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Research Article

CHITOSAN-POLY(N,N-DIMETHYLACRYLAMIDE-CO-DIALLYL DIMETHYL AMMONIUM CHLORIDE) AND CHITOSAN-POLY(N,N-DIMETHYLACRYLAMIDE) SEMI-IPN FILMS: THE COMPARISON OF THEIR PROPERTIES

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ABSTRACT

In this study, cationic semi-IPN films (CS-DA-DAD) containing chitosan (CS), N,N-dimethylacrylamide (DA), and diallyldimethylammonium chloride (DAD) were prepared for the first time at initial molar concentrations of 0.06, 0.12, 0.18, and 0.21 M, using ammonium persulphate (APS) as initiator, and N,N,N',N'-tetramethylethylenediamine (TEMED) as accelerator. For comparison, CS and CS-DA films were also prepared.

The characterization of films was performed by FTIR, DSC, and XRD methods. Electrical properties of the films were determined by the measurements of dielectric constant (ε') and dielectric loss (ε'') between 12 Hz and 100 kHz at room temperature under dry air atmosphere.

Dielectric constant values of all films decreased with frequency. While the dielectric constants of CS-DA-DAD increased with the increase in DAD content, those of CS-DA films decreased with the increase in DA content due to the decrease in the ionic charge density of the film.

It has been determined that the increase in DAD content of CS-DA-DAD films shifted the frequency values corresponding to the maximum value of the imaginary part of the electric modulus (M'') to the higher values. This result indicates the increase in conductivity and the decrease in relaxation time of the films with DAD. In the case of CS-DA films, the increase in DA content led to shift the frequency values corresponding to the maximum value of the imaginary part of the electric modulus to lower values, which is indicating the decrease in the conductivity of the films and the increase in their relaxation times.

Keywords: Chitosan, N,N-dimethylacrylamide, diallyldimethylammonium chloride, dielectric constant, dielectric loss.

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1. INTRODUCTION

Chitosan (CS) is the second most abundant bio-polymer in the world. Since it is prepared by alkaline deacetylation of chitin, the deacetylation degree (DD) of CS determines its many properties such as solubility and reactivity [1]. During the deacetylation, N-acetyl groups in chitin are converted to $–NH_2$ groups, and the chitin with 75% deacetylation degree is called as chitosan [2]. For that reason, CS consists of glucosamine and *N*-acetyl glucosamine units linked by β- (1–4) glycosidic bonds. Although CS is a linear polymer, it does not dissolve in water, but in acidic aqueous solutions. CS dissolved in aqueous acetic acid solution is known as chitosonium acetate [3]. It is a non-toxic, biodegradable, and bio-compatible polymer, and has a good film-forming property. These properties make it a good candidate for many applications in biomedicine, waste water treatment, and packaging. Due to protonation property of $–NH_2$ groups of CS in acidic medium, it responds to changes in the pH of medium, and for that reason it is called as pH-responsive (smart) polymer [4,5].

N,N-dimethylacrylamide (DA) is a neutral-polymer forming monomer. Since the biocompatibility and hydrophilicity of the poly(N,N-dimethylacrylamide) (PDA), it has many drug-release applications in medical and pharmaceutical fields [6,7].

Diallyldimethylammonium chloride (DAD) is a cationic, and water soluble monomer with high-charge density [8]. It polymerizes by ring-opening reaction (cyclopolymerization), and the backbone of poly(diallyldimethylammonium chloride) (PDAD) contains quaternary ammonium groups and cyclic rings [9]. While it is mainly used as flocculant and coagulant in potable water treatment, it is also used in cosmetic, personal care and biomedical applications, food industry, and in membrane technology [10,11].

Smart polymers such as pH-responsive or electric field-responsive polymers are the subject of many studies in recent years [12]. Due to pH-dependent ionization property of chitosan, as a pH-responsive polymer, it responds to electric field as bending or motion [3]. Electric field-responsive polymers have potential applications in artificial muscles etc. The response rate and the intensity of the polymer to electric field are important parameters for electric field-responsive polymers. The most important property of a polymer necessary for fast response to electric field is to have a high charge density. In a previous work [13], we have synthesized CS-DA semi-IPN polymer films and investigated their electrical properties such as dielectric properties and response to electric field. In order to increase the ionic charge density of polymer, and to obtain a fast responsive polymer to electric field, an ionic monomer DAD was introduced to the structure of CS-DA polymer, and CS-DA-DAD semi-IPN films were prepared for the first time at four initial monomer concentrations (0.06-0.21 M) composed of 40 mol % DA and 60 mol % DAD. There are few papers on CS-DA [6,14,15] polymers, but there is no paper on the synthesis and electrical properties of CS-DA-DAD polymer. The swelling behavior and thermal properties of CS-DA-DAD semi-IPN films were investigated by swelling measurements in distilled water and buffer solutions with pH of 2-10, and DSC method, respectively. The dielectric properties of CS-DA-DAD semi-IPN films were also determined in order to estimate the response rate of polymer to electric field, and they were compared with those of CS-DA films in order to observe the presence of ionic DAD monomer in the polymer structure on the electrical properties.

2. MATERIALS AND METHODS

2.1. Materials

Chitosan (CS) (low viscosity), N,N'-methylenebisacrylamide (NMBA), N,N-dimethylacrylamide (DA), diallyldimethylammonium chloride (DAD), and ammonium persulphate (APS) were purchased from Sigma-Aldrich. Acetic acid (AAc) and N,N,N',N'-Tetramethylenediamine (TEMED) were of Merck (Hohenbrunn, Germany) and Serva

Electrophoresis GmbH (Heidelberg, Germany) products, respectively. Distilled water was used in the preparation of semi-IPN films.

2.2. Synthesis of Chitosan-poly(N,N-dimethyl acrylamide-co-dialildimetilamonyum klorür) (CS-DA-DAD) semi-IPN Films

For the preparation of CS-DA-DAD semi-IPN gel films, at first, CS (0.25 g) was dissolved in 25 ml, 2% (v/v) aqueous AAc at room temperature by stirring with a magnetic stirrer. The aqueous solution of crosslinker NMBA (1g NMBA/50 mL distilled water) (in 1 mol % of DA+DAD monomers) was added to this CS solution, and stirred for 5 minutes to obtain homogeneous solution. Then, DA and DAD monomers at 40 mole % and 60 mole %, respectively, was added to the solution of CS and NMBA at four initial total monomer concentrations of 0.06. 0.12, 0.18, and 0.21 M. After that, APS (in 3 mol% of initial total monomer content) solution (2.25g/50 mL distilled water), and the accelerator TEMED (in equal amounts with APS in weight) solution (5 mL/20 mL solution) were added by stirring, respectively, and the mixture was further stirred for 5 minutes at 750 min^{-1} stirring rate in order to obtain a completely homogeneous mixture. Then, the reaction mixture was cast into a Teflon petri dish with inner diameter of 9.8 cm, and left to dry at first at room temperature, and then in an oven at 35^{o}C to form a film by the copolymerization of DAD and DA monomers, and the evaporation of water in reaction mixture, simultaneously.

CS-DA films were prepared by the same procedure given above using DA monomer instead of DAD and DA monomers. CS film was obtained by leaving CS solution (1 wt. %) to dry at room temperature at first, and then in an oven.

In films' codes, the numerals seen after CS-DA-DAD/CS-DA/CS such as 0.06, 0.12, 0.18, and 0.21 show the initial total monomer concentration (in M) in monomer feed. The film codes and the amounts of materials used in the preparation of films were given in the table below (Table 1).

Table 1. Feed composition of CS-DA and CS-DA-DAD semi-IPN films

Film Code	[CS]^a (wt./v %)	[DA]^b (mole/L)	[DA]+[DAD]^c (mole/L)	[NMBA]^d (mole %)	[APS]^e (mole %)
CS	1	-		-	
CS-DA-DAD-0.06	1		0.06	1	3
CS-DA-DAD-0.12	1		0.12	1	3
CS-DA-DAD-0.18	1		0.18	1	3
CS-DA-DAD-0.21	1		0.21	1	3
CS-DA-0.06	1	0.06		1	3
CS-DA-0.12	1	0.12		1	3
CS-DA-0.18	1	0.18		1	3
CS-DA-0.21	1	0.21		1	3

a: CS concentration in wt./v dissolved in 2 (v/v) % aqueous acetic acid solution ; b: Initial monomer concentration in mole/L in CS solution; c: Initial total monomer concentration in mole/L in CS solution; d: mole percentage of DA or DA+DAD monomers; e: mole percentage of DA or DA+DAD monomers

2.3. The Characterization of semi-IPN Films

2.3.1. Film thicknesses

The thicknesses of the films were determined by a micrometer screw gauge (“a” brand, 0-25mm, ±0.001 mm), and they were measured from at four different positions over the film surface using four films. The mean thickness values were given in Table 2 , and they were used in the calculation of dielectric parameters.

2.3.2. FTIR analysis

FTIR spectra of CS, CS-DA, and CS-DA-DAD films were taken by KBR pellet method between 400 and 4000 cm^{-1} using Agilent-Cary 630 FTIR equipment.

2.3.3. Differential scanning calorimetry (DSC) analysis

The thermal properties of the films were determined by DSC measurements in two steps of heating using ca. 15 mg film sample using DSC equipment (DSC 131, Setaram). In the first step of heating, the sample was heated from 30^{o}C to 150^{o}C with the heating rate of 10°C/min under nitrogen gas atmosphere (40 mL N_2/min) in order to delete the thermal history of the sample, and then cooled back to 30^{o}C. In the second step, that sample was heated from 30^{o}C to 350◦C at the heating rate of 10 ^{o}C/min under nitrogen gas atmosphere (40 mL N_2/min).

2.3.4. Swelling measurements

Swelling measurements of the semi-IPN films gave both swelling behavior and gel percentages of the films. In order to investigate the swelling behavior of CS-DA-DAD films, their equilibrium swelling values (ESVs) were determined in distilled water, and in buffer solutions with different pH values (pH=2.2, 4.1, 7.0, and 10.0) at constant ionic strength (0.08 M), at room temperature by gravimetric method using three replicates. The compositions and the preparation of buffer solutions used in the swelling measurements as swelling media were given in one of our previous papers [13]. The ESVs of the films were also determined in NaCl solutions at 0.1 and 0.2 M concentrations. For the comparison purpose, ESVs of CS-DA films were also determined under the same conditions.

A given amount (W_{d1}) of dry film was immersed in distilled water (dw)/buffer solution/NaCl solution at 25^{o}C for 24h. The swollen film was with-drawn from the distilled water or salt solution, and the excess of surface water was removed by lightly blotting the film with a filter paper, and then it was weighed (W_s). Finally, the swollen gel films were dried at first at room temperature, and then in vacuum oven at 35^{o}C until no change in weight was observed. The dry gel films were re-weighed (W_{d2}). The ESVs and gel percentages of the films (in wt. %) were calculated according to the equations 1 and 2 given below:

$$\text{ESV } (gH_2O/g \text{ polymer}) = [W_s - W_{d1}]/ W_{d1} \tag{1}$$

$$\text{Gel percentage } (\%) = [W_{d2} / W_{d1}] \times 100 \tag{2}$$

2.3.5. Dielectric measurements

The dielectric property of a material is defined by the following equation;

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \tag{3}$$

where ε' represents the energy storage property or relative permittivity, ε'' represents the energy dissipation property or dielectric loss. The ratio of dielectric loss to relative permittivity gives the dissipation factor (*D*) or loss tangent of the material;

$$D = \varepsilon'' / \varepsilon' \tag{4}$$

For a closer inspection of the conduction mechanism the electric modulus can also be analyzed. The electric modulus is basically the reciprocal of permittivity;

$$M^* = 1 / \varepsilon^* = M' - jM'' \tag{5}$$

The electrical properties of CS-DA-DAD and CS-DA semi-IPN films were investigated by the measurements of capacitance (*C*) and loss tangent (*D*) of the built parallel-plate cell which consisted of the films to be studied in a tailor made vacuum glove box to provide a dry air atmosphere at room temperature. All measurements were carried out in the frequency range of 12 Hz–100 kHz by a 4-probe LCR-meter (Instek LCR-819) equipped with a parallel plate capacitor structure in the vacuum glove box (Fig. 1). The films dried well just before the measurements in a vacuum oven at 35◦C for 24h duration in order to eliminate the possible effect of water on the electrical properties of films. Before the measurements, the films were cut into size of 2cm×3 cm and sandwiched between two rectangular (2cm×3cm) copper plates that forms a parallel plate capacitor. Measurement mode of the LCR-meter was adjusted to capacitance mode with equivalent parallel RC circuit, and the amplitude of the measuring signal to 1Volt. Capacitance (*C*) and loss tangent (*D*) values were obtained from the averages of ten sets of measurements.

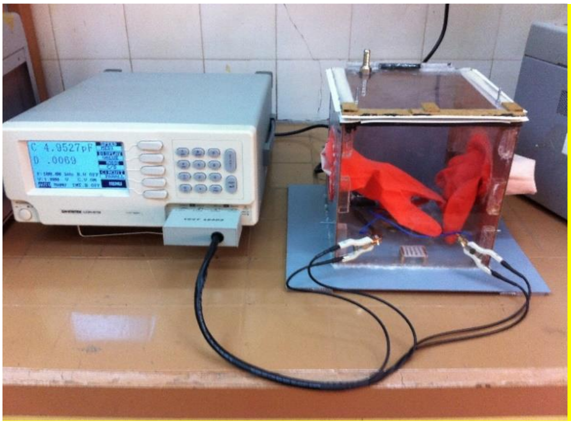

Figure 1. LCR-meter and vacuum glove box used in the measurements of dielectric properties of semi-IPN films

The dielectric constant and dielectric loss values of films were calculated by using capacitance and loss tangent values which were measured according to equation given below:

$$\varepsilon' = C/C_o \tag{6}$$

$$\varepsilon'' = D.\varepsilon' \tag{7}$$

where *C* and *D* is measured capacitance and loss tangent of parallel plate capacitor, ε': dielectric constant, .ε'': dielectric loss, C_o: capacitance of air gapped vacuumed parallel plate cell with $C_o=\varepsilon_o A/d$, ε_o: permittivity of free space (8.854×10^{-12} F/m), *d*: the thickness of the film in mm, and *A*: surface area of film (6 cm^2).

3. RESULTS AND DISCUSSION

3.1. Characterization of the Films

The thicknesses of CS-DA-DAD semi-IPN films (Table 2) were found to be 1.5 times of those of CS-DA films since the molecular weight of DAD monomer (167.5 g/mole) is higher than that (99.1 g/mole) of DA monomer although the content of CS in both CS-DA-DAD and CS-DA films were the same (0.25 g).

The comparison of FTIR spectrum of CS-DA and CS-DA-DAD semi-IPN films with that of CS film was given in Figure 2. FTIR bands of CS-DA films were explained in one of our previous papers [13]. A new band at 3024 cm^{-1} due to the stretching vibration of C-H bond in the compounds with aromatic ring appeared in the FTIR spectra of CS-DA-DAD films except in that of CS-DA-DAD-0.06 [16-18]. The band assigned to the bending vibration of N-H bond at 1565, 1560, 1553, 1546, and 1638 cm^{-1} existed in the spectra of CS and CS-DA films disappeared in those of CS-DA-DAD films. The intensity of the band at 962 cm^{-1} assigned to the out of plane bending of aliphatic C-H bond increased with DAD concentration in monomer feed. This increase can be attributed to the increase in PDAD content of CS-DA-DAD film [18]. Another increase with DAD content in monomer feed was observed in the intensity of the band at 1479 cm^{-1} ascribed to the stretching vibration of C-H bond in $–CH_3$ groups [18]. All these changes confirm the presence of PDAD units in CS-DA-DAD semi-IPN films.

Table 2. Film thicknesses of dry CS-DA and CS-DA-DAD semi-IPN films and their theoretical CS and DAD contents in percentage.

$[DA]_i$ or $[DA+DAD]_i$ (mole/L)	**Film Thickness (mm)**		**CS (wt.%)**		**DAD (wt.%)**
	CS-DA	**CS-DA-DAD**	**CS-DA**	**CS-DA-DAD**	**CS-DA-DAD**
0.06	0.0647±0.0056	0.1000±0.0065	63	47	42
0.12	0.0765±0.0043	0.1320±0.0183	46	31	55
0.18	0.1200±0.0234	0.1780±0.0088	36	23	61
0.21	0.1520±0.0176	0.2180±0.0157	33	20	63

$[DA]_i$ or $[DA+DAD]_i$: Initial molar concentration of DA or DA+DAD monomer(s) in the feed of CS-DA/CS-DA-DAD semi-IPN films.

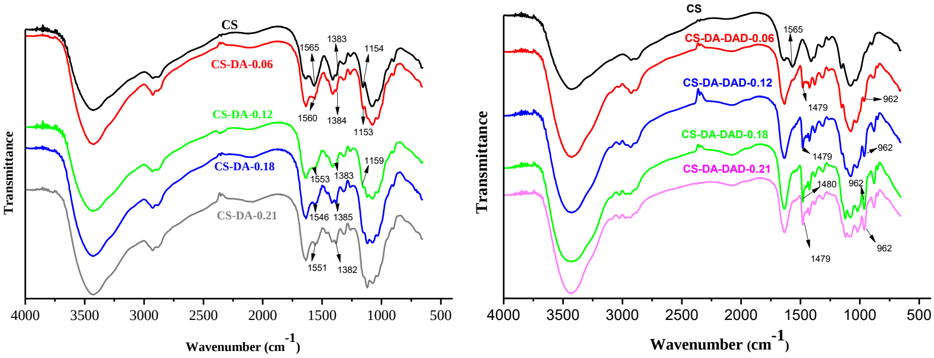

Figure 2. FTIR spectra of CS-DA (left) and CS-DA-DAD (right) semi-IPN films

3.2. Swelling Measurements

ESVs of CS-DA and CS-DA-DAD films in distilled water and in salt solutions with 0.1 and 0.2 M NaCl concentrations at room temperature were given in Figure 3. ESVs of CS-DA films in both distilled water and in NaCl solutions decreased with DA content in monomer feed, namely with the increase in PDA content of the semi-IPN film. It is known that PDA is more hydrophobic than CS [13]. For that reason, the increase in PDA content of CS-DA semi-IPN film makes the film more hydrophobic, and the ESVs of CS-DA film decrease. In addition, the increase in monomer concentration in feed leads to the formation of self-crosslinking reactions during polymerization, namely the increase in crosslink-density of the polymer. The decrease in ESVs of CS-DA films with initial DA concentration in feed can also be attributed to the increase in physical crosslinking due to the formation of hydrogen bonds between –OH and/or $–NH_2$ groups of CS and –C=O group of PDA. The same decrease in ESVs of films with initial momomer concentration was also observed for CS-DA-DAD films. Although CS-DA-DAD films contain PDAD units which are ionic in structure, and the presence of ionic units in polymer structure positively contributes to the swelling of polymer, the lower EVSs of CS-DA-DAD films than those of CS-DA films both in distilled water and in salt solutions indicate that the crosslink densities of former films are higher than those of latter films. The increase in the crosslink density of CS-DA-DAD semi-IPN films in comparison to that in CS-DA films can be explained by the presence of extra hydrogen bonds, namely physical crosslinks, between CS and P(DA-co-DAD) as claimed by H. Zhang et al ([19]. It is known that chitosonium acetate forms during the dissolution of CS in aqueous acetic acid solution [3] by the reaction between $–NH_2$ groups of CS and acetic acid as given below:

$$CS\text{-}NH_2 + CH_3COOH \longrightarrow CS\text{-}NH_3^+CH_3COO^-$$

The increase in the crosslink density of CS-DA-DAD films occurs by the formation of intermolecular hydrogen bonds between $-CH_3COO^-$ groups of CS and $-N^+(CH_3)_2$ group of PDAD unit of P(DA-co-DAD). [19].

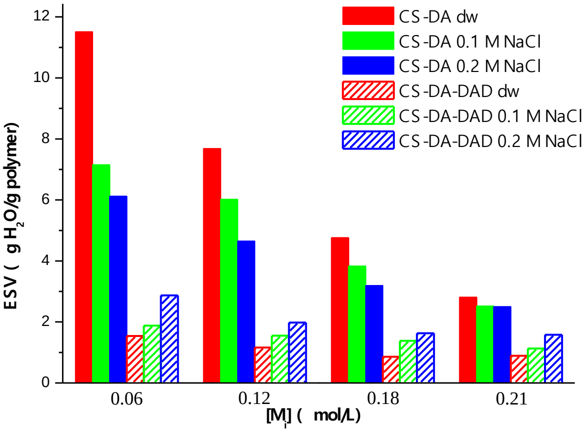

Figure 3. ESVs of CS-DA and CS-DA-DAD films in distilled water (dw) and in 0.1 M and 0.2 M NaCl solutions

ESVs of CS-DA films in distilled water are higher than those in salt solutions since the driving force for swelling in case of distilled water is higher than that in salt solutions due to the higher difference in the concentrations of mobile counter ions between the polymer film and the distilled water (swelling medium).

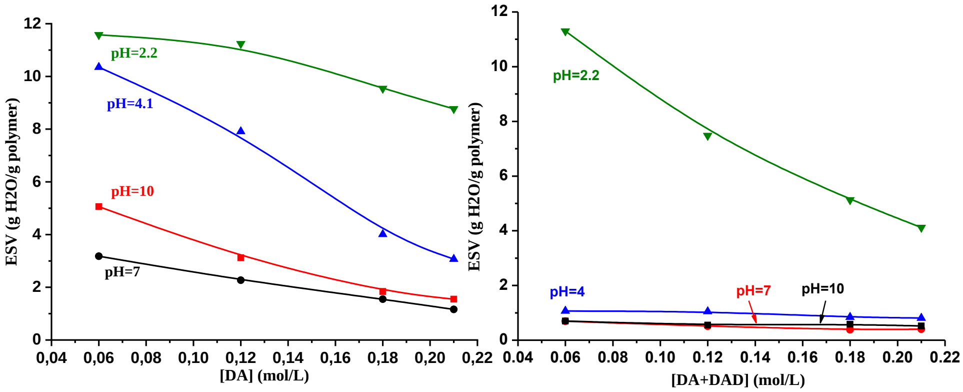

Figure 4. ESVs of CS-DA (left) and b) CS-DA-DAD (right) films in buffer solutions at pH range of 2-10.

In the swelling of salt solutions, ESVs decreased with the concentration of NaCl in the solution since the difference in the concentrations of mobile counter ions between the inside and outside of the polymer film decreases with NaCl concentration, namely the driving force for the swelling of the film. It is also interesting that the ESVs of CS-DA-DAD films in NaCl solutions are higher than those in distilled water on the contrary of general expectation since both PDAD units of CS-DA-DAD film and the swelling medium, aqueous NaCl solution, have the same ion, Cl^-. Therefore, in the swelling of PDAD in NaCl solution, the concentration of mobile counter ions inside and outside of the polymer film decreases in the presence of NaCl in the swelling medium, and this affects swelling in a less amount than that in distilled water. It is also probable that in the case of swelling of CS-DA-DAD film in salt solution, polymer film can exist in a lesser crosslinked form due to inhibition of the formation of hydrogen bonds. Therefore, the swelling values of CS-DA-DAD films in salt solutions are higher than those in distilled water.

ESVs of CS-DA and CS-DA-DAD films in buffer solutions with pHs of 2-10 are given in Figure 4. As can be seen from Figure 4, the highest swelling is observed in the solution with pH of 2.2 since CS exists in positive charged at that pH. The repulsion forces between positive charged polymer chains lead to increase in the swelling of CS-DA film. The swelling values of these films decrease with pH of swelling medium since the protonation of NH_2 groups of CS decreases, namely the repulsion forces between the polymer chains disappear with pH. Further increase in pH can lead to hydrolysis of N-acetyl groups of CS to more hydrophilic $-NH_2$ groups. For that reason, ESVs at pH=10 are slightly higher than those at pH=7.

The decrease in ESVs of CS-DA-DAD films with initial monomer concentration at pH=2.2 is higher than that of CS-DA films. Although $-NH_2$ groups of CS in acidic medium exist in protonated form ($-NH_3^+$), this finding indicates that physical crosslinking through intra- or inter-molecular hydrogen bondings between CS and P(DA-co-DAD) polymers increases. ESVs of CS-DA-DAD films at pH=4-10 are nearly the same at all initial monomer concentrations unlike those of CS-DA films at those pHs. It is expected that the presence of ionic PDAD will increase the ESVs of CS-DA-DAD films, but it is not the case. ESVs of CS-DA-DAD films at neutral and alkaline pH indicate that they have nearly the same crosslink density independent from the initial monomer concentration.

Gel percentages of both kind films in both distilled water and salt solution decreased with the increase in initial monomer concentration during the preparation of semi-IPN films. It means that the amount of crosslinked polymer decreases with the increase in initial monomer concentration contrary to the general expectation. It can also be concluded from the gel percentages values given in Figure 5 that amount of sol fraction increases with initial monomer concentration. The decrease in gel percentages is more apparent and reasonable for CS-DA-DAD films due to the repulsion forces between the positive charged DAD monomer and the same charged growing polymer chain. This finding is suitable with the expected values.

The highest gel percentages in buffer solutions for both kinds of films were observed at pH 4.1. Gel percentages of CS-DA-DAD films decreased with the introduction of DAD units to the semi-IPN film. It is known that during the copolymerization of DA and DAD monomers, DA monomer incorporates in copolymer structure faster than DAD, and DAD is introduced in the polymer structure after the consumption of DA monomer during polymer formation [20] as can be understood from the reactivity ratios of r_{DA}= 6.3 and r_{DAD}= 0.3. For that reason gel percentages values of DAD containing films are lower than those of films without DAD

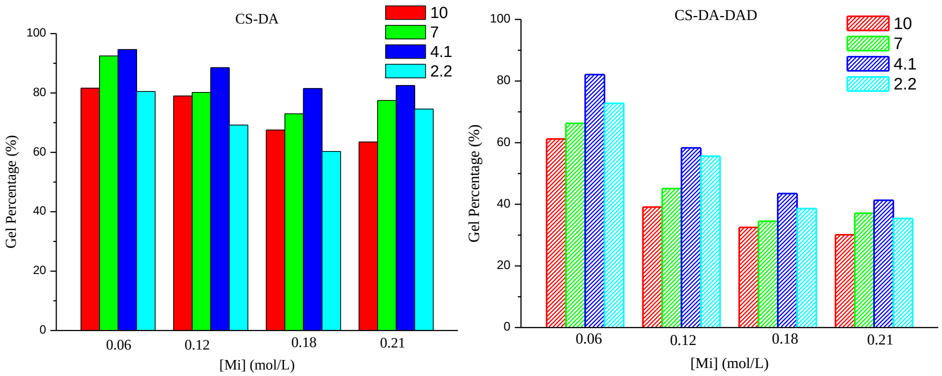

Figure 5. Gel Percentages of CS-DA (left) and CS-DA-DAD (right) films in buffer solutions at pH range of 2-10.

3.3. DSC Analysis

Thermal behavior of CS-DA and CS-DA-DAD films was investigated by DSC method, and their DSC curves were given in Figure 6. The exothermic peak in DSC curve of CS at 286.9^{o}C is attributed to the decomposition of amine groups CS [21-23] It is known that CS films decomposes mainly in two steps, the first and the maximum amount of decomposition occurs between 180 and 300^{o}C, and the second in the temperature range 540–810^{o}C [24]. In the first degradation step of CS, the dehydration of saccharide rings, decomposition of N-acetyl and amine units, and depolymerization of CS takes place [24].

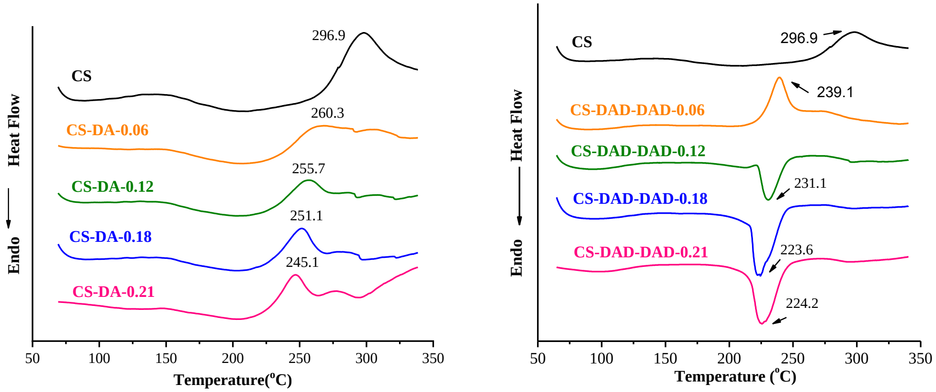

Figure 6. DSC curves of CS-DA (left) and CS-DA-DAD (right) semi-IPN films.

Since all the DCS curves were obtained during the second step of heating, no endothermic peak is observed up to 150-200^{o}C which is assigned to the loss of moisture or adsorbed water. The introduction of DA into CS film decreased the decomposition peak temperature to 260^{o}C, and further increase in DA in monomer feed led to decrease in thermal stability of CS-DA film, and decomposition temperature to 245^{o}C. While the introduction of DAD into CS-DA semi-IPN film led to decrease in the decomposition peak temperature from 296.9^{o}C to 239.1^{o}C, its further increase led to convert the decomposition reaction from an exothermic to an endothermic one by accompanying a highly great decrease in decomposition peak temperature to 224.2^{o}C. The endothermic peak in DCS curve of CS-DA-DAD films can be attributed to the decomposition reaction which occurs by the release of small molecules such NH_3 and HCl. The appearance of endothermic decomposition reaction in DSC curves of CS-DA-DAD films confirms the presence of PDAD in the film structure.

3.4. XRD Analysis

X-ray diffraction curves of CS, CS-DA and CS-DA-DAD films were given in Figure 7. CS is a polymer with low crystallinity (semi-crystalline), and the characteristic diffraction peaks of CS film at 2θ=14.4 and 20.1 (Figure 7) are attributed to the crystal forms of I and II [25-27], respectively. The diffraction peak at 2θ=14.4 in XRD pattern of CS film shifted to about 2θ = 11, and its intensity decreased with DA in feed. In addition, the diffraction peak at 2θ=20.1 lost its sharpness with DA, and it is seen as a shoulder in XRD pattern of CS-DA-0.21 film due to the breakage of hydrogen bonds between hydroxyl and amino groups, and the conversion of crystalline regions to amorphous ones in the film. In XRD pattern of CS-DA-DAD films, the peak at 2θ=14.4 assigned to the crystal form I completely disappeared even at the film with lowest DAD content (Figure 7). It can be concluded from the comparison of XRD patterns of CS-DA and CS-DA-DAD films, the introduction of DAD to the CS-DA film led to the formation of a semi-IPN film with higher amorphous content in comparison to CS-DA films.

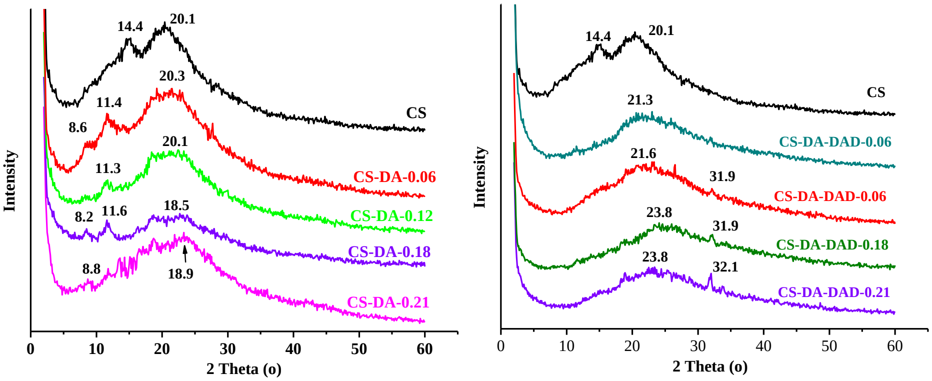

Figure 7. XRD patterns of CS-DA (left) and CS-DA-DAD (right) semi-IPN films.

3.5. Dielectric Measurements

Dielectric properties of CS-DA and CS-DA-DAD semi-IPN films were determined at room temperature in a glove box under dry air atmosphere since the high moisture adsorption property of CS-DA-DAD films. The dielectric constant (ε') and the dielectric loss (ε'') of the films as a function of frequency and initial monomer concentration in feed were given Figures 8 and 9.

In all the CS-DA films, the dielectric constant decreased with the increase in frequency and initial monomer concentration in the feed of polymer film due to the dielectric relaxation which causes an irregular distribution. The dielectric relaxation affects the orientation polarization of dielectric materials which is dependent on the molecular ordering. At high frequencies, the orientation motion of polar molecules in a dielectric material is not fast enough to attain an equilibrium. For that reason, the polarization and dielectric constant of CS-DA films decrease with frequency [28, 29]. In CS-DA films, the crosslinked unit content of the film increases, and total ionic charge density of the film decreases with the increase in DA due to the non-ionic structure of PDA.

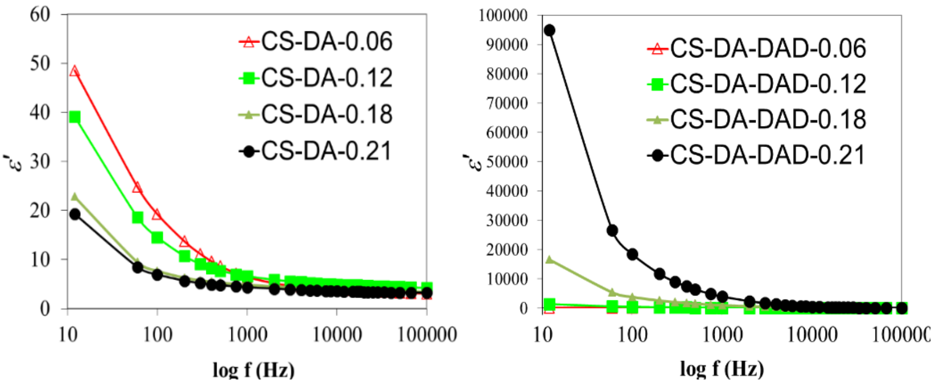

Figure 8. The variation of dielectric constant of CS-DA (left) and CS-DA-DAD (right) films with frequency.

The increase in crosslinked unit content of the film leads to decrease in the polarizability of the film. The decrease in ionic charge density of the film leads to a similar effect. Therefore, the dielectric constant of CS-DA films decreases with the increase in DA. $-NH_2$ groups of CS in acidic medium exist in positive charged form ($-NH_3^+$), and CS has a high electric conductivity property due to its polycationic structure. PDA is a neutral and non-ionic polymer. The conductivity decreases with the increase in the crosslink density and PDA content of polymer gel. The dielectric constant of a material is related with its conductivity, a decrease in the conductivity leads to decrease the dielectric constant [30].

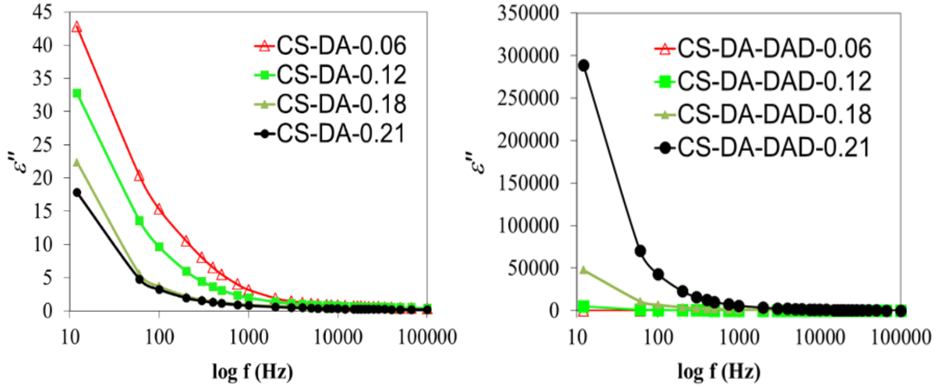

Figure 9. The variation of dielectric loss of CS-DA (left) and CS-DA-DAD (right) semi-IPN films with frequency.

The dielectric constant of CS-DA-DAD films decreased with frequency (Figure 8) as seen in CS-DA films, but it increased with the introduction of DAD into the polymer structure. Since PDAD is a cationic polyelectrolyte, its increase in polymer film increases the ionic charge density, and consequently its conductivity. The increase in the conductivity of polymer film improves the polarizability, and rate of polarizability of polymer and it leads to observe high dielectric constant values.

The dielectric loss values of both films decreases with frequency as seen in Figures 9, and it is related with the decrease in the motion of free charges in the material [30]. The heat which is lost and released due to friction of molecules during the polarization is known as dielectric loss. The dielectric loss decreases with frequency since the decrease in polarization with frequency leads to decrease in the heat loss liberated due to the friction of molecules during polarization. The dielectric loss decreases with frequency since the decrease in the polarization of molecules with frequency decreases the heat loss liberated due to the friction of molecules. At low frequency values, the highest dielectric loss was observed for CS-DA-0.06 film; the lowest one is for CS-DA-0.21 film. This finding is resulting from the easier and more polarizability of CS-DA-0.06 film with lowest crosslink density, and it indicates high amount of heat loss in that film. The polarization is getting difficult in CS-DA-0.21 semi-IPN film due to its high crosslink density, and for that reason the dielectric loss of that film is the lowest amongst the films with DA. These findings are suitable with the dielectric constant & frequency curves given in Figure 8. In CS-DA-DAD semi-IPN films, the highest dielectric loss was observed for CS-DA-DAD-0.21 film (Figure 9) and it is an expected finding since that film polarize faster and easier due to its highest ionic charge density amongst the CS-DA-DAD films.

The variation of imaginary parts of electric modulus of CS-DA and CS-DA-DAD semi-IPN films with frequency are given in Figure 10. While the real parts of CS-DA films are nearly the same for a wide frequency range, but for DAD-containing films the *M'* values of the film with lowest monomer concentration are apparently higher than those of films with higher DAD contents. In CS-DA films, with the increase in DA content of polymer film, the frequency values at maximum *M''* values shifted to the lower frequencies (Figure 10).

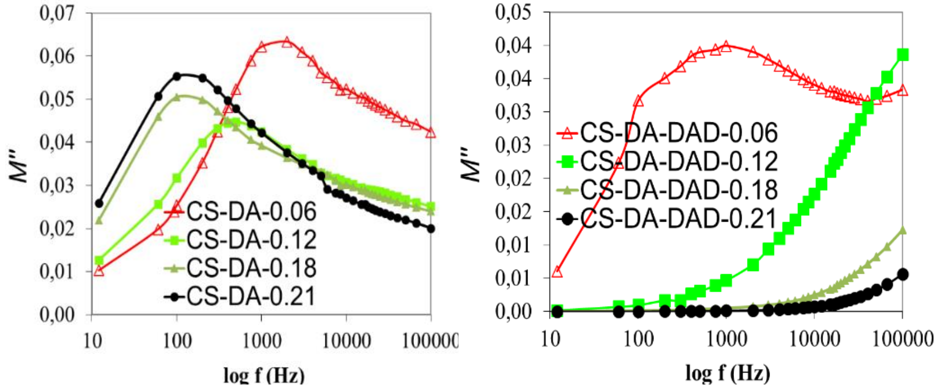

Figure 10. The variation of imaginary part of electric modulus of CS-DA (left) and (b) CS-DA-DAD (right) semi-IPN films with frequency.

This result indicates that the increase in DA decreases the conductivity of the film and increases the relaxation time which is the time necessary for returning back to the previous free orientation of polymer dipoles. With the increase in DA, the crosslink density of the polymer films increase, but their ionic charge density decrease. The increase in crosslink density makes the orientation of polymer chains difficult, and polymer chains return from the oriented from to non-oriented form in a longer time. The decrease in ionic charge density has similar effect on the relaxation time. In one of our previous works, we have determined the same finding for CS-DA semi-IPN films [13]. In the case of CS-DA-DAD films, only one maximum *M''* value was observed for the film with lowest monomer concentration, and no maximum for higher DA+DAD concentrations. It means that the frequency at maximum *M''* shifted to higher values, and indicates that the conductivity and polarizability of the polymer film increase with the introduction of DAD into the polymer structure. It also shows that the relaxation time of CS-DA-DAD films decrease due to the presence of DAD. For that reason, the polymer chains returns back to the previous orientations in a shorter time. This finding is an expected result since the ionic charge density of CS-DA-DAD films is higher than those of CS-DA films.

4. DISCUSSION

Two types of CS-based semi-IPN polymer (CS-DA and CS-DA-DAD) films were successfully prepared by free radical polymerization in aqueous solution, and they were characterized by FTIR, DSC, and XRD methods. Their equilibrium swelling values in distilled water and buffer solutions with pH between 2 and 10 were determined at room temperature. Dielectric properties of the films were investigated by the variation of dielectric constant, dielectric loss, and electric modulus values with frequency.

All the characterization methods confirmed the introduction of DAD monomer into the polymer structure. At high initial monomer concentrations, while CS-DA films were brittle, CS-DA-DAD films were in an elastic structure. In addition, the thicknesses of latter films were higher than those of former films due to higher molecular weight of DAD than that of DA at the same monomer composition. ESVs of both types of semi-IPN films decreased with initial monomer concentration due to crosslinking reactions during polymerization. Introduction of DAD monomer into CS-DA polymer decreased the gel percentage of polymer film. Since the reactivity ratios for the polymerization of DA and DAD monomers are r_{DA}=6.3 and r_{DAD}=0.3, in the case of polymerization of DA and DAD monomers, it is expected that DA polymerizes faster than DAD, and DAD content of the copolymer will be lower than that in monomer feed. Although FTIR, DSC, and XRD analyses confirmed the presence of DAD in CS-DA-DAD semi-IPN films, the reactivity values of monomers and the decrease in gel percentages with DAD indicate that the presence of DAD decreases the crosslinking reactions, and leads to the formation of higher amount of linear chained polymer. The presence of DAD in the polymer films was also confirmed by the increase in dielectric constant of CS-DA-DAD films due to their high conductivity resulting from the cationic polyelectrolyte structure of PDAD. The decrease in relaxation time of CS-DA-DAD films with DAD content indicates that these films would respond fast to electric field, and this finding has important contribution to the further studies on the electric field responsive gels.

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