

On the Compatibility of Polysaccharide/Maleic Copolymer Blends. II. Thermal Behavior of Pullulan-Containing Blends

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ABSTRACT: The compatibility of pullulan with maleic acid/vinyl acetate copolymers in the solid state in the form of thin films was studied with thermogravimetry, differential scanning calorimetry, infrared spectroscopy, and optical microscopy. With respect to morphology, blends with a content of pullulan greater than 85 wt % exhibited an even distribution of finely dispersed particles. The thermal prop-

erties were dependent on the mixing ratio, and the interactions between components were quite pronounced in the pullulan-rich blends. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1782–1791, 2002

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

INTRODUCTION

Blends and composites of biopolymers and synthetic polymers constitute a promising area of material science. Properties of pure synthetic polymers and pure biological polymers are often inadequate for producing materials with good chemical, mechanical, thermal, and biological performance characteristics, so researchers have been trying to prepare blends of synthetic polymers with biological macromolecules to obtain new materials with enhanced functional properties and biodegradability at a relatively low cost, so-called bioartificial polymeric materials. They are produced in different forms, including films, sponges, and hydrogels, and have been evaluated as biomaterials for dialysis membranes, wound dressings, drug delivery systems, and so forth.

Although the potential of pullulan in plastics or as coatings and film-forming materials has been recognized,¹ its compatibility with other components and its phase behavior in multicomponent systems have not been widely explored. Biliaderis et al.² studied pullulan/gelatinized corn starch blends and the effect of polyol plasticizers (sorbitol and xylose) on the water sorption, gas permeation, and thermal and mechanical properties of these blends. Toshio³ developed a new environmentally friendly packaging material based on a sodium alginate/pullulan mixture that

keeps the degree of freshness function by forming a biodegradable film on the usual linear boards.

In our previous studies,^{4,5} we prepared new potential biomaterials based on mixtures of poly(vinyl chloride) (PVC) and pullulan with different maleic anhydride (MA) copolymers as compatibilizing agents. We found that the mixtures compatibilized with alternating MA/styrene and MA/methyl methacrylate copolymers or with an ethylene/propylene copolymer grafted with MA (Exxelor) exhibited a higher hydrophilicity and biocompatibility than the pullulan/PVC mixture (Exxon Chem., Houston, TX).

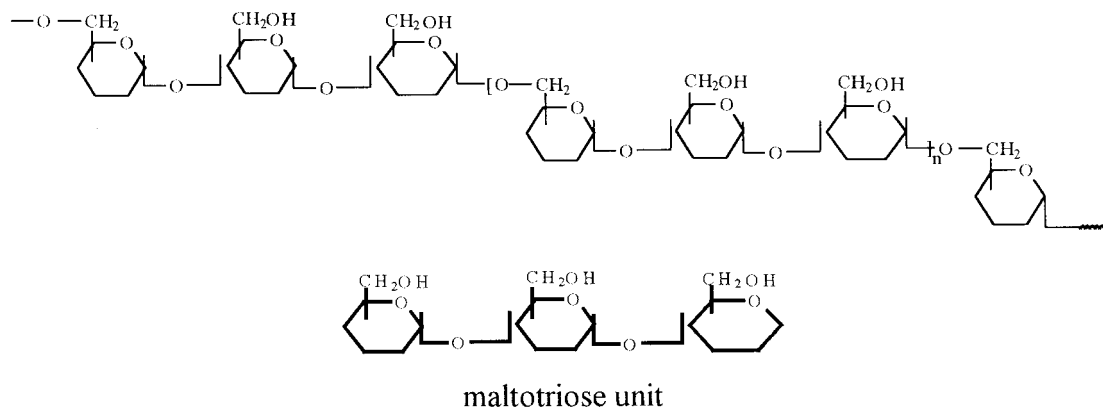
This article deals with the study of the compatibility of blends of pullulan and maleic acid (MAc)/vinyl acetate (VA) copolymers in the solid state. The following investigation methods were used: thermogravimetry (TG), differential scanning calorimetry, infrared (IR) spectroscopy, and optical microscopy.

EXPERIMENTAL

Polymers

Pullulan PF-20 (P), with a viscosity-average molecular weight (M_v) of 114,300 g/mol, was kindly supplied by Hayashibara Laboratory (Okayama, Japan) and was used as provided. Pullulan is a linear polysaccharide. It consists of glucopyranosyl units that are bounded with regular alternation between one (1→6) α and two (1→4) α glycosidic linkages or a maltotriosyl unit connected by (1→6) α linkages and has the following molecular structure:⁶

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The alternating MA-VA copolymer with an M_n value of 101,300 g/mol was synthesized by radical copolymerization in benzene, at 80°C, to a high conversion⁷ and was purified by extraction with chloroform (for details, see ref. 8). The fully water-soluble MAC-VA copolymer was obtained after 24 h by the hydrolysis of MA moieties from the MA-VA copolymer to MAC.⁹

Blend preparation

The blends were obtained as follows: 10 wt % aqueous solutions (twice distilled water) of each partner were mixed in different ratios ranging from 95 to 25 vol % pullulan and 5 to 75 vol % MAC-VA copolymer and were then stirred for 10 min and kept under stirring at 40°C for half an hour. The films were obtained through casting from these solutions onto glass plates. So that adherence of the films to the glass plate surface was avoided, a hydrophobic surface was obtained. The plates had been previously rinsed with a 10 wt % solution of trichloromethylsilane in acetone and then dried under air at room temperature. The advanced drying of the film samples was performed in a desiccator in the presence of phosphorus pentoxide. So that the degradation of polymers was avoided, no drying by heating was used. The film moisture was checked by TG and IR measurements. The thicknesses (determined with a micrometer gauge screw) of the sample films used for thermal analyses and IR spectroscopy were between 0.09 and 0.19 mm.

Methods

The TG and derivative thermogravimetry (DTG) curves were recorded on a Paulik-Paulik-Erdey-type derivatograph (MOM, Budapest, Hungary) under the following operational conditions: a heating rate (β) of 12°C min⁻¹, a temperature range of 25–600°C, a film sample mass of 50 mg, platinum crucibles, and an air flow of 30 cm³ min⁻¹. A kinetic analysis of the TG data was carried out on a single curve with both integral Coats-Redfern (CR)¹⁰ and differential Swaminathan-

Modhavan (SM)¹¹ methods (for more details, see ref. 8). The subscript of the overall kinetic parameters—the activation energy (E_a), pre-exponential factor (A), and reaction order (n)—indicates the evaluation method.

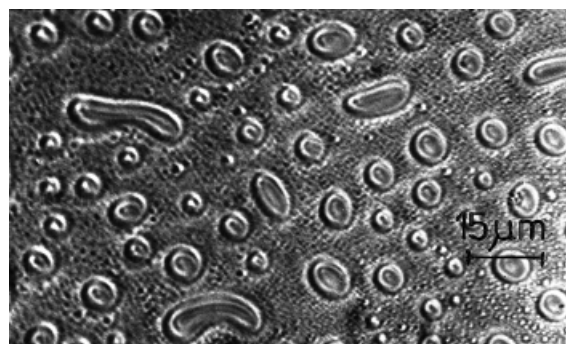
IR spectra of the unheated and heated blends (150°C for 5 min followed by more heating at 160°C for 5 min), in KBr tablets, were recorded with a SPECORD M-80 (Karl-Zeiss, Jena, Germany) spectrometer.

An optical examination of the very thin film samples obtained via casting from solution on the microscope glasses was performed with a microscope (IOR, Bucharest, Romania) in phase contrast with a magnification of 300×.

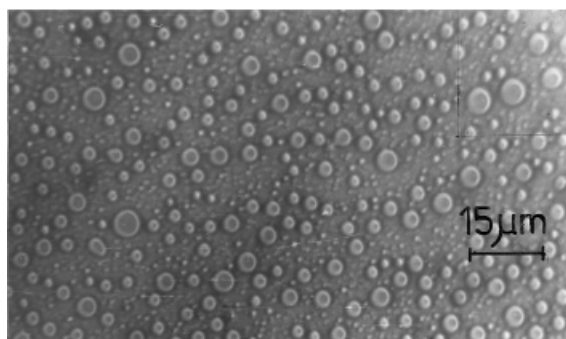
RESULTS AND DISCUSSION

Morphology

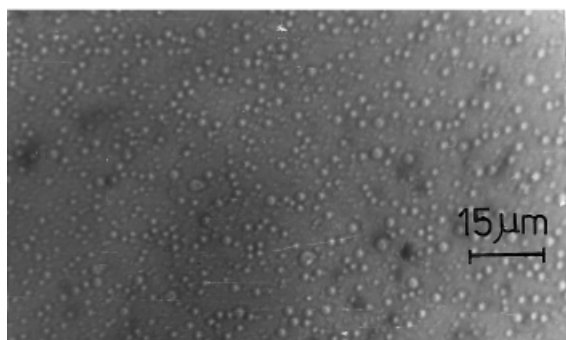
From an examination of the microscopic aspects of the films with a counter chamber, it is evident that the morphology of the blends is dependent on the mixing ratio. The following discussion is based on an examination of three or five micrographs for each sample. The blends with a pullulan content greater than 85 wt % are homogeneous, whereas the blends with a content of pullulan lower than 80 wt % can be described as finely dispersed phases in a continuous matrix. The 80 wt % pullulan-containing blend exhibits a fine and even distribution of particles of regular shape (5.2–1.5 μm) in a homogeneous matrix, the average diameter of the particles varying between 4 and 3 μm . The percentage of the disperse phase in the continuous matrix is approximately 24%. For the 60 P/40 MAC-VA blend, the percentage of the disperse phase is 26%, less than that of the minor component in the blend composition. The size of the particles varies between 6.3 and 1.5 μm , and the coarse disperse phase is distributed unevenly in the continuous matrix. The curve of distribution of the particle size is bimodal, with an average particle diameter of approximately 4 or 6.6 μm .



50 P/50 MAC-VA



40 P/60 MAC-VA



25 P/75 MAC-VA

Figure 1 Microscopic aspects of 50 wt % P/50 wt % MAC-VA, 40 wt % P/60 wt % MAC-VA, and 25 wt % P/75 wt % MAC-VA blends.

The 50 P/50 MAC-VA blend (Fig. 1) shows a morphology different from all the other blends, with big islands of one component distributed in the other one. The disperse phase is 49%, very close to that of the component in the mixture, and the size of the particles is 17–4 μm . At this mixing ratio, the partners exhibit a pronounced phase separation.

The blends with a prevalent content of MAC-VA copolymer (60–75 wt %) exhibit a fine and uniform distribution of the particles in the matrix. The percent-

age of the disperse phase is around 20%, different from that of the mixture. The size of the particles decrease with the increase in the MAC-VA copolymer content from 5.2 to 1.5 μm for a 40 P/60 MAC-VA blend to 2.2–1.5 μm for a 25 P/75 MAC-VA blend. The average diameter of the particles is lower than that of the other blends with a similar percentage of the disperse phase, namely, 2–3 μm .

The difference between the percentage of the dispersed component in the blends and that found by optical examination could be explained by partial solubilization of the components or by the existence of particles with dimensions below the detection limit for the employed conditions.

It is expected that the morphology will influence the thermal properties of the blends, as established for other blends too.^{12,13}

Thermal properties

DSC results

The MAC-VA copolymer presents a glass-transition temperature (T_g) around 100°C.⁸ Under our experimental conditions, for pullulan we have not detected any T_g , although in the literature a transition is mentioned at approximately 166°C, obtained by the extrapolation to zero humidity of T_g 's of various pullulan samples with different degrees of moisture.² The film blends with a high content of pullulan (>50 wt %) do not present any glass transition. This could be justified by the crosslinks that appear between the components due to an esterification reaction. The 50 P/50 MAC-VA and 25 P/75 MAC-VA blends exhibit a T_g at about 103°C that could be assigned to the copolymer. This agrees with the phase-separation behavior that we noticed with optical microscopy.

TG

In Figure 2 are displayed the DTG curves of the polymers and several blends. For each TG stage, the following thermal characteristics have been determined: the onset temperature (T_i); the temperatures corresponding to the maximum mass loss (T_M) and the end of the stage (T_F ; error in temperature determination = $\pm 2^\circ\text{C}$); the mass loss (Δw ; error = $\pm 1\%$); and the overall kinetic parameters E_a (error of determination = ± 10 –15 kJ/mol), A , and n .

The main TG stage of pullulan occurs in the 230–330°C temperature interval, with a T_M value of 273°C, a mass loss of 44.4 wt % (Table I), and an E_a value of 221.9 kJ/mol (Table II). This could be ascribed to the scission of the backbone of the polysaccharide.¹⁴ Between 35 and 223°C, a process takes place with a mass loss of 6.8 wt % that could be assigned to the absorbed water loss.

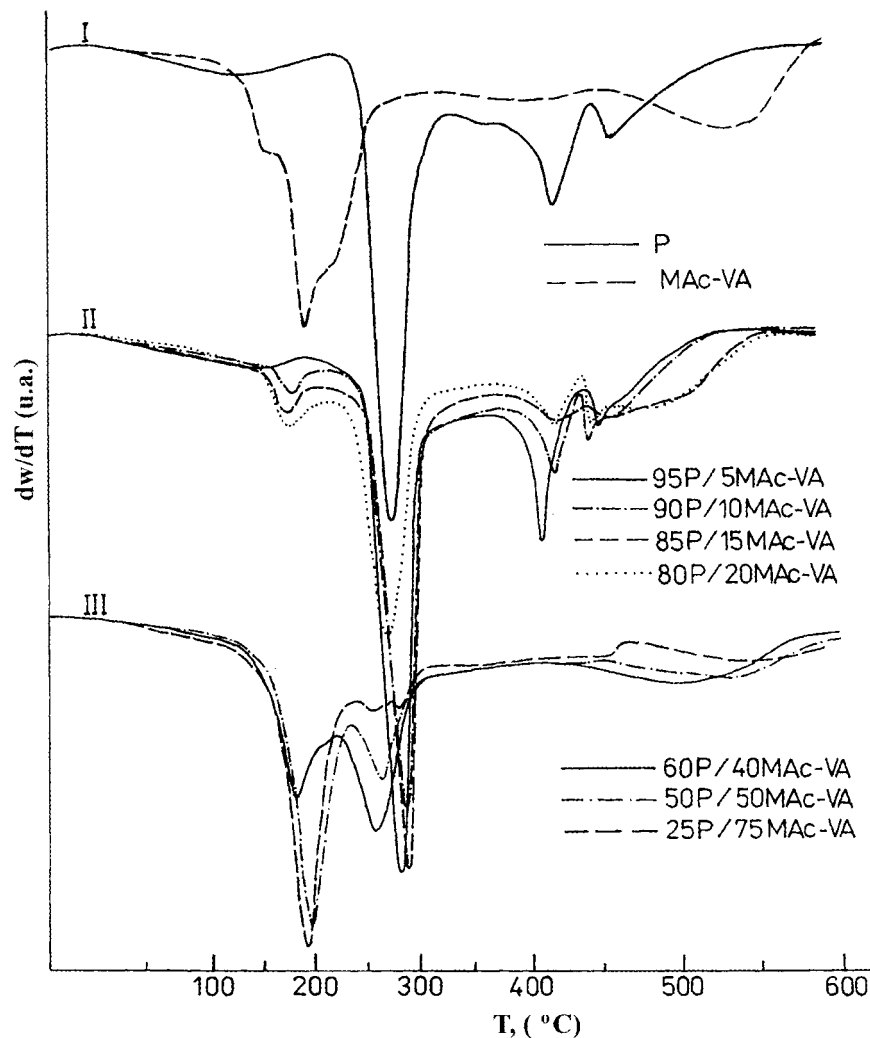


Figure 2 DTG curves of (I) individual polymers, (II) 90–80 wt % P/10–20 wt % MAc-VA blends, and (III) 60–25 wt % P/40–75 wt % MAc-VA blends.

The DTG curve of the MAc-VA copolymer exhibits only one distinct TG stage in the 20–400°C temperature range, but the process of decomposition seems to be very complex; the DTG peak looks very compli-

cated. It lies in the 68–300°C temperature interval, with a T_M value of 194°C, a shoulder at 159°C, and an inflexion at 218°C; the total mass loss is 47 wt %. We have shown in previous articles^{8,15} that this DTG peak

TABLE I
TG Data of Pullulan/MAc-VA Blends

Sample	First stage				Second stage			
	Characteristic temperatures				Characteristic temperatures			
	$T_{5\%}$ (°C)	T_M (°C)	T_F (°C)	Δw (%)	T_I (°C)	T_M (°C)	T_F (°C)	Δw (%)
Pullulan	160	—	223	6.8	223	273	330	44.4
95P/5MAc-VA	156	161	200	7.25	200	283	346	49.8
90P/10 MAc-VA	160	180.5	207	9.25	207	283	360	50.8
85P/15 MAc-VA	172	182	226	10.75	226	282	351	45.8
80P/20MAc-VA	179	183	224	14.75	224	272	330	34.9
60P/40MAc-VA	154	182.5	222	23.4	222	258	320	25.6
50P/50MAc-VA	163	197	237	33.5	237	264	312.5	17
25P/75MAc-VA	144	190	240	35.4	240	259	277	7.75
MAc-VA	155	194	300	47	—	—	—	—

TABLE II
Kinetic Data of the Second TG Stage of Pullulan/MAC-VA Mixtures

Sample	Characteristic temperatures				$E_{a_{CR}}$ (kJ/mol)	n_{CR}	$E_{a_{SM}}$ (kJ/mol)	$\ln A$	n_{SM}	Semi width
	T_I (°C)	T_M (°C)	T_F (°C)	Δ_w (%)						
Pullulan	223	273	330	44.4	221.9	2.0	194.7	42.8	2.1	10
95P/5MAC-VA	200	283	346	49.8	199.1	2.4	188.4	41.0	2.4	8.25
90P/10 MAC-VA	207	283	360	50.8	173.2	1.5	199.5	43.4	1.9	8
85P/15 MAC-VA	226	282	351	45.8	182.5	2.2	249.6	54.5	2.9	7
80P/20MAC-VA	224	272	330	34.9	157.3	1.7	140.1	30.4	1.7	10.5

appears because of two overlapping processes: the recyclization of MAC units to MA and the loss of acetic acid from VA moieties.

In the studied temperature range (20–400°C), pullulan/MAC-VA copolymer blends present two distinct TG stages (Fig. 2). The first TG stage of the blends occurs in the 40–240°C temperature domain and mainly corresponds to MAC-VA copolymer decomposition, whereas the second one (200–360°C) could be ascribed to pullulan decomposition.

The T_M value of the first TG process is situated between 180.5 and 197°C. It increases with an increas-

ing copolymer content in the blends. In a comparison of the experimental curves and those calculated according to the additivity rule (Fig. 3), it appears that the experimental curves lie over the calculated ones for the blends rich in pullulan [Fig. 3(a)] and below the calculated curves for blends with a prevalent content of the copolymer [Fig. 3(c)]. As a general trend, the temperature at which 5% of the process has occurred ($T_{5\%}$; Table I) increases with an increasing content of MAC-VA in the blends up to a 20 wt % value; then, it decreases. Blends with a content of pullulan lower than 60 wt % present an experimental mass loss 6–8

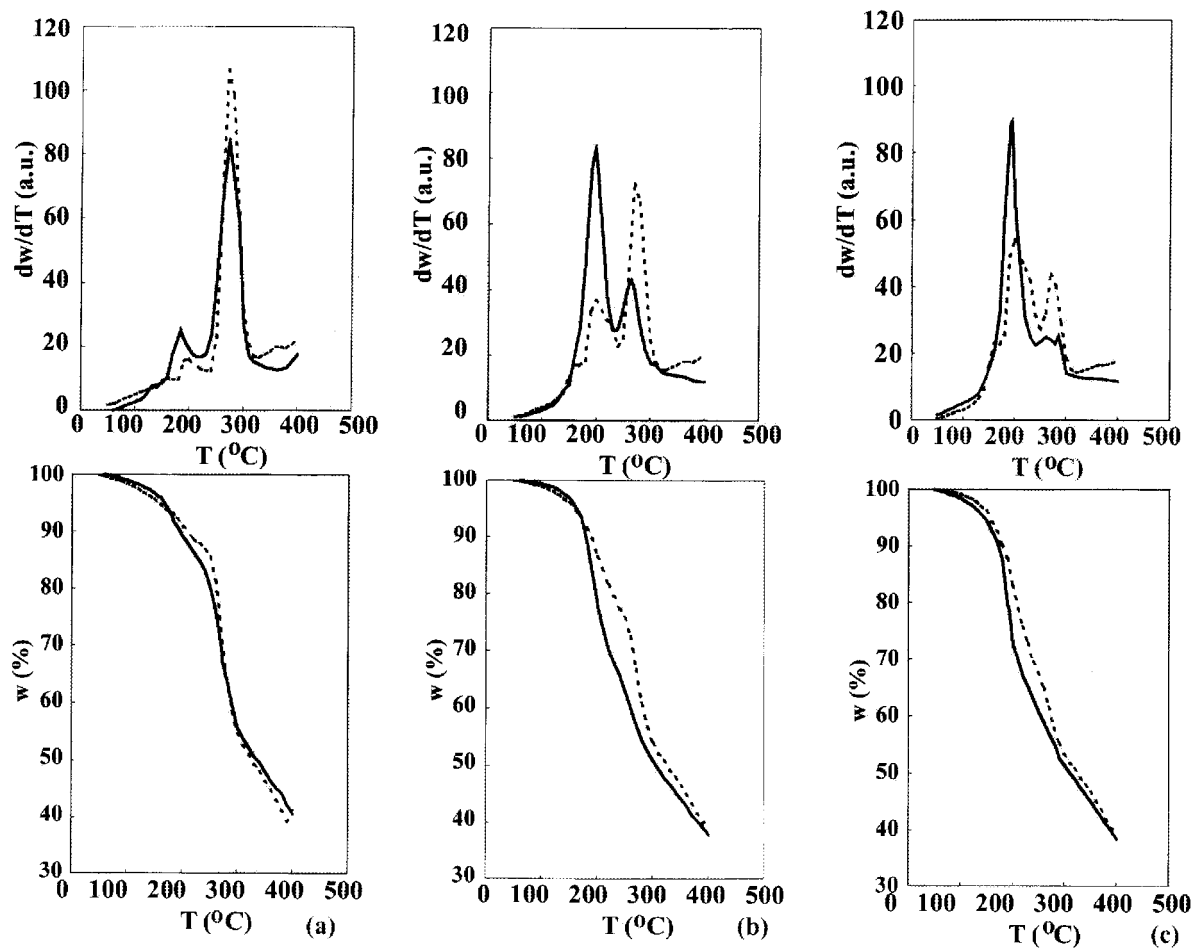


Figure 3 Experimental (solid lines) and calculated (dashed lines) TG/DTG curves of (a) 80 wt % P/20 wt % MAC-VA, (b) 50 wt % P/50 wt % MAC-VA, and (c) 25 wt % P/75 wt % MAC-VA blends.

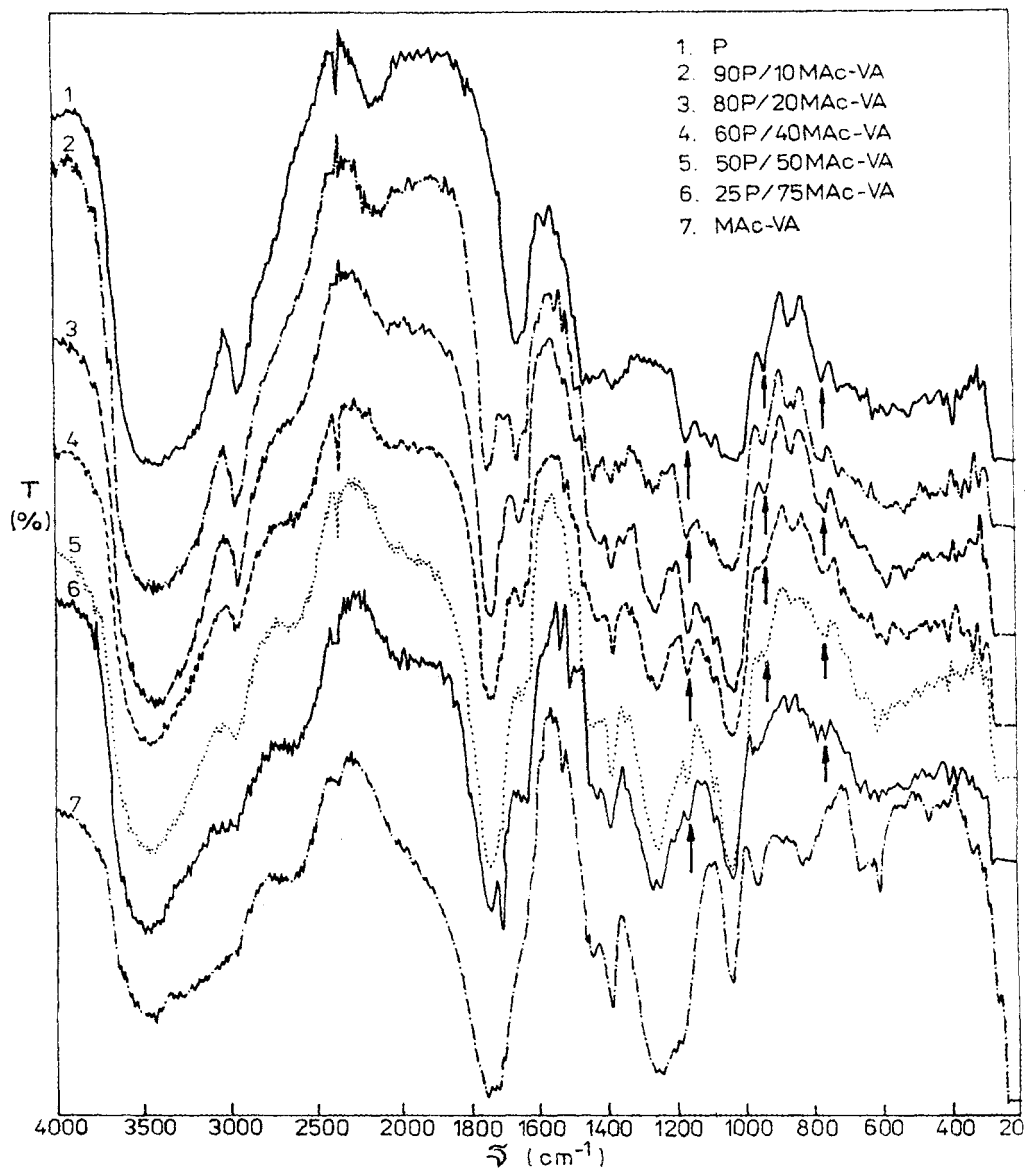


Figure 4 IR spectra of pullulan, MAc-VA copolymer, and their blends in various ratios.

wt % higher than the calculated loss. All this means a higher thermal stability of the blends with a prevalent content of pullulan and a lower stability for the blends rich in MAc-VA copolymer in comparison with the components. We can presume that the appearance first of the DTG peak of the blends at a different temperature with respect to those of the components is induced by the occurrence of a new structure during the mixing and heating processes. It can be supposed that a physical association by hydrogen bonding or a chemical reaction takes place between the OH groups (especially the primary ones) of pullulan and COOH or COO⁻ groups of MAc-VA copolymers, especially during the drying process of the films. The formation of this new structure in the mixture depends on the mixing ratio of the components. IR spectral measurements of the films from blends compared with those of

the components and solubility tests provide proofs as shown in the data listed later.

The second DTG/TG stage of the blends occurs in the 200–360°C temperature range. There are two distinct groups of blends with respect to thermal behavior in this temperature domain: blends with a content of pullulan greater than 85 wt % (first group) and blends with a content of pullulan lower than 85 wt % (second group; Fig. 3).

The experimental T_M value of the blends from the first group is 14–15°C higher than that evaluated according to the additivity rule from the TG data of the components; the experimental T_i value is lower than that calculated, and the experimental mass loss is higher than that calculated. Therefore, these blends are less stable than the components. The overall activation energy and the half-width of this stage are

TABLE III
Effect of the Mixing Ratio and Heating on the Log E_{1160} /Log E_{930} and Log E_{1160} /Log E_{765}
Ratio of Several P/MAC-VA Blends

Sample	Log E_{1160} /log E_{930}			Log E_{1160} /log E_{765}		
	Initial	After heating at 150°C for 5 min	After heating at 160°C for 5 min	Initial	After heating at 150°C for 5 min	After heating at 160°C for 5 min
Pullulan	1.4455	2.0668	2.1477	1.3194	1.53755	1.9487
95P/5MAc-VA	2.8736	3.0372	3.6733	2.1231	1.7041	4.03590
90P/10 MAc-VA	2.07476	—	3.5738	2.4877	2.9621	4.02214
85P/15MAc-VA	1.3965	3.1695	3.7433	2.04798	1.6076	3.13399
80P/20MAc-VA	3.1473	5.0043	3.0094	3.6283	2.8993	4.0444
60P/40 MAc-VA	—	3.2326	2.54797	1.7504	2.9224	3.7872
50P/50 MAc-VA	—	1.6305	1.0215	3.1750	2.5302	2.7190
40P/60 MAc-VA	2.7805	2.2075	1.1516	1.7874	2.7963	2.73098
25P/75 MAc-VA	—	—	—	—	—	—
MAc-VA	—	—	—	—	—	—

lower than those of pullulan, decreasing with a decreasing pullulan content in the blends. The apparent reaction order is fractionary and higher than unity (Table II). This indicates a complex mechanism of decomposition.

For the blends from the second group, the experimental T_M value is 3–8°C lower than that calculated. The experimental T_I value and the mass loss are also lower than those evaluated according to the additivity rule [Fig. 3(b,c)]; therefore, these blends are more stable than the partners.

IR spectroscopy

In the IR spectra of the blends (Fig. 4), all the characteristic bands of the IR spectra of the components are present,¹⁶ and the intensity of the bands varies in the same way with the mixing ratio of the components, many of them being overlapped. In the 1300–1550- cm^{-1} wave-number region, the characteristic domain for OH and COOH groups, the IR spectra of the blends have specific shapes depending on the mixing ratio of the partners. The peaks at 1460 cm^{-1} assigned to primary OH groups of pullulan¹⁶ and those at 1440

cm^{-1} ascribed to secondary and primary OH groups from pullulan and to COOH and COO^- groups from MAc-VA copolymers shift to lower wave numbers or vanish, especially for the blends with a medium content of pullulan (60–40 wt %). The modified shape of the IR spectra of the blends in this region could be due to the physical (hydrogen bonding) or chemical interactions between carboxylic and hydroxylic groups.

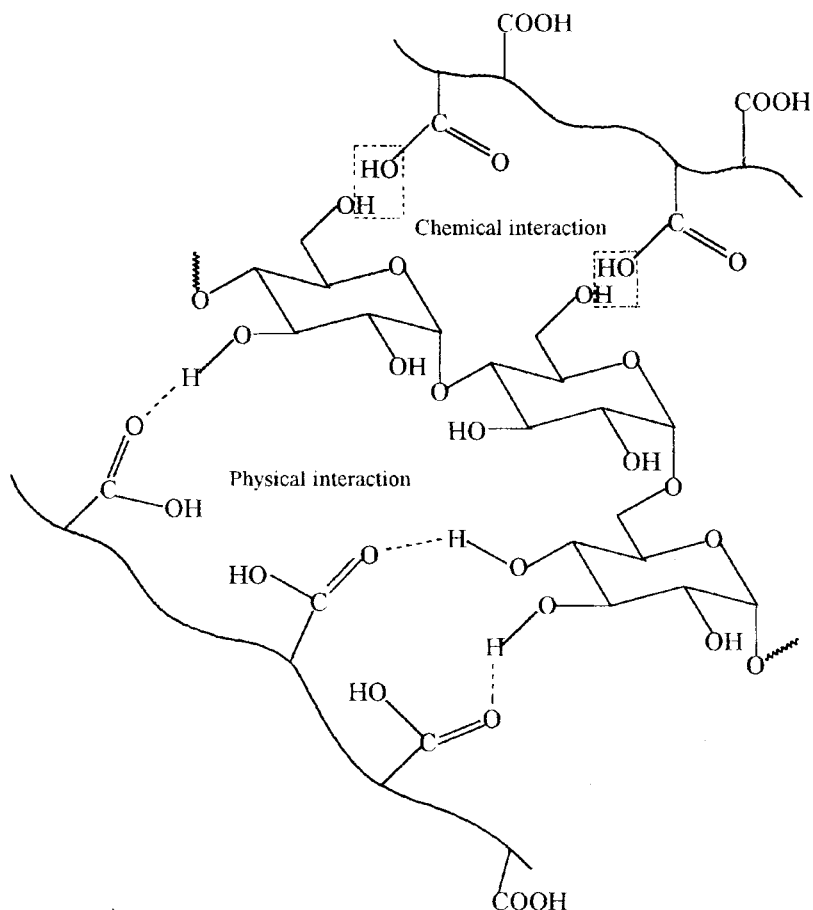
In the spectra of all the blends, the peak at 1160 cm^{-1} is more evident. This peak could be assigned to the ether and secondary OH groups¹⁶ of pullulan. At the same time in this region, the characteristic band of maleate ester group at 1160 cm^{-1} is also present;¹⁶ therefore, the increase in the intensity of the peak could be ascribed to the appearance of this type of ester group. A reaction is possible between the COOH groups from the MAc-VA copolymer and primary OH groups from pullulan. The acid pH (3.72–3.92) of the solution of the blends favors the development of an esterification reaction, especially when solutions of the mixture undergo the drying process of the films, as shown also for dextran-containing blends.⁸

To compare the relative amounts of the maleate ester groups that could appear in various blends, we

TABLE IV
Solubility Data of the Unheated and Heated Blend Films in Water

Sample	Blend unheated at room temperature	Blend unheated at 70°C	Blend heated at 150°C, at room temperature	Blend heated at 150°C, at 70°C
Pullulan	+	+	—	—
95P/5MAc-VA	+-	+-	+-	+
90P/10 MAc-VA	+-	+-	—	—
85P/15MAc-VA	+-	+	—	—
80P/20MAc-VA	+-	+-	—	—
60P/40 MAc-VA	+-	+-	—	—
50P/50 MAc-VA	+-	+	—	—
40P/60 MAc-VA	+-	+	—	—
25P/75 MAc-VA	+-	+	+-	+-
MAc-VA	+	+	+	+

+ = Water soluble; +- = partially water soluble; — = water insoluble.



Scheme 1 Schematic representation of possible physical and chemical interactions between pullulan and MAC-VA copolymer.

have calculated the ratios between the extinction of the band at 1160 cm^{-1} and the characteristic band of the $(1\rightarrow6)\alpha\text{ D}$ or $(1\rightarrow4)\alpha\text{ D}$ link of the main chain of pullulan at 765 or 930 cm^{-1} in the blend, $\log E_{1160}/\log E_{765}$ and $\log E_{1160}/\log E_{930}$, which are reported in Table III.⁶ When the ratio $\log E_{1160}/\log E_{765}$ or $\log E_{1160}/\log E_{930}$ is higher than that of pullulan, ester bonds can appear, and it is possible that the water solubility of the films will be changed (Table IV).

All the blends are partially soluble in cool water, but with heating at 70°C , their solutions have different behaviors depending on the mixing ratios of the components. Physical associations between the partners were also followed by solubility tests of the films of the blends at room temperature and at 70°C (Table IV). Both pullulan and MAC-VA are highly hydrophilic; therefore, the main interactions between their moieties are hydrogen bonds. At temperatures higher than 70°C , the hydrogen bonds are broken, and the physical associations are destroyed.

Films with a content of pullulan greater than 15 wt % are partially soluble (transparent with small unsolved particles) both at room temperature and at 70°C . The ratio $\log E_{1160}/\log E_{765}$ or $\log E_{1160}/\log E_{930}$

is higher than that of pullulan itself, and so we can suppose that a number of intermolecular ester groups appear.

The 80 P/20 MAC-VA blend is partially water soluble at room temperature, giving a cloudy solution; its solution keeps the same aspect after heating at 70°C and even at higher temperatures. The ratio $\log E_{1160}/\log E_{765}$ or $\log E_{1160}/\log E_{930}$ has the highest value in comparison with pullulan and the other blends. We can conclude that this ratio of mixing is the most favorable for a chemical reaction because it is relatively close to the stoichiometric ratio of the COOH groups of MAC-VA and the primary OH groups of pullulan.

The 60 P/40 MAC-VA and 40 P/60 MAC-VA blends have the same value for $\log E_{1160}/\log E_{765}$ and $\log E_{1160}/\log E_{930}$ (~ 1.7), a little bit higher than that of pullulan. By dissolution in water at room temperature, they form a cloudy solution with swollen pieces of films. Heating at 70°C , they become clear, and the films are totally water-soluble. Therefore, we can suppose that at these mixing ratios the formation of partially soluble interpolymeric complexes by hydrogen bonds is favored. The linear structure of pullulan and

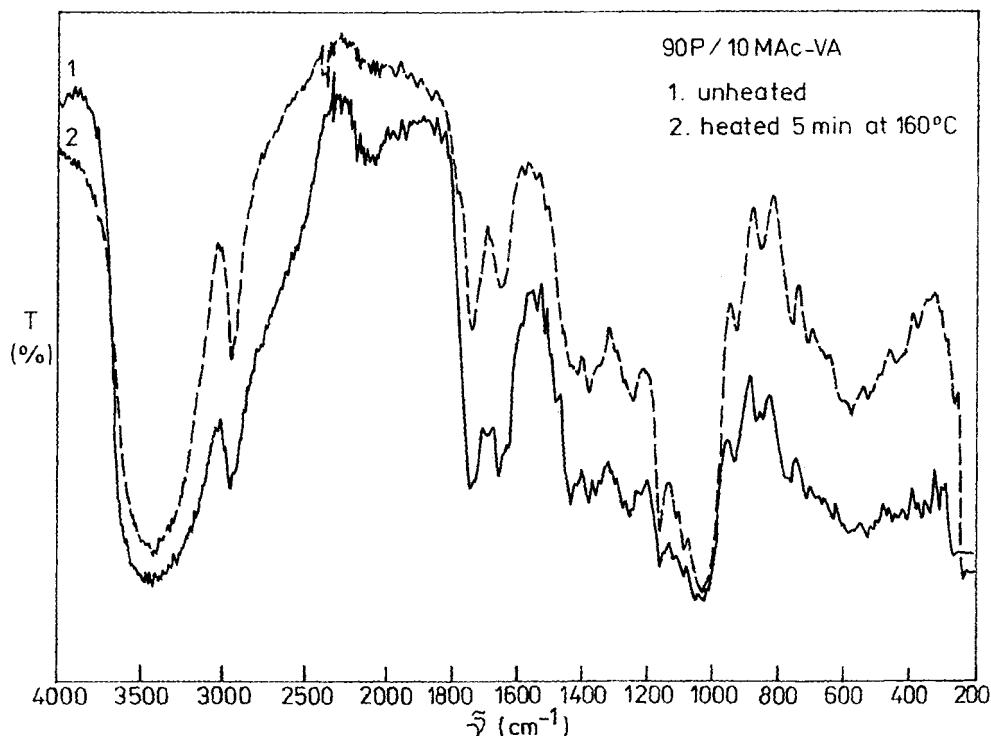


Figure 5 IR spectra of 90 wt % P/10 wt % MAC-VA blends before and after heating at 150°C and then at 160°C for 5 min.

the large number of primary OH groups from this polysaccharide favor this kind of interaction with COOH groups of the polyelectrolyte (MAC-VA copolymer), as shown in Scheme 1.

The esterification reaction is favored also by the heating of the blends. To provide evidence of this behavior, we recorded IR spectra of the heated blends (at 150°C for 5 min followed by heating at 160°C for 5 min). The values of $\log E_{1160}/\log E_{765}$ or $\log E_{1160}/\log E_{930}$ were calculated, and solubility tests were performed.

In the IR spectra of the heated blends with a high content of pullulan (≥ 85 wt %), the bands at 1675 cm^{-1} assigned to COOH groups and the peak at 1460 cm^{-1} ascribed to the primary OH groups of pullulan disappeared (Fig. 5). Although the pullulan content of the blends decreases and the MAC copolymer content increases, the characteristic bands of COOH (1690–1675, 1415–1430, and 1205–1275 cm^{-1}) vanish, and those of MA (1790–1800 cm^{-1}) appear. When the content of the MAC copolymer from the blends is higher than 40 wt %, the characteristic band of MA at 1860 cm^{-1} appears also via heating at 160°C (Fig. 6). With increasing temperature, the intensity of the characteristic bands of MA increases. At the same time, another important modification is observed. The characteristic bands of the OH groups of pullulan at 1445, 1430, 1345, 1275, and 1040 cm^{-1} vanish. The $\log E_{1160}/\log E_{765}$ and $\log E_{1160}/\log E_{930}$ ratios of the heated blends increase in comparison with those of unheated blends

and those of heated films of pullulan (Table III); therefore, the number of maleate ester groups increases. The esterification reaction could be particularly favored by the appearance of the MA groups, which are more reactive than the acid groups. The heated films of the blends are water-insoluble, whereas the heated film of the MAC-VA copolymer is water-soluble. This difference could be due to the crosslinks that appear between the partners because of the intermolecular reaction of esterification.

Generally, the esterification reaction and the physical associations depend on the mixing ratios of the partners. With heating, the formation of ester bonds is favored. The number of intermolecular ester links formed during the preparation of the blends will influence both the first stage of decomposition and the behavior during the second decomposition stage of the blends. In the blends with a high content of the MAC-VA copolymer, the reaction of MA or carboxyl moieties with OH groups of pullulan occurs concomitantly with the recyclization of MA groups.

CONCLUSIONS

Comparing the results obtained previously for dextran/MAC-VA blends with the presented data for pullulan/MAC-VA blends, we can remark that the type of glycosidic linkage from the main chain of a polysaccharide with the same structural unit is decisive for the morphology and thermal behavior of their blends

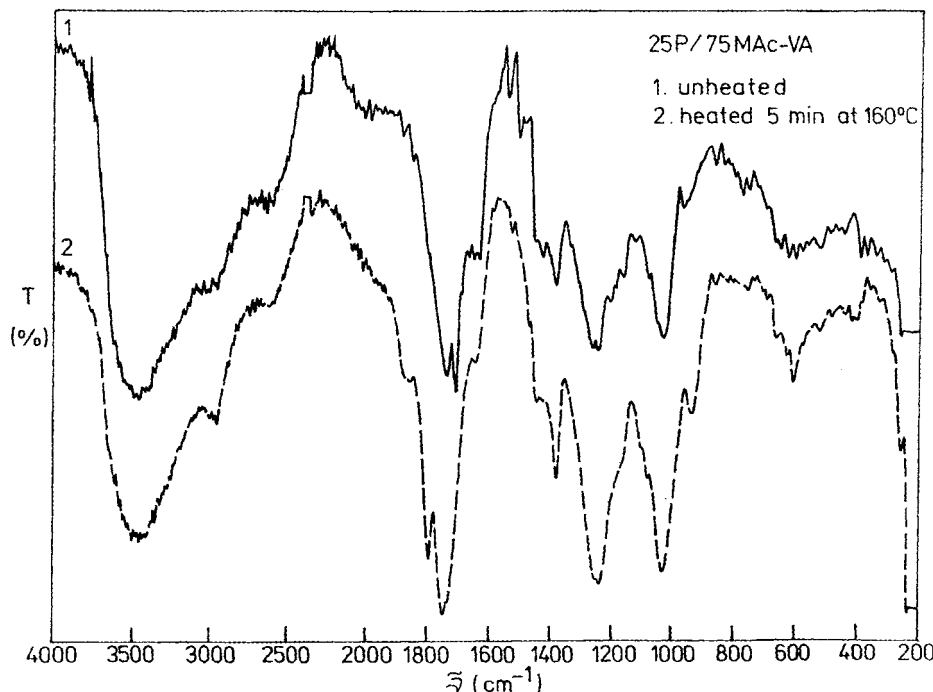


Figure 6 IR spectra of 25 wt % P/75 wt % MAc-VA blends before and after heating at 150°C and then at 160°C for 5 min.

with MAc-VA copolymers. Both pullulan and dextran backbone consist of glucopyranosil units linked in different positions; this leads to a different number of primary —OH groups.

Pullulan contains a larger number of primary OH groups [ca. 27.8% of the total of OH groups¹⁷ due to the presence of a large number of (1→4) α linkages in the main chain] than dextran [the main chain of dextran consists of glucopyranosil units linked in the (1→6) α position; therefore, it has primary OH groups only at the end of the macromolecular chain and at the ends of branches]. Therefore, in blends containing pullulan, the intermolecular crosslinking reaction between the primary OH groups of polysaccharides and the COOH groups of MAc copolymers is favored at room temperature in comparison with those containing dextran. This leads to a lower solubility of the pullulan-containing films, whereas those based on dextran are water-soluble at room temperature. The linear structure of pullulan also favors physical association by hydrogen bonding, whereas the branched structure of dextran does not allow this. Both pullulan-containing and dextran-containing films can undergo a crosslinking esterification reaction via heating.

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