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SCIENTIFIC PAPER

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SYNTHESIS AND CHARACTERIZATION OF HEMICELLULOSE-BASED POLYMERIC GEL FILM FROM TEA LEAF BREWING WASTE

Article Highlights

- Tea leaf brewing waste occurring as a result of the tea brewing process is a domestic waste
- There is no economic use area of tea leaf brewing waste
- Tea leaf brewing waste is a potentially suitable waste for the production of bio-film
- The characterization results of production films are promising for the packaging sector

Abstract

In this study, hemicellulose-based polymeric gel films were synthesized using the free radical polymerization mechanism. Hemicellulose was obtained from tea leaf brewing waste by using delignification process. Polymeric gel films were produced in accordance with solution-casting technique. The effects of synthesis parameters were investigated on the structure and properties of gel films. For this purpose, the hemicellulose-based synthesized gel films were characterized by analytical test. Experimental results indicated that hemicellulose-based gel films absorbed moisture at the rate of maximum 1% in 100% relative humidity environment. The lowest water vapor permeability (WVP) value was measured to be 5.88×10^{-10} *g/(s Pa m), for the hemicellulose-based film including chitosan. The average solubility values of the produced polymeric films varied between approximately 0.4 and 1.8%. It was observed that the optical transparency of hemicellulose-based polymeric gel films changed from about 45 to 65% and the opacity/thickness values were from 0.0027 to 0.0011* μm^{-1}*. As a result, it was found that the physicochemical and morphological properties of the synthesized films are greatly influenced by the composition of the films.*

Keywords: biodegradable, hemicellulose, polymer, gel film, characterization.

Especially in the last fifteen years, in order to overcome both the raw material reserve bottleneck and environmental problems, new and sustainable resources are investigated in the production of polymer products. For this purpose, the studies on the production of environmentally friendly natural polymeric materials with biodegradablity have been intensified by evaluating the resources available in the nature [1,2]. The most common investigated biodegradable polymeric materials are starch and polylactic acid-based plastics, although these are commercially used in a limited area. Although the strength and optical properties of starch and polylactic acid-based plastics are good, it is thought that their use in the production of polymeric materials will cause problems in the near future and will compete with food functions. Due to the concerns related to possible and serious food shortage that may arise in the future, research and development studies have shifted towards the biodegradable plastics obtained from natural sources that do not have nutritional functions. In previous studies, it was pointed out that the different parts (bodies and roots) of lignocellulosic biomass sources were used to produce biodegradable polymeric materials. The fact that the economic values of

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the waste biomass resources are extremely low and that they do not have any food-related functions have caused their evaluation in the production of biodegradable plastic products [3,4]. Specific investigations have been started to be caried out within the framework of the evaluation of agricultural wastes as natural resources in the production of plastic materials [5]. Although specific studies have been started to improve the mechanical, elastic and water resistance properties of the produced polymers in order to compete with the petroleum-based polymeric products in the commercial field, there are ongoing questions of commercial, technical and sustainable economic resources yet to be evaluated.

Turkey is a country with a wide variety of agricultural products. As a result of agricultural activities, a large amount of waste is released. According to biomass energy potential atlas (BEPA), Turkey has reserves of about 62 million tons of agricultural waste per year. The annual energy equivalent to this waste potential is approximately 25 MTPE. The residual tea leaf, as a side product of the tea brewing process, is an agricultural waste. According to the Global Tea Statistics Report (2019) [6] and a statistical report published by tea manufacturers (2018) [7], the consumption of tea is approximately 3.5 kg per person per year. In addition, 270,000 tons of dry tea are produced each year in Turkey. In the light of these reports, it is understood that “tea leaf brewing waste reserve” has a significant potential to be evaluated in Turkey. However, the waste (tea leaf brewing waste) does not yet have an economic value and a suitable using area. To generate more income from agricultural activities, to protect the environment and nature, and to accelerate socio-economic development, it is necessary to collect and evaluate these wastes. Apparently, although the collection of agricultural wastes leads to additional costs, the fact remains that these wastes can be used in the production of biopolymers.

In this study, the aim was to produce polymeric gel films from tea leaf brewing waste which is a domestic waste. Tea leaf brewing waste has previously not been evaluated for the production of polymeric materials. Produced gel films have been predicted to have highly water-resistant and optical properties, low vapor water permeability and moisture holding capacity (which acts as a water vapor barrier).

MATERIAL AND METHODS

The study was carried out in two stages. In the first phase of the study, the tea leaf brewing waste was obtained from the local commercial enterprises and then hemicellulose was isolated from tea leaf brewing waste by delignification method. In the second stage, the polymeric gel films were produced by polymerization of hemicellulose. Polymeric gel films were produced in accordance with the solution-casting technique. The effects of various synthesis parameters, such as type and amount of co-monomer, crosslinker and initiator, were investigated on the physicochemical and optical properties of the gel films. For this purpose, the produced gel films were characterized. The water vapor permeability test, moisture retention capacity test, equilibrium and dynamic swelling tests, and light permeability tests of the gel films were performed.

Materials

The following chemicals (Table 1), which were used in polymeric film synthesis as co-monomer, crosslinker or initiator, were purchased from Sigma--Aldrich. The chemicals used in the synthesis process were analytical grade or high purity degree. Chitosan with a molecular weight of 100-300 kDa and a degree of deacetylation of 75-85%, which was used as additive material, was purchased from Acros (New Jersey, USA).

Table 1. The main chemicals and their properties

Chemical	Purity	Chemical formula
Acrylamide (AAm)	99%	$CH_2=CHCONH_2$
N-Isopropyl acrylamide (NIPAm)	≥ 99%	$H_2C=CHCONHCH(CH_3)_2$
N,*N*′-Methylenebis (acrylamide) (BIS)	99%	$H_2C=CHCONH)_2CH_2$
Ammonium persulfate (APS)	98%	$(NH_4)_2S_2O_8$
Asetic acid	≥99.85%	CH_3CO_2H
Ethanol	Absolute	CH_3CH_2OH
Hydrochloric acid	37%	HCl
Sodium chlorite	80% (RT)	$NaClO_2$
Sodium hydroxide	≥98% pellets	NaOH
Toluene	99.8%	$C_6H_5CH_3$

For tea plants, it is known that the values of these effective parameters vary depending on the climatic conditions, the composition of the soil and the kind of waste from the tea plants, such as field waste and brewing waste. Table 2 provides the characteristic properties of the TLBW (tea leaf brewing waste). The results of the chemical, elemental and proximate analyses of the TLBW seem to have characteristics similar to other biomass samples which are known to have a lignocellulosic structure. The chemical analysis of TLBW indicated that the cellulosic structure was predominant, which is consistent with the volatile substance. It was also understood from the results of the characterization that the TLBW was suitable for evaluation as a raw material in this study.

Table 2. Main characteristic properties of TLBW

Component	Value (%)
Ultimate analysis of TLBW	
C	48.69
H	5.906
N	3.048
O*	42.086
S	0.270
Proximate analysis of TLBW, preliminary analysis	
Volatile matter	73.65
Ash	3.42
Moisture	3.70
Fixed carbon	19.23
Structure analysis of TLBW	
Extractive components	10.03
Hemicellulose	37.20
Cellulose	24.93
Lignin	24.42
Ash	3.420

Extraction of tea leaf brewing waste hemicellulose

The tea leaf brewing waste was collected from local commercial enterprises in Elazığ. The tea leaf brewing waste was pre-dried on polyethylene tarpaulin under atmospheric conditions in the laboratory. Then it was dried in an oven at 80 °C for 48 h. The dried tea leaf brewing waste was ground using a food mill (Renas brand), homogenized and fractionated using a laboratory scale vibratory screen series. The tea leaf brewing waste which has -30+50 mesh particle size was treated for 6 hours with a mixture of toluene and ethanol to remove the oil, wax and resins in the structure of the residual solids. At this step, a Soxhlet extractor was used. After this first step, the hemicellulosic fraction was isolated by delignification process which is one of the chemical pretreatment methods.

The method's operating conditions are presented in detail in Figure 1. The hemicellulosic fraction was isolated by delignification process which is one of the chemical pretreatment methods. Sodium chlorite extraction processes were used for the isolation of the major components (hemicellulose, cellulose and lignin) from various biomass species in previous studies [8-10].

Synthesis of polymeric gel film

Polymeric gel films were produced in accordance with solution-casting technique. The effects of the type and amount of co-monomer, crosslinker, additive material and initiator were investigated on the structure, morphological and thermal properties of the gel films produced.

In order to prepare hemicellulose-based gel films, hemicellulose was dissolved in 10% NaOH solution (solid/liquid ratio: 1/10) at 55-60 °C and 800 rpm stirring speed for 120 min. After complete dissolution of hemicellulose, the solution was cooled to room temperature. Comonomer (AAm or NIPAAm) and crosslinker (BIS) were added to the cooled solution in certain amounts. After that, as additive, a calculated amount of chitosan dissolved in 2% acetic acid solution was added to the solution. Finally, a calculated amount of ammonium persulfate (APS) as a redox initiator was added to the solution. The mixture was homogenized by an ultrasonic homogenizer (Bandelin HD2200). Then the homogenous mixture was quickly poured into the petri dish before the gelation process began. The poured gel films were allowed to dry completely in an oven at 60 °C for 24 h. The gelled films were washed with distilled water to remove the impurities completely. After washing, the polymeric films were again dried under the same conditions. In order to keep the thickness and dimensions of the polymeric films to be produced, standard sized petri dishes of 90 mm×15 mm were used. The compositions of the polymeric gel films synthesized are given in Table 3. The preparation steps are given schematically in Figure 2.

During the synthesis experiments, all pH measurements were performed by a Thermo Scientific Orion 1112000 3-star pH meter. Weighing operations were carried out by an Ohaus brand Analytical Plus model balance with ±0.0001 grams sensitivity. Daihan brand magnetic stirrer and Nuve brand oven were used in the synthesis and drying stages of polymeric gel, respectively.

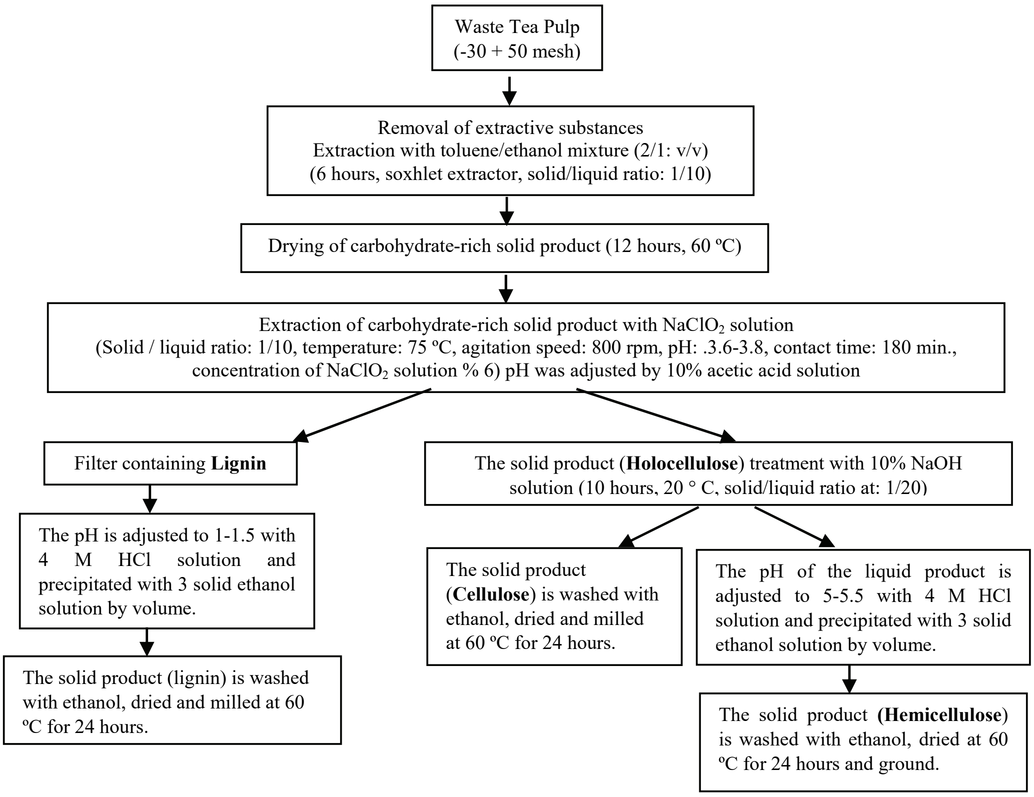


Figure 1. Isolation stages of the hemicellulosic fraction from the tea leaf brewing waste.

Table 3. The composition of hemicellulose-based gel films; CM: comonomer, HC: hemicellulose, C: crosslinker, I: initiator A: additive materials

Polymerization parameter	Type	Range Rate
Comonomer type and ratio	NIPAAm (*N*-*N*-isopropyl acrylamide), AAm (acrylamide)	CM/HC mass ratio: 0/3-3/0
Crosslinker type and ratio	*N*-*N*-methylene bisacrylamide (BIS)	C/HC: 0-5 mass%
Initiator type and rate	Ammonium persulfate (APS)	I/HC: 0-4 mass%
Type and ratio of additive	Chitosan	Chitosan/HC mass ratio: 0/1-0.5/1

Analytical methods

Thickness test. The thickness of the gel films produced in a standard size by casting method was determined using digital thickness gauge (caliper/micrometer). For this aim, the thicknesses of the gel films were measured at five different points for each gel film using a digital thickness gauge with ±0.001 mm accuracy. All analyses and tests applied for the characterization of polymeric gel films were carried out using the films of standard thickness. It was aimed to produce a standard thickness film and to normalize the results obtained depending on the thickness of the films analyzed during the experiments. The opacity test and water vapor permeability test results were presented considering the film thicknesses.

Moisture content test. Moisture content of polymeric films was determined by gravimetric method. For this purpose, a Mettler LJ16 brand moisture analyzer was used. The synthesized films were kept at room conditions (25 °C and 1 atm) until the moisture content reached equilibrium value. The polymeric gel films having the equilibrium moisture content were dried at 60 °C and then the amount of moisture absorbed under atmospheric conditions was read from a Mettler LJ16 brand moisture analyzer. Since the gel film synthesis was carried out at 60 °C, thus the drying temperature was chosen as 60 °C. In addition, the raw materials of biological origin and gel film are dried generally between 40-80 °C.

The film resolution test. The produced gel films were cut to 15 mm in diameter and weighed after drying for 24 h at a temperature of 50±5 °C (W_i). The

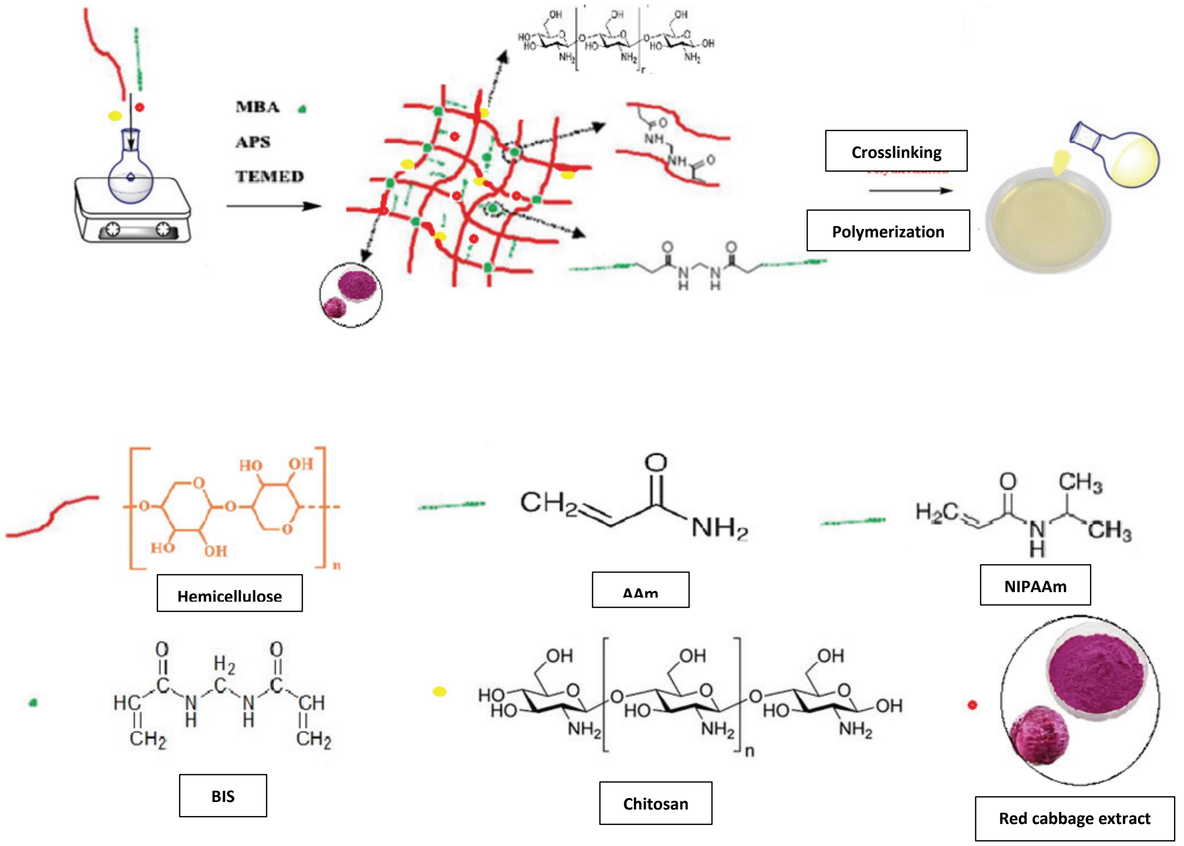


Figure 2. Schematic illustration of gel films preparation.

weighed film samples were put into 20 ml of distilled water for 24 hours at a temperature of 25±2 °C. Then the films were removed from the water, dried at 50±5 °C for 24 h and weighed to determine the final weights (W_f). The % resolution values of the films were calculated from the difference between the first and the last weighing of the films with the following equation (Eq. (1)). All the measurements of gel film samples were performed in duplicate.

$$\text{Resolution}\,(\%) = 100\frac{W_i - W_f}{W_i} \qquad (1)$$

The film's moisture holding capacity test. All samples subjected to this test were conditioned for 24 h at room temperature (approximately 30 °C), then the initial weight of the films was taken (W_i). Each conditioned sample was placed in a glass cabinet at 100% RH at room temperature (about 30 °C). The increase in the weight of the gel films (W_t) was recorded during the conditioning period. For each polymeric gel film, at least two parallel samples were run. The time-dependent moisture retention capacity (MHC) of the films was calculated from the following equation (Eq. (2)). All the measurements of gel film samples were performed in duplicate:

$$\text{Moisture holding capacity } (MHC)(\%) = 100\frac{W_t - W_i}{W_i} \qquad (2)$$

The film's water vapor permeability test. The water vapor permeability test of the prepared films was carried out by gravimetric method which was used in different studies in literature [11-13]. The test was performed using glass tubes filled with silica gel. Hemicellulose-based gel films cut with a diameter of 2 cm were fixed to the glass tubes with the help of tape. Glass tubes prepared in this way were placed in a glass cabinet maintained at 100% RH at room temperature (about 30 °C). The changes in the weight of the glass tubes were monitored for 24 h. The water vapor permeability value of the polymeric films was calculated using the slope values of the lines depending on the difference between the measured final weight of the tubes and the tube weight at the initial conditions of the analysis. The water vapor permeability of the films (WVP) was calculated by Eq. (3) and Eq. (4). As the experiments were carried out with the films of different thickness values, in order to eliminate the effect of film thickness on the permeability, the values were normalized considering the film thickness. Water vapor transfer rate and film thickness normalized water vapor permeability ($NWVP$) values were calculated by considering the equation Eq. (5). All the measurements of gel film samples were performed in duplicate:

$$WVP\left(\frac{\text{g}}{\text{day m}^2}\right)=\frac{\text{Slope}\left(\frac{\text{g}}{\text{h}}\right)\times 24\left(\frac{\text{h}}{\text{day}}\right)}{\text{Film area (m}^2\text{)}} \tag{3}$$

$$VP\left(\frac{\text{g}}{\text{m Pa h}}\right)=\frac{WVP\left(\frac{\text{g}}{\text{h m}^2}\right)\times\text{Film thickness}(\text{m})}{\text{Steam pressure at }30^{\circ}\text{C}(\text{Pa})} \tag{4}$$

$$NWVP=\frac{WVP\left(\frac{\text{g}}{\text{day m}^2}\right)}{\text{Film thickness (m)}} \tag{5}$$

The film's light permeability test. Chebios brand UV-Vis spectrophotometer was used to determine the light transmittance of synthesized gel films. The light absorption values of the gel films were read by scanning in the 200-800 nm wavelength range. The percent permeability of the gel films was calculated using light absorption data (Eq. (6)). The opacity values were determined by taking the permeability values and film thicknesses by considering the following equation, Eq. (7). All the measurements of gel film samples were performed in duplicate:

$$A=-\log T=2-\log\%T \tag{6}$$

$$\frac{\text{Opacity value}}{\text{Film thickness}}=\frac{1-\left(\%\frac{T}{100}\right)}{\text{Film thickness}(\mu\text{m})} \tag{7}$$

where A - absorbance value, T - permeability.

The film's color scale test. In order to determine the universal color scales of the gel films, the photos of synthesized films using different additive ratios under different conditions were taken under the same conditions. Image analysis was performed with the help of MATLAB-R2017 version and Red Green Blue (*RGB*) values of the films were determined.

FTIR analysis. FTIR analyses were used to reveal the functional groups and chemical structure of polymeric gel films. Analyses of polymeric gel films were performed using the ATI Unicam Mattson 1000 model FTIR spectrophotometer. All measurements were conducted in the range from 400 to 4000 cm^{-1} using 16 scans. For this purpose, background screening was performed to prevent interferences from airborne components and this was followed by screening the sample pellets that include the samples under the same conditions.

RESULTS AND DISCUSSION

In this study, based on hemicellulose isolated from tea leaf brewing waste, an environmentally friendly and biodegradable polymeric film, an alternative to existing commercial polymers, was produced. By means of comonomers added to the structure of polymeric gel films, the films were made to be sensitive to environmental temperature changes. By optimizing the cross-linking ratio and adding additives, the physical and water resistance properties of the gel films were tried to be improved. The physicochemical and optical properties of gel films produced in the study were determined and interpreted. As a result, the obtained data and the reached general comments were presented under the main headings as follows.

Thickness and moisture content of gel films. The thickness and moisture content (%) of the produced gel films was given in Table 4. At observations made during experimental studies, it was determined that no gelling was to be formed in the film prepared by

Table 4. Thickness of produced gel films depending on film composition; I: indicator, CM: comonomer, HC: hemicellulose, C: crosslinker, NIPAAm:N-N-isopropyl acrylamide, AAm: acrylamide

Variable	Variable range	Thickness (mm)	Moisture, %	Variable	Variable range	Thickness (mm)	Moisture, %
I/HC mass ratio	0.04/1	0.28	0.349	C/HC mass ratio	0.0135/1	0.25	0.482
	0.03/1	0.27	0.357		0.025/1	0.27	0.440
	0.02/1	0.26	0.347		0.05/1	0.27	0.373
	0.015/1	0.26	0.358		0.1/1	0.28	0.347
	0.01/1	0.25	0.353		0.15/1	0.28	0.337
AAm/HC mass ratio	0.25/1	0.33	0.292	NIPAAm/HC mass ratio	0.25/1	0.36	0.499
	0.5/1	0.38	0.288		0.5/1	0.39	0.326
	1/1	0.42	0.178		1/1	0.41	0.220
	2/1	0.49	0.147		2/1	0.43	0.176
Type of additive	Chitosan	0.38	0.072	Chitosan /HC mass ratio	0.1/1	0.36	0.072
	Montmorillant	0.28	0.108		0.2/1	0.38	0.065
	Chitin	0.26	0.112		0.3/1	0.38	0.067
	Bentonite	0.27	0.097		0.5/1	0.39	0.063

dissolving hemicellulose in pure water and pouring into a Petri dish without using initiator and crosslinker. Only depending on the drying, an approximately 0.2 mm thick film layer was formed in the Petri dish. This result was not presented in the table, since no gelling occurred.

It was determined that the thickness of the cross-linked films, in which gel formation was observed, changed in the range of 0.25-0.49 mm depending on the polymeric composition. It was seen that the thickness of the hemicellulose-based films was largely dependent on the comonomer type and ratio and the type of additive. However, it was found that the crosslinker and initiator ratio had no effect on the thickness of the gel films which were measured in the range of 0.25-0.28 mm. In the literature, it was reported that the thickness of the xylan-based films obtained from cotton stalk was 0.29-0.38 mm and the thickness of hemicellulose-based films isolated from oil palm leaves and sugar beet pulp was between 0.13-0.15 mm [14,15]. The thickness of the produced films in this study was in conformity with the previous studies.

But, Mendes *et al.* (2017) [16] reported the thickness of the hemicellulose films in range from 0.061-0.077 mm in their paper. These values are far lower than the values for our hemicellulose-based film. Table 4 shows that the moisture content of the gel films is less than 1%. The obtained MC values of gel films are far lower than previous with those presented by other authors for chitosan and hemicellulose-based films [17,12]. Unlike our current work, in these previous studies presented in literature, the films were produced without a cross-linking agent. The produced films are not in gel form. Therefore, the produced films have a high water affinity and are water soluble.

Result of solubility of gel films. The solubility value of the films in water is important if used in packaging material or biomedical fields. In food packaging film applications, polymeric films are generally used to increase the water resistance of the package. Thus, it is desirable that the water solubility of the packaging film is very low. However, polymeric coating film applications are generally made to extend the shelf life of foods (usually fruits). In film coating applications, it is aimed that the film protects the food during its shelf life, and the film must be able to be completely removed from the food surface with water before consumption. Therefore, it is desirable that the polymeric films to be used in food coating applications have a very high solubility in water. For this reason, it is important to know the purpose for which the produced film will be used to improve the properties of the film [18].

In this study, it was aimed to produce gel film which can be used as food packaging material. For that reason, great effort has been made to reduce the water solubility of the produced films as much as possible by increasing water resistance. The solubility of the produced films was calculated from the change of the weight of the polymeric gel films which stood in 20 ml of distilled water at 25 °C for 24 h. The solubility values of hemicellulose-based polymeric gel films in distilled water, which were obtained at different compositions, are summarized in Table 5. As seen from Table 5, the average resolution values of the produced films ranged between 0.4 and 1.8%.

It was observed that the solubility values of gel films in water were not very different from each other. Due to the cross-linked structure of the produced gel films, it was seen that their solubility in water had very low values compared to that of the films presented in

Table 5. The solubility values in distilled water of hemicellulose-based polymeric gel films and the moisture-holding capacities of the gel films; HC: hemicellulose, C: crosslinker, I: initiator, NIPAAm:N-N-isopropyl acrylamide, AAm: acrylamide, M: monomer

Variable	Variable Range	% Solubility	% *MHC*	Variable	Variable Range	% Solubility	% *MHC*
I/HC mass ratio	0.04/1	0.64	0.6426	AAm/HC mass ratio	0.25/1	1.04	0.7914
	0.03/1	0.62	0.6620		0.5/1	0.91	0.8394
	0.02/1	0.59	0.7738		1/1	0.72	0.6862
	0.01/1	2.82	0.5839		2/1	0.50	0.4959
C/HC mass ratio	0.0135/1	1.05	0.6018	NIPAAm/HC mass ratio	0.25/1	1.47	0.9339
	0.025/1	0.95	0.5980		0.5/1	0.78	0.8913
	0.05/1	0.77	0.5880		1/1	0.54	0.8324
	0.1/1	0.55	0.7299		2/1	0.48	0.6220
	0.15/1	1.30	0.6657	Chitosan/M mass ratio	0.05/1	0.59	0.0055
					0.1/1	0.55	0.0079
					0.2/1	0.48	0.062
					0.25/1	0.43	0.057

the literature [14,18,19]. While the ratio of the crosslinker used in the synthesis of gel films was increased, a decrease was observed in the solubility values of the gel films.

However, when the crosslinker mass ratio reached 0.15/l, it was observed that the elasticity of the gel films decreased and fragility increased. The increased fragility of the gel films caused them to break up in distilled water. On the other hand, as the ratio of comonomer and chitosan used in polymeric film synthesis was increased, the solubility values of the gel films were decreased. It was observed that the amount of initiator did not have a significant effect on gel film solubility, *i.e.*, there was no important relationship between the amount of initiator and the solubility of the gel films. Due to the cross-linked structure of the produced films, it was observed that the water resistance of the gel films is very high, they are hardly soluble in distilled water and the addition of chitosan increases their physical strength.

Result of the moisture holding capacity of gel films. Determining the water vapor permeability of the films is particularly important when the films are to be used as food packaging materials. Polysaccharides are hydrophilic in character due to their high hydroxyl content. Therefore, they are very sensitive to changes in relative humidity [20,21]. Hemicellulose is a hygroscopic natural biopolymer and easily soluble in water at high temperatures. Due to these properties, it can be obtained easy by extraction from lignocellulosic biomass [22]. However, the moisture-holding capacity of the biodegradable polymeric materials, in particular hemicellulose-based films, significantly limits its use. For example, the high moisture retention of the polymeric films used as packaging material results in damage to the packaging and the product becoming non-consumable. The high moisture content of the packaging material reduces the physical strength of the packaging, causing the packaging to undergo formal deformation, *i.e.*, the dimensional stability of the package is lost. Therefore, it is stated that the moisture holding capacity of the films to be used in packaging production should not exceed the critical value [23,24].

In this study, the moisture-holding capacities of the gel films were investigated by exposing the gel films to 30 °C, 100% relative humidity for 24 h (1440 min). The results regarding the moisture-holding capacity of hemicellulose based biodegradable gel films obtained from tea leaf brewing waste are given in Table 5. As shown in Table 5, it was observed that, all the produced gel films have a moisture-holding capacity of less than 1%. It was determined that the moisture-holding capacity of the produced gel films was found to be quite low compared to the hemicellulose- and cellulose-based films in the literature. It is thought that the absence of the free hydroxyl group in the polymeric structure as a result of the polymeric crosslinking results in a decrease in the hydrophilicity of the polymeric film and thereby reducing the moisture-holding capacity of gel film. In contrast to gel films which were produced in this work, the films which were produced in the literature have been based on the casting of the hemicellulose which are usually dissolved in suitable solvents without cross-linking. Therefore, the moisture-holding capacity of the films presented in the literature is significantly higher than the moisture-holding capacity of the films obtained in this study.

Result of the water vapor permeability of gel films. The determination of the water vapor permeability (*WVP*) of the produced gel films helps to understand how the water absorption, dissolution and diffusion characteristics in the polymeric gel film matrix change with the film composition [12,25]. It is known that many enzymatic activities of foodstuffs are associated with water in the environment. In order to protect foods, it is important to reduce the water activity of foods or to keep the existing water under control. Therefore, water vapor permeability values of the films to be used in food packaging applications are very important parameters. Because the low water vapor permeability of the packaging materials limits the passage of moisture between the product and the atmosphere, as a result, it helps to extend the shelf life of the product. The water vapor permeability (*SBG*) of films is a function of resolution (*S*) and diffusion coefficient (*D*). According to experimental results and calculated data, it was determined that the factors affecting these two basic parameters, such as structure of gel film and cross-link density of gel film, were affected by the SBG values of the films. The normalized water vapor permeability values obtained by film thickness correction and the water vapor permeability values calculated by taking into consideration the equations derived by using Fick law are presented in Table 6.

The water vapor permeability values (*SBG*) of the hemicellulose-based films produced within the scope of the study were determined to be between 1.77×10^{-9} and 5.08×10^{-10} g/(s Pa m). The water vapor permeability values of the commercial alternatives were found to be between 3.1×10^{-10} and 3.5×10^{-11} g/(s Pa m). It was concluded that *SBG* values of the produced gel films were 10 to 100 times higher than the commercial alternatives. Also, unfortunately, it

Table 6. The normalized water vapor permeability and the water vapor permeability values; M: monomer, HC: hemicellulose, AAm: acrylamide

Synthesis condition	*WVP* (g/(d m^2))	*NWVP*×10^{-6} (g/(d m^3))	*WVP*×10^{10} (g/(m Pa s))
AAm/HC mass ratio: 3/1	1302.42	3.62	12.7
AAm/HC mass ratio: 0.33/1	1559.24	5.03	13.1
AAm/HC mass ratio: 0/1	1394.14	4.50	11.7
Chitosan/M. mass ratio: 0.05/1	1008.92	2.73	10.1
Chitosan/M. mass ratio: 0.1/1	1705.99	8.98	8.81
Chitosan/M. mass ratio: 0.2/1	1082.29	5.41	5.88
Commercial alternative materials			
Stretch film	385.22	0.770	0.82
Plastic bag	146.75	7.34	0.31
Aluminium foil	275.16	0.275	0.59
Greaseproof paper	1632.61	0.408	3.5
Filter paper	1650.96	7.86	3.5

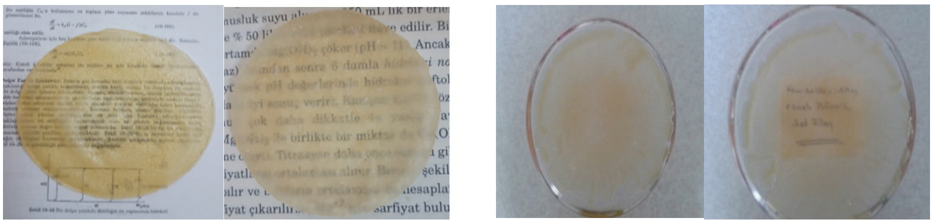
was not possible to obtain a significant relationship between the film composition and the *WVP* that could be converted into an equation because the values obtained were not very different from each other. Additionally, it was determined that in chitosan-containing films, when the mass ratio of chitosan/monomer was increased from 0.05/1 to 0.2/1, the water vapor permeability was decreased from 1.01×10^{-9} to 5.88×10^{-10} g/(s Pa m). The water vapor permeability value of the chitosan-containing films was found to be close to the water vapor permeability value of the oily paper (3.5×10^{-10} g/(s Pa m)) [24]. Although the *WVP* value achieved for chitosan-containing films are in agreement with the literature [12,26], the produced film in this study has higher water vapor permeability values than the sugar beet-based hemicellulose films produced by Sabiha-Hanim and Siti-Norsafurah (2012) [14].

Hemicellulose films were expected to have higher water vapor permeability than commercial alternatives. In the previous studies, it was concluded that hemicellulose-based films produced without crosslinker, which have a strong hydrophilic character, cannot be used in the production of high-volume packaging. It was stated that the properties of hemicellulose-based films to be used in this field should be improved [27]. It was also said that packet materials of high *WVTR* values such as hemicellulose-based films are beneficial for vegetable or fruit packaging due to the continuation of respiration and some of the metabolic activities [14].

Light permeability test and color scale analysis of films. Polymeric films are commonly used in some applications such as food packaging, coating, biomedical applications, drug release etc. It is well known that the optical properties of the produced gel films vary depending on the area of use. For example, during the packaging of nutrients which are decomposed with light, the opaque films are preffered. But, transparent packaging is preffered for the packaging of other nutrients [28]. Because these materials are aesthetically beautiful and consumers can easily visually control the product, it is important to determine the light transmission, *i.e.*, transparency/opacity values of the gels produced. Especially in recent years, researches have been conducted to determine and improve the optical properties of the films produced. Therefore, the transparency of the gel films produced in this study was attempted to be determined either visually or by instrumental analysis methods.

The transparency of the hemicellulose-based and acrylamide (AAm)-doped films produced is presented visually in Figure 3. In the visual test, it was determined that the writing under the film could be read easily, and after the synthesis of the film, the holes of the Büchner funnel could be seen in the washing process. Hemicellulose-based films were observed to be more yellowish than AAm-doped films. A series of films which were synthesized under different conditions were selected and photographed. The color scales (Red, Green, Blue values) of the produced films were determined using the R2017 version of the MATLAB program. The values are presented in Table 7. As a result of these analyses, it was concluded that the additives which were added to the structure of the produced gel films had a significant effect on the color scale of the films.

The opacity/thickness values of films in Table 8 are given for the wavelength range of 200-800 nm. It was determined that the maximum transmitance of light for the films was 200-250 nm. When the permeability values corresponding to this value were



Hemicellulose based films AAm and hemicelulose based films

Figure 3. The transparency of the hemicellulose-based and acrylamide (AAm) gel films.

Table 7. The color scales of the produced gel films

Synthesis condition	RGB numbers			Color	Film image
	R	G	B		
AAm/HC mass ratio: 0/1 I/M mass ratio: 0.5/1 C/M mass ratio: 0.05/1 Chitosan/M mass ratio: 0.2/1	225	210	179	🟫	
AAm/HC mass ratio: 1/1 I/M mass ratio: 0.5/1 C/M mass ratio: 0.05/1 Chitosan/M mass ratio: 0.2/1	218	215	198	⬜	

Table 8. The opacity/thickness values (10^4/μm) of the produced gel films

Synthesis condition	Wavelength (nm)												
	200	250	300	350	400	450	500	550	600	650	700	750	800
AAm/HC mass ratio: 1/1 I/M mass ratio: 0.5/1 C/M mass ratio: 0.05/1 Chitosan/M mass ratio: 0.1/1	18	**14**	28	27	27	27	27	27	27	27	27	27	27
AAm/HC mass ratio: 1/1 I/M mass ratio: 0.5/1 C/M mass ratio: 0.05/1 Chitosan/M mass ratio: 0.05/1	**11**	15	32	32	32	32	31	31	31	31	30	30	30
AAm/HC mass ratio: 1/1 I/M mass ratio: 0.5/1 C/M mass ratio: 0.05/1 Chitosan/M mass ratio: 0.2/1	**11**	13	27	27	27	27	27	26	25	25	25	25	25
AAm/HC mass ratio: 3/1 I/M mass ratio: 0.5/1 C/M mass ratio: 0.05/1 Chitosan/M mass ratio: 0.1/1	26	**23**	52	52	51	49	48	46	45	44	45	44	44
AAm/HC mass ratio: 3/1 I/M mass ratio: 0.5/1 C/M mass ratio: 0.05/1 Chitosan/M mass ratio: 0.1/1	**21**	24	50	49	49	49	49	49	48	48	48	48	48

examined, the light transmittance value in the selected sample films was determined to be in the range of about 45 to 65%. It was found that the lowest opacity/thickness value was in the range of about 0.0023 to 0.0011 μm^{-1}. As a result, it was determined that the light permeability values of the gel film samples were lower than the values given in the literature due to the surface morphology of the gel films [29]. It was observed that different additives added to the gel film structure decreased the homogeneity of the film surface. Because of the surface was more rough and the light sent to the surface reflected at

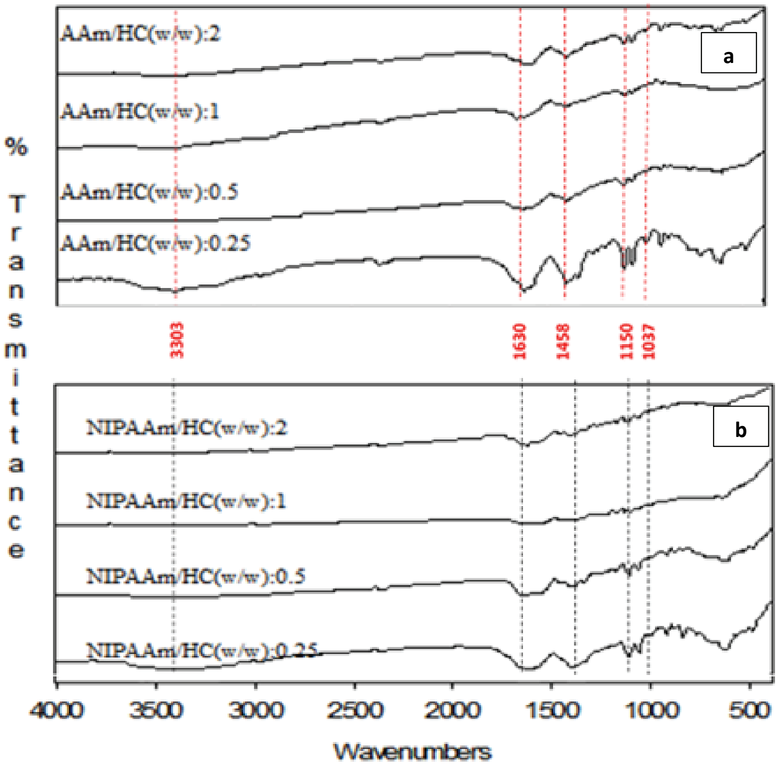


Figure 4. FTIR spectrum of hemicellulose co-AAm-based (a) and hemicellulose co-NIPAAm-based gel films (b).

different angles, the opaque values of films were read as higher than their real values.

Figure 4 presents the FTIR spectrum of hemicellulose-based gel films obtained using AAm (a) and NIPAAm (b) as comonomers. Various main peaks were attributable for the hemicellulose co-Aam-based films (a) and the hemicellulose co-NIPAAm-based films (b) at 3303, 1630, 1458, 1150 and 1037 cm^{-1}. The main peak shows the FTIR spectrum, indicating the presence of C=O bond, C-N bonds, C=C bond and C-H bond. The functional groups, vibrational frequency and their assignment that were obtained from the FTIR spectrum were summarized as follows.

The attributes of the main absorption are characteristic of glycosidic structures of hemicellulose and related to OH stretching at 3303 cm^{-1} and C-O-C stretching at 1037 cm^{-1}. In addition to the the valence vibration at 3303 cm^{-1} corresponding to the NH groups from the crosslinking bridges, the peak at 1630 cm^{-1} can be attributed to absorbed water, since hemicellulosic based gel film usually have a strong affinity for water. The peak at 1428 cm^{-1} can be attributed to C-N stretching vibrations. Cyano groups (C-N) on the chains of PAAm give the absorption band. The two low-intensity shoulders at 1150 cm^{-1} were assigned to the deformation vibrations of the -C-N- links and CH_2 groups. Lan *et al.* (2011) [30], Dudu *et al.* (2017)[31], Dumitrescu *et al.* (2015) [32], and Taşar and Orhan (2020)[33] interpreted the bands observed in this region in a similar way.

CONCLUSION

Hemicellulose-based gel films absorbed maximum 1% in 100% relative humidity environment.

It has been determined that the average solubility values of the polymeric films produced within the scope of the thesis vary between approximately 0.4% and 1.8%.

Among the films, the lowest water vapor permeability (*WVP*) value was measured to be 5.88×10^{-10} g/(s Pa m) for the hemicellulose-based film which contained chitosan.

It has been determined that the optical transparency of hemicellulose-based polymeric gel films varies from about 45 to 65% and the opacity/thickness values range from 0.0027 to 0.0011 μm^{-1}.

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NAUČNI RAD

SINTEZA I KARAKTERIZACIJA POLIMERNOG GEL-FILMA NA BAZI HEMIKELULOZE IZ OTPADA DIGESTIJE LIŠĆA ČAJA

U ovom radu, sintetizovani su polimerni gel-filmovi na bazi hemiceluloze koristeći mehanizam polimerizacije slobodnih radikala. Hemiceluloza je dobijena iz otpada iz digestije lišća čaja postupkom delignifikacije. Polimerni gel-filmovi su proizvedeni tehnikom livenja rastvora. Ispitivan je uticaj parametara sinteze na strukturu i svojstva gel-filmova. U tu svrhu, sintetizovani gel filmovi na bazi hemiceluloze okarakterisani su analitičkim testom. Eksperimentalni rezultati su pokazali da su gel-filmovi na bazi hemiceluloze apsorbovali vlagu brzinom od najviše 1% u okruženju sa relativnom vlažnošću od 100%. Izmerena je najniža vrednost propustljivosti vodene pare za film na bazi hemiceluloze, uključujući hitosan, od $5,88\times10^{10}$ g/(s Pa m). Prosečne vrednosti rastvorljivosti proizvedenih polimernih filmova varirale su između 0,4 i 1,8%. Primećeno je da se optička prozirnost polimernih gel-filmova na bazi hemiceluloze promenila sa 45 na 65%, a vrednosti neprozirnost/debljina su 0,0027-0,0011 mm^{-1}. Kao rezultat, utvrđeno je da na fizičko-hemijske i morfološke osobine sintetizovanih filmova u velikoj meri utiče sastav filmova.

Ključne reči: biorazgradiv, hemiceluloza, polimer, gel film, karakterizacija.