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INFLUENCE OF CASTING SOLUTION CHARACTERISTICS ON CELLULOSE ACETATE MEMBRANES: RHEOLOGY AND ATOMIC FORCE MICROSCOPY

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Cellulose acetates with different substitution degrees were investigated as to their rheological properties and morphology. Atomic force microscopy (AFM) studies on membranes showed ordered domains, in which pores and nodules with different sizes and intensities are distributed. The substitution degree, as well as the history of the membranes formed from the solutions in acetone and water nonsolvent mixtures, influenced the aspect of surface images.

Keywords: Atomic force microscopy; Cellulose acetate; Rheology

INTRODUCTION

The increasing need of materials for new applications requires polymers with diverse architectures, inducing specific properties.^[1–4] Among such materials, cellulose acetate evidences excellent properties such as biocompatibility, good desalting, and relatively low cost. Usually this material is molded and extruded into various consumer products, such as brush and tool handles, toys, steering wheels, or other items. Cellulose acetates are used in lacquers and protective coatings for various substrates, such as paper, glass, metal, leather, and wood. Also, photographic and cinematographic films, as well as X-ray films, microfilms, and graphic films, are made from cellulose acetate. Special castings of cellulose acetate films are also used for water purification, blood purification, dialysis, air separation, and for a large range of biotechnological applications.

As known, solvents contribute essentially to the modification of the solution behavior (association, complex, micelle, and core-shell structure of the polymer chains) and also to processes that determine the membrane morphology of cellulose derivatives. Most of the parameters that play an important role in the formation of cellulose acetate (CA) membranes have been studied in great detail. Among these variables, one should mention the nature of cellulose and the

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substitution degree of CA, the nature of the casting solvent mixture, and their composition and temperature.^[5-8]

Extensive studies have been conducted on the effect of the used solvents on the morphology and performance of these polymers in different applications, such as ultrafiltration membranes,^[9-11] reverse-osmosis membranes,^[10] gas-separation membranes,^[11] and pervaporation membranes.^[12,13] Addition of a second solvent to the casting solution increases the permeation flux of a membrane.^[14] Literature data^[15,16] have pointed out that the structures, boiling point, content of solvents mixture, and intrinsic viscosity may affect performance in some applications.

Some previous articles^[17-20] studied the homogeneous hydrolysis of highly acetylated cellulose in the presence or absence of a hydrocarbon (toluene, benzene), besides acetic acid and water, and using sulfuric acid as a catalyst. The conformational behavior and unperturbed dimensions of these cellulose acetates with different substitution degrees were investigated by viscometry and interferometry, in 2-methoxyethanol and acetone/water nonsolvent mixtures. The influence of concentration and temperature on coil densities and dimensions as well as that of solvent mixture composition on the solution properties were also discussed.^[21] In the present work, a series of cellulose acetate (CA) membranes with different substitution degrees were prepared, using acetone/water as casting solutions. The results of previous studies on the solution properties were correlated with the rheological characteristics and morphological aspects by atomic force microscopy for determining the influence of the cellulose acetate substitution degree and of the mixed solvent compositions.

EXPERIMENTAL SECTION

Cellulose acetate (CA) with different substitution degrees and number average molecular weight of about 40000 was synthesized in acetic acid/water and acetic acid/water/benzene media, using the compositions presented in Table I, as described in detail elsewhere.^[17,18]

Viscometric and oscillatory data for cellulose acetate with different substitution degrees in acetone/water were obtained with a Bohlin instrument, by the cone and plate measuring system; the cone had an angle of 4° and a diameter of 40 mm. The dependencies between viscosity, η , and shear rate, $\dot{\gamma}$, were determined at a shear stress, σ , of 30 Pa, at 25°C, over the concentration domain of 8–15 g/dL. Oscillatory measurements were performed over the frequency range of 0.1–150 Hz.

Table I. Hydrolysis conditions of cellulose acetate in homogeneous systems^[17,18]

Code ^a	T, °C	Time, h	Composition, wt.%			H ₂ SO ₄ , wt. %
			Acetic acid	Water	Benzene	
CA _{1.73}	60	24	57	8	35	10
CA _{1.88}	40	19 (phase 1)	90	10 (phase 1)	—	10
		20 (phase 2)	80	20 (phase 2)	—	10
CA _{1.90}	40	35	90	10	—	10
CA _{2.21}	40	63	98	2	—	10

^aSubscripts express the substitution degrees.

Table II. Huggins constants (K_H) and Huggins plot regressions, r^2 , for cellulose acetate with different substitution degrees (DS), as a function of the volume fraction of water from acetone/water mixed solvents, at 25°C^[21]

DS	ϕ_2				
	0.05	0.10	0.15	0.20	0.25
1.73	Insoluble	Insoluble	$K_H = 0.656$ $r^2 = 0.998$	Small regression	Small regression
1.88	Insoluble	Insoluble	$K_H = 0.548$ $r^2 = 0.891$	Small regression	Small regression
1.90	Insoluble	Insoluble	$K_H = 1.138$ $r^2 = 0.986$	$K_H = 0.628$ $r^2 = 0.750$	$K_H = 0.940$ $r^2 = 0.940$
2.21	$K_H = 0.893$ $r^2 = 0.999$	$K_H = 0.829$ $r^2 = 0.970$	$K_H = 0.848$ $r^2 = 0.940$	Insoluble	Insoluble

The composition range of the used mixed solvents was selected as a function of the solubility of the cellulose acetate with different substitution degrees (DS). According to previous investigations,^[21] Table II shows, for a few CA dilute solutions, the small regression of the Huggins plots, which prevented the determination of intrinsic viscosity and of Huggins constants. Thus, the main factors of solvation power are the polarity of the solvents and their interactions with the cellulose acetate. In this context, Table II shows the composition range of nonsolvent mixtures in which cellulose acetates are insoluble. Also, at lower DS values, cellulose acetate is partially dissolved and, as the DS increases, the content of undissolved structures decreases, along with an increase in intrinsic viscosity, $[\eta]$.^[21] Reduction in intrinsic viscosity at higher substitution degrees was explained by the modification of the nonsolvent mixture power.^[22]

Although the CA_{1.88} and CA_{1.90} samples evidence close substitution degrees, the differences that appear in dilute solution studies (Table II) are due to the synthesis conditions (Table I). Thus, CA_{1.90} is obtained by hydrolysis in media with lower water content, determining a less free OH group content and therefore a higher number of substituents at the primary carbon atom (C₆).

The membranes used for atomic force microscopy (AFM) investigations were prepared from cellulose acetate solutions of 10 g/dL concentration in acetone/water, at different composition ranges of these solvent mixtures. The polymer solutions were cast on a flat glass and gradually oven-dried at different temperatures to control the solvent evaporation rate. Finally, the membrane was placed in a vacuum oven for two days at 50°C. AFM images were obtained on an SPM SOLVER Pro-M instrument. An NSG10/Au silicon tip with a 35 nm curvature radius and 255 kHz oscillation mean frequency was used to investigate membrane surface morphology. The apparatus was operated in semi-contact mode, over $10 \times 10 \mu\text{m}^2$ scan areas, 256×256 scan point size images being thus obtained. The differences in membrane surface morphology were expressed in terms of various roughness parameters, such as the root-mean-square roughness (rmn), which represents the mean value of the surface relative to the central plane, the nodule height from the height profile (nhp), the nodules' average height from the histogram (nhh), and the number of pores (N) with their characteristics: area, volume, depth, and diameter.

RESULTS AND DISCUSSION

Dynamic Viscosity

Cellulose acetate exhibits particular solubility characteristics depending on the substitution degrees. This polymer is characterized by partial or full replacement of the hydroxyl (OH) groups on the C2, 3, and 6 positions with acetyl groups.^[23,24] It has been observed that cellulose acetates having a DS between 0.5 and 1 are soluble in aqueous solutions.^[25,26] Studies have shown that solubility in aqueous medium may depend on the uniform distribution of the substituents and on the substitution of the OH groups at the C3 position.^[26] On the other hand, when the $DS > 1$, CA tends to be insoluble in aqueous solutions, but soluble in various other solvents. Pintaric et al.^[27] mentioned that basic solvents (e.g., acetone) interact primarily with the hydroxyl groups on the chain, while water tends to dissolve the acetyl groups. Therefore, the use of specific solvents can induce structural changes in the solution, due to the presence of both acetyl and hydroxyl groups on the partially substituted CA chains.

According to previous data,^[21] acetone and water are poor solvents for CA. Addition of water increases the quality of the solvent mixtures. Thus, the

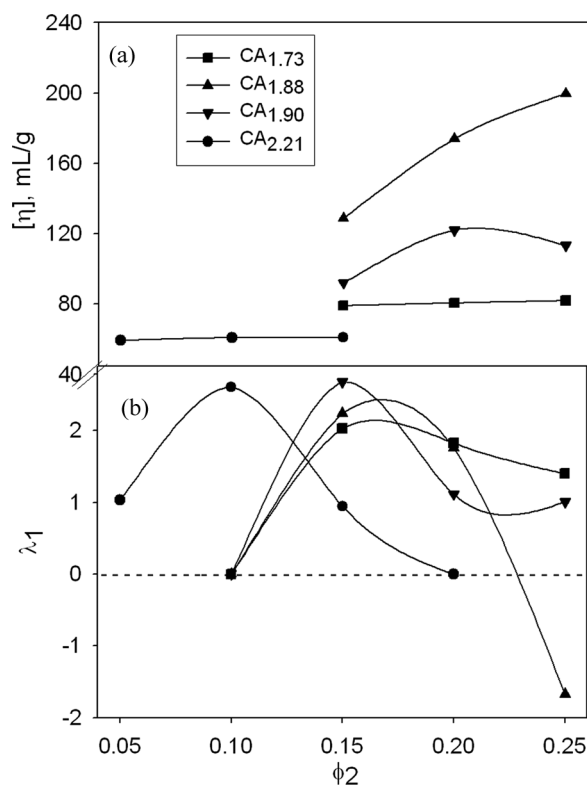


Figure 1. Intrinsic viscosity (a) and experimental values of the preferential adsorption coefficients for acetone (b) in acetone/water binary mixtures as a function of the volume fraction of water, at 25°C, for cellulose acetates with different substitution degrees.^[21]

acetone/water mixture evidences good solvation properties in a 0.15–0.25 volume fraction of the water domain for $CA_{1.73}$, $CA_{1.88}$, and $CA_{1.90}$, as well as in a 0.05–0.15 volume fraction of the water domain for $CA_{2.21}$; acetone is preferentially adsorbed within the mentioned domains, and both solvents tend to minimize the preferential adsorption at the extreme values of ϕ_2 (Figure 1).

The results of rheological measurements, either in the form of dynamic viscosity or as viscoelastic behavior, depend on the applied shear stress and on the frequency range, as well as on the structure of the polymer chain, solvent nature, polymer concentration, and temperature.

Figure 2(a) and (b) illustrate the logarithmic plots of dynamic viscosity as a function of shear rate for CA with a 1.90 substitution degree ($CA_{1.90}$), in acetone/water 80/20 and 85/15 (v/v), respectively, while Figure 3(a)–(c) show the same dependencies for CA with a 1.73 substitution degree ($CA_{1.73}$) in acetone/water 75/25, 80/20, and 85/15 (v/v), respectively.

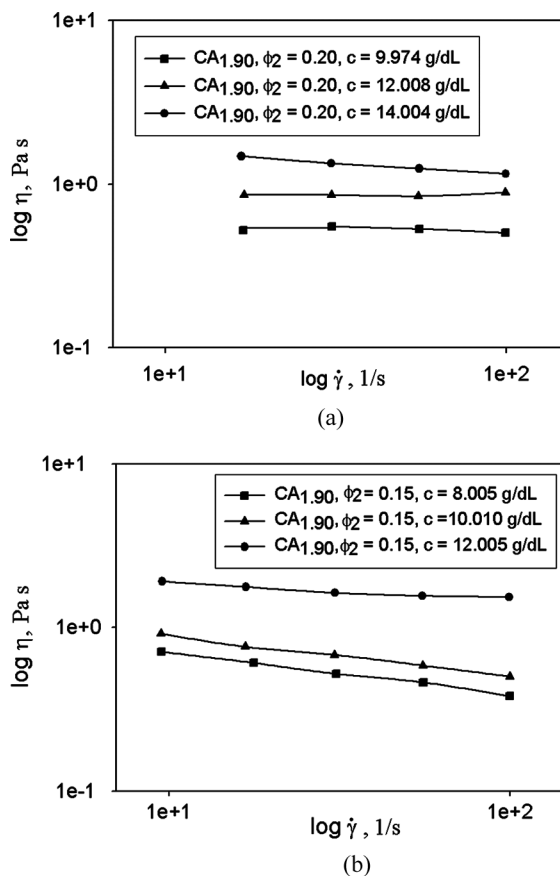


Figure 2. Effect of different concentration values on steady shear viscosity for $CA_{1.90}$ in: (a) 80/20 v/v acetone/water solvent mixtures; (b) 85/15 v/v acetone/water solvent mixtures.

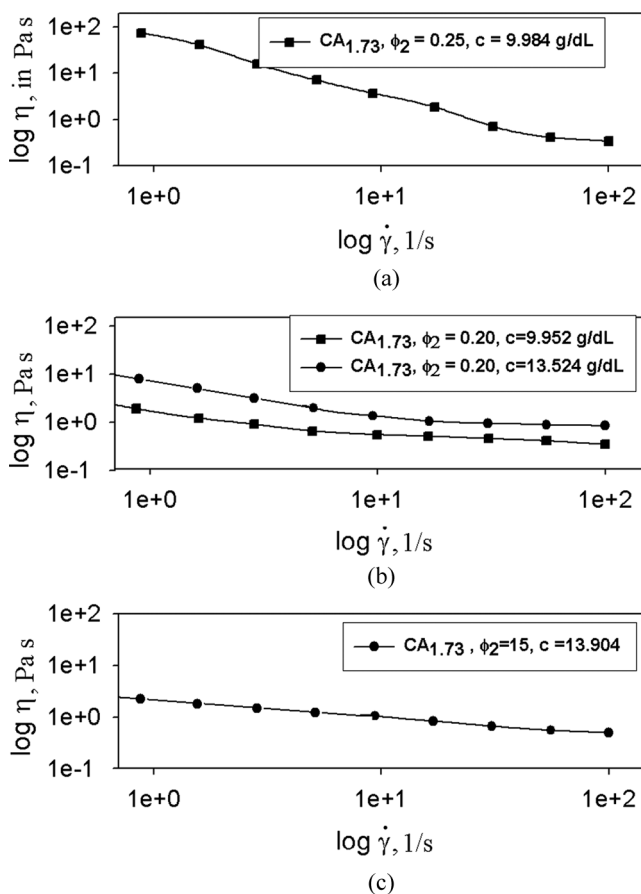


Figure 3. Effect of different concentration values on steady shear viscosity for CA_{1.73} in: (a) 75/25 v/v acetone/water solvent mixtures; (b) 80/20 v/v acetone/water solvent mixtures; and (c) 85/15 v/v acetone/water solvent mixtures.

At lower concentrations and higher substitution degrees, the solution exhibits constant viscosity region at the studied shear rates and Newtonian behavior. Increasing the concentration (see Figure 2(a) at 14.004 g/dL concentration) results in the emergence of cloudiness in the system, leading to gel materials. Cloudiness may be also induced by the substitution degree and by solvent mixture composition. The phenomenon is more intense for some solvent mixtures identified from the Huggins plots of cellulose acetates.^[21] Thus, in Table II, a small regression in the linear dependencies of reduced viscosity, η_{sp}/c , versus c indicated a cloudy polymer solution.

Moreover, at higher values of the substitution degree, dynamic viscosity increases with decreasing water content (Figure 1(a) for $c = 12.008$ g/dL and Figure 2(b) for $c = 12.05$ g/dL) while at lower values dynamic viscosity increases with increasing water content (Figures 3(a)–(c) for close concentrations of the polymer solutions).

Viscoelastic Behavior

Previous works on the gelation mechanism of cellulose acetate have shown an interesting behavior with respect to the sol-gel transition. Cellulose acetate gels exhibit thermally reversible properties, which depend on factors such as the concentration of solutions, acetyl content, and type of solvent. It is postulated that gel formation is induced by the existence of strong intermolecular associations in the system.^[28] In polymeric systems, physical gel formation can arise as a result of phase separation. This phenomenon leads to polymer aggregation and formation of large macromolecular assemblies.^[29] In some CA/solvent systems, the addition of a non-solvent (e.g., water) can induce gelation in which phase separation characteristics are exhibited prior to gel formation. Phase separation is characterized by a gradual to extreme cloudiness of the system, which is dependent on the concentration of the polymer and solvents used. Such phase separation-induced cellulose acetate gelation is used in the production of wet-phase inversion membranes.^[30]

To quantify the sol-gel behavior, Figures 4 and 5 show the plots of the elastic (G') and viscous (G'') moduli of the CA_{1.90} and CA_{2.21} solutions, respectively, as a function of frequency, for three compositions of water. At all water contents,

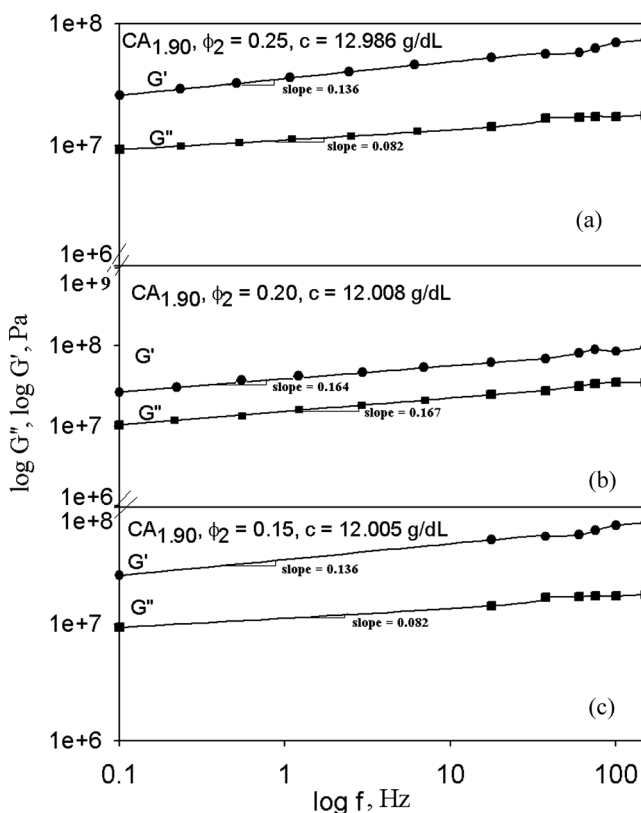


Figure 4. Dependencies of viscous (G'') and elastic (G') moduli on frequency for CA_{1.90} in different compositions of acetone/water solvent mixtures, at approximately equal concentrations.

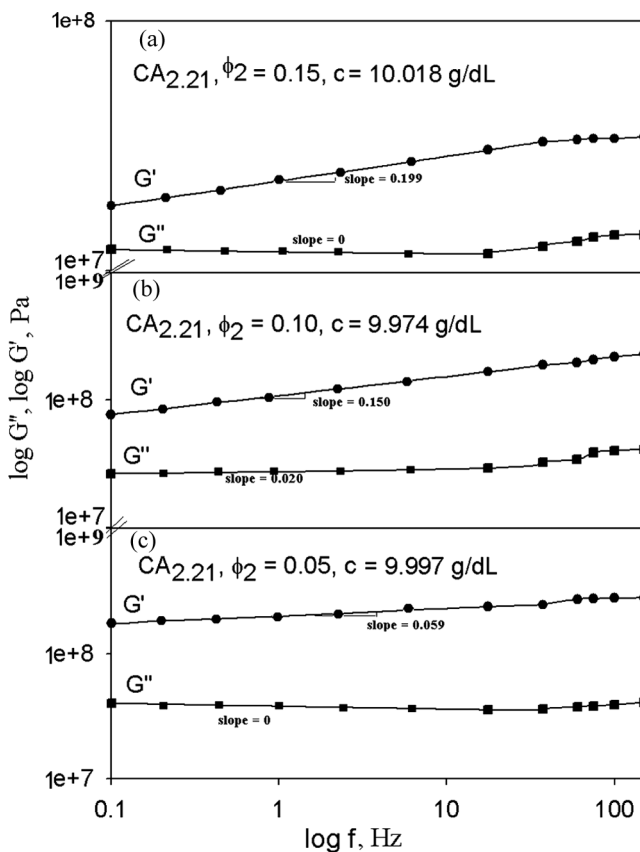


Figure 5. Dependencies of viscous (G'') and elastic (G') moduli on frequency for $CA_{2.21}$ /acetone/water system at approximately equal concentrations.

G' is larger than G'' over the entire frequency range studied, and, according to the obtained slopes, both manifest a slight dependence on frequencies, which is actually a characteristic of a three-dimensional elastic gel.^[31–34] In fact, the higher slope of the elastic modulus was obtained for a better solvent mixture (according to Table II, where K_H takes a minimum value), i.e., for $CA_{1.90}$ in a 80/20 v/v acetone/water solvent mixture and for $CA_{2.21}$ in a 85/15 v/v acetone/water solvent mixture.

Figure 6 shows the dynamic frequency spectrum of $CA_{1.88}$ and $CA_{2.21}$ in 85/15 v/v acetone/water solvent mixtures at approximately equal concentrations. As the substitution degree of CA increases, the slope decreases, indicating that gels are formed due to more intense intermolecular interactions between CA and solvents. Stronger gels also appear as CA concentration increases, for a constant composition of the solvent mixtures (see Figures 5(a) and 6(b) for $CA_{2.21}$ in 85/15 v/v solvent mixtures, at 10.018 g/dL and 11.985 g/dL concentrations, respectively).

To pinpoint the gelation intensity, Figure 7 plots the variation of the elastic modulus and of slopes from Figures 4 and 5 as a function of water content for $CA_{1.90}$ and $CA_{2.21}$.

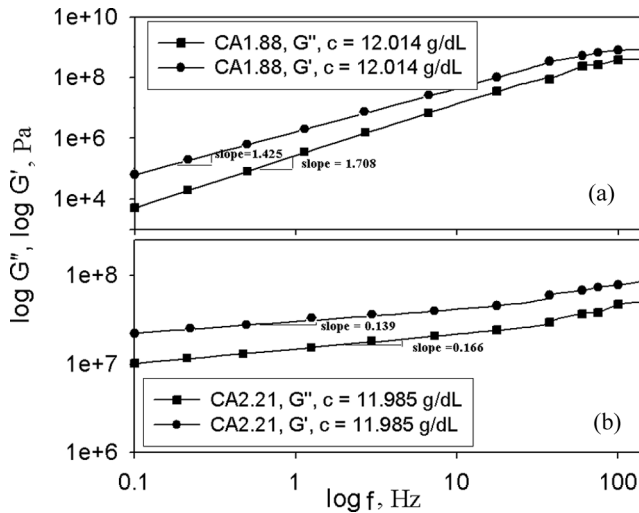


Figure 6. Effect of the substitution degree of CA in 85/15 acetone/water solvent mixture on the viscous (G'') and elastic (G') moduli, at approximately equal concentrations.

Two distinct regimes in terms of G' modification were observed for both samples. As the water content increases, initially G' decreases more intensely, followed by a regime of slow decreases. Also, at the water content at which these modifications appear, the slopes attain the maximum values. Thus, at an intermediary

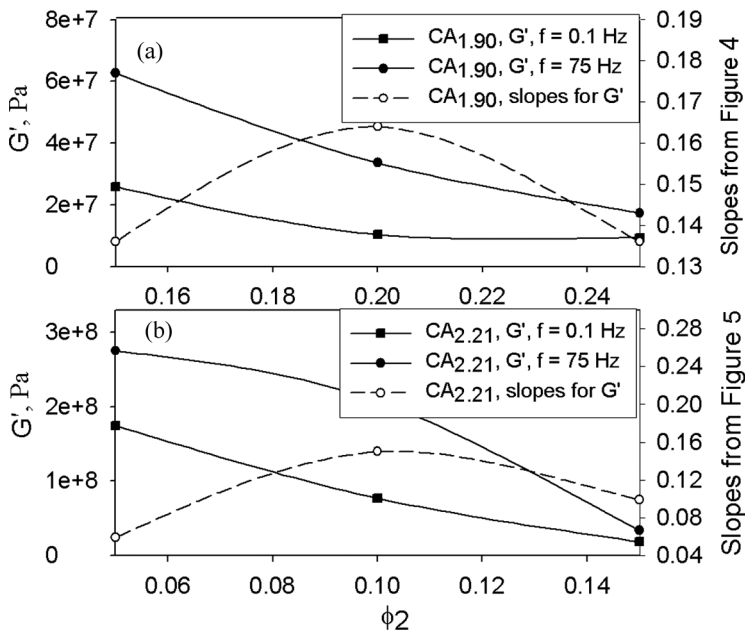


Figure 7. G' versus water content at frequencies of 0.1 and 75 Hz for 12.008 g/dL CA_{1.90}/acetone/water system (a) and for 9.974 g/dL CA_{2.21}/acetone/water system (b).

composition of the solvent mixtures, solvation of cellulose acetate is improved, attenuating the gelation process, while, at lower composition of acetone or at higher water content, the slight interaction with solvent mixtures generates a more compact gel network.

The possible explanation for these processes may be that CA interacts differently with acetone and water, depending on mixture composition. With increasing water content, a competition of all interactions from the system occurs in the direction of the thermodynamically most effective mixture. The intermolecular interactions may be one of the important mechanisms for gel formation.^[35] Thus, CA behavior in solvents that selectively interact with the specific functional groups on the CA chain can generate the gelation process.^[36] One may assume that acetone preferentially interacts with the OH groups on the CA molecule. Addition of water (beyond a certain limit) to CA/acetone solutions weakens this interactive bond and shifts some acetone molecules to interact rather with the OH groups on water. The bond-breaking process gets progressively worse with water content increase, leading to intramolecular interactions between the unbonded or “free” CA chains, some of which had displaced from acetone. This process is also accompanied by intermolecular interactions between the CA units, acetone, and water. It is postulated that, at equilibrium, such interactions lead to a uniform aggregation of CA within the entire volume, and, invariably, gelation occurs, more pronounced at extreme compositions of water.

Surface Morphology

It has been reported that the chain shape of a polymer in solution could affect the morphology of the polymer in bulk.^[15,37,38] The cellulose acetate membranes used in atomic force microscopy examination were prepared from acetone/water

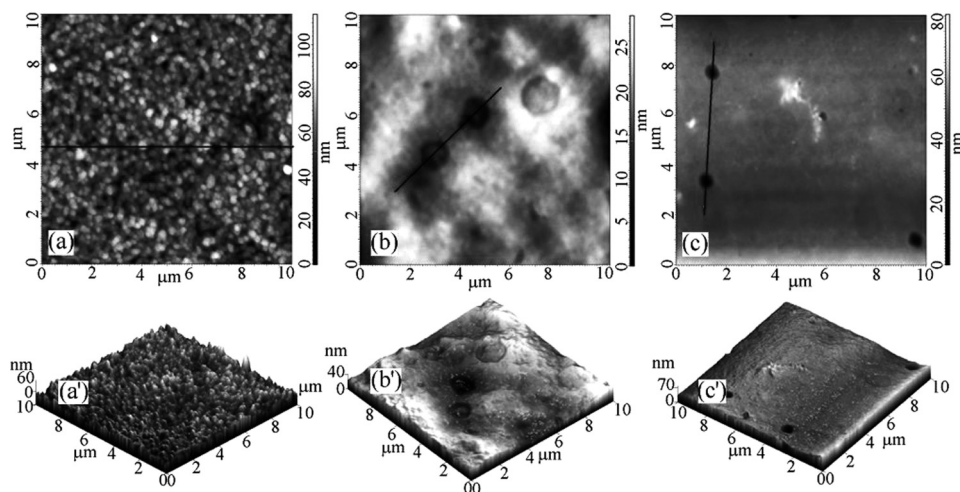


Figure 8. 2-D (a, b, c) and 3-D (a', b', c') AFM images of CA_{1.73} membranes obtained from different acetone/water solvent mixtures: $\phi_2 = 0.15$, $\phi_2 = 0.20$, and respectively, $\phi_2 = 0.25$.

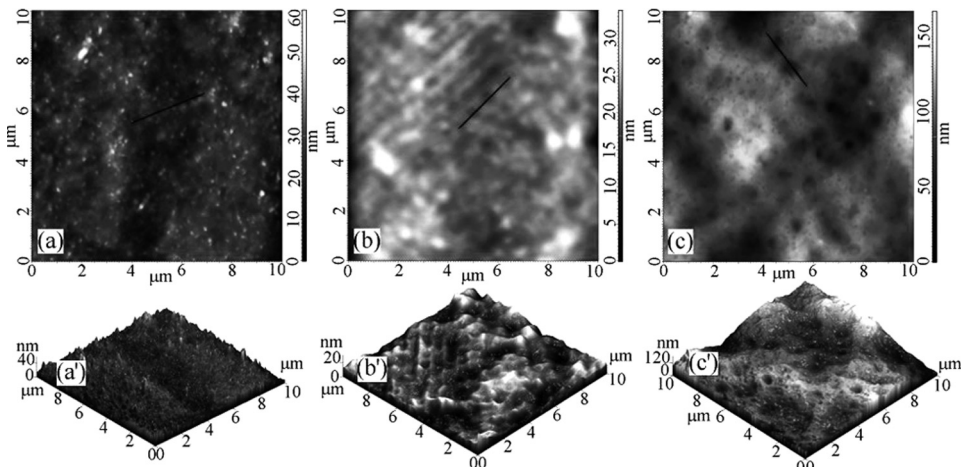


Figure 9. 2-D (a, b, c) and 3-D (a', b', c') AFM images of CA_{1.88} membranes obtained from different acetone/water solvent mixtures: $\phi_2=0.15$, $\phi_2=0.20$, and respectively, $\phi_2=0.25$.

nonsolvent mixtures. The composition of the nonsolvent mixtures was selected as a function of the substitution degrees of CA. Thus, for the studied cellulose acetates, intrinsic viscosity and the preferential adsorption coefficient versus water content show modification of chain conformation in dilute solution and over the composition range of the solvent mixtures (see also the experimental section), as illustrated in Figure 1(a) and (b).^[21]

AFM was used to examine the film surface and to measure its surface topography. All images presented in Figures 8–11 were recorded under ambient conditions, over $10 \times 10 \mu\text{m}^2$ scan areas, to provide morphological details.

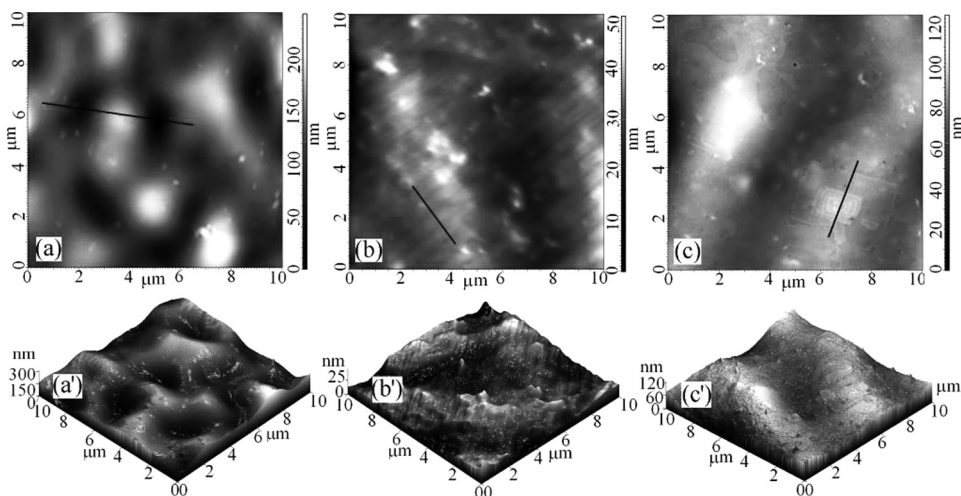


Figure 10. 2-D (a, b, c) and 3-D (a', b', c') AFM images of CA_{1.90} membranes obtained from different acetone/water solvent mixtures: $\phi_2=0.15$, $\phi_2=0.20$, and respectively, $\phi_2=0.25$.

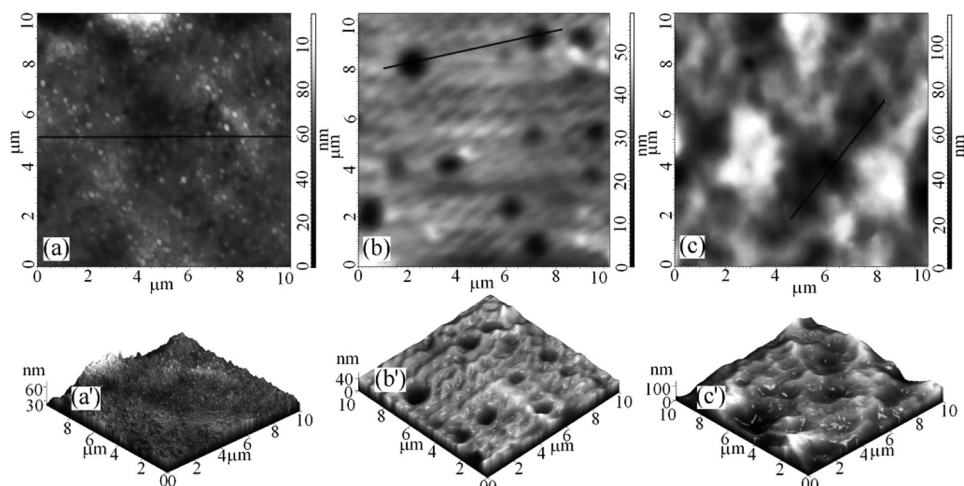


Figure 11. 2-D (a, b, c) and 3-D (a', b', c') AFM images of CA_{2.21} membranes obtained from different acetone/water solvent mixtures: $\phi_2=0.05$, $\phi_2=0.10$, and respectively, $\phi_2=0.15$.

Each micrograph shows that the membrane surface is not smooth, with ordered domains, in which pores and nodules of different size and intensity are distributed, being evidenced.

According to our data, the water content in the casting solutions favored the occurrence of ordered domains, more visible for intermediary compositions of the nonsolvent mixtures, which corresponds to better cellulose acetate dissolution (see discussion in the experimental section) and acetone adsorption (Figure 1(b)), as well as for cellulose acetate with higher degrees of substitution.

Table III. Pore characteristics, including area (μm^2), volume ($\mu\text{m}^2 \times \text{nm}$), depth (nm), and diameter (μm), and surface roughness parameters, including root-mean-square roughness (nm), nodule height from the height profile (nhp, in nm), and nodule average height from the histogram (nhh, in nm) of the membranes prepared from cellulose acetate with different solvent mixtures

Sample	ϕ_2 in cast solvents	Pore characteristics				Surface roughness		
		Area	Volume	Depth	Diameter	rms	nhp	nhh
CA _{1.73}	0.15	0.035	1.000	0.157	9.021	11.480	106	160
	0.20	0.535	4.416	0.627	3.990	6.533	18	356
	0.25	0.167	2.309	0.471	23.045	6.836	49	270
CA _{1.88}	0.15	0.057	0.708	0.118	1.446	27.432	24	310
	0.20	0.149	1.624	0.314	1.388	2.976	20	450
	0.25	0.206	8.464	0.275	7.287	5.833	78	70
CA _{1.90}	0.15	0.984	56.397	0.863	22.207	47.721	190	42
	0.20	0.372	2.384	0.353	1.099	4.874	37	330
	0.25	0.126	5.770	0.157	2.429	16.414	99	105
CA _{2.21}	0.05	0.185	4.945	0.196	2.602	20.860	72	200
	0.10	0.640	12.203	0.784	11.797	4.525	40	110
	0.15	0.823	24.752	0.863	17.407	10.623	50	128

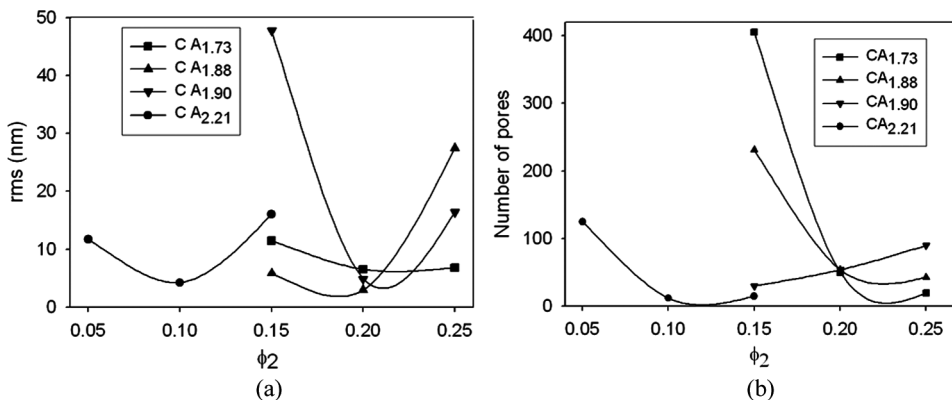


Figure 12. Root-mean-square roughness (in nm) (a) and number of pores (b) for cellulose acetate with different substitution degrees, at different water contents.

On the other hand, AFM images show that, at extreme water compositions and especially at lowest water content, when dissolution is the worst, a higher number of pores, with lower areas, volumes, diameters, and depths appear. Also, for extreme water contents, the root-mean-square roughness of the surface (rms) increases, the phenomenon being more intense at lower water contents.

Table III and Figure 12 give the average values of pore characteristics and the surface roughness parameters of membranes prepared from water and acetone nonsolvent mixtures, identified in AFM images.

All investigations indicate that the membrane properties depend not only on the substitution degrees of the cellulose acetate, but also on the composition of the solvent mixtures. In particular, it was found out that decreasing the solvation power, observed from viscometric studies in dilute solution, and increasing the gelation process, detected by rheological data, favored increase of pore numbers.

CONCLUSIONS

This study describes the rheological properties of some cellulose acetate with different substitution degrees in acetone/water nonsolvent mixtures. The AFM results obtained for cellulose acetate membranes prepared by a dry-cast process in the same solvent mixtures show the influence of nonsolvent mixture composition on membrane morphology.

The solubility of cellulose acetate depends on the water content and on substitution degrees. Thus, the water volume fractions favorable for dissolution occur in the 0.15–0.25 range for CA_{1.73}, CA_{1.88}, and CA_{1.90}, and in the 0.05–0.15 range for CA_{2.21}. Modifications of the solubility domains determine the rheological properties as a function of the water content, substitution degrees, and solution concentration. Thus, at higher substitution degrees, dynamic viscosity increases with decreasing water content, while at lower concentrations, the solution exhibits Newtonian behavior. On the other hand, at lower values of the substitution degree, dynamic viscosity

increases with increasing water content, showing a non-Newtonian flow. Moreover, increased concentration induces cloudiness in the system, thus self-supporting the gel materials.

According to AFM data, the water content in the casting solutions favored the occurrence of ordered domains, more visible for intermediary compositions of the mixed solvents, which corresponds to better cellulose acetate dissolution. Furthermore, the phenomenon is more visible for cellulose acetate with higher degrees of substitution. Also, at extreme water compositions and especially for lowest water content, when dissolution is the worst, a higher number of pores, with lower areas, volumes, diameters, and depths appears. Moreover, the root-mean-square roughness of the surface (rms) increases, the phenomenon being, again, more intense at lower water contents.

One may also consider that the interactions and association phenomena of acetone and water over different composition domains of their mixtures should be among the factors affecting the morphology of the cellulose acetate membrane surface. Knowledge of these properties is necessary for some biomedical applications, such as obtaining semipermeable membranes.

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