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Polyvinyl alcohol/chitosan/montmorillonite nanocomposites preparation by freeze/thaw cycles and characterization

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Abstract: Polyvinyl alcohol (PVA) and chitosan (CS) based hydrogels are often chosen to obtain hydrogels as being considered non-toxic for human body. The present study aims the preparation and physical chemical characterisation of hydrogels based PVA and CS by using an environmental friendly method i.e. freeze/thaw. In this method the only parameters affecting the hydrogels' properties is the PVA concentration in solution, time and number of cycles of freezing / thawing. Repeated freezing and thawing cycles resulted in production of a highly elastic polyvinyl alcohol hydrogel with higher degree of crystallization. Adding chitosan in polyvinyl alcohol hydrogel is giving to the newly formed material, biocompatibility and antibacterial properties due to the free amino groups of chitosan. Higher mechanical and thermal characteristics of PVA/CS based hydrogels were obtained by addition of a small amount of inorganic nanoparticles (montmorillonite clay, C30B) into the matrix (i.e. 1%). Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), near-infrared chemical imaging spectroscopy (NI-CI), X-ray diffraction (XRD),

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thermogravimetric analysis (TG), swelling and rheological measurements were used to characterize the polyvinyl alcohol/chitosan/montmorillonite properties. The swelling degree increased with decreasing chitosan content in hydrogels and the variation is opposite in nanocomposites, decreasing after introducing the nanoclay. The swelling behaviour was influenced by the presence of the nanoparticles. The plasticizer effect of the nanoparticles was reflected by obtaining a more compact hydrogel network with higher mechanical and thermal properties. The proposed materials can be a promising alternative in biomedical applications.

Introduction

Hydrogels are formed by crosslinking polymer chains and have the ability to absorb water or biological fluids as a result of the high number of hydrophilic groups. However, the hydrogel is resistant to dissolution due to the presence of crosslinks.[1] Hydrogels can be obtained either by chemical crosslinking of the polymers by using a crosslinker agent (e.g. glutaraldehyde) or by using physical methods i.e. freeze-thawing techniques which are considered cost-free and non-invasive for environment.

Poly (vinyl alcohol) (PVA) is a hydrophilic, semi crystalline synthetic polymer which contains a large number of hydroxyl groups and can easily form hydrogen bonds with free water molecules. It has been widely used in biomedical and pharmaceutical industry for its good biocompatibility and physical properties.[2,3] The physically crosslinked PVA hydrogel prepared by cyclic freezing/thawing method has attracted much attention in the past years, due to the remarkable properties of the freeze/thawed PVA hydrogels such as the good mechanical strength and the lack of toxicity.[4] These properties depend on the PVA's molecular weight, the PVA concentration in water and the freeze-thaw cycles, etc.[5] It is well known that blending is an efficient method to improve the performance of polymer materials. In order to improve the properties of the PVA hydrogels,

many researches reported successfully blended PVA with other polymers such as *cassava* starch,[6] hyaluronic acid,[7] and polyurethane,[8]etc.

Chitosan, a linear polysaccharide consisting of (1,4)-linked 2-amino-deoxy-b-D-glucan, is commercially obtained from shrimp and crab shell chitin (a N-acetylglucosamine polymer). Chitosan is a well known polymer which has many unique properties such as high molecular weight, high viscosity, high crystallinity, and high capacity to form intermolecular hydrogen bonds and also special properties such as biocompatibility, antibacterial activity, mucoadhesivity, etc. These properties make chitosan a very promising biomaterial with a wide range of application in the biomedical field e.g. wound dressings or tissue engineering. Blending chitosan with PVA, the prepared hydrogel will have the biocompatibility of chitosan and will confer to the materials' antibacterial, antiinflamatory, antidiabetic properties, etc.

In the last decade many researchers reported nanocomposite hydrogels with enhanced properties by incorporating nanoparticles into the polymeric matrix.[9,10]

The addition even of a very small amount, up to 5 wt% of nanoparticles give superior mechanical and thermal characteristics of the new nanocomposite materials as compared with conventional composites. Additionally, the nano-meter size and high surface area of the silicate layers of montmorillonites (e.g. C30B) enhance also flame-retardant, tensile and barrier properties of the nanocomposite materials.[11]

The aim of this study is to obtain nanocomposite hydrogels based on polyvinyl alcohol/chitosan/montmorillonite by using non-invasive and low cost methods i.e. freeze/thawing. The newly prepared PVA/CS-C30B's morphology and properties were investigated by means of scanning electron

microscopy (SEM), FT-IR and NIR spectroscopy, X-ray diffraction (XRD), thermogravimetry (TG), DMTA analysis, swelling and rheological measurements.

Experimental

Materials

- Polyvinyl alcohol (PVA) was commercially purchased from Romacril Râşnov company and has the following characteristics: Mw = 18,300 Da, 95% degree of hydrolysis, 1.3 g/cm^3 density. - Chitosan (CS), a product of low molecular weight, was purchased from Aldrich. It has a dynamic viscosity of a 5 wt% concentration solution of 20,000 cPs.

- Organically modified montmorillonite (C30B) was obtained from Southern Clay Products. C30B has a moisture content of < 2 % and a density of 1.98 g/cm^3.

Preparation of PVA/CS hydrogels

PVA/CS hydrogels and PVA/CS-C30B nanocomposite hydrogels were prepared in two steps: 1) preparation of the PVA/CS and PVA/CS-C30B mixtures (with C30B nanoclay content of 1 wt%); 2) crosslinking the PVA/CS and PVA/CS-C30B mixtures by cyclic freezing-thawing method to form the hydrogels.

A PVA solution of 5 wt% was prepared by mixing PVA in double distilled water followed by heating it up to 90 °C for 2 hours, under continuous mechanical stirring, to obtain a clear solution. 5 wt% CS solution was prepared by dissolving chitosan in 1% acetic acid solution at ambient temperature by stirring it overnight. The mixed solutions of PVA and CS mentioned above were stirred for 60 minutes at ambient temperature, the homogeneous solutions being obtained according to the designed blending ratio: PVA/CS (polyvinyl alcohol/chitosan) of 90:5, 90:10, 80:20, 60:40 (v/v %).

In parallel, the nanoclay powder (C30B) was first dispersed in 1% acid acetic solution by stirring it at room temperature for 12 hours, followed by ultrasonication for 10 min. The dispersion was added into chitosan solution mentioned above, the resulted CS-C30B dispersion being further stirred for 5 hours, followed by ultrasonication for 10 min. The PVA solution and the CS-C30B dispersion were then mixed to obtain the blends with weight ratios of PVA/CS-C30B (90:5, 90:10, 80:20, 60:40 v/v %). The resultant mixtures were stirred for 5 hours. In order to homogenize and to remove the air bubbles, the mixtures were placed in an ultrasonic water bath for 15 min.

The formed mixtures of PVA/CS and PVA/CS-C30B were casted onto glass Petri dishes. Repeatedly, three cycles of freezing and thawing were performed by keeping the solutions of the blends at - 20°C for 12 hours and then maintaining them at room temperature for the same time interval to complete one cycle. Prior physicochemical characterization, all hydrogels were dried by lyophilization for 24 hours, using a LABCONCO 117 freezing-dryer.

The properties analysis of the freeze / thawed hydrogels based on PVA/CS-C30B

The freezed-thawed obtained membranes based on PVA and CS and montmorillonite were thermally characterized by means of thermogravimetry and DMTA; the evaluation of the nanoclay distribution in the polyvinyl alcohol matrix was made by near infrared chemical imaging (NIR-CI); the morphological aspects were investigated by scanning electron microscopy (SEM), followed by X-ray diffraction (XRD) tests and completed by swelling and rheological measurements.

Thermogravimetric analysis: The thermogravimetric study was performed by means of a TGA-40S Shimadzu thermogravimetric analyzer. Amounts of about 12 mg PVA/CS-C30B nanocomposite hydrogels were heated by 10 °C/min up to 110 °C and the temperature was kept constant for

30 minutes in order to remove the moisture and then the temperature increased up to 550 °C in an open Al_2O_3 crucible, under 200 mL/min nitrogen flow. Mass loss of nanocomposites was recorded against the temperature.

Dynamic mechanical thermal analysis (DMTA): The DMTA tests of the PVA/CS-C30B nanocomposite hydrogels were performed with a Rheometer Anton Paar MCR301 instrument equipped with dynamic mechanical analysis accessories for extensional deformation (UXF) at a constant frequency of 1Hz within the -50 to 100 °C temperature range with a heating rate of 4 °C/ min. Due to the brittle character of the dried films of these materials, based on PVA and CS and C30B nanoclay, the specimens for DMTA tests were prepared as swollen membranes with the excess of water mechanically removed.

NIR-CI characterization: The evaluation of the nanoclay distribution in the polyvinyl alcohol / chitosan matrix was performed by *near infrared chemical imaging (NIR-CI)* using different chemometric analysis methods. The NIR-CI data were collected on a SisuCHEMA device which employs SPECIM's hyperspectral imaging technology on full NIR range, respectively from 1000 to 2500 nm. The system is equipped with a spectral camera. The chemical images were collected at 320 × 640 pixel spatial resolution with a rate of 60–350 Hz. The optical and spectral data have been processed with the EVINCE program, used as powerful chemometrics and image processing software package. The data processing program deals with the investigation of imagistic maps for the classification and quantification of the images, exploring the spectral and spatial data. Based on multivariate analysis techniques, two processing methods, principal component analysis (PCA), and partial least squares - discriminant analysis (PLS-DA) respectively, have been used to extract quantitative and qualitative information.

FT-IR spectroscopy: The nanocomposites hydrogels were analyzed by FT-IR spectroscopy, using the KBr pellet technique. The spectra were

scanned on a Bruker VERTEX 70 (USA) device, over the 4000–500 cm^{-1} range, at a resolution of 4 cm^{-1}.

Scanning electron microscopy: The cross-sections of the nanocomposites hydrogels were coated with gold, then observed and photographed on a QUANTA 200 scanning electron microscope (SEM).

X-ray diffraction patterns of the hydrogels and raw materials were obtained using a Bruker AXS D8 Advance X-ray Diffractometer, with Cu-K α radiation source. The data was collected at 2θ between 0-40 degrees.

Swelling behaviour was tested gravimetrically. The freeze-dried hydrogels based on PVA/CS-C30B were immersed in distilled water at 37°C. After immersion, at different time intervals, the samples were periodically removed from the medium and was gravimetrically weighed (W_S). The swelling degree (SD) was calculated according to Equation 1.

$$SD = (W_S - W_D)/W_D \times 100 \qquad (1)$$

where W_S is the weight of the sample after swelling in water and W_D is the weight of the dried hydrogel.

Rheology: The rheological behaviour of PVA/CS-C30B nanocomposite hydrogels was monitored with an Anton Paar MCR301 Rheometer, using plate–plate geometry of 50 mm as a measurement system. Dynamic modulus, storage modulus (G′) and loss modulus (G″) of the nanocomposite samples were measured as a function of angular frequency (ω = 0.01–100 rad/s) using oscillatory tests. To perform the frequency sweep tests, the linear viscoelastic range of the samples (LVE) was obtained from amplitude sweep tests (with a strain amplitude between 0.01 and 100%) using a constant angular frequency ω = 10 rad/s. The influence of temperature on the dynamic viscosity of the mixtures with different compositions (temperature sweep test, T_{swp}) 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 discussions

NIR-CI studies

The nanoclay (C30B) distribution into PVA/CS hydrogels and the matrix homogeneity were evaluated by the near infrared chemical imaging technique, by using two models, the partial least squares-discriminate analysis (PLS-DA) and the principal component analysis (PCA).

The PLS-DA mathematical model is based on PCA classification and codifies the observations and variables with ''0'' and ''1'' in order to obtain quantitative estimation of the nanocomposite hydrogel' components, Table 1. The qualitative estimation was observed optically in nuances of gray (Figure 1). The 2D image of nanocomposites hydrogels surface obtained based on PCA (a) and PLS-DA (b) modelling for 80/20 and 60/40 PVA/CS compositions are plotted in Figure 1.
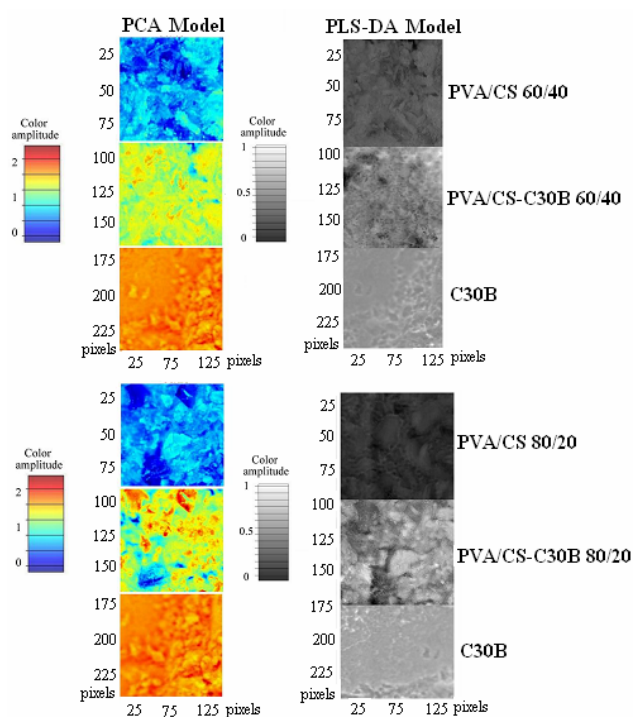

Figure 1. PCA and PLS-DA model for 60/40 and 80/20 PVA/CS-C30B hydrogels.

As we can see in Figure 1, from the PCA model, the pixels with higher and lower score values are coded with light and dark blue colours and represent the colour code for the components of the matrix (PVA and CS). The orange score images correspond to the optical image of nanoclay powder surface. The predominantly yellow score on nanocomposite hydrogel

images indicates the distribution of the nanoclay in the polyvinyl alcohol/chitosan matrix. The predicted values of the nanoclay contents into the polyvinyl alcohol and chitosan matrix derived from the PLS-DA model estimation are presented in Table 1. It is a relatively good correlation between incorporated nanoclay content and that found by using the PLS-DA model. The PVA/CS 80/20 nanocomposite hydrogels, after optical evaluation on PCA model, reveal the existence of nanoclay in agglomerated state in the polymeric matrix. In the case of PVA/CS 60/40 nanocomposites hydrogels, the nanoclay is relatively homogeneously distributed in the polymer matrix, which means that 2.2 wt % is the optimal concentration of inorganic material to obtain a uniform hybrid material, Table 1.

Table 1. The quantitative estimation of the nanoclay amount in the polymeric matrix using the PLS-DA model.

Sample	Polymeric matrix (%)	Nanoclay (%)	Nanoclay in hydrogels experimental (g)
PVA/CS-C30B 60/40	98.68 ± 1.63	2.2 ± 0.03	2.66
PVA/CS-C30B 80/20	98.15 ± 2.71	1.8 ± 0.1	1.33
PVA/CS-C30B 90/10	98.7 ± 0.2	0.89 ± 0.014	0.66
PVA/CS-C30B 95/05	99.27 ± 0.56	0.65 ± 0.23	0.33

The spectral bands corresponding to the clay and polymeric matrix are summarized in Table 2. Slight deviations of absorption bands were observed between the nanocomposite hydrogels with different ratio of PVA/CS polymers. The band from 1908 nm corresponds to –OH group from the water molecules inside the nanoclay structure. The absorption band corresponding to O-H stretch from 1834 nm shifted to 1823 nm (nanocomposite hydrogels) revealing hydrogen interaction between the inorganic nanoparticles and the polymeric matrix. The absorption band

attributed to O-H stretch from clay (1908 nm) is overlapped with the absorption band corresponding to C-O stretch from the chitosan structure.

Table 2. The wavelength corresponding to the functional groups on NIR spectra for PVA/CS-C30B hydrogels.[12]

		Sample			Band assignment and comments
C30B	PVA/CS 60/40	PVA/CS-C30B 60/40	PVA/CS 80/20	PVA/CS-C30B 80/20	
2384vw	2375sh	2375sh	2377sh	2375sh	C-H stretch/C-C stretch combination – polymeric matrix Al-OH - nanoclay
-	2352w	2352w	2352w	2357w	CH$_2$ bend second overtone
-	2314s	2312s	2311s	2313s	C-H bend second overtone
2094w	2096vs	2098vs	2096vs	2098vs	O-H bend
-	1950s	1950s	1951s	1947s	C=O stretch second overtone
1908vs	-	-	-	-	O-H stretch first overtone
1834sh	1823sh	1823sh	1831sh	1829sh	O-H stretch/C-O stretch second overtone combination
-	1760w	1760w	1760w	1760w	C-H stretch first overtone
-	1715w	1715w	1719w	1717w	
-	1418sh	1418sh	1421sh	1425sh	C-H combination
-	1204w	1206w	1208w	1206w	C-H second overtone

s – strong, w – weak, vw – very weak, sh – shoulder

FT-IR analysis

In our previous study,[13] the FT-IR spectra of the polyvinyl alcohol, chitosan and their blends were analyzed and the formation of inter-molecular bonds between components was observed. In this work, the FT-IR technique was used to qualitatively analyse the interactions between the C30B nanoclay and PVA/CS matrix. FT-IR spectra of nanocomposite hydrogels based on PVA, CS, and C30B nanoclay are shown in Figure 2.
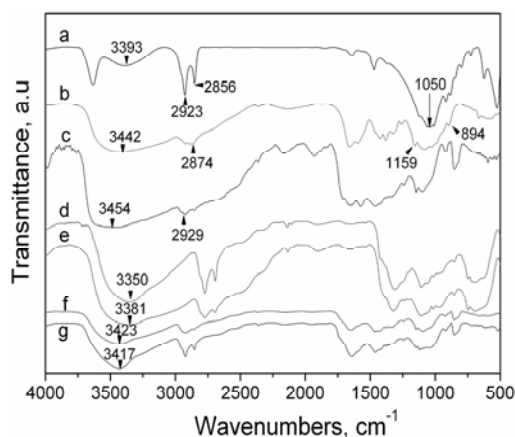
Figure 2. FT-IR spectra of C30B (a), CS (b), PVA (c), and PVA/CS-C30B hydrogels: (d) PVA/CS 80/20, (e) PVA/CS-C30B 80/20, (f) PVA/CS 60/40, (g) PVA/CS-C30B 60/40 in spectral range of 4000 - 500 cm^{-1}.

FT-IR spectrum of clay (Figure 2) indicated typical bands: in the region of 3650 - 3200 cm^{-1}, a broad absorption band, which is assigned to H bonding OH stretching, mostly due to the intrinsic structure of the nanoclay (hydroxyl groups) and also a strong peak at 1050 cm^{-1}, assigned to the Si-O-Si vibrations, explained by the chemical composition of the nanoclay. A set of two peaks in the region 3000-2800 cm^{-1} (approximately 2930 and 2860 cm^{-1}) is assigned to compounds containing long linear aliphatic chains. This region is representative for the organically modified clay C30B.

It was also possible to find characteristic bending vibrations of Si–O bonds at $\upsilon_1 = 625$ cm^{-1} and $\upsilon_2 = 523$ cm^{-1}.[14] In the spectrum of pure PVA, the bands at 3440 cm^{-1} and 2921 cm^{-1} are attributed to the –OH and CH$_2$ stretching vibrations, respectively. The infrared spectrum of chitosan shows around 894 cm^{-1} and 1159 cm^{-1} peaks assigned to the saccharine structure and amino characteristic peak at around 1597 cm^{-1}.[15] From the FT-IR spectra of pure components and PVA/CS-C30B hydrogels it can be observed that the intensity of –OH absorption band ($\upsilon_1 = 3454–3350$ cm^{-1}) is lower in the hydrogels as compared to –OH stretching vibration band in PVA, CS and C30B nanoclay. This can indicate that soluble parts of the biopolymer containing OH from polyvinyl alcohol and NH$_2$ groups from

chitosan may form hydrogen bonds with the nanoclay. Compared with clay spectra, in the spectrum of the nanocomposite hydrogels there can be observed slight changes in the intensity of the bands near 1050 cm^{-1} and 570 cm^{-1} which can be attributed to Si–O vibrations originating from clay addition.[16]

Scanning electron microscopy (SEM)

Figure 3 presents the SEM images of nanocomposite hydrogels based on polyvinyl alcohol, chitosan and nanoclay at two magnifications, respectively 5000X and 2500X. The hydrogels prepared from polyvinyl alcohol/chitosan/clay clearly show a homogenous morphology in comparison with the hydrogels without clay. This result is consistent with the conclusion of XRD.
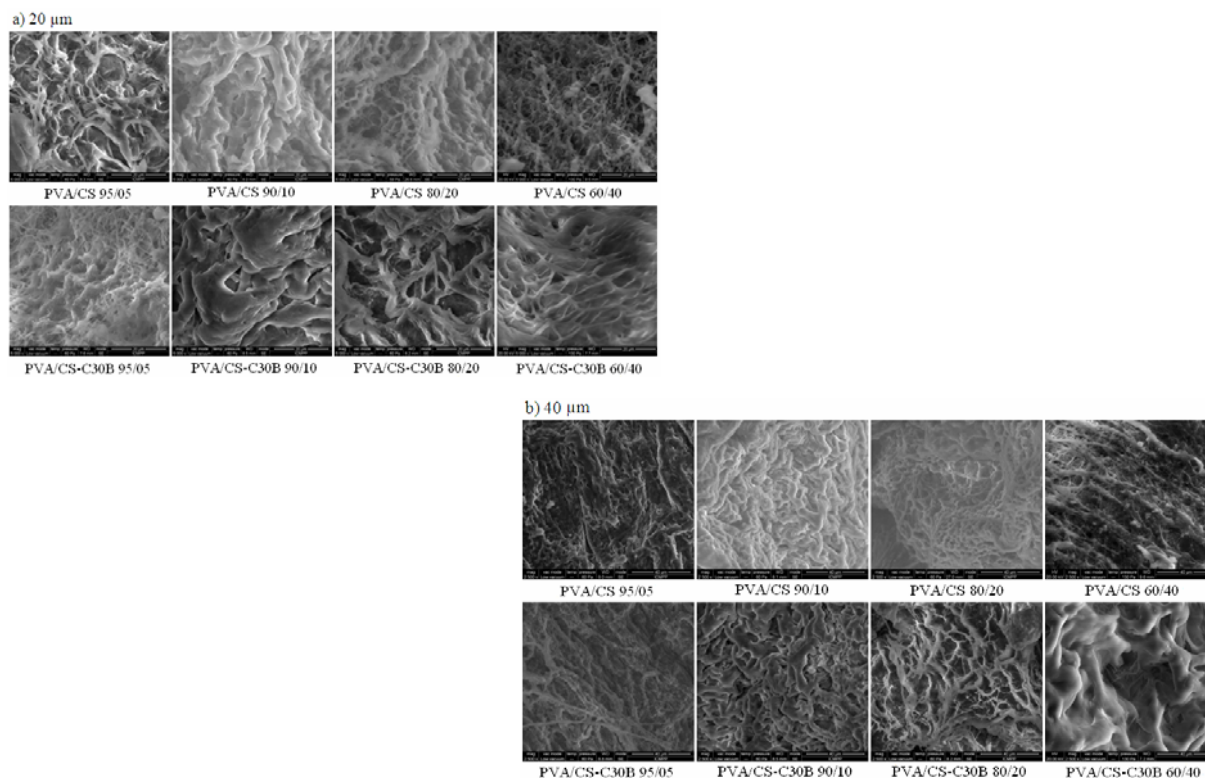

Figure 3. SEM images of nanocomposite hydrogels based on polyvinyl alcohol, chitosan and C30B at magnification of (a) 5000X and (b) 2500X.

X-ray diffraction (XRD)

The degree of intercalation/exfoliation and its effect on the nanocomposites properties is an important factor in the obtaining of

polymer/nanoclay nanocomposites. X-ray diffraction (XRD) analysis is widely used to characterize the micro structure of nanocomposites as well as pure nanoclay.
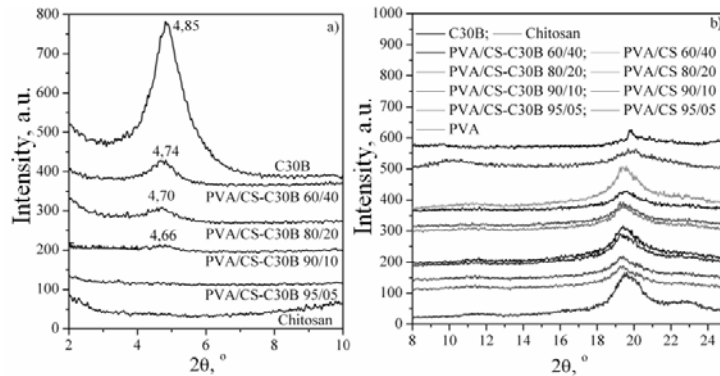

Figure 4. XRD patterns of nanocomposite hydrogels based on polyvinyl alcohol, chitosan, and C30B in two 2θ regions.

Wide angle X-ray diffraction is probably the most indicated technique to investigate the interactions between the polymer and inorganic layers. The XRD patterns of the pure components (PVA, CS and C30B) and the nanocomposite hydrogels prepared in this study are shown in Figure 4. The XRD pattern of the C30B shows a reflection peak at about 2θ = 4.85° (Table 3).

Table 3. The obtained values for 2θ angles and basal spacing (d_{001}) for nanocomposite hydrogels based on polyvinyl alcohol, chitosan and clay.

Sample	2θ, °	d_{001}, nm
C30B	4.85	1.81
PVA/CS-C30B 60/40	4.74	1.86
PVA/CS-C30B 80/20	4.70	1.87
PVA/CS-C30B 90/10	4.66	1.89
PVA/CS-C30B 95/05	-	-
CS	-	-

The interlayer distance was estimated from Bragg's law, $2d\sin\theta = \lambda$, corresponding to a d-spacing of 1.81 nm. Chitosan powder shows two main

diffraction peaks around $2\theta = 10.1°$ and $19.7°$. PVA showed an obvious diffraction peak at $2\theta = 19.59°$ and a shoulder at $2\theta = 22°$, typical of the crystalline atactic PVA.[17] After the incorporation of CS and nanoclay solution, the (001) peak of C30B moves to a lower angle from $2\theta = 4.85°$ to $2\theta = 4.66°$, corresponding to a d_{001} value of 1.81-1.89 nm (Table 3). The increase of 1.81-1.89 nm in the interlayer spacing for the nanocomposites indicates the intercalation of bilayers of CS into interlayers of clay and the formation of an intercalated nanostructure.

TG/DTG results

TG measurements were performed in order to determine the compatibility of the PVA, chitosan, and C30B nanoclay components. Figure 5 shows TG curves and their derivative (DTG) of PVA, PVA/CS, and PVA/CS-C30B nanocomposite hydrogels.
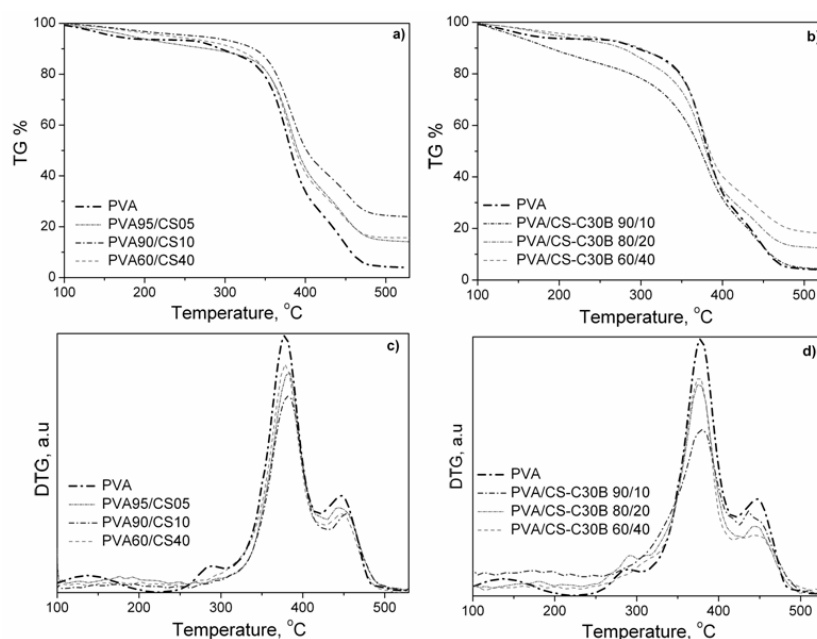

Figure 5. TG/DTG curves for PVA, PVA/CS, and PVA/CS-C30B nanocomposites hydrogels.

All the samples showed a weight loss of more or less 10% within 100 °C – **Figure 5a**. The major weight losses are observed in the range of

250–500 ºC. It is also clear that the onset degradation temperature of the nanocomposites is slightly increased by the incorporation of the nanoclay (Table 4), indicating an enhancement of the thermal stability by C30B incorporation in PVA matrix.

Table 4. Values of T_i (onset temperature), T_{max} (peak temperature), T_f (final temperature) from DTG curves for PVA and PVA/CS-C30B nanocomposites.

System	Peak 1				Peak 2				w_r
	T_i (°C)	T_m (°C)	T_f (°C)	Δw_1 (%)	T_i (°C)	T_m (°C)	T_f (°C)	Δw_2 (%)	(wt %)
PVA	239sh	286sh	306sh	4.7	420	444	493	27	4.3
	314	376	419	57.9					
PVA/CS 95/05	265	382	424	50.9	422	443	499	25.8	14.6
PVA/CS 90/10	266	383	429	47.6	429	453	499	23.2	24.5
PVA/CS 60/40	270	379	427	48.9	431	448	500	29.5	15.8
PVA/CS-C30B 90/10	276	380	426	52.3	426	446	499	30.4	4.8
PVA/CS-C30B 80/20	300	376	425	50	430	444	499	25.2	12.6
PVA/CS-C30B 60/40	287	376	420	44.8	435	445	500	25.5	18.4

T_i- onset temperature, T_m temperature corresponding to maximum mass loss rate, T_f final temperature, Δw –mass loss; w_r – residual mass loss at 510 ºC.

Swelling experiments

Figure 6 shows the swelling behaviour of nanocomposite hydrogels based on polyvinyl alcohol, chitosan, and nanoclay. This figure shows that the swelling degree increases with time, reaching the equilibrium swelling degree after ~ 225 min for all samples.
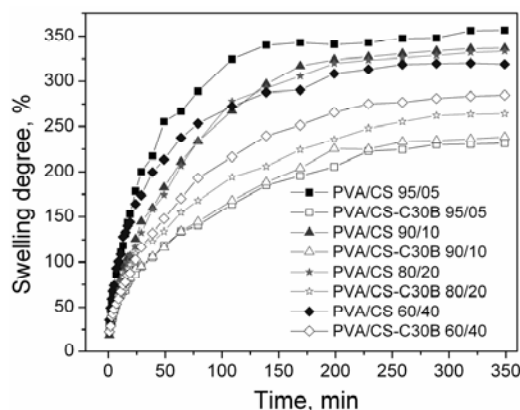
Figure 6. Swelling behaviour of nanocomposite hydrogels based on polyvinyl alcohol, chitosan, and nanoclay, swollen in bidistilled water at 37 °C.

Table 5. Parameters Q_{max} (%), n, k (min^{-1}) for hydrogels swollen at 37 °C.

Sample	Swelling parameters at 37°C		
	Q_{max} (%)	n	k (min^{-1})
PVA/CS 95/05	352	0.31	0.21
PVA/CS 90/10	335	0.3	0.19
PVA/CS 80/20	329	0.26	0.21
PVA/CS 60/40	317	0.24	0.29
PVA/CS-C30B 95/05	232	0.2	0.3
PVA/CS-C30B 90/10	236	0.221	0.27
PVA/CS-C30B 80/20	260	0.222	0.027
PVA/CS-C30B 60/40	279	0.27	0.028

It can be clearly seen from Table 5 that values of the swelling exponent range between 0.2 and 0.31, indicating a quasi-Fickian diffusion mechanism without relaxation of polymeric chains.[18]

DMTA analysis

DMTA analysis was mainly used to establish the effect of clay content on the polymer network stability. Effect of the clay on the stability and consistency of the hydrogels was tested by means of dynamical mechanical analysis (DMTA) showing the dependence of dynamic moduli on temperature and angular frequency. Additionally, the PVA/CS membranes were characterized by temperature sweep tests, with the rheological

analysis, measuring the dependence of storage modulus (G′) and viscosity (η) on the temperature in the oscillatory regime Figure 7 and Table 6.

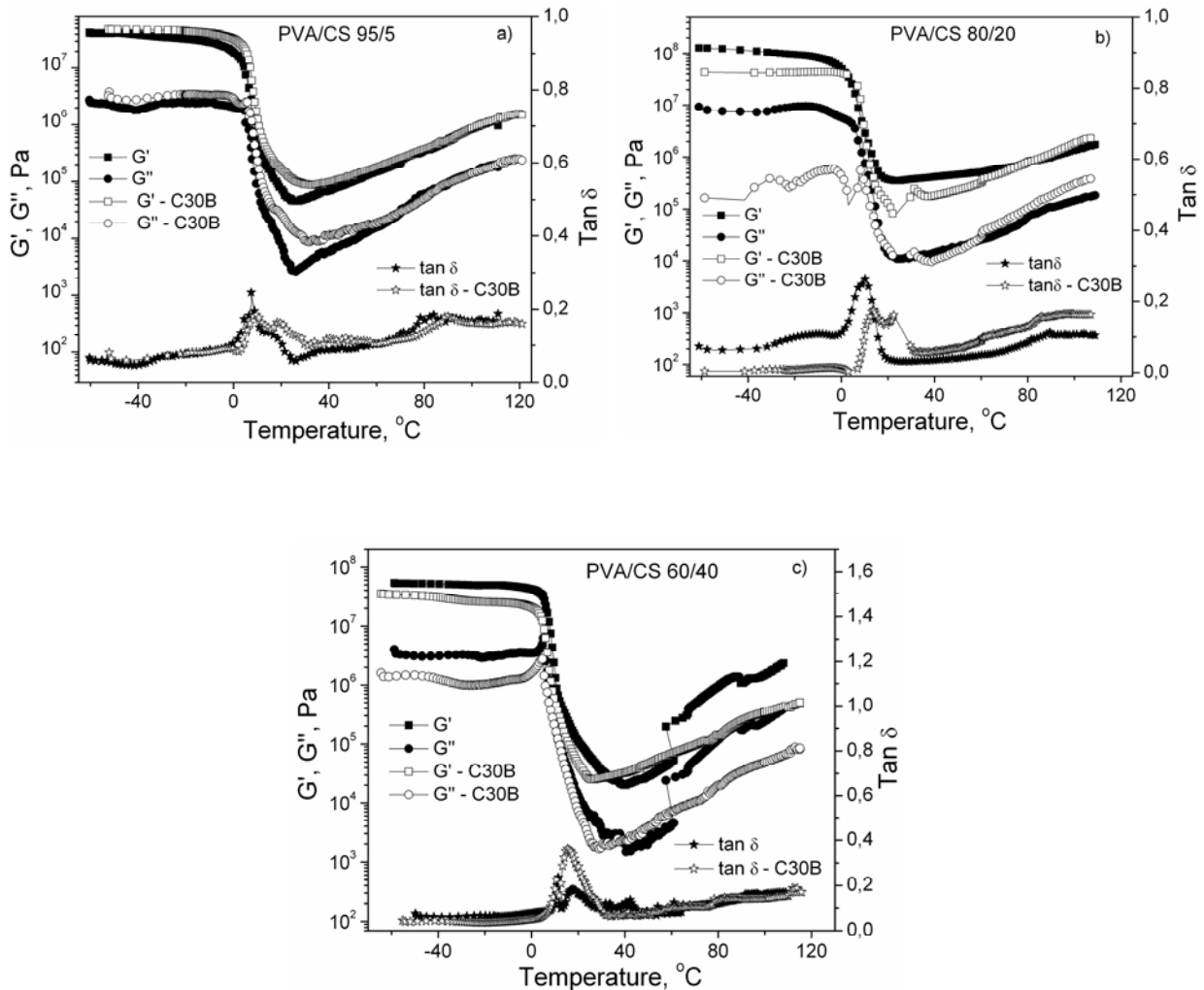Figures 7a-c represents the obtained DMTA curves for the studied systems based on PVA/CS with and without nanoclay.

Figure 7. Storage (G'), loss (G'') and damping factor (tan δ) moduli dependences on temperature for systems PVA/CS with different compositions (a) 95/5 (b) 80/20 (c) 60/40 with and without nanoclay.

Based on these dependences, the characteristic transition temperatures were summarized in the Table 6.

Table 6. Transition temperatures measured from dynamic moduli dependences on temperature (e.g. damping factor) and temperature sweep tests.

Sample	T (ºC)						From T sweep tests	
	From tanδ							
PVA			24.6				72.9	87
PVA/CS 95/5	7.4	16.8sh		41.2		81.3	83.2	92.9
PVA/CS-C30B 95/5	-3.8sh	9.5	19	42		89.3		86
PVA/CS 90/10							72.2	89
PVA/CS-C30B 90/10							72	86
PVA/CS 80/20	-12.4	9.5			60.3sh	89.6	70 sh	87
PVA/CS-C30B 80/20	-5.7sh	13.8	22.5		61.3sh	85.6sh	72.2	86.7
PVA/CS 60/40	5.7	12.1	28.6	37.9	57.7		68sh	103
PVA/CS-C30B 60/40	4.74	9.8			61.2	80.3	72.8	107

sh – shoulder

The DMTA curves showed similar trend lines for all systems showing higher transition temperatures at ~72 – 107 ºC with the increasing of chitosan/clay content, which indicates an important modification of mechanical properties.

In order to establish the effects of the nanoclay on the PVA/CS hydrogels' stability (Figures 8a-d), the samples were rheological tested within oscillatory regime and the obtained dynamic moduli (G′ and G″) were used to appreciate the behaviour of the samples. Within the previous study,[16] the systems based on PVA and CS were analyzed and it was observed that the gel character of the PVA/CS blends, increased with increasing CS amount.[19]
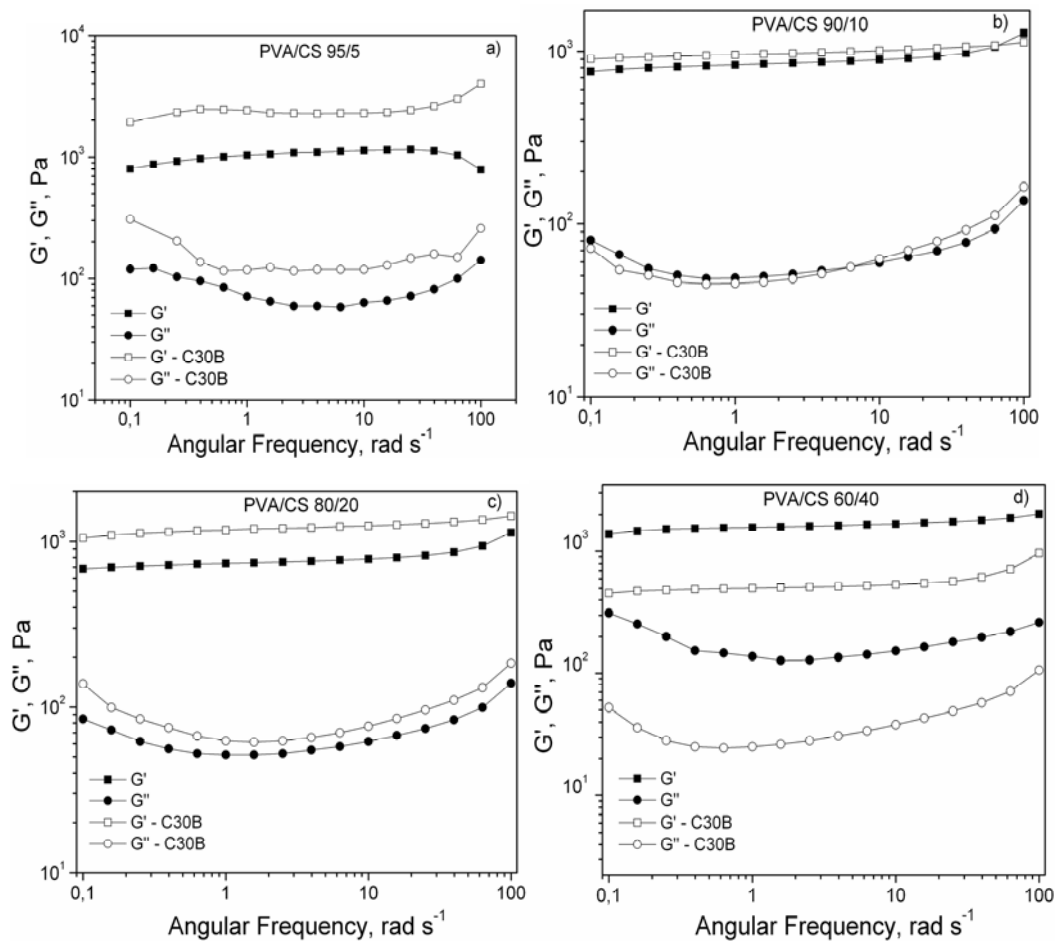
Figure 8. Variation of storage and loss moduli with angular frequency.

By analyzing Figures 8a-d, the dynamic moduli curves of the four systems show similar viscoelastic character, predominantly gel, as G′ takes higher values than G″ and the nanoclay induce a slight increase of the values of the both moduli. This behaviour shows that the addition, even of a small amount of clay (up to 3 % - Table 1), has a slight reinforcing effect on the polymeric matrix, soft and elastic membranes being obtained. As it is shown in Figure 8b, even though the loss modulus, G″ of the system PVA/CS 90/10 containing clay takes lower values in the low frequency region simulating a sparsely gel character, the higher values of G′ confirm the increase in mechanical strength of formed gel when clay was added.

In order to establish the best option in composition, it was chosen for comparison the viscosity dependence on composition by temperature sweep tests (Figure 9).
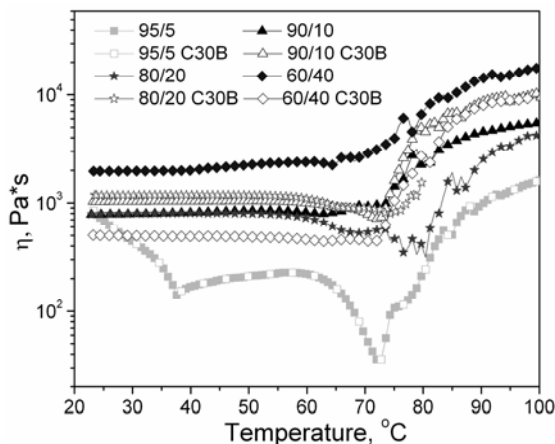

Figure 9. The dependence of viscosity on composition of PVA/CS systems.

The system based on PVA/CS with different compositions (Figure 9), had quite different behaviour. With the increasing content of chitosan and nanoclay, the viscosity increased 10 times and transition temperature is shifted to higher temperature from 87 ºC for PVA/CS to 103 ºC for PVA/CS clay (see also Table 6).

Conclusions

Nanocomposite hydrogels based on PVA/CS-C30B were obtained by the freeze-thaw method. FT-IR spectra evidenced of the interactions, like hydrogen bonds, between the components of the hydrogels, as PVA, CS and C30B nanoclay. The PVA/CS-C30B nanocomposite hydrogels indicated an increase of thermal stability and mechanical properties, by introducing C30B nanoclay in the polymeric matrix. The systems, which look like soft membranes, have predominantly gel character due to the higher G′ than G″. Comparing with the previous studies regarding the blends of PVA with CS, it seems that the freeze-thawing method was more efficient in

blending/crosslinking the two components, the new systems being toughened, more elastic, resistant to solvents and water.

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