.

(hydrogen bonding) and/or chemical interaction between the carboxyl group of MAC-VA and hydroxyl groups of HPC.

The characteristic band of COOH at  $1430\text{ cm}^{-1}$  (marked on figure with an arrow on spectra 1–3) appears only in the blends with a content of MAC-VA of

**TABLE III**  
Solubility in Water Data of the Unheated  
and Heated Film Blends<sup>a</sup>

Sample code	At room temperature	Blend heated, at 80 °C
HPC	+	+
95HPC/5MAc-VA	+	+
90HPC/10 MAc-VA	+	-
85HPC/15MAc-VA	+ -	-
80HPC/20MAc-VA	+ -	-
60HPC/40 MAc-VA	-	-
40HPC/60 MAc-VA	-	-
25HPC/75 MAc-VA	-	-
MAc-VA	+	+

<sup>a</sup> Key: (+) water soluble; (+-) partially water soluble; - water insoluble.

>60 wt %. A supplementary band is evidenced in the spectra of the blends at 1650 cm<sup>-1</sup>.

In all IR spectra of the blends, many differences appear in the shape of bands 1000–1300 cm<sup>-1</sup>. These differences are clearly pointed out by the deconvolution of the overlapped constitutive bands (Figure 6). It is evident that the band at 1239 cm<sup>-1</sup>, corresponding to the acetate ester, is present in all the blends with a MAc-VA copolymer content of >40 wt % (Figures 6c–f) but is not evidenced in blends with a MAc-VA content of <20 wt % (Figure 6b). The weak band at 1176 cm<sup>-1</sup>, which could be ascribed to the small residual amount of normal anhydride from MAc-VA copolymer (Figure 6g), vanished in all blends. Simultaneously, a new band at 1168–1170 cm<sup>-1</sup> appears in the blends with a MAc-VA content of >40 wt percent; (Figures 6c–f). This new band could be assigned to a new kind of ester group, namely the maleate ester,<sup>23</sup> that could appear because of a reaction between the COOH groups from MAc-VA copolymer and the OH groups from HPC. The low pH of the solution of the blends (pH = 2.5–2.8) favors the development of an esterification reaction, especially when solutions of the mixture undergo the drying process (e.g., during the preparation of the films). The 1148 cm<sup>-1</sup> band, corresponding to the secondary —OH of HPC, disappears in blends with an HPC content of <60 wt %. The other characteristic bands of ethers groups from HPC (1120, 1058, 1090 cm<sup>-1</sup>) are present in all IR spectra of the blends. The bands at 1058 and 1090 cm<sup>-1</sup> are strongly shifted to a lower wave number. All these results combined support the hypothesis of chemical reactions between components.

Chemical associations/reactions between the partners could also be followed by solubility tests of the films of blends at room temperature and at temperatures up to 80°C (Table III). A different solubility behavior of the films was observed depending on the mixing ratios between components. The blends with an HPC content of 95 or 80 wt % are water soluble or partly soluble at room temperature, but the solutions,

are slightly cloudy. By increasing the temperature to 40°C, the turbidity increases and, therefore, phase separation occurs. The films with an HPC content of <60 wt % are transparent but insoluble at room temperature and remain insoluble even at 80°C.

The MAc-VA copolymer is hydrophilic, whereas HPC is a hydrophobic compound that presents a low critical solution temperature (LCST) of ~40°C depending on the degree of substitution and its molecular weight.<sup>13,24</sup> These two partners could interact by H-bonds. Hydrophobic forces could also appear, strengthening the interaction between the components. By increasing the temperature, two opposite effects appear. At high temperature, the H-bonds are broken and the H-bonding physical associations are destroyed, whereas the hydrophobic forces become stronger, thereby strengthening the physical associations.

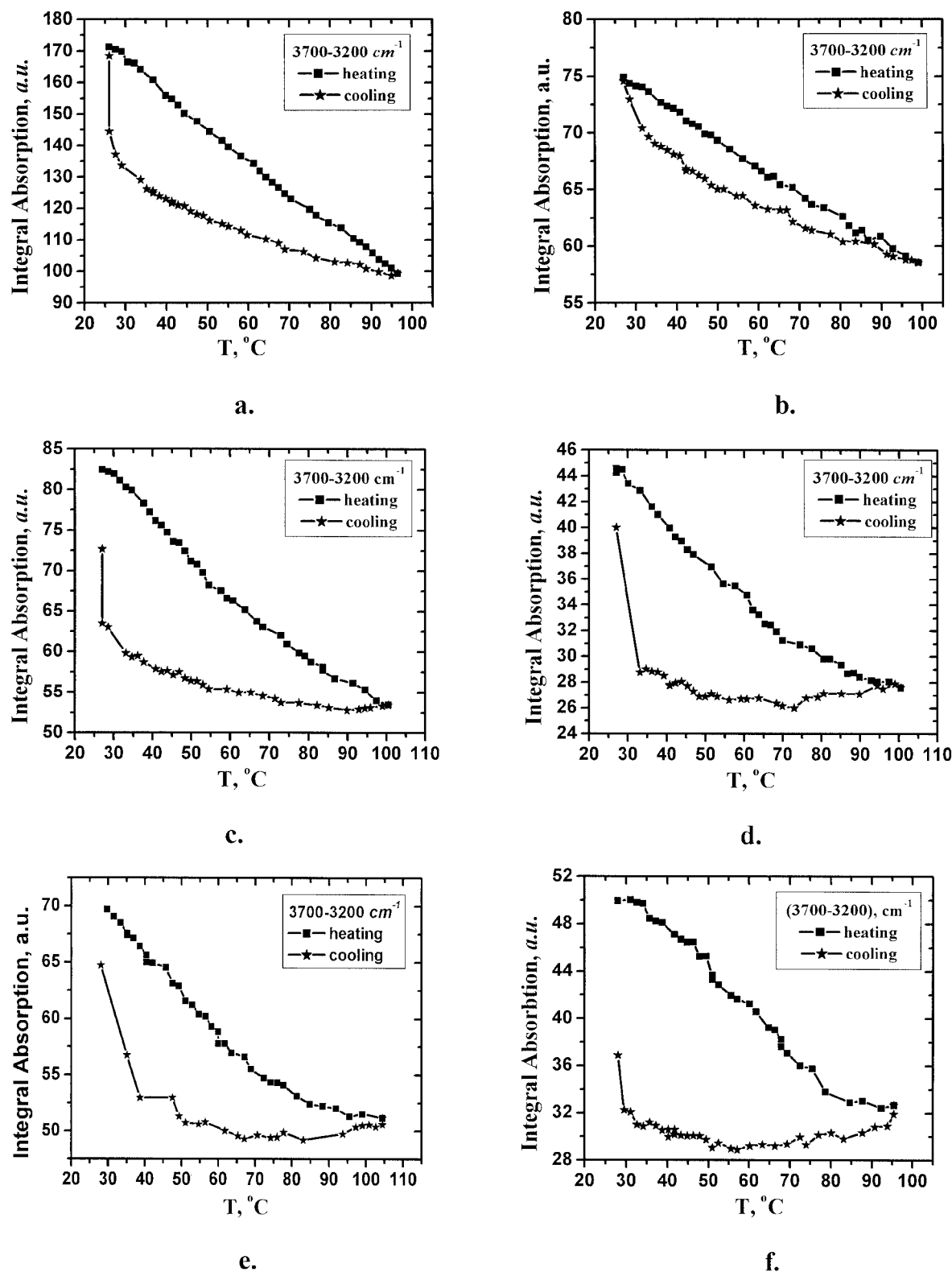
To evidence mainly the role of the physical interaction, like H-bonding, for the compatibility of the blends and to follow the evolution of the blends with increasing temperature, the samples were heated to 100°C at a heating rate of 1°C min<sup>-1</sup> and then cooled. Significant changes in the 3200–3700 cm<sup>-1</sup> region are noted following heating of the components and blends.

In the FTIR spectra of the heated HPC, the characteristic band of the self-associated OH at 3446 cm<sup>-1</sup> shifted to higher wave number at 3501 cm<sup>-1</sup>, corresponding to free OH group vibrations. A plot of the integral absorption of the 3700–3200 cm<sup>-1</sup> band versus temperature reveals a decrease of this intensity by increasing temperature up to ~100°C (Figure 7a). On cooling, the integral absorption of this band slightly increases and, after 1 day, it reaches the initial value and the band regains its initial position at 3446 cm<sup>-1</sup>. This result indicates that the intermolecular H-bonding of HPC is rebuilt on cooling.

The integral absorption of the wide band at 3700–3200 cm<sup>-1</sup> of the associated COOH groups from the MAc-VA copolymer also decreases with heating (Figure 7f) and remains constant at a low value with cooling. A slight increase was noticed after a day of keeping the sample at room temperature. These results suggest that the H-bonds were not entirely rebuilt, possibly because some of OH groups from the MAc-VA copolymer were consumed during heating due to reaction or because traces of physically absorbed water that contributes to the H-bonds are eliminated.

The variation of the integral absorption of the bands at 3700–3200 cm<sup>-1</sup> (Figures 7b–e) in the FTIR spectra of the blends depends on the mixing ratio of the components. The values of the integral absorption of the blends decreased with heating of the blends. For blends with an HPC content of >60 wt %, the integral absorptions of the bands increase with cooling, but the values are lower than those of the heated samples at

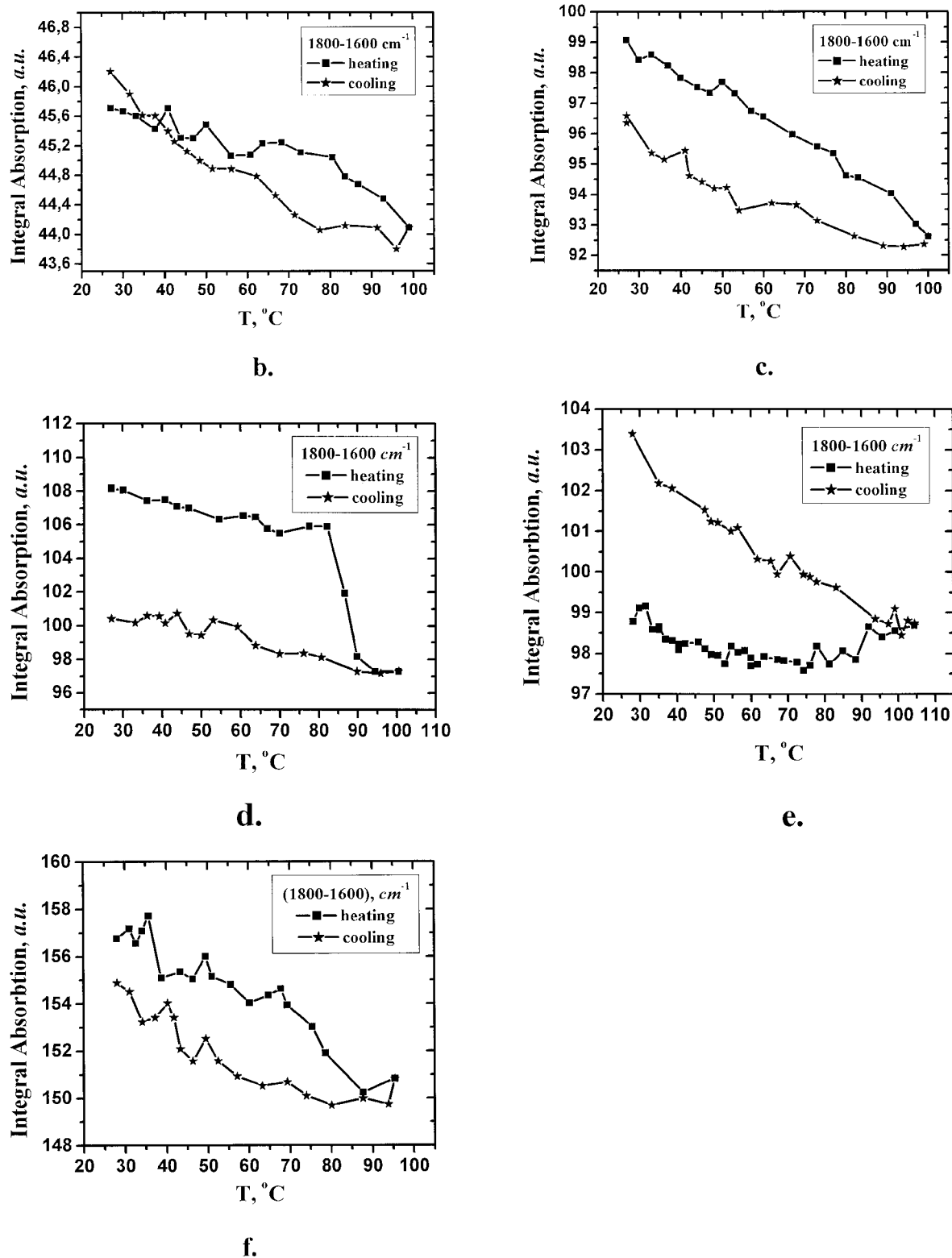




**Figure 7** Integral absorbance versus temperature for the 3700–3200  $\text{cm}^{-1}$  region of the IR spectra of (a) HPC, (b) 80 wt %; HPC/20 wt %; MAC-VA, (c) 60 wt %; HPC/40 wt %; MAC-VA, (d) 40 wt %; HPC/60 wt %; MAC-VA, (e) 25 wt % HPC/75 wt % MAC-VA, and (f) MAC-VA.

the same temperatures. This difference signifies that not all H-bonds are restored with cooling. After 1 day, the H-bonds are entirely recovered only in the case of

80 HPC/20 MAC-VA blend (Figures 7b). For blends with an HPC content of <60 wt %, the integral absorption of the 3700–3200  $\text{cm}^{-1}$  bands remains con-



**Figure 8** Integral absorbance versus temperature for the 1600–1800  $\text{cm}^{-1}$  region of the IR spectra of the (b) 80 wt % HPC/20 wt % MAc-VA, (c) 60 wt % HPC/40 wt % MAc-VA, (d) 40 wt % HPC/60 wt % MAc-VA, (e) 25 wt % HPC/75 wt % MAc-VA, and (f) MAc-VA. (Fig. 8(a) not included because the HPC does not have an absorption band at 1600–1800  $\text{cm}^{-1}$  region.)

stant on cooling, with lower values than that obtained with heating even if recording was made the second day. Therefore, the H-bonds are not rebuilt (Figures 7c and e). The biggest difference between values of the

integral absorption before and after cooling was observed for the 60HPC/40MAc-VA blend (Figure 8c).

In the 1600–1800  $\text{cm}^{-1}$  spectral region, the changes are particular and are observed mainly for blends

(Figure 8). The HPC does not present any band in this region. The initial and final absorbance of the bands corresponding to the 80 HPC/20 MAc-VA blend (Figure 8b) and MAc-VA copolymer (Figure 8f) are similar, whereas values obtained by heating and consecutive cooling of the other blends are totally different (Figures 8c-e). These differences could be due to a reaction between the functional groups of the two components.

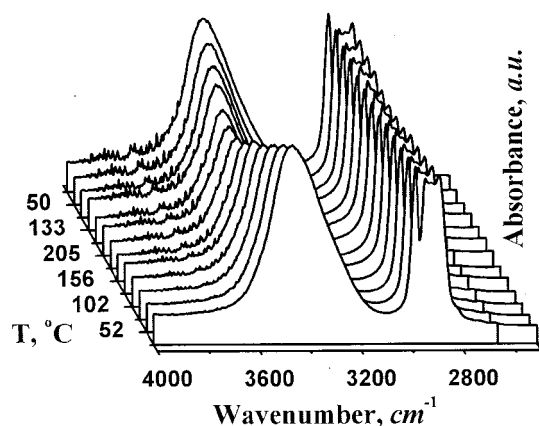
By heating the samples at a temperature  $>100^{\circ}\text{C}$ , intra- and intermacromolecular thermochemical reactions between the functional groups of the partners are favored.<sup>26</sup> The thermochemical reaction between partners was followed by heating the sample to  $200^{\circ}\text{C}$  and then cooling following the procedure already described. The IR spectra of the heated HPC indicate that the sample did not suffer any structural changes by heating to  $200^{\circ}\text{C}$  (Figures 9a-c) in any region examined, whereas the MAc-VA copolymer suffers important changes at temperatures  $>140$ – $150^{\circ}\text{C}$  (Figures 10a-c).

After  $120^{\circ}\text{C}$ , the integral absorption of the band at  $1733\text{ cm}^{-1}$  of the MAc-VA copolymer decreases and the other peaks appear at  $1665$  ( $\text{COO}^-$ ),  $1795$  (normal anhydride) and  $1835$  (cyclic anhydride)  $\text{cm}^{-1}$  (Figure 10a). This result indicates that the water elimination takes place not only between vicinal  $\text{COOH}$  groups from the same chain, but also between the  $\text{COOH}$  groups belonging to the different chains. The intensity of the band at  $1665\text{ cm}^{-1}$  increases and remains constant to  $150^{\circ}\text{C}$  and then decreases. A small band appearing at  $1100\text{ cm}^{-1}$  is characteristic of the normal anhydride (Figure 10b).

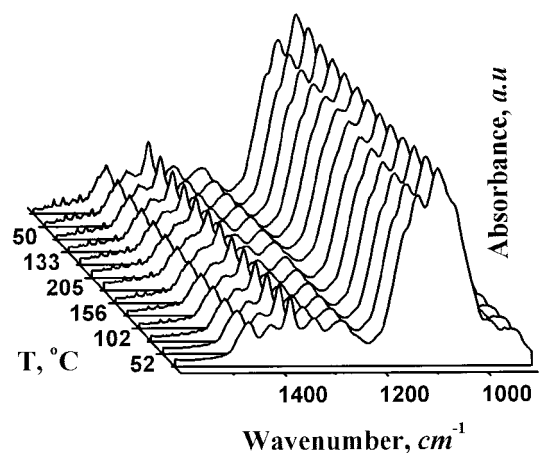
The band at  $1235\text{ cm}^{-1}$ , assigned to overlapped  $\text{COOH}$  and ester groups, decreases and splits with heating. The shoulder of  $\text{COOH}$  at  $1180\text{ cm}^{-1}$  vanishes. As evident in Figure 10c, the obtained changes in IR spectra by heating the MAc-VA copolymer are irreversible compared with the changes in IR spectra for HPC; that is, the initial shapes of the IR spectra are not found after cooling.

The IR spectra of the blends with a high content of HPC (60–80 wt %) do not present important changes in the  $1500$ – $1800\text{ cm}^{-1}$  wave number range by increasing the temperature. During the heating of all other blends at  $T > 100^{\circ}\text{C}$ , the band at  $\sim 1730\text{ cm}^{-1}$  splits in two other bands, one at  $\sim 1775$ – $1778\text{ cm}^{-1}$  and another at  $\sim 1726\text{ cm}^{-1}$  (Figures 11a and b). The band at  $1775$ – $1778\text{ cm}^{-1}$  could be assigned to cyclic and normal anhydride and that at  $1726\text{ cm}^{-1}$  to ester and carboxylic groups.

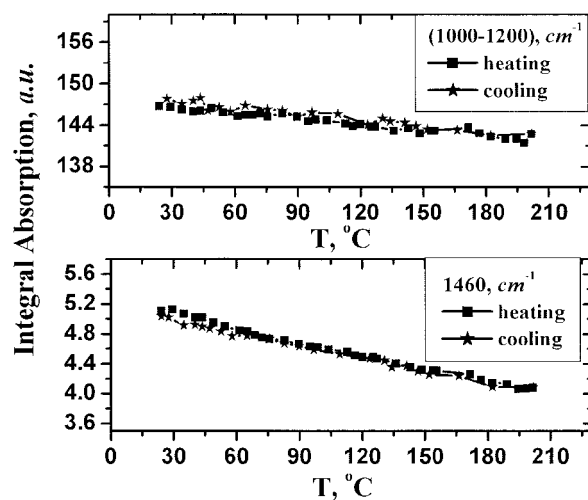
Plots of the evolution of the integral absorption of the  $1778$  and  $1733\text{ cm}^{-1}$  bands (Figure 11c) with heating indicates a very slow decrease of the band at  $1733\text{ cm}^{-1}$  between  $100$  and  $150^{\circ}\text{C}$ . After  $160^{\circ}\text{C}$ , the integral absorption of the  $1733\text{ cm}^{-1}$  band drastically decreases up to  $200^{\circ}\text{C}$ . With cooling, the integral absorption of this band remains constant. These results indi-



a.



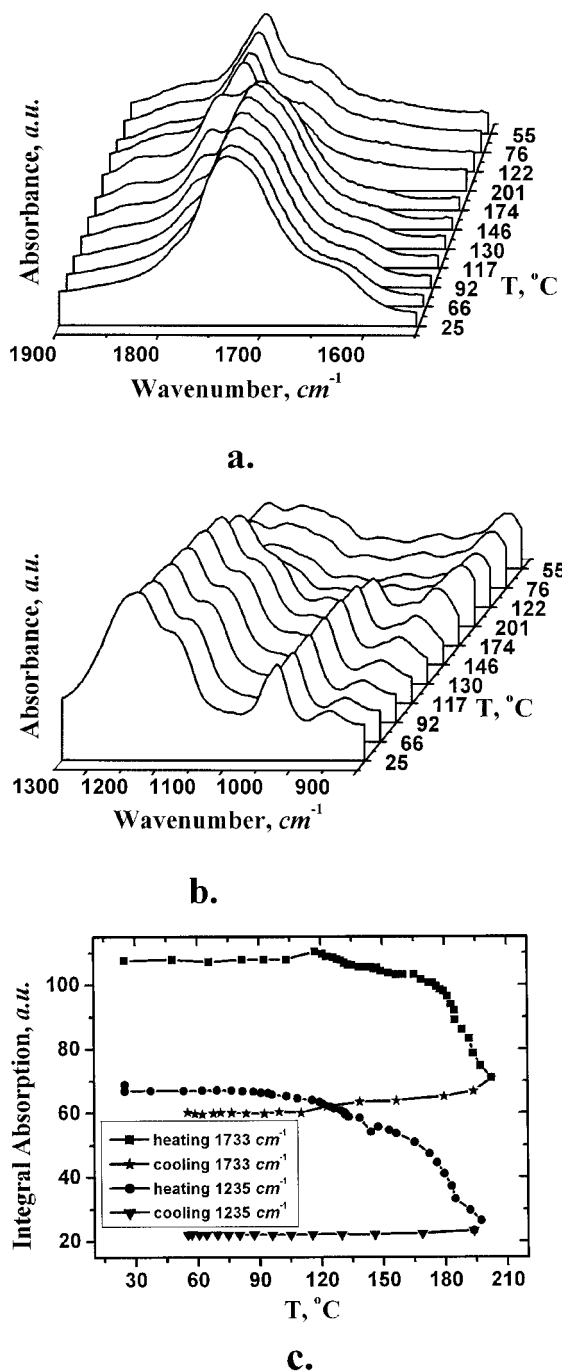
b.



c.

**Figure 9** FTIR spectra of the HPC heated from 20 to  $200^{\circ}\text{C}$  at  $1^{\circ}\text{C}/\text{min}$  and cooled to room temperature: (a)  $2800$ – $4000\text{ cm}^{-1}$ ; (b)  $1000$ – $1500\text{ cm}^{-1}$ . The variations of the integral absorbance of the bands are indicated on the figure versus temperature.

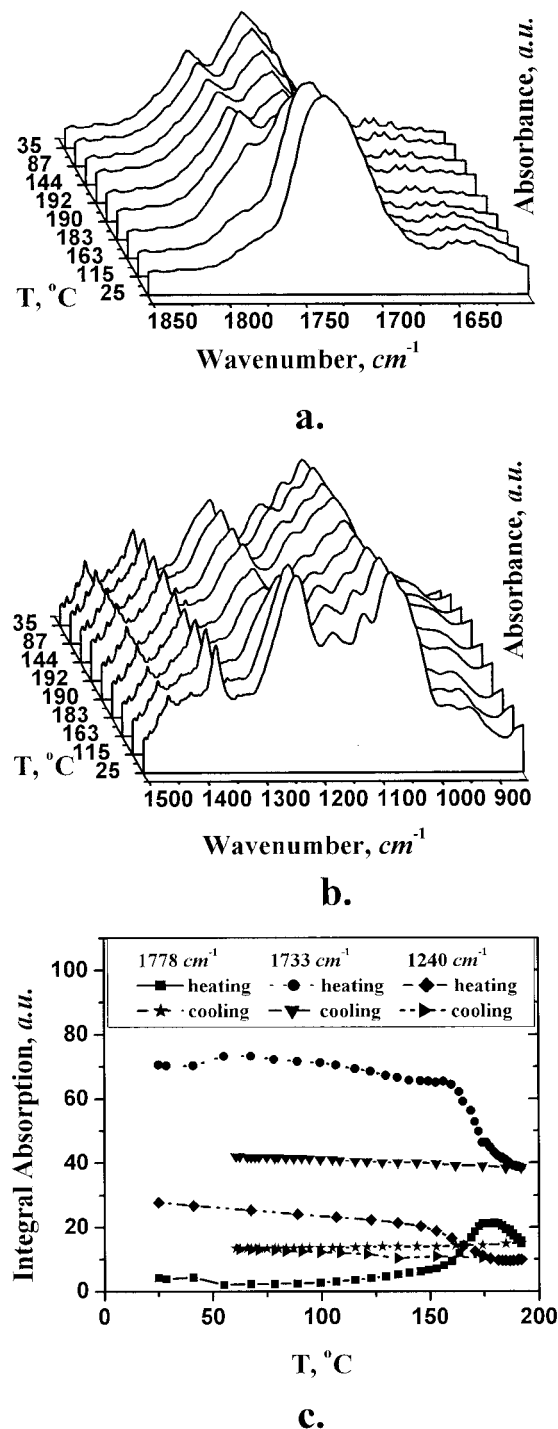
cate that these groups are consumed by a chemical reaction occurring during heating. The integral absorption of the band at  $1730$ – $1740\text{ cm}^{-1}$  has a different



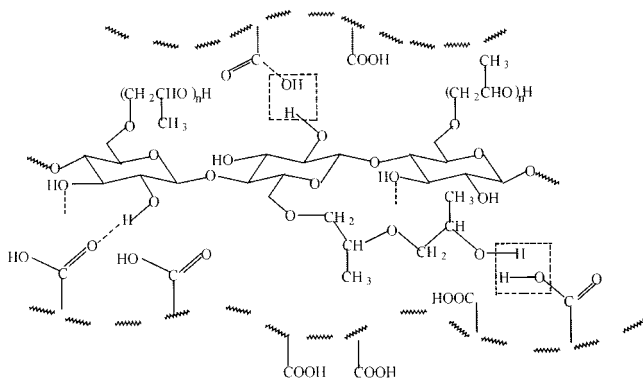
**Figure 10** FTIR spectra of the MAC-VA copolymer heated from 20 to 200  $^{\circ}\text{C}$  at 1  $^{\circ}\text{C}/\text{min}$  and cooled to room temperature: (a) 1600–1900  $\text{cm}^{-1}$ ; (b) 900–1300  $\text{cm}^{-1}$ . The variations of the integral absorbance of the bands are indicated on the figure versus temperature.

behavior depending on the content of the MAC-VA copolymer on the blends (not shown). In blends with a low content of MAC-VA copolymer ( $\leq 20$  wt %), the integral absorbance at 1770–1780  $\text{cm}^{-1}$  slowly increases up to  $\sim 170^{\circ}\text{C}$  and then remains constant. Therefore, we can assume that the COOH groups corresponding to the bands from 1730  $\text{cm}^{-1}$  are consumed.

In blends with a high content of MAC-VA ( $>40$  wt %) (Figure 11), the integral absorbance of the bands at 1778  $\text{cm}^{-1}$  increases between 160 and 180  $^{\circ}\text{C}$ , presents a maximum at 180  $^{\circ}\text{C}$ , and then decreases. These results support the idea that the anhydride units that could appear during heating from dehydration of the



**Figure 11** FTIR spectra of the 60 wt % HPC/40 wt % MAC-VA heated from 20 to 190  $^{\circ}\text{C}$  at 1  $^{\circ}\text{C}/\text{min}$  and cooled to room temperature: (a) 1600–1900  $\text{cm}^{-1}$ ; (b) 900–1500  $\text{cm}^{-1}$ . The variations of the integral absorbance of the bands are indicated on the figure versus temperature.



Scheme 2

MA moieties could easily be later involved in an esterification reaction. Schematic representation of the possible interactions between HPC and MAC-VA copolymer is given in the Scheme 2.

### CONCLUSIONS

All blends are less thermally stable than parent components, and their thermal stability decreases by increasing the MAC-VA content. The domain of heterogeneity is wider in HPC/MAC-VA blends than in dextran or pullulan/MAC-VA blends (see refs. 15 and 27) and is caused by different kinds of interactions.<sup>15,27</sup> In the blends with a high content of HPC, physical interactions are prevalent because these films are partially water soluble. In contrast, in blends with medium and low contents of HPC, chemical interaction leads to new structures because the films are water insoluble.

The presence of hydrophobic interactions that could appear between the backbone of the MAC-VA copolymer and the propylene oxide side chain of HPC contribute greatly to the strengthening of the H-bonding interactions between partners. The presence of a high number of physical and chemical crosslinks between components in the HPC/MAC-VA blends (films that are water insoluble) compared with the dextran (pullulan)/MAC-VA blends could be justified by the different conformation of main chain of the polysaccharides with a (1→4) $\beta$ -linked glucopyranosyl backbone (HPC) and (1→4) $\alpha$ - or/and (1→6) $\alpha$ -linked glucopyranosyl backbone (dextran and pullulan). Cellulose derivatives, such as HPC, generally have a much more ordered structure that is sterically more favorable to physical and chemical interactions compared with the other two polysaccharides. Tempera-

ture favors the inter- and intramacromolecular reactions.

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