

MORPHOLOGICAL, THERMAL AND RHEOLOGICAL CHARACTERIZATION OF POLYVINYL ALCOHOL/CHITOSAN BLENDS

ELENA PARPARITA, CATALINA NATALIA CHEABURU and CORNELIA VASILE

*“Petru Poni” Institute of Macromolecular Chemistry, Physical Chemistry of Polymers Department,
41A Gr. Ghica Voda Alley, 700487, Iasi, Romania*

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The present study deals with the preparation of polyvinyl alcohol (PVA)/chitosan (CS) blends with different compositions. The physico-chemical characterization and compatibility have been studied by means of polarized light optical microscopy, FT-IR spectroscopy, DSC, DMTA, TG/DTG and rheological measurements. The film-forming ability of the blends was confirmed by rheological tests, as they showed higher viscosity and improved viscoelastic properties in comparison with pure PVA. The obtained films were transparent and homogenous with enhanced mechanical properties and thermal stability.

Keywords: poly(vinyl alcohol), chitosan, blends, film-forming

INTRODUCTION

The polymer modification by mixing two or more distinct polymers to obtain compounds with improved or special properties, arises an increasing interest reflected by the large number of publications.¹⁻⁵ Blends of natural polymers (e.g. chitosan, starch, cellulose, alginates, etc) and synthetic polymers (polyvinyl alcohol, polyethylene, polystyrene, polypropylene, etc) are intensively investigated as biodegradable materials, due to their various biomedical and pharmaceutical applications, in food industry (packaging), environment conservation, etc.⁶⁻⁸

Polyvinyl alcohol (PVA) is a biodegradable, biocompatible, synthetic polymer, non-carcinogenic and non-toxic, with excellent film-forming properties. It is useful in many applications, such as adhesives, binding and coating agents, controlled drug delivery systems, recycling of polymers, packaging etc.^{9,10} Due to its water-solubility and outstanding chemical stability, it was blended with different synthetic and natural polymers.

Chitosan is obtained by deacetylation of chitin. The sugar backbone consists of β -1, 4-linked D-glucosamine with a high degree of N-acetylation, a structure very similar to cellulose, except that the acetamino group is replaced by hydroxyl group on the C-2 position. Thus, chitosan is poly(N-acetyl-2-amino-2-deoxy-D-

glucopyranose), a copolymer where the N-acetyl-2-amino-2-deoxy-D-glucopyranose (or Glu-NH₂) units are linked by (1 \rightarrow 4)- β -glycosidic bonds.¹¹ It is one of the most studied among naturally derived polymers, due to its biodegradability, biocompatibility, bioadhesivity and responsiveness.^{12,13} It is non-toxic for the human body, so that, chitosan and its derivatives are preferred to be used in biomedical applications. Chitosan is insoluble in water, aqueous alkaline solutions and common organic solvents, but it readily dissolves in aqueous inorganic and organic acid media. Chitosan is degraded by enzymatic hydrolysis.¹⁴ However, its tensile strength and elasticity is not suitable for some biomedical applications, such as wound dressing, skin tissue replacement, etc. Chitosan joined to other polymers opened a window of research for altering or tailoring the property of interest.⁸

Given the good biological activity of chitosan, a combination of chitosan and PVA should have beneficial effects on the biological characteristics of blend films.¹⁵⁻¹⁹ Hence, by combining hydrophilic polymers of different origins, one synthetic (PVA) and the other natural (CS), a class of hybrid organic-organic network can be produced with properties not present in either one separately.²⁰ Hydrogel blend systems containing PVA have been explored for medical

and pharmaceutical application, due to the advantage of non-toxic, non-carcinogenic, bioadhesive and antimicrobial properties.²¹

This study aims to obtain polymer blends based on polyvinyl alcohol and chitosan and to investigate their compatibility and physico-chemical properties in solid state by FT-IR spectroscopy, thermal characterization, by DSC, DMTA and TG, optical microscopy in polarized light (POM) and in solution by rheological measurements.

EXPERIMENTAL

Materials

Chitosan (CS), a product of low molecular weight was purchased from Aldrich. The dynamic viscosity of a solution with a 10 wt% concentration was of 20000 cP.

Polyvinyl alcohol (PVA), purchased from the company Romacril Râșnov, and had the following characteristics: Mw = 18300 Da, degree of hydrolysis of 95%, density of 1.3 g/cm³.

Preparation of PVA/CS mixtures

A 10 wt% polyvinyl alcohol aqueous solution was prepared by mixing PVA and water, followed by heating up to 70 °C under continuous mechanical stirring to obtain a clear solution. A 1% glacial acetic acid solution was used to prepare a 10 wt% chitosan solution.

The blends were prepared by mixing the 10 wt% polyvinyl alcohol solution (PVA) and 10 wt% solution of chitosan (CS) in the desired weight ratios namely, PVA/CS (polyvinyl alcohol/chitosan) w/w of: 90:5, 90:10, 85:15, 80:20, 70:30, 60:40, 50:50.

Mixtures were allowed to stand for several days, to observe any changes in their stability, phase separation, color, etc. The solutions were found to be homogenous and no phase separation was observed. Thin films of PVA/CS blends with different weight ratios were prepared by casting the solutions on glass plates, followed by solvent evaporation, at room temperature. Transparent, uniform and slightly yellowish films were obtained.

Methods of investigation

The blends were characterized by optical microscopy, FT-IR spectroscopy and thermal analyses: differential scanning calorimetry (DSC), thermogravimetry (TG) and dynamic mechanical thermal analysis (DMTA) and rheological measurements.

Optical microscopy

Investigations on the morphological aspects of the films based on PVA/CS were realized by optical microscopy studies by means of a Leica DM 2500 M

microscope, with polarized light at a magnification of 500X.

FT-IR spectra

ATR-FT-IR spectra were recorded for films of approximately constant thickness, using a spectrometer Bruker Vertex 70, by attenuated reflection on a diamond crystal with an angle of 45 degrees, at a resolution of 4 cm⁻¹.

Thermal analysis

DSC was performed using a Du Pont Instrument 912 Differential Scanning Calorimeter, in the temperature range 25 °C-325 °C. The films were previously dried at 70 °C for 60 minutes. The curves were recorded for 6 mg of sample, at a heating rate of 20 °C/min.

Dynamic mechanical thermal analyses (DMA) were performed using Anton Paar MCR301 rheometer equipped with specific accessories, namely a device for testing the extended films in a temperature range from -50 °C to 220 °C.

Thermal degradation of polymers was performed using a TG/FTIR system in the temperature range of 30-600 °C (303-873 K) at a heating rate of 3 °C/min in nitrogen atmosphere. The system consists of a device for simultaneous thermal analysis thermogravimetry (TG), Jupiter (Netzsch – Germany) coupled with a FT-IR spectrophotometer model Vertex 70 (Bruker – Germany).

Rheology

The rheological behavior of PVA and chitosan mixtures was monitored with an Anton Paar MCR301 rheometer, using a plate-plate geometry of 50 mm as a measurement system. Thus, rotational tests with variable shear rate and dynamic oscillatory tests with variable amplitude oscillations (amplitude sweep) or with different angular frequency (frequency sweep) were done. The amplitude sweep tests provide information on the amplitude-linear viscoelastic range and can be calculated in the “LVE range”, which is subsequently used in the angular frequency tests (frequency sweep, FSwp).

Strain sweep tests were performed at 25 °C at 1 Hz (10 rad/s) over the strain range 0.01-100% to determine the linear viscoelastic region (LVE), in which G' and G'' are practically constant and independent of the strain amplitude; the results showed a LVE regime up to a strain value of 0.01%. The results obtained from oscillatory dynamic measurements carried out in the angular frequency range 0.01-100 rad/s at a constant strain of 0.01%.

The amplitude sweep tests were performed at variable amplitudes in the range 0.01-100%, maintaining the frequency at a constant value of 10 rad/s.

Analyzing the behavior in the LVE range, the following relations can be used to describe the “character” of a sample:²²

a. Gel character: $G' > G''$ (G' , storage modulus and G'' , loss modulus): the elastic behavior dominates over the viscous behavior, the structure shows certain rigidity and the sample is stable.

b. Liquid character: $G'' > G'$: in this case, the viscous behavior dominates over the elastic behavior, the sample shows the character of a liquid in the LVE range.

c. $G' = G''$: in the LVE range, if the values of the two moduli are balanced, the behavior is sometimes called “at the gel point”.

The influence of temperature on the dynamic viscosity of the mixtures with different compositions (temperature sweep test, TSwp) was also observed. The temperature sweep tests were performed in a temperature range from 25 °C to 100 °C, at a heating rate of 5 °C/min.

RESULTS AND DISCUSSION

Polarized light microscopy

The microscopic examination of the films based on polyvinyl alcohol and chitosan in different ratios gives information about the homogeneity of the samples, highlighting any phase transformation. Figures 1-5 (a and b) provide the microscopic images of the PVA/CS film blends and the corresponding curves of the particle size distribution of the dispersed phase, while Table 1 summarizes the most probable average diameter values of these particles. The films based on chitosan and PVA are homogeneous upon microscopic examination. From the analysis of optical microscopy images and the corresponding distribution curves, it can be seen that the chitosan particle distribution in the PVA matrix is uniform and the chitosan particles present various sizes and shapes, usually as globules. Particle counts were graphically drawn versus their average diameter for several mixtures – Figures 1b-5b.

Phase separation is very evident for the mixture PVA/CS 50/50 – Figure 1a – the distribution

curve being large – Figure 1b, while the average particle size ranges from 8 to 25 microns. Particle size distribution curve for PVA/CS 60/40 mixture is large – Figure 2b, with the most probable diameter ranging between 6-8 microns, which also indicates a clear phase separation, Figure 2a. Starting with the mixture PVA/CS 70/30, the films become more homogeneous (Figure 3a), particle sizes are smaller than 2 and 10 microns, but in this case the curve is bimodal – Figure 3b. The films of the PVA/CS 80/20 and 85/15 blends are more homogeneous – Figure 4a – the distribution curves are unimodal with frequently found particles of 3-4 micron size (diameter) – Figure 4b. The mixtures PVA/CS 90/10 and 95/5 are even more homogeneous – Figure 5a – with a unimodal distribution curve with particles having an average diameter of 2-3 microns – Figure 5b.

Depending on the mixture composition, the particle diameter of the dispersed phase is modified, the lowest values being obtained for blends with a small amount of chitosan (1.8-2.6 microns for the mixture PVA/CS 85/15-95/5). Also, the distribution curves take different shapes depending on the composition; a unimodal curve is obtained for systems PVA/CS 50/50, 60/40, 80/20 and a narrow unimodal curve for 90/10 and 95/5 blends. Bimodal curves were obtained for system PVA/CS 70/30.

FT-IR spectroscopy

FT-IR spectra of the PVA, CS and their blends are shown in Figure 6 for two spectral regions and in Table 2 the main spectral bands and their assignments are given. The infrared spectrum of PVA shows an absorption peak at 3328 cm^{-1} , which refers to the intermolecular hydrogen bonding and –OH stretch vibration.²³ The vibrational band observed at 2930 cm^{-1} is associated with the C-H stretching from alkyl groups.

Table 1
Particle diameter of the dispersed phase at the maximum of the distribution curves for various PVA/CS blends

Sample (PVA/CS)	The most probable diameter of the particles of dispersed phase (microns)
50/50	8
60/40	7.3
70/30	6.3
80/20	3.3
85/15	1.7
90/10	1.8
95/5	2.6



Figure 1: Microscopic image (a) and distribution curve (b) of the dispersed phase of PVA/CS 50/50 blend

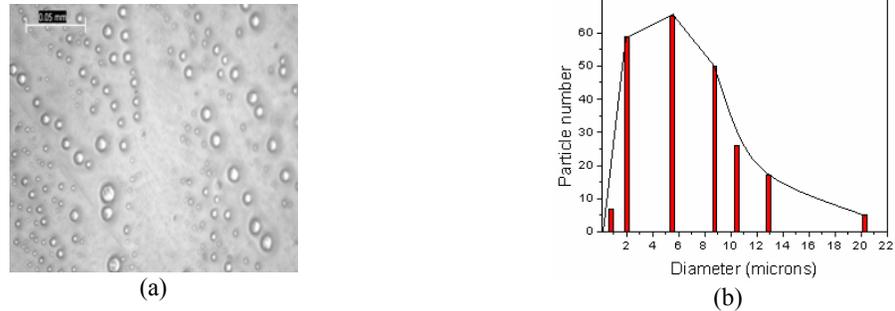


Figure 2: Microscopic image (a) and distribution curve of the dispersed phase (b) of PVA/CS 60/40 blend



Figure 3: Microscopic image (a) and distribution curve of the dispersed phase (b) of PVA/CS 70/30 blend

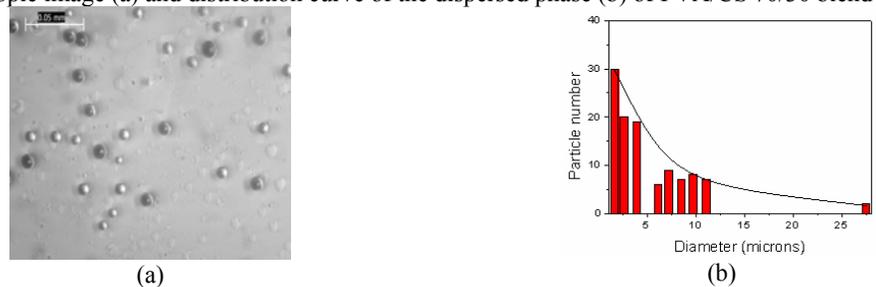


Figure 4: Microscopic image (a) and distribution curve of the dispersed phase (b) of PVA/CS 80/20 and 85/15 blends



Figure 5: Microscopic image (a) and distribution curve of the dispersed phase (b) of PVA/CS 90/10 and 95/5 blends

The absorption corresponding to the -C-O stretching occurs at 1083 cm^{-1} .²⁴ The spectrum of the pure chitosan film shows a broad band at 3320 cm^{-1} , which is due to the OH stretching. The band at 1560 cm^{-1} is assigned to the NH bending (amide II) (NH_2).²⁵

As can be seen from the data of Table 2, the decrease in the PVA concentration in the blended films caused an increase in the intensity of the band arising from the NH bending (amide II) at 1560 cm^{-1} of chitosan. Also, an increase in the intensity of CH group at around 2925 cm^{-1} was observed as the PVA content increased. Furthermore, the band at 840 cm^{-1} , assigned to the C-H rocking region of PVA, disappeared from the spectra of the pure chitosan film and the PVA/CS 50/50 blend film.

Thermal analysis

DSC and DMTA

The DSC curves (Figure 7) showed a region with a sudden decrease of the heat flow due to the modification of heat capacity around $60\text{ }^\circ\text{C}$, which was related to the glass transition (T_g) process in the sample. Also, an endothermic process was observed at about $180\text{-}190\text{ }^\circ\text{C}$ assigned to PVA melting. The transition temperatures were read at the inflexion for T_g from the DSC curves (Figure 7) and as peak temperature from G'' vs. temperature curves (Figure 8a) and $\tan \delta$ vs. temperature curves (Figure 8b).

From all the data in Table 3, the decrease of T_g and T_m is observed with an increasing amount of chitosan in the blend composition, because of the mutual interactions between the components and their partial compatibility.

The dynamic-mechanical thermal analysis of polymer materials is of great interest and importance, resulting from its great sensitivity in detecting changes of internal molecular mobility and in probing a phase structure and morphology of polymers.

The DMA spectra: loss modulus G'' or loss factor $\tan \delta = G''/G'$ can show a few peaks, which are attributed to the relaxation processes, the main being known as α and β . The β process has been assigned to the local mode of relaxation in the amorphous phase. The α relaxation related to the glass transition of the amorphous phase, is controlled by both intra- and intermolecular interactions. It is accompanied by a distinct decrease of the storage modulus G' with increasing temperature and the presence of G'' peak. The data obtained over a broad temperature range can also be used to ensure the molecular response of a polymer in blends with other polymers. In heterogeneous (phase separated) blends the molecular motions of the components remain unchanged, whereas in miscible blends the motions should be strongly affected and a single α transition appears.²⁶

Table 2
Characteristic bands in spectra of PVA, CS and their mixtures and their assignment

Sample	Band centered at (cm^{-1})						
PVA	3328	2930	1734	-	1245	1083	842
PVA/CS 95/5	3320	2930	1732	1554	1253	1080	823
PVA/CS 90/10	3320	2929	1732	1555	1253	1083	800
PVA/CS 85/15	3320	2929	1732	1555	1253	1083	825
PVA/CS 80/20	3320	2921	1734	1555	1253	1080	796
PVA/CS 70/30	3320	2920	1732	1556	1253	1066	797
PVA/CS 60/40	3319	2918	1734	1556	1253	1060	799
PVA/CS 50/50	3319	2915	-	1557	-	1066	-
CS	3320	2912	-	1560	-	1066	-
Assignment	OH - polymer (intermolecular bond)	ν_{CH}	ν_{CO}	ν_{NH} "Amide band II"	- OH	C-OH (primary alcohol)	C-C

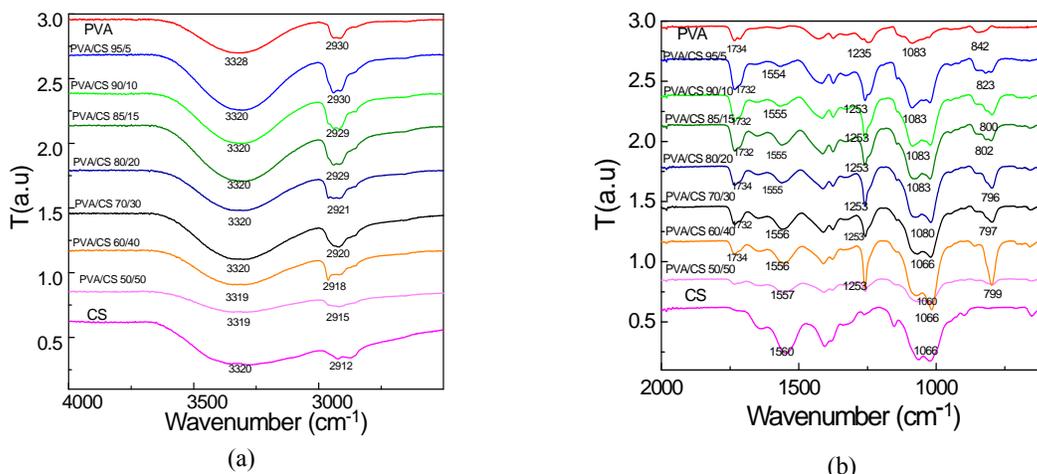


Figure 6: FT-IR spectra of pure components (chitosan and polyvinyl alcohol) and their mixtures within two spectral regions (a) 4000-2500 cm^{-1} and (b) 2000-500 cm^{-1}

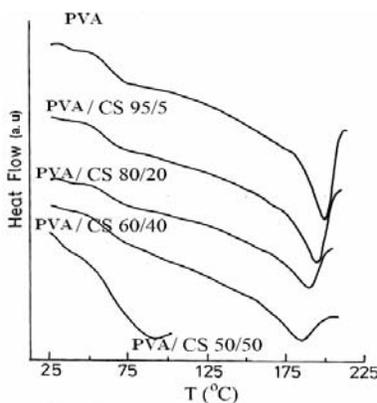


Figure 7: DSC curves of PVA and PVA/CS mixtures

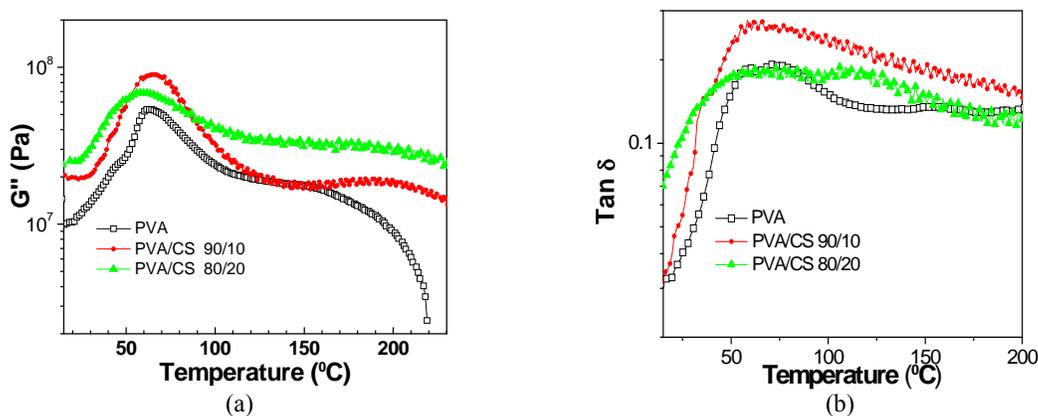


Figure 8: Variation of dynamic loss modulus G'' (a) and $\tan \delta$ (b) with temperature for polyvinyl alcohol films and PVA/CS 90/10, 80/20 blends

By comparing the shape of DMA curves presented in Figure 8 (a), an increase in the dynamic modulus of the blends *vs* PVA was

remarked. The storage modulus curve (not shown) had an increased value of storage modulus (G') from $3.1 \cdot 10^8$ (Pa) for PVA to $6.38 \cdot 10^8$ (Pa) or

6.84×10^8 (Pa) for PVA/CS 90/10 blend and PVA/CS 80/20, respectively. The dynamical loss modulus (G'') showed also increased values from 5.42×10^7 (Pa) for pure PVA to 6.87×10^7 (Pa) and

8.96×10^7 (Pa) for PVA/CS 90/10 respectively (Figure 8 a). The increase of dynamic moduli indicates a good stability of the blends owing to the compatibility of the components.

Table 3
Transition temperatures of PVA, CS and their blends

Method of determination System	DSC		T _g from DMTA (°C)		T _{swp}
	T _g (°C)	T _m (°C)	From E''	From Tan δ	T _g from T _{swp} (°C)
PVA	62	199	64	69	67
PVA/CS 95/5 wt%	60	195			64
PVA/CS 90/10 wt %		191	63	65	67
PVA/CS 80/20 wt%	61	189	60	60	65
PVA/CS 85/15 wt%					64
PVA/CS 70/30 wt%					60
PVA/CS 60/40 wt%	59	184			60
PVA/CS 50/50 wt%	69				59

Table 4
Values of T_i (onset temperature), T_{max} (peak temperature), T_f (final temperature) from DTG curves for PVA, CS and PVA/CS blends

System	Peak 2				Peak 3			
	T _i (°C)	T _{max} (°C)	T _f (°C)	Δw (%)	T _i (°C)	T _{max} (°C)	T _f (°C)	Δw (%)
PVA	250.8	287	340	33.6	340	366.9	404.3	12
PVA/CS 90/10 wt%	266.7	318.2	361.8	69.12	414.7	428.4	495.3	13.98
PVA/CS 50/50 wt%	258	282	355.7	48.65	426.9	439.7	470.2	10.52
CS	253.1	279.7	310.8	52.68				

The tan δ curves of the blends- Figure 8(b)- showed a relaxation at about 69 °C, which corresponds to the glass transition of PVA. It is known that DMA analysis detects molecular relaxations, such as the T_g processes, with a higher sensitivity than the DSC/DTA methods.²⁷ The T_g values obtained by DMA analysis also decreased with increasing CS content of the blends, therefore T_g is dependent on composition, indicating at least partial compatibility of the components. A satisfactory agreement was found between the T_g values obtained by different methods (Table 3).

TG/DTG

The thermogravimetric data of PVA have been recorded under the same experimental conditions as those used for PVA/CS blends in our previous paper.²⁸

Figure 9 shows mass loss vs temperature (TG) curves and their derivative (DTG) of CS and PVA/CS blends. The thermograms of PVA/CS blends showed three stages of degradation. The first stage involved dehydration and occurred at

temperatures of about 100 °C, then in the second step, degradation took place by ring scission and decomposition reactions. As can be seen, the degradation of CS occurred in a single step in the range from 253 °C to 310 °C, with the peak temperature at 279 °C (T_m) – (Table 4).

The blends with a higher amount of polyvinyl alcohol (90/10 wt%) had two stages of decomposition. The first one occurred in the range from 266 °C to 361 °C with the peak temperature at 318 °C (Table 4). Then a residue was obtained, which decomposed in the third stage at 429 °C. The blend PVA/CS 50/50 also presented two stages of degradation, the first one in the range of 258-355 °C. A shoulder was observed above 318 °C, being influenced by the presence of PVA. As known, the DTG thermograms evidence more clearly the degradation pattern than the TGA curves and they are more complex than those of components, therefore the degradation mechanism of PVA in the presence of chitosan is changed and becomes more complex.

Some mixtures have higher decomposition temperatures than polyvinyl alcohol which indicates a better thermal stability of the PVA/CS blends in respect with parent PVA (Table 4).

Rheological data

Controlled shear rate tests (CSR)

The variation of dynamic viscosity with shear rate for the 10 wt% solutions of CS, PVA and their blends is shown in Figure 10. The CS solution had the highest viscosity, while the PVA

solution viscosity had the lowest. The curves of the mixtures lay between those of the components.

The solutions of CS and of blends PVA/CS 50/50 and 60/40 showed a sudden decrease of viscosity at a shear rate higher than 9 s^{-1} , because of their instability at such a shear rate. The viscosity of the other solutions remained constant over the entire shear rate range studied, i.e. they were stable.

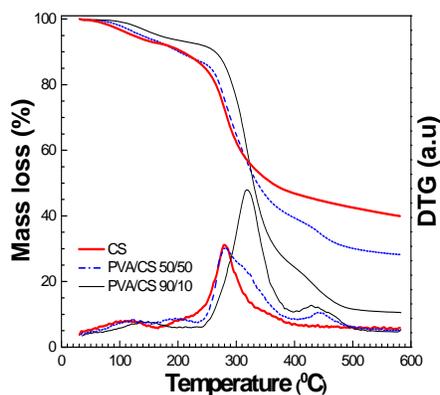


Figure 9: TG/DTG curves for CS and several PVA/CS mixtures

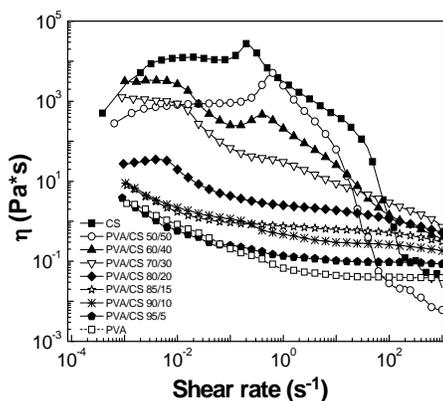


Figure 10: Variation of dynamic viscosity with shear rate for PVA, CS and their blends

To obtain information about the compatibility of the components, viscosity was determined from the curves in Figure 10, both at low shear rates, of $\gamma = 0.01\text{ (s}^{-1}\text{)}$ and at high shear rates, of $\gamma = 100\text{ (s}^{-1}\text{)}$, and the values obtained were drawn vs. mixture composition in Figure 11.

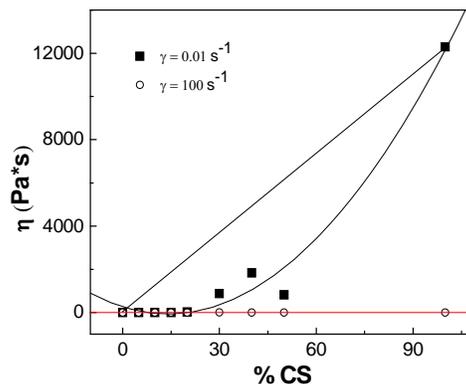


Figure 11: Dynamic viscosity vs composition of PVA/CS mixture

It can be noticed that the mixtures have lower experimental viscosity values than those calculated in the hypothesis of additivity, supposing no interactions between components. The lower values could be an indication of phase separation at low shear rates or formation of a

compact structure, while the mixtures became homogeneous at high shear viscosity, where the values for the blends lay on the same line as those obtained by the additivity rule.

Oscillatory tests

By the oscillatory testing, the viscoelastic behavior of the PVA/CS blends can be determined. The tests were performed at variable amplitudes and a constant frequency (ω), of 10 rad/s (amplitude sweep tests), and at different frequencies and a constant amplitude (frequency sweep tests).

The LVE range of the samples within which the frequency tests were performed was determined by amplitude sweep tests, where the curves of G' and G'' remained on a constant plateau.

At low amplitudes in the linear viscoelastic (LVE) range, the curves of both dynamic moduli

(storage modulus, G' , and loss modulus, G'') showed a plateau for all blends on different levels. The amplitude gamma strain (γ_L) was found to be below 0.1% for all compositions of PVA/CS blends; while the CS solutions showed a γ_L slightly higher than 0.1%, due to its viscous appearance. On the other hand, PVA had a γ_L of 0.01%, showing its liquid character. G' took higher values than G'' in the case of the blends with a higher amount of chitosan, starting with PVA/CS 70/30, suggesting the formation of a gel-like structure after blending.

γ_L of 0.01% was chosen, a value within the LVE range of all blends and pure components, and it was used as constant strain for frequency sweep tests at low frequencies.

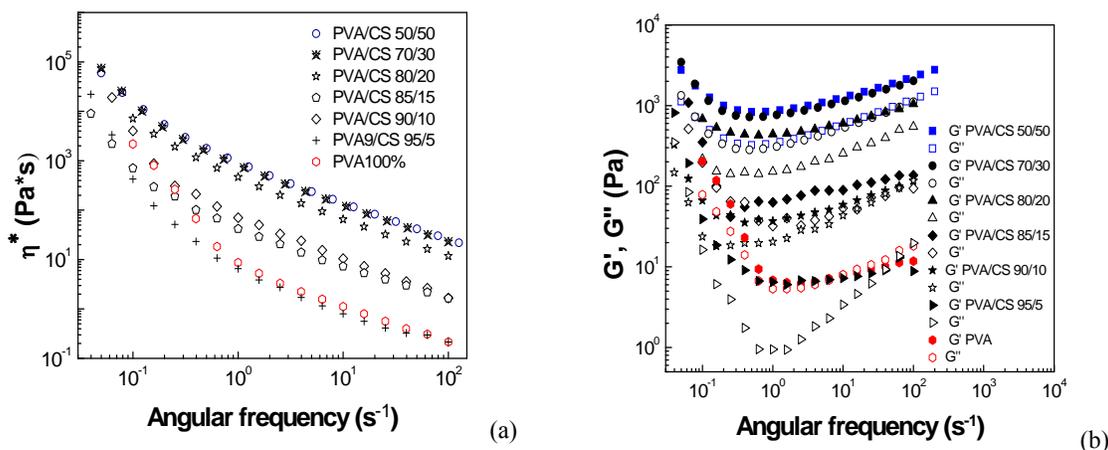


Figure 12: Variation of viscosity (a) and loss and storage moduli (b) with angular frequency

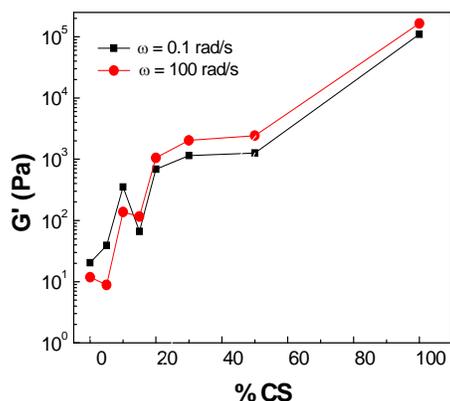


Figure 13: Variation of storage modulus with mixture composition at angular frequency of 0.1 s^{-1} and 100 s^{-1}

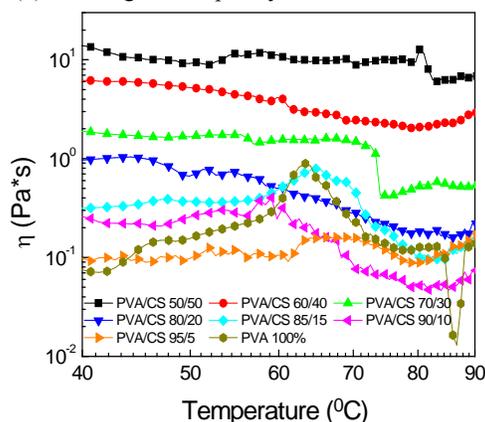


Figure 14: Variation of dynamic viscosity with temperature for PVA and PVA/CS blends

Generally, for materials showing a network of physical-chemical superstructures or chemical bonds, gels and crosslinked polymers above glass

transition temperature, γ_L was described to be below 1%, and for polymers below glass transition temperature or materials showing a very

inflexible structure, $\gamma L \leq 0.1\%$; materials showing values $G' > G''$ in whole frequency range, with a slight increase in the slope at higher frequencies.²²

As can be seen in Figure 12 (a), the values of the complex viscosity of the blends $[\eta^*]$ increased with increasing the amount of chitosan in the blend composition. The same dependence was observed in the case of dynamic moduli (G' and G'') – Figure 12 (b), which took higher values once the chitosan content within the mixture increased due to the increase in the gel character with a higher strength. Storage modulus, G' , is indicative of the gel strength and its higher values with increasing chitosan content within the mixture explain the formation of blends with gel character.

For pure PVA, both moduli G' and G'' had very close values showing a liquid-like character. In the case of the blends with 5, 10 and 15% chitosan, at high frequency, G'' took higher values than G' , following a trendline, so that at very low frequency G' became slightly higher than G'' . This type of behavior is specific for sparsely cross-linked polymers, flexible gels or dispersions showing a low structural strength at rest. In the case of the mixtures with 20, 30 and 50 wt% of chitosan, G' was higher than G'' throughout the range of angular frequency and the two curves of the moduli are parallel, without any crossover point, indicating a strong gel character.

The cross-over point of the two moduli is indicative of gel formation. The values of cross-over points found are summarized in Table 5.

Table 5
Cross-over points of PVA and PVA/CS blends

Sample	$G'=G''$ (Pa)
PVA	9.17
PVA/CS 95/5	8.32
PVA/CS 90/10	60.28
PVA/CS 85/15	92.92

As can be observed both from Figure 12 (b) and Table 5, the samples with a higher amount of chitosan didn't show any cross-over point, which can be explained by the presence of the gel character of the blends, while at lower amounts of chitosan within the system, a transition point from solution to gel state is observed.

Figure 13 presents the variation of storage modulus with composition at low angular frequency, of 0.1 rad/s, and high angular frequency, of 100 rad/s.

At small angular frequency the dependence emphasis on the gel character described by a three-order polynomial dependence, storage modulus values and hence gel strength increase with increasing chitosan content in the mixture PVA/CS.

Temperature sweep tests

The variation of rheological properties with temperature is given in Figure 14.

All samples have a transition around 60 °C (see Table 3, last column), which can be associated with the glass transition temperature of PVA.²⁹ The T_g values decrease with increasing CS amount in blend composition, according to DSC results. This transition is dependent on blend composition, therefore the blends exhibit at least partial compatibility.

CONCLUSION

Morphological observations showed that the polyvinyl alcohol/ chitosan blends with different compositions behave as distinct phase systems, those containing up to 20% chitosan exhibited a higher degree of compatibility, being considered as optimum compositions for obtaining materials with satisfactory properties.

Blends based on polyvinyl alcohol/chitosan (PVA/CS) with various compositions had increased thermal stability.

The dynamic moduli (G' and G'') exhibited higher values for blends, compared with values of the pure polyvinyl alcohol, which is an indication of a good stability and a tendency of gel formation. The mixtures showed visco-elastic behavior of a predominantly gel character, becoming more compact with increasing chitosan content.

The mixtures showed enhanced thermal stability and also improved mechanical and visco-elastic properties, in comparison with PVA.

Blends based on chitosan and polyvinyl alcohol could be proposed for applications in food industry, for active packaging, wastewater purification membranes, in medicine and pharmacy as carriers of active principles.

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REFERENCES

- ¹ J. W. Barlow and D. R. Paul, *Polym. Eng. Sci.*, **21**, 985 (1981).
- ² Y. S. Lipatov and A. E. Nesterov, in “Thermodynamics of Polymer Blends”, Technomic Publishing Company Inc., 1998, pp. 227-271.
- ³ E. Parparita, C. N. Cheaburu and C. Vasile, in “Noi ambalaje polimerice pentru alimente”, edited by C. Vasile and C. N. Cheaburu, PIM, 2010, pp. 153-175.
- ⁴ L. A. Utracki, in “Polymer Blends Handbook”, edited by L. A. Utracki, Kluwer Academic Pub, 2003, pp. 1-96.
- ⁵ L. Robeson, in “Polymer Blends: A Comprehensive Review”, edited by L. M. Robeson, Hanser Verlag, 2007, pp. 109-210.
- ⁶ E. M. Chiellini, P. Cinelli, F. Chiellini and S. H. Imam, *Macromol. Biosci.*, **4**, 218 (2004).
- ⁷ D. W. Lee, H. Lim, H. N. Chong and W. S. Shim, *Open Biomater. J.*, **1**, 10 (2009).
- ⁸ C. Vasile, in “Environmentally Degradable Materials Based on Multicomponent Polymeric Systems”, edited by C. Vasile and G. E. Zaikov, Brill Academic, 2009, pp. 512-529.
- ⁹ V. Goodship, in “Polyvinyl Alcohol: Materials, Processing and Applications”, Smithers Rapra Press, 2009, p. 142.
- ¹⁰ S. Patachia, in “Handbook of Polymer Blends and Composites”, edited by C. Vasile and A. K. Kulshereshta, Rapra Technol. Ltd, 2003, pp. 288-365.
- ¹¹ R. Hejazi and M. Amiji, *J. Control. Release*, **89**, 151 (2003).
- ¹² A. Domard and M. Domard, in “Polymeric Biomaterials”, edited by S. Dumitriu, Marcel Dekker Inc., 2002, pp. 187-212.
- ¹³ E. S. Gil and S. M. Hudson, *Prog. Polym. Sci.*, **29**, 1173 (2004).
- ¹⁴ J. K. F. Suh and H. W. T. Matthew, *Biomaterials*, **21**, 2589 (2000).
- ¹⁵ S. B. Bahrami, S. S. Kordstani, H. Mirzadeh and P. Mansoori, *Iran. Polym. J.*, **12**, 139 (2003).
- ¹⁶ E. I. Kulish and S. V. Kolesov, *Russ. J. Appl. Chem.*, **78**, 1486 (2005).
- ¹⁷ S. Tripathi, *Int. J. Biol. Macromol.*, **45**, 372 (2009).
- ¹⁸ E. S. Costa-Júnior, *Carbohydr. Polym.*, **76**, 472 (2009).
- ¹⁹ S. Tripathi, *Carbohydr. Polym.*, **79**, 711 (2010).
- ²⁰ H. S. Mansur, C. M. Sadahira, A. N. Souza and A. A. P. Mansur, *Mat. Sci. Eng. C*, **28**, 539 (2008).
- ²¹ H. S. Mansur, R. L. Oréface, A. P. Mansur, *Polymer*, **45**, 719 (2004).
- ²² T. Mezger, in “The Rheology Handbook”, Vincentz Network GmbH & Co. KG, 2006, pp. 80-102.
- ²³ A. L. Ahmad and B. S. Ooi, *J. Membrane Sci.*, **255**, 67 (2005).
- ²⁴ M. Ilcin, O. Hola, B. Bakajova and J. Kucerik, *J. Radioanal. Nucl. Chem.*, **283**, 9 (2010).
- ²⁵ Z. Cui, Y. Xiang, J. Si, M. Yang, Q. Zhang and T. Zhang, *Carbohydr. Polym.*, **73**, 111 (2008).
- ²⁶ K. P. Menard, in “Dynamic Mechanical Analysis: A Practical Introduction”, edited by K. P. Menard, CRC Press, 1999, pp. 17-37.
- ²⁷ T. Hatakeyama and F. X. Quinn, in “Thermal Analysis. Fundamentals and Applications to Polymer Science”, edited by T. Hatakeyama, F. X. Quinn, Wiley, 1999, pp. 5-24.
- ²⁸ C. Vasile, A. Stoleriu, M. C. Popescu, C. Duncianu, I. Kelnar and D. Dimonie, *Cellulose Chem. Technol.*, **42**, 549 (2008).
- ²⁹ C. E. Wilkes, J. W. Summers, C. A. Daniels and M. T. Berard, “PVC Handbook”, Hanser Verlag, URL: http://en.wikipedia.org/wiki/Glass_transition, 2005.