Preparation and Characterization of Polysaccaride Interpolymer Complexes: I-PVA/ι-Carrageenan

Ömer Kantoğlu,[1] Tuncer Çaykara,[2] Olgun Güven[3]

[1]Turkish Atomic Energy Authority, Sarayköy Nuclear Research and Training Center, 06983, Kazan, Ankara, Turkey
[2]Department of Chemistry, Gazi University, Faculty of Art and Science, Beşevler Ankara, Turkey
[3]Department of Chemistry, University of Hacettepe, Beytepe, 06532, Ankara, Turkey

Correspondence to: Ömer Kantoğlu (E-mail: omer.kantoglu@taek.gov.tr)

ABSTRACT: Thermal and spectroscopic charaterization of PVA, iota carrageenan (IC), and their interpolymer complexes were studied in terms of stability, complex formation, and species determination by XRF, FTIR, Raman, DSC, and TGA. Thermogravimetry analysis showed that initial thermal degradation temperature of PVA/IC decreased from 276 to 256°C with an increase of IC content. The complexation of IC to PVA significantly increased, the thermal stability of IC, where as the thermal stability of PVA increased rather insignificantly. Fourier Transform Infrared (FTIR) and Raman spectroscopic results showed that PVA interacted with IC through —OH groups of PVA and IC as shown by the frequency and scattering shift at —OH band of FTIR and Raman spectra of each complex. The involvements of ester sulfate and ether groups of IC in interaction were not significant. In the results of the thermal and spectroscopic analysis, 17% content of PVA/IC is the most miscible and intercomplexable weight fraction of PVA/IC. The natural source of IC, which was unknown was characterized by XRF and found to be as potassium salt and *Euchema* specie of marine red algee of the class *Rhodophceae*. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

During the past decades, the combination of natural and synthetic macromolecules has become of increasing interest for the great potential of these blends in the close related fields of bioengineering, biomaterials and biotechnologies. The comprehension of their interactions and an increase in their reciprocal material compatibility is therefore a crucial point to develop polymer blends suitable to the perspective applications.[1] Polymeric materials are widely used for biomedical applications, but, in the past, synthetic and natural polymers have been used separately as potential biomaterials. Nowadays, the importance of polymeric interpolymer complexes is now well-established and both practical and fundamental studies have been conducted with a number of pairs of polymers. The success of synthetic polymers as a biomaterial mainly relies on their wide range of mechanical and thermal properties and transformation processes that allow a variety of different shapes to be easily obtained at low production costs.[2,3] On the contrary, biological polymers present good biocompatibility but their mechanical and thermal properties are often poor; the necessity of preserv-

ing biological properties complicates their processability and increases their production or recovery costs. Designed new materials based on interpolymer complex of biological and synthetic polymers with the final objective of producing new processable polymeric materials that hopefully possess both good mechanical and thermal properties and biocompatibility. Such materials are prepared through simple mixing. This class of materials is called bioartificial polymeric materials. Poly(vinyl alcohol) (PVA) is mainly used in aqueous solution and is commercially prepared by hydrolysis of poly(vinyl acetate) (PVAc). Its solubility in water depends on its degree of polymerization and degree of hydrolysis; it exhibits excellent chemical resistance and complete biodegradability.[4] PVA has been investigated for a variety of membrane applications in which its environmentally responsive behaviour is of interest.[5,6] Carrageenan belongs to the group of polysaccharides which shows enzymatic degradation behavior and relatively good biocompatibility. It is widely under investigation as a polymeric carrier, both as a macromolecular prodrug and in the form of a hydrogel.[7] However, interpolymer complexes containing ι-carrageenan (Scheme 1) as one
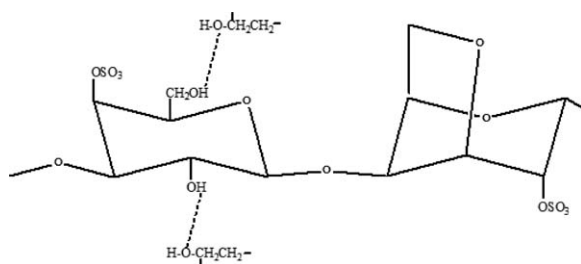
Scheme 1. Interaction among iota (ι)-carrageenan (IC) and polyvinyl alcohol (PVA).

component have received relatively low attention. Nevertheless, PVA/IC polymer interpolymer complexes are attractive and important not only because of potential applications but more specifically as models for the investigation of interpolymer complexes containing polymers with functional groups that can engage in strong intermolecular interaction such as hydrogen bonding. Therefore, for present system, it is also of interest to ascertain whether molecular interaction based on hydrogen bonding takes place between the two different polymers, contributing to enhancement of the state of complexibility in the interpolymer complexes.

For thermodynamic miscibility in polymer interpolymer complexes a basic prerequisite is that Gibbs free energy of mixing be negative. For this purpose, it is usually necessary to have some kind of favorable interaction between segments of the component polymer chains. Because of the abundance of hydroxyl groups in carrageenans, interpolymer complexes with the synthetic polymer offer the interesting possibility of studying the effects of strong hydrogen bonding as a major factor in inducing complexibility. Thus for interpolymer complexing with carragenans, it is important to choose synthetic polymers containing functional groups that can potentially interact with the hydroxyl groups of the carrageenan chains. Conversely, carrageenans have some extent of rigidity and brittleness. For these reasons, it is expected that properties of carrageenans can be improved through interpolymer complexing with PVA, which is highly elastic and also known as biocompatible.

Hydrogen bonding interaction is an important aspect of miscibility. Hydroxyl containing polymers are capable of forming miscible blends with proton accepting polymers through hydrogen bonding interactions involving their hydroxyl groups.[8] In this kind of studies, Fourier transform infrared spectroscopy (FTIR) was until recently the most widely used vibrational technique for studying natural products. Hydrogen bonding is a very important effect in infrared spectroscopy. This bonding influences the bond stiffness and so alters the frequency of vibration. Many solvents are capable of forming hydrogen bonds to solutes. Apart from solvent effects, concentration and temperature also affect the degree of hydrogen bonding in a compound. The lower the concentration, the less chance there is of two molecules colliding. It follows that the degree of hydrogen bonding decreases with decreasing concentration.[9] The structural properties of polymers can be useful for their identification, particularly, if they are used in conjugation with

other techniques such as Raman spectroscopy. Raman spectroscopy has provided valuable information on polymer properties such as their macro and supermolecular structure. For example, it has been found useful for the identification of polymer–polymer interactions, polymer–solvent interactions, and additives in polymers and has been applied in a number of recent studies to the investigation of the sorption certain liquids into polymer. Raman spectroscopy is particularly an ideal technique for examining the effect of water on polymers. Unlike infrared spectroscopy, which suffers from the disadvantages that the infrared spectrum of water is strong and masks the polymer spectrum, the Raman spectrum of water is weak and causes no interference.

The objective of this study is to prepare and characterize the PVA/IC interpolymer complexes. The miscibility of two interpolymer complexes in the solid state due to intermolecular and intramolecular interactions and the influence of water on the spectrum of polymers in the determination of interactions between polymer couples are discussed by means of FTIR, FT-Raman, Dispersive Raman, DSC, and TGA. Conversely, the origin of the carrageenans used in this study was identified by using XRF spectroscopy.

EXPERIMENTAL

Reagents
Polymers used in this study, PVA purchased from Merck (Mn = 72,000 g/mole, 99% soluble in water) and potasssium salt of IC (Mn = 216,000 g/mole) were obtained from Shemberg Corporation, Philippines.

Preparation of Interpolymer Complexes
In the preparation of PVA/IC interpolymer complex films (w_l/w_{tot}%; 0, 17, 50, 75, and 100), polymer samples were mixed in 10 mL deionized water. Then, the interpolymer complex solutions were kept for at least 3 h at 90°C. The interpolymer complex films were obtained by slow casting method under reduced pressure in polystyrene petri dishes over a period of day. Once casting was complete, the films were kept at 50°C in vacuum for an additional day.

Materials and Methods
During the dissolving of PVA, and IC at 90°C, intramolecular hydrogen bonds of PVA, IC homopolymers are destroyed and are turn to amorf structure. Afterwards the solution casting, polymer couples reorganize and form an interpolymer complex. All these deformation and reorganization processes, film samples were investigated in terms of the interactions of the homopolymers and interpolymer complexes, whether intramolecular or intermolecular hydrogen bonding by means of FTIR and Raman in the 4000–400 cm^{-1} range used in a structural analysis of biopolymers of the polygalactane type and also DSC and TGA. Conversely, the natural source of IC, which was unknown, was also investigated by X-ray fluorescence.

XRF analysis was performed with an Oxford ED2000 XRF spectrometer at a power of 50 W (max. 50 kV and 1 mA). FTIR spectra of PVA, IC and their interpolymer complexes were measured with FTIR Thermo Nicolet 8700 spectrometer on KBr pellets in 4000–400 cm^{-1} range, where 64 scans were taken at

4 cm^{-1} resolution. FT-Raman spectra of samples were recorded with Thermo Nicolet NXR FT-Raman spectrometer in the 4000–400 cm^{-1} range, where 64 scans were taken at 4 cm^{-1} resolution and at 1.5 kW power of 1064 nm laser source. Dispersive Raman spectra of samples were taken with Thermo Nicolet Almega XR spectrometer equipped with confocal microscope at a 532 nm laser source. All spectra of samples were scanned at 100 (m slit width, at 4000–500 cm^{-1} range and at 10× magnification. The glass transition temperatures of pure PVA and its interpolymer complexes with IC were determined by using of Thermal Analyzer TA DSC 2010 differential scanning calorimeter system. The samples were thermally analyzed in a nitrogen atmosphere in two scans between 20 and 175°C. The first scan showed a broad endotherm between 50 and 160°C due to the presence of residual water. The second scan showed no such endotherm. Between two heating scans the samples were kept at 175°C for 3 min and then quenched to 20°C with ice. The reported glass transition temperatures were those from the second heating scan. Dynamic weight loss tests were conducted on a Thermal Analyzer TA TGA 2050 thermogravimetric analyzer system. All tests were performed under nitrogen condition (25 mL/min) using sample weights of 5–10 mg over a temperature range 20–600°C at a ramp rate of 10°C/min.

RESULTS AND DISCUSSION

XRF Analysis

Carrageenan used was natural local product of Philippines and the source of their raw materials was unknown. To characterize the origin of $\imath$-carrageenan, sample has been subjected to elemental analysis by X-ray fluorescence. As it is well-known, carrageenan from *Euchema* specie of marine red algae of the class *Rhodophyceae* is extracted only by using of potassium hydroxide. Conversely, carrageenan from the other species (e.g., *Chondrus*, *Gigartina*, and *Fucellaria*) of marine red algae of the class *Rhodophyceae* is extracted only by using of sodium hydroxide.[10] In the XRF spectra of IC, two peaks at 3.3 and 3.6 kV were observed which were characteristic peaks of potassium K and K1α. Regarding to this result, It could be said that IC was a potassium salt of IC. It also demonstrated that $\imath$-carrageenan was *Euchema* specie of marine red algae of the class *Rhodophyceae*.

Differential Scanning Calorimetry (DSC) Analysis

Differential scanning calorimetry (DSC) was used to assess the extent of interpolymer complexing between IC and PVA. It sensitively detected the small heat capacity change due to glass transition of PVA and its interpolymer complexes with IC (Figure 1). Interpolymer complexes of PVA/IC and IC are amorphous and do not exhibit melting endotherm, whereas PVA is semicrystalline and exhibits a melting endotherm. Generally, the observation of a single glass transition temperature for an interpolymer complex of a pair, between those of the homopolymers, is regarded as decisive evidence of unique environment and of polymer complexibility.[11] In the present DSC study, however, a single T_g is not necessarily a sign of complexibility, since cast IC itself does not show any features to which the glass transition temperature could be related. Conversely, T_g of film form PVA (1.7 wt %) was estimated to be 76°C. Additional DSC analysis of PVA sample was run in powder form and T_g
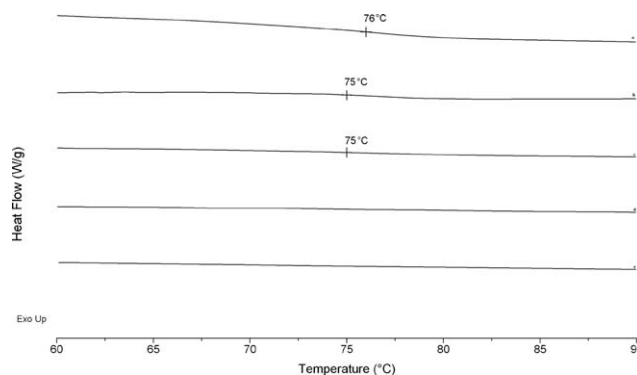
Figure 1. DSC thermograms of PVA/IC IPCs containing various percent of IC between 60 and 90 °C: (A) 0%, (B) 17%, (C) 50%, (D) 75%, (E) 100%.

was estimated to be 102°C. This difference (26°C) was most probably due to the plasticizing effect of the bound water in PVA film sample. Despite the PVA was dried in a vacuum at 50°C for a day, it was clear that this treatment was not sufficient to completely remove the bound water.[12] For interpolymer complexes with an increasing amount of IC, the T_g gradually lost its prominence and became more diffuse. Consequently, it became increasingly difficult to determine exactly the location of the discontinuity in heat flow as the IC content in the interpolymer complexes increases, and it was impossible to locate it in the interpolymer complexes with more than 75% IC.

Thermogravimetric Analysis

To examine the composition effect on thermal degradation of PVA/IC interpolymer complexes, typical weight loss (TG) and derivative of weight loss (DTG) curves were shown in Figures 2 and 3 for PVA/IC, respectively. From the TG curves initial degradation temperature and final degradation temperature, and from DTG curves, the maximum temperatures of weight loss were also determined.

Two reaction stages [Figure 2(Aa,Ba)] in TGA thermogram and double peaks in the DTG curve [Figure 3(A)] were observed from the TG curve of PVA homopolymer. The first stage, which began at 236°C and reached maximum at 267°C, mainly involved dehydration accompanied by predominately polymers with conjugated unsaturated structures. In the second stage, the polyene residues were further degraded at 456°C to yield carbon and hydrocarbons. Thermal decomposition of PVA was also deduced by Tsuchiya and Sumi and results were in agreement with those of reported.[13]

Typical weight loss curves of IC were shown in Figures 2(Ae,Be) for IC. From Figures 2(Ae–Be), the mass loss of IC began at ~ 244°C and reached maximum at 247°C. One reaction stage was observed from the TG curves of IC, which was reflected single peak in DTG curves. Conversely, for interpolymer complexes, degradation took place in two stages. The first stage began at 236°C and the second stage started at 412°C and completed at 458°C. The first and second stage was attributed to the PVA segments and IC in the interpolymer complexes, respectively. As could be seen from Figure 2(A,B), the initial thermal
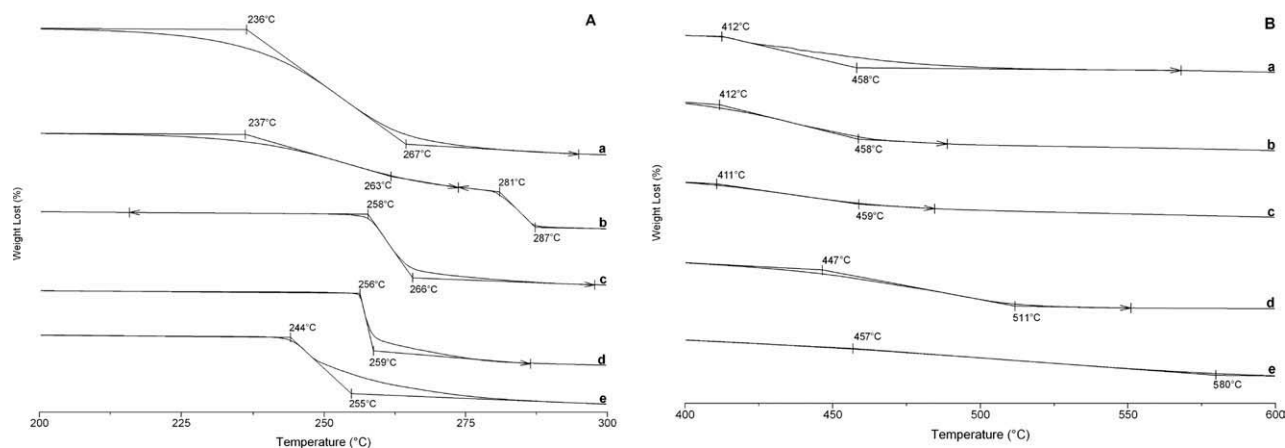
Figure 2. TGA thermograms of PVA/IC interpolymer complexes containing various percent of IC between 200 and 300°C (A) and 400 and 600°C (B): (a) 0%, (b) 17%, (c) 50%, (d) 75%, (e) 100%.

degradation temperature of PVA/IC interpolymer complexes decreased from 276 to 256°C with IC content. Maximum thermal degradation temperature of PVA/IC interpolymer complexes were also noted from Figure 3, and it was found that the maximum thermal degradation temperature of PVA/IC interpolymer complexes decreased from 279 to 257°C with IC content.

As could be depicted from Figures 2 and 3, weight lost and derivative weight lost curves of 17% PVA/IC interpolymer complexes was different with the other content of IC interpolymer complexes. Their decomposition regimes are in three stages. In the first stage, bound water is removed, and then PVA is decomposed to hydrocarbons and in the third stage IC component of the interpolymer complex is decomposed.

Degradation Studies
To support TGA results, a series of FT-IR analysis of 17% PVA/IC interpolymer complexes were conducted at ambient temp., 200, 225, 255, 275, and 300°C and their FT-IR spectrum were recorded (Figure 4). These temperatures were selected according to initial and final temperature of each decomposition stages of 17% PVA/IC interpolymer complexes. In this estimation, the spectral band dissappearance was based on against to temperature rise. In this regard, 1438 cm^{-1} (CH$_2$ deformation) bands for PVA, 1565 cm^{-1} (C=O deformation), 1730 cm^{-1} (C=O stretching) of carbonyl stretching for poly(vinyl acetate) (PVAc), which was unhydrolized residue of PVA, 1250 cm^{-1} (O=S=O), 1070 cm^{-1} (C—O—C linkage), 930 cm^{-1} (C—O stretching), 850 cm^{-1} (C—O—S), and 805 cm^{-1} (C—O—S) bands for IC were followed to characterize the FT-IR spectrum. Between ambient temp. and 200°C, dehydration of residue and bound water was observed. At 200°C, it was seen that the decomposition of the carbonyl and CH$_2$ group of unhydrolized PVAc and PVA started and this decomposition was followed by the vibrations bands at 1730 and 1565 cm^{-1} for PVAc and 1438 cm^{-1} for PVA. At 225 and 255°C, the decomposition of the functional groups at 200°C accelerated and was more evident. At 275°C, vibrations bands of PVA and PVAc completely dissappeared. Ethoxy group on the β(1-4)-D-glycosidic ring of IC at 930 cm^{-1} was also destroyed and dissappeared at 275°C. In the final heating step at 300°C, sample was evaluated to the identify the

ester sulphate decomposition at 1250, 850, and 805 cm^{-1} for IC, and also the ether linkage decomposition at 1070 cm^{-1} for IC. It is observed that all vibration bands dissappeared. Regarding to results, decomposition slightly started at 200°C and finalized around 300°C and it caused to carbon–carbon double bond (—C=C—) formation at 3022 cm^{-1}. When temperature was rised gradually, the intesity of (—C=C—) band was more evident.

PVA was more thermally stable than IC because the max. decomposition peak of PVA appeared at higher temperature than that of IC. As the component of IC increased in the interpolymer matrix, the peak of PVA in interpolymer complex appeared at higher temperature and after 50% of IC content in the interpolymer complex, the peak of PVA appeared at lower temperature. This behavior was attributed the synergistic effect of both pairs in the interpolymer complex. To better understanding of thermal stability and decomposition of the interpolymer complex as the content increament of IC, a serial of interpolymer complexes were prepared varied from 0 to 100%. Their initial and maximum decomposition temperatures were
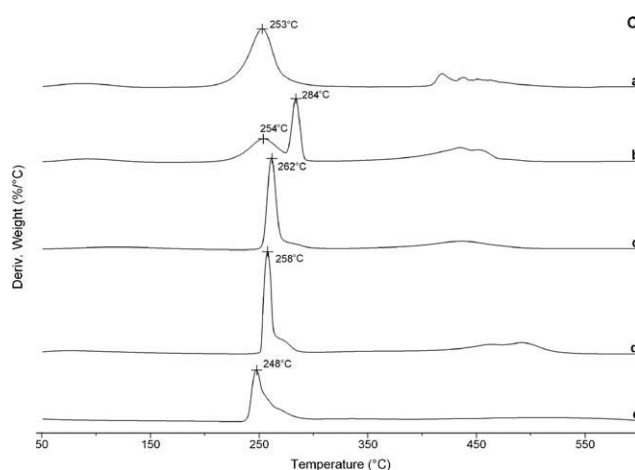
Figure 3. DTG thermograms of PVA/IC interpolymer complexes containing various percent of IC: (A) 0%, (B) 17%, (C) 50%, (D) 75%, (e) 100%.
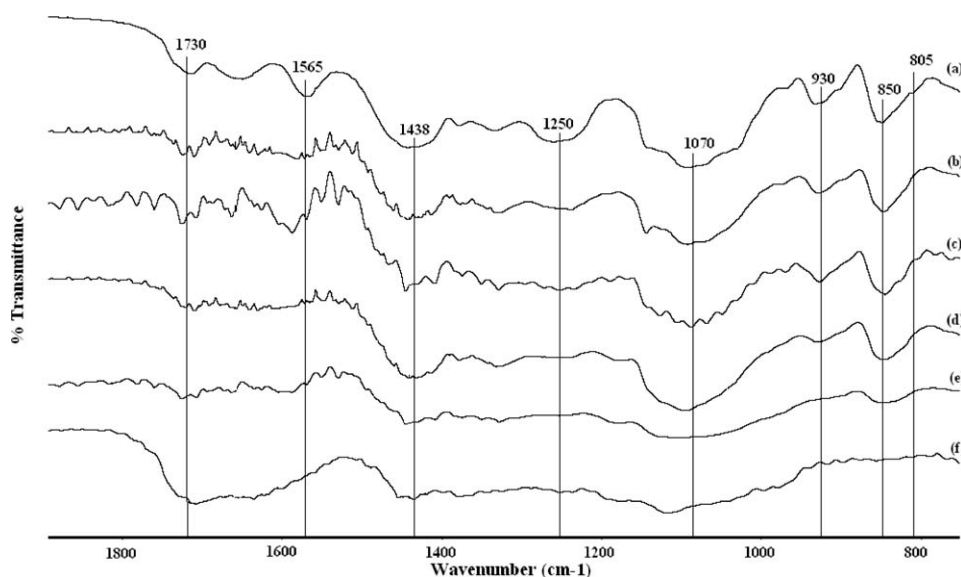
Figure 4. FT-IR spectrum of 17 % PVA/IC interpolymer complex heated up to (a) ambient temp., (B) 200°C, (C) 225°C, (D) 255°C, (E) 275°C, (F) 300°C.

calculated and presented at Table I. As it is seen from Table I, the most stable interpolymer complex is at 17% content of IC because of a sharp increment at initial and maximum decomposition temperature. This stability is attributed to the strongest hydrogen bonding interaction between polymer pairs. In addition, this stability is enhanced because sufficient hydroxyl groups on each chain are suitable placed to form a hydrogen bond rather than those of other IC content of interpolymer complexes.

FTIR Analysis

FTIR spectroscopy is one of the most powerful techniques for investigation of multicomponent systems, because it provides information on the polymer–polymer and polymer–solvent interaction as well as on the blend and interpolymer complex composition. In this part of the study, our discussion will mainly concentrate on the hydroxyl stretching vibration bands, which are expected to be affected by hydrogen bonding interactions. FTIR spectra for IC, and PVA/IC interpolymer complexes and PVA were recorded and shown at Figure 5. As it is seen from Figure 5, the O—H stretching region of the pure PVA consisted of a broad band centered at 3385 cm^{-1}, was attributed to a wide distribution of hydrogen bond hydroxyl groups. Stretching vibration of hydroxyl groups appearred at around 3395 and 3565 cm^{-1} for IC. The —OH stretching vibration at 3565 cm^{-1} peak in the pure IC did not appear in the interpolymer complex samples and not only the characteristic shape of the spectrum of IC change in the interpolymer complex but also the center of the broad hydroxyl band of the interpolymer complex broaden and also shifted to a higher frequency with an increasing concentration of IC. This change reflected an increase in hydrogen bonding between PVA hydroxyl group and IC hydroxyl groups. Such an interaction indicated that the PVA/IC was miscible, and there was also comprised a stronger hydrogen bonding interaction between —OH of PVA and IC in the interpolymer complex. In this study, ester sulfate and ether groups contribution to hydrogen bonding was also investigated. Stretching vibration

bands of sulfate ester group of IC appeared at 1255 and 805 cm^{-1} (Figure 6) while that of interpolymer complex appearred at same frequency. Ether group interaction could be identified by a strong C—O stretching band near 1070 cm^{-1} (Figure 6) in this type of polymer. But, there was no significant peak shift of sulfate ester groups and ether group band in the interpolymer complex, indicated that the involvement of the sulfate ester groups and ether group in interaction with PVA was not significant. To better understanding of interaction, spectra subtraction technique was applied to 50% PVA/IC interpolymer complex. Intermolecular interactions in the interpolymer complexes may be elucidated by comparing the spectra of the IC with the subtraction spectra that should represent the spectra of IC resulting from intermolecular interactions with PVA in the interpolymer complex. In this regard, spectra of PVA was subtracted from the spectra of interpolymer complex to give spectrum of IC. It was known that 1438, 1569, and 1715 cm^{-1} bands of PVA were the only absorption bands without any superposition of those due

Table I. Initial and Maximum Decomposition Temperature of PVA/IC Interpolymer Complexes

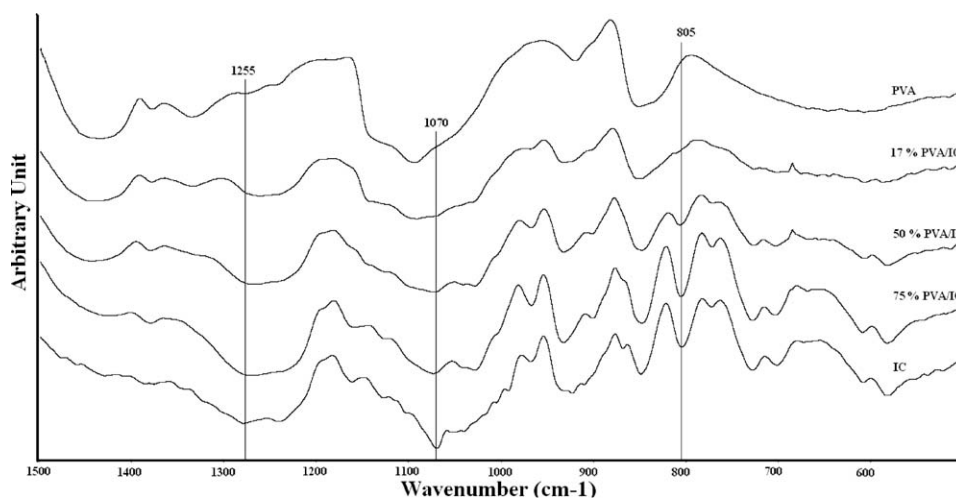|	PVA/IC	
IC (%)	Initial decomp. temp. (°C)	Max. decomp. temp. (°C)
0	236	253
9	234	252
17	237–281	254–284
25	276	278
40	266	268
50	258	262
57	265	266
62.5	257	259
75	256	258
100	244	248
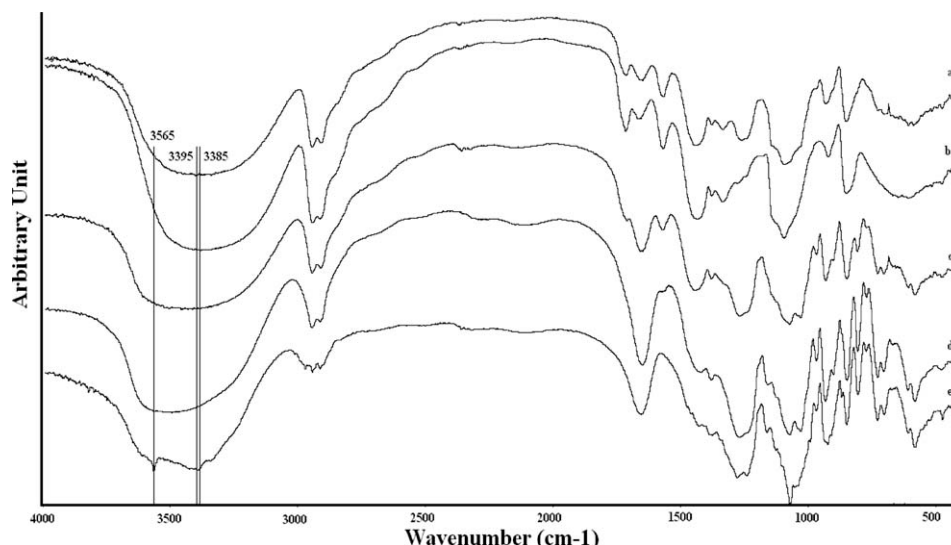
Figure 5. FTIR spectra of (A) PVA, (B) 17% (% w_l/w_{tot}) PVA/IC, (C) 50% (% w_l/w_{tot}) PVA/IC, (D) 75% (% w_l/w_{tot}) PVA/IC, (E) IC.

IC. In the subtraction spectrum, the 1438, 1569, and 1715 cm^{-1} bands were cancelled out. The spectra of interpolymer complex was very similar to that of PVA, and the subtraction spectra shown the characteristic IC spectrum. The detailed characteristic feature in the 1800–800 cm^{-1} region of IC in spectra was well reproduced in the subtraction spectrum. The differences between the subtraction and IC spectra were attributed to arise from intermolecular interactions of —OH groups between IC with PVA in the interpolymer complex.

Hydrogen bonding formation is also possible between the appropriate groups within the one molecule. This is known as intramolecular hydrogen bonding. To identify, the intramolecular hydrogen bonding in the prepared film samples was investigated by following the band shift of hydroxyl, ester sulfate and ether groups of homo polymers and interpolymer complexes. If there is an intramolecular hydrogen bonding interaction in any polymer complex, there must be a band shift toward to upper

or lower frequency value when the samples prepared in a unit volume and increasing amount of solute. When the amount of solute is increased in a constant volume, the contingency of intramolecular interaction of functional group accompanying the hydrogen bonding increases.[14] In concentrated samples, the distance between the functional groups responsible from the hydrogen bonding shorthens and leads to better interaction than the lower concentrated samples in liquid or solid form. In this regard, a new set of film samples were prepared containing equal amount (50% w/w) of PVA with IC in constant volume of water. Solute content was varied from 100 to 300 mg for homo polymers, and 50% (w/w) of interpolymer complexes in a constant volume (10 mL) of solvent. By comparing those of prepared samples spectrum, —OH band wavenumber value of the prepared PVA/IC (50/50, w/w) interpolymer complex samples in three different weights (100, 200, and 300 mg) shifted to 3450 cm^{-1} from 3400 cm^{-1}. This change in the —OH band

Figure 6. The change at the sulfonic acid groups (805 and 1255 cm^{-1}) and ether (1070 cm^{-1}) vibration bands of PVA/IC interpolymer complexes by increasing the IC concentration.

wavenumber trending to increase or decrease in the prepared samples of PVA/IC in same mass and ratio was the evidence of intramolecular hydrogen bonding. Ueda and Brady computed the molecular mechanic and dynamic calculations of nonsulfated ι-carrageenan by computer simulation method. The hydroxyl group of polymer and solvent interaction were shown beside the intramolecular interactions for polymer solutions by using Monte Carlo simulation method.[15] Ester sulfate and ether bands were also evaluated. But, any significant contribution to the intramolecular hydrogen bonding was not observed.

As mentioned in materials and methods, PVA used in this study is 99% hydrolized and 1% is poly(vinyl acetate) (PVAc). The carbonyl group of PVAc may also contribute to interpolymer complex formation. It is therefore, the investigation of carbonyl group contribution to interpolymer complex formation is also important. In this regard, 1730 cm^{-1} carbonyl stretching was followed. Hovewer, any band shift toward to higher or lower frequencey at 1730 cm^{-1} was not observed. This result was attributed to PVAc content in PVA which was insufficient to create a hydrogen bond with the functional groups of IC.

Raman Analysis

PVA is a hydrophilic polymer and has a tendency to intramolecular as well as intermolecular hydrogen bonding. It is therefore, determination of the polymer interaction origin is difficult while water is used as solvent.[16] In this study, homo polymer of PVA, IC and interpolymer complex of PVA/IC were prepared by using water. Thus, the source of the —OH band shift and broadening of IR spectra of the homopolymer and interpolymer complex were tought to be the interactions among the water molecules and the —OH group of PVA, and IC. Two methods were applied to determine the source of interaction. First was to use an apolar and/or IR inactive solvent in the preparation of the samples. Several solvents were examined, but any homogeneous solution was not obtained to be used in the solution casting technique. Second was to record of the Dispersive and FT-Raman spectra free from the bounded water or water and to compare the band shifts with FT-IR results.

FT-Raman Analysis

PVA, IC, and their interpolymer complex samples used were prepared in different weight fractions by solution casting technique. The recorded spectrum of PVA/IC films were presented at Figure 7(A). As it could be seen from Figure 6(A), Raman band of —OH group of interpolymer complex components shifted to lower and higher frequency value. As it was clearly seen from Figure 7(A), the maximum interaction between PVA/IC was observed at the weight fraction of 17%. As it was defined before, shifting to lower frequency value means lower vibrational energy used in the interactions of each interpolymer complex component and exhibits the increment of interaction among the PVA/IC. As in elucidated in FTIR analysis by comparing the spectrum of the pure IC with the subtraction spectrum, same methodology was also applied to FT-Raman spectrum. It was found that the differences between the subtraction and IC spectra were aroused from intermolecular interactions —OH groups between IC and PVA. Other sources of interaction among IC with PVA due to potential tendency of hydrogen bonding groups of ester sulfate,
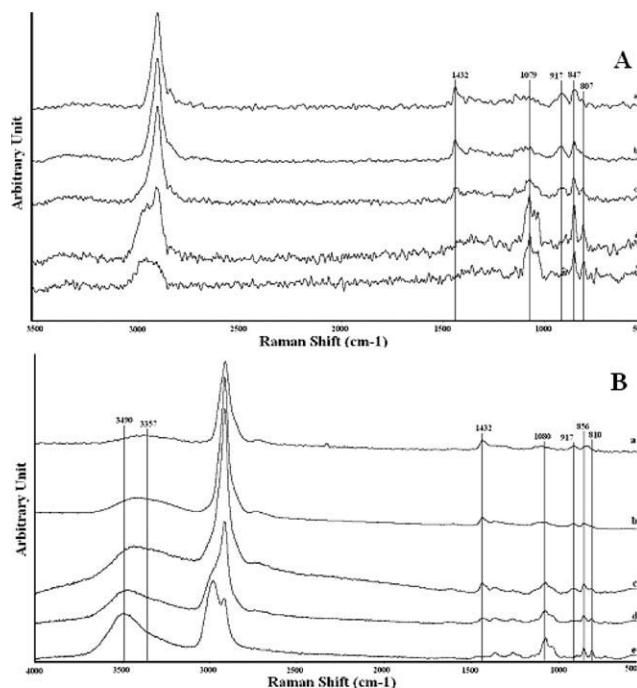
Figure 7. FT-Raman (A) and Dispersive Raman (B) spectra of (a) PVA, (b) 17% (% $w_(/w_{tot}$) PVA/IC, (c) 50% (% $w_(/w_{tot}$) PVA/IC, (d) 75% (% $w_(/w_{tot}$) PVA/IC, (e) IC.

and ether of IC were also investigated by FT-Raman. 1432 cm^{-1} (CH_2 deformation), 917 cm^{-1} (CH_2 symetric ring vibration), 847 cm^{-1} (C—O—S ring stretching), 807 cm^{-1} (C—O—S ring stretching of second ester sulfate group of IC), and 1079 cm^{-1} (C—O—C stretching) were followed. As could be seen from Figure 6(A), there was no frequency shift at the followed frequency band values. By this result, interaction among the polymer couples was attributed to —OH group of PVA and —OH groups of IC responsible from the hydrogen bonding resulting with the interpolymer complexation.

Dispersive Raman Analysis

For the correlation of FT-Raman results, Dispersive Raman analysis was performed. In this regard, Dispersive Raman spectra was recorded under confocal microscope at 10× magnification [Figure 7(B)]. Confocal microscope allowed the imaging and homogenity analysis of surface and depth profiling. As it was determined from Figure 7(B), Raman band of —OH group of interpolymer complex components shifted to lower and higher frequency value. But the maximum interaction between PVA/IC was observed at the weight fraction of 17%. Spectrum subtraction methodology was also performed for Dispersive Raman spectrum. The results were alike FT-Raman results and it was found to be the same intermolecular interaction —OH groups of PVA and IC) between IC with PVA in the interpolymer complex. Ester sulfates and ether groups contribution to the interaction were also investigated and was followed the bands at 856 and 810 cm^{-1} (C—O—S ring stretching of IC), 1080 cm^{-1} (C—O—C stretching of IC). As could be seen from Figure 6(B), there was no frequency shift at the followed frequency band values. By this result, interaction among the

polymer couples was attributed to ─OH group of PVA and ─OH groups of IC as found FTIR and FT-Raman analysis.

Stoichiometry of IPC formed at pH = 6.0

The ratio between the structural units interacting to fort the IPC structure, known as stoichiometry of the complex, is an important characteristic of IPCs. To determine the stoichiometry among the polymer pairs, pyrene probe method of luminescence technique has been applied. In the IPC film preparation, pyrene (1 μM) was added to IPC solutions and then casted. In these experiments, the excitation wavelength of pyrene added IPCs was $\varepsilon_{ex} = 276$ nm. The polarity was determined through the intensity ratio (I_3/I_1) of the third (550 nm) to the first vibronic peak (403 nm) of emission fluorescence spectrum of pyrene in the presence of polymers.

The pyrene solubilized in PVA/IC film gives the information on the stoichiometry and also hydrophobicity. In this study, it is foud that the stoichiometry of PVA/IC complex formed at pH = 6.0 is 2 : 1 mole units for each composition indicating that the hydrophobicity of IPCs is slightly more than the polymer components. Khutoryanskiy's research group found that the stoichiometry of PAA/HPC complex formed at pH = 3.4 is 4 : 1 mole units, whereas at pH = 3.6 it reaches 10 : 1 mole units and also reached the same conclusion.[17]

General Remarks

Thermal and spectroscopic characterization of PVA/IC interpolymer complexes as well as homopolymers of PVA and IC was performed by DSC, TGA, FTIR, Raman, and XRF techniques. The natural source of ι-carrageenan was determined by XRF analysis, and found to be as potassium salt and *Euchema* specie of marine red algae of the class *Rhodophyceae*.

The thermal stability and decomposition of PVA, IC, and their interpolymer complexes were investigated by means of TGA and DTG techniques. IC exhibited a single peak, indicating a single degradation mechanism, whereas the interpolymer complexes exhibited two peaks except 17% content of IC (three stages decomposition), whose shapes and positions dependent on composition.

FTIR, Raman, DSC, TGA, and DTG measurements shown that the PVA/IC interpolymer complexes exhibited considerable miscibility in the amorphous regions above 17 wt % IC content. But the strongest interactions between those polymer pairs were observed on 17% IC content.

In the result of the spectral analysis of FTIR and Raman, the hydroxyl band of IC progressively shifted to a higher frequency up on interpolymer complexing with PVA and was determined that the existence of hydrogen bonding interactions was between hydroxyl group of PVA and IC. But, the contribution of sulfate ester and ether groups of IC to the hydrogen bonding interactions was not significant. Conversely, the degree of miscibility was pointed out by the increament in the degree of intermolecular hydrogen bonding. In this regards, it was observed that 17% of PVA/IC was the most miscible and intercomplexable weight fraction of PVA/IC. After hydrogen bond formation between PVA and IC, the stretching of the hydroxyl group bond reduced.

As concluded by the results of thermal and spectroscopic techniques, interaction among both polymer pairs goes through ─OH groups on the macromolecular structure of both polymers. But in the IPC formation, atoms interact and generate hydrogen bonding. As energy and frequency are directly proportional, high frequency has a high energy. When ─OH bands in the Raman and FTIR spectrum were interpretated, an increase in ─OH vibration band frequency of PVA by decreasing of PVA content in the IPCs and a decrease in ─OH vibration band frequency of IC by increasing of IC content were determined. Regarding to results, it could be said that the interaction mainly was occured between hydrogen atom of the IC hydroxyl groups and the oxygen atom of PVA hydroxyl group (Scheme 1).

The results reported here provide a clear indication that interpolymer complexes of IC with PVA are miscible and complexable over the whole composition range and that the miscibility and complexibility is driven by hydrogen bond formation most probably due to the interaction between the hydroxyl groups of IC and the hydroxyl functionalities of PVA.

REFERENCES

1. Giusti, P.; Lazzeri, L.; Barbani, N.; Lelli, L.; De Petris, S.; Cascone, M. G. *Macromol. Symp.* **1994,** *78,* 285.

2. Paul, D. R.; Newman, S. Polymer Blends; Academic Press: New York, **1978.**

3. Olabisi, O.; Robeson, L. M.; Shaw, M. T. Polymer-Polymer Miscibility; Academic Press: New York, **1979.**

4. Hoffman, A. S. *Adv. Drug Del. Rev.* **2002,** *54,* 3.

5. Gudeman, L. F.; Peppas, N. A. *J. Memb. Sci.* **1995,** *107,* 239.

6. Gudeman, L. F., Peppas, N. A. *J. Appl. Polym. Sci.* **1995,** *55,* 919.

7. Larsen, C. *Adv. Drug Delv. Rev.* **1989,** *3,* 103.

8. Coleman, M. M.; Painter, P. C. *Prog. Polym. Sci.* **1995,** *20,* 1.

9. Stuart, B. Infrared Spectroscopy: Fundamentals and Applications; Wiley: New York, **2004.**

10. Kantoğlu, Ö. Ph.D. Dissertation, Department of Chemistry, Gazi University: Ankara, Turkey, **2006.**

11. Stoelting, J.; Karasz, F. E.; MacKnight, W. *J. Polym. Eng. Sci.* **1970,** *10,* 133.

12. Park, J. K.; Kim, D. W.; Kim, C. H.; Maeng, K. S.; Hwang, T. S.; Kim, Y. C. *Polym. Eng. Sci.* **1991,** *31,* 867.

13. Tsuchiya, Y.; Sumi, K. *J. Polym. Sci.* **1969,** *7,* 3151.

14. Janaswamy, S.; Chandrasekaran, R. *Carbohydr. Res.* **2001,** *335,* 181.

15. Ueda, K.; Brady, J. W. *Biopolymer* **1996,** *38,* 461.

16. Malfait, T.; Vandael, H.; Vancauwelaert, F. *Carbohydr. Res.* **1987,** *163,* 9.

17. Dubolazov, A. V.; Nurkeeva, Z. S.; Mun, G. A.; Khutoryanskiy, V. V. *Biomacromol* **2006,** *7,* 1637.