



Effect of Glycerol on the Functional Properties of Chitosan/PEO Films

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Polymer blending is a productive technique for granting attractive properties in polymeric materials which are advantageous for the packaging industry. In the present investigation, blended films of chitosan/poly (ethylene oxide) (PEO) were synthesized in different proportions of weight in the presence and absence of glycerol. Presence of distinctive peaks of chitosan and PEO at 1656 cm^{-1} and 843 cm^{-1} separately confirms the blending of chitosan/PEO. Simultaneously widening of peaks at 3380 cm^{-1} and 1656 cm^{-1} can be credited to the inter-molecular hydrogen bonding between chitosan/PEO films which thereby support blending. The physico-mechanical, barrier, optical, thermal, surface morphology and biodegradation properties of chitosan and PEO blended films with and without glycerol were estimated. It was seen that the tensile strength of the blended films diminished. Haze values of chitosan/PEO blended films with glycerol (20%) diminished from 17.7% for C100 to 3.7% for pure PEO bringing about an increase in transparency of the films that could be due to the plasticized effect. The outcomes indicate that in the presence of glycerol (20%), there is an increment of the elongation at break by more than 150%, inferring that these chitosan/PEO films could be suitably used in elastic and stretchable packaging. These films with high WVTR values can be utilized for fresh produce to control moisture evaporation and upgrades their shelf life. These films biodegrade or disintegrate within five weeks.

Keywords: Biodegradation, Barrier, Mechanical properties, Packaging, Surface morphology

Introduction

The non-degradable petroleum-based packaging films are severely increasing environmental pollution and therefore require the replacement by safe, non-toxic, eco-friendly packaging materials for enhanced applications. Packaging materials made from biodegradable and renewable raw materials seem to draw greater attention than before from the technologists, polymer chemists and environmental scientists as they favour pollution free environment. Subsequently, an environmentally cognizant option is to plan or synthesize polymers that can be degraded biologically. Blending or mixing of polymers is a viable way for the creation of new polymeric materials with customized features, minimal expense, not as much of tedious and easy to process. The blends between natural and artificial polymers are of specific importance, since they can bring about biocompatibility along with easy processing and enhanced mechanical properties. Considering the current drive on ecofriendly packaging materials, one

such fascinating blend turns out to be chitosan/PEO blend.^{1,2}

Chitosan is the second most abundant natural polymer available from the shells of crab, shrimp, prawn, etc., It is a de-N-acetylated form of chitin consisting mainly of β -(1-4)-2 amino-2-deoxy-D-glucose units and with some N-acetyl glucosamine residues. It is a non-toxic, biodegradable, and commercially available polymer having a widespread applications.³ It forms transparent films, which might find various packaging applications as it forms inter and intra-molecular hydrogen bonds.^{4,5}

Polyethylene Oxide (PEO) has been widely utilized in medical field as a result of its biocompatibility, brilliant hydrophilicity, high viscosity and capacity to form H-bonds with oxygen of ether. Additionally, it has applications in various aspects of cosmetics industry.^{6,7} By and large, the formation of explicit inter-molecular associations through H-bonding among polymeric chains is accountable for the noticed blending features of the mixes produced from aqueous solutions.⁸ Studies by Kondo & Sawatari⁹ and Caykara *et al.*⁸ have recognized that the primary alcoholic group on cellulose, methyl cellulose, and

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sodium alginate can form hydrogen bond with oxygen of PEO. Similarly, hydroxyl group on chitosan can also form a H-bond with the oxygen of PEO. Therefore, PEO was selected as suitable polymer for blending with chitosan.

In the present study, the emphasis was on the synthesis of chitosan /PEO blends (with and without glycerol) as well as to examine their surface morphology, mechanical, barrier, thermal properties as well as biodegradation. Glycerol is used as being a good plasticizer provides flexibility in the films for better packaging application.

Materials and Methods

Prawn shell Chitosan powder (batch number BX 12AN-24) with a 88% deacetylation property and 195 mPa viscosity (further confirmed in laboratory by Rheology international RI: 3: M viscometer at ambient temperature of $(25 \pm 2^\circ\text{C})$) was obtained from India Sea Food, Cochin, India. Polyethylene oxide (PEO) of molecular weight (≈ 200 kDa) was procured from Sigma Aldrich, St. Louis, MO, USA. All other chemicals were of analytical grade obtained from M/s S D fine Chemicals, Bangalore, Karnataka (India).

Preparation of Chitosan/PEO Blended Films

Chitosan solution at 2% concentration was prepared in 1% acetic acid with constant stirring followed by filtration through cheese cloth. Similarly, 2% PEO solution was prepared in distilled water with constant stirring at $60\text{--}70^\circ\text{C}$ for 2 h. Both the solutions were then degassed through vacuum pump and were mixed in different proportions and stirred for 1 h at room temperature to obtain homogeneous solutions of 20% to 90% (w/w) of PEO in chitosan. Approximately 200 ml of solution from each of chitosan, PEO and the blends were filtered through cotton and poured on separate glass plates ($27\text{ cm} \times 20\text{ cm}$) lined with a polyethylene film. After drying for 3–4 days at room temperature transparent film with uniform thickness were obtained and stored at ambient conditions (25°C , RH of 50%).

Preparation of Chitosan/PEO Blended Films with Glycerol

To study the effect of glycerol on the chitosan/PEO blends the above process was repeated additionally including 10 and 20% glycerol (on weight basis of total polymer) during the chitosan/PEO blending process and films were made.

FT-IR Spectral Studies

Thin films of uniform thickness of ($75\ \mu\text{m}$) chitosan/PEO blends were used for obtaining the IR

spectra using FTIR-RAMAN Nicolet 5700 instrument.

Physico-Mechanical Properties

Physico mechanical properties like density, tensile strength, percentage elongation ($\%\epsilon$) at break, barrier properties (Water vapour transmission rate), optical properties and thermal properties (DSC) of chitosan/PEO blends with and without glycerol was measured as per methods described in research paper of Jagadish *et al.* as well as ASTM standards.^{10,11} The mean and standard deviation of five measurements of above-mentioned properties is reported.

Surface Morphological Analysis

Scanning electron microscopy was used to study the surface morphological analysis of the chitosan/PEO blended films with and without glycerol. By spreading the dried film samples over double-sided conducting adhesive tape pasted on a metallic stub and coated with gold in a sputter coating unit for 2 min the surface morphological analysis was done in scanning electron microscope (LEO 435, VP LEO Electronic microscopy Ltd. Cambridge, UK.,) at 15kV and magnification of 100 X.

Biodegradation

Chitosan/PEO blended film samples with and without glycerol of size $3 \times 3\text{ cm}^2$ were completely buried inside the compost/mud (in 50:50 ratio) mixture. Control sample were kept separately. Moisture content of the compost/mud was maintained at 25% throughout the study period. The samples were observe for biodegradation at specific intervals through visual changes and weight loss (%) if any.¹²

Results and Discussion

Chemical Characterization of Chitosan/PEO Blends by FT-IR Spectroscopy

Characterization of blended films was carried out by IR spectroscopy to spot any change in the position of the bands which could be accredited to weak interactions between two polymers. The FTIR spectra of chitosan, PEO and chitosan/PEO blended films fall in the range of $4000\text{--}800\text{ cm}^{-1}$ that are represented in Fig. 1. In the IR spectrum of chitosan, a broad band at 3380 cm^{-1} is ascribed to N-H and OH (involved in intermolecular hydrogen bonding). A very feeble band at 2879 cm^{-1} due to CH_2 stretching, at 1656 cm^{-1} due to $>\text{C}=\text{O}$ stretching (amide-I) and other at 1555 cm^{-1} due to N-H bending (amide-II) were observed. In pure PEO film spectrum, a characteristic band at

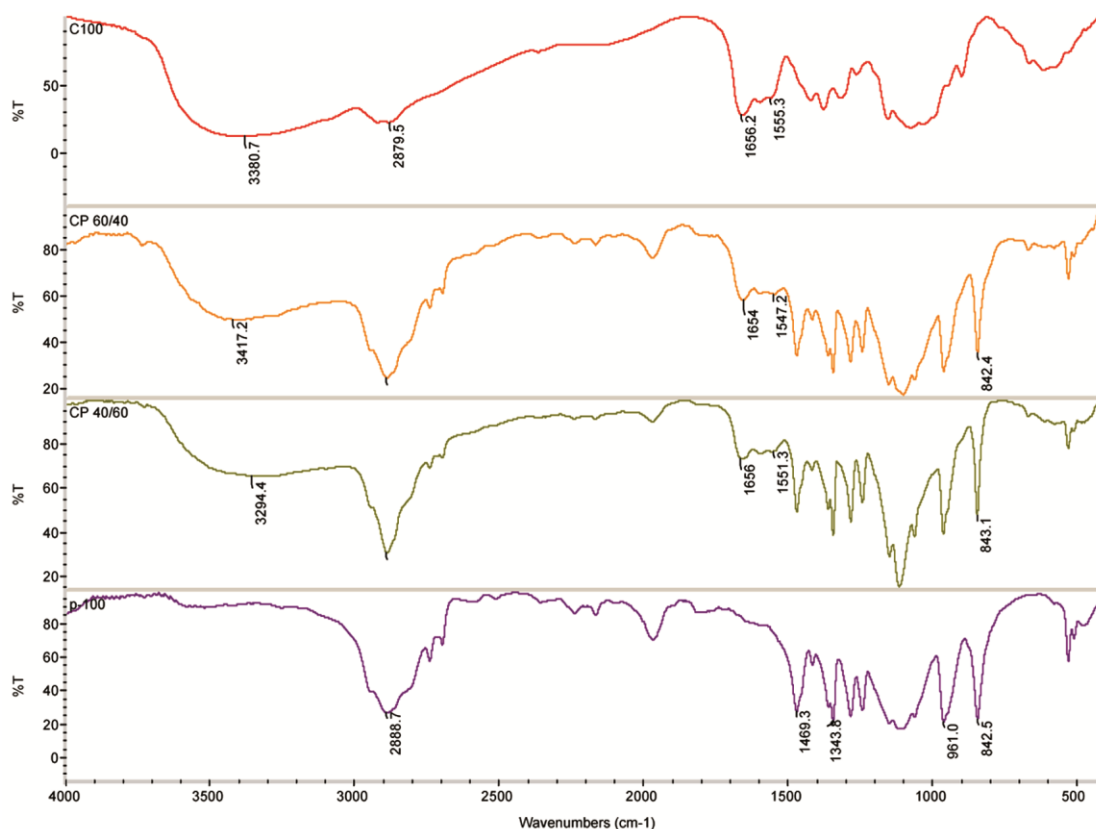


Fig. 1 — Comparison of IR spectra of Pure Chitosan and pure PEO with CP film

2888 cm^{-1} due to CH_2 stretching, C–H bending at 1469 cm^{-1} , 1343 cm^{-1} and 961 cm^{-1} were also observed. The typical absorption at 843 cm^{-1} due to C–O–C bending was also seen.⁸ In the IR spectrum of blends of chitosan/PEO, presence of characteristic peaks of chitosan and PEO at 1656 cm^{-1} and 843 cm^{-1} correspondingly supports the blending. Broadening of bands at 3380 cm^{-1} and 1656 cm^{-1} can be accredited to the inter-molecular H-bonding between chitosan and PEO which also supports blending.^{8,13} On increasing the percentage of PEO in blend, the absorbance intensities of CH_2 stretching (2888 cm^{-1}) and C–O–C bending (843 cm^{-1}) were amplified. But, the absorbance intensity of NH_2 bending (1555 cm^{-1}) diminished in the blends.

Physico-Mechanical Properties

The values of measured density, tensile strength (TS) and percent elongation ($\%\epsilon$) of chitosan/PEO (CP) films (with and without glycerol) are recorded in Table 1. From Table 1, it was observed that there was no major difference between the densities of CP films (with and without glycerol) as the density of CP films with glycerol lies between 1.409 – 1.289 g/ml and

without glycerol in the range of 1.407 – 1.321 g/ml. on increasing the PEO content in the CP blend, density was found to be declining. The change in density profile of any of the CP films with and without glycerol had a maximum difference of ± 0.0072 g/ml. It is because densities of unadulterated PEO and glycerol are lesser than the density of pure chitosan (1.26 g/ml).

CP films without glycerol displayed higher TS of 45 MPa in C-100, 38.22 MPa for CP 80/20 (than those of CP films with glycerol) and fall to 9.36 MPa in CP 10/90. The TS values CP films with glycerol (10%) decreased from 36.54 MPa for C-100, 32.8 MPa for CP 80/20 and to 6.66 MPa in CP 10/90. Likewise, the TS values of glycerol (20%) added CP films decreased from 24.74 MPa for C-100, 21.54 MPa for CP 80/20 and to 2.91 MPa in CP 10/90. This steady decrease in TS in both the films (with and without glycerol) is perhaps due to the lesser strength of PEO and presence of plasticizer that diminishes the intermolecular bonds amongst the polymer chains.

It is detected that percent elongation of CP films with glycerol remarkably increased ($>150\%$) when compared with CP films without glycerol. The CP

Table 1 — Density, Tensile strength and Percent elongation of CP films with and without glycerol

Material films	Density (g/ml)		Tensile Strength (MPa)			% Elongation		
	Glycerol		Glycerol			Glycerol		
	0 %	20 %	0%	10 %	20 %	0%	10 %	20 %
CP-100/0	1.4073	1.4090	45 ± 0.79	36.54 ± 0.98	24.74 ± 0.87	16.31 ± 0.92	36.20 ± 1.15	42.27 ± 1.04
CP-80/20	1.3981	1.3969	38.22 ± 1.05	32.80 ± 1.10	21.54 ± 0.98	13.56 ± 0.91	30.60 ± 1.19	35.41 ± 0.96
CP-60/40	1.3871	1.3871	24.27 ± 1.09	15.64 ± 1.28	07.46 ± 0.87	5.45 ± 0.88	28.14 ± 1.40	30.07 ± 0.99
CP-40/60	1.3642	1.3648	16.30 ± 0.91	10.66 ± 0.98	05.85 ± 0.79	3.84 ± 0.94	15.16 ± 0.93	22.02 ± 0.87
CP-20/80	1.3371	1.3265	13.34 ± 0.86	8.98 ± 0.82	03.96 ± 0.94	2.36 ± 0.65	11.42 ± 0.73	15.67 ± 0.99
CP-10/90	1.3296	1.3151	09.36 ± 0.94	6.66 ± 0.87	02.91 ± 0.96	2.04 ± 0.7	7.44 ± 0.77	9.73 ± 0.90
CP-0/100	1.3210	1.2890	NA	NA	NA	NA	NA	NA

NA= Not Available, C = Chitosan, P=PEO

Table 2 — Burst and Tear strength of CP films with and without glycerol

Material films	Burst Strength (Kg/cm ²)			Tear Strength (g)		
	Glycerol			Glycerol		
	0%	10 %	20 %	0%	10 %	20 %
CP-100/0	6.1	5.9	5.7	12	10.5	9
CP-80/20	5.2	4.8	4.2	12	9.0	7.5
CP-60/40	1.7	1.5	1.0	7.5	7.5	6.0
CP-40/60	1.2	0.9	0.8	6.0	4.5	3.0
CP-20/80	0.8	0.7	0.5	4.5	3.0	—
CP-10/90	0.5	0.2	0.2	3.0	—	—
CP-0/100	—	—	—	—	—	—

C = Chitosan, P=PEO

blended films with glycerol (20%) showed percent elongation of 35.41 in CP 80/20 and decreased to 9.73 in CP 10/90. Also, the CP films with 10% glycerol showed percent elongation from 30.60 in CP 80/20 and decreased to 7.44 in CP 10/90. The percent elongation of CP films without glycerol exhibited fairly lesser values as compared to CP films with glycerol (10% and 20%). The percent elongation values of CP films without glycerol decreased from 13.56 for CP 80/20 to 2.04 in CP 10/90. The values of TS and percent elongation are in harmony with literature.^{5,9,14-16}

The measured Burst Strength (BS) and Tear strength of CP films (with and without glycerol) are recorded in Table 2. CP films without glycerol displayed greater BS of 5.2 Kg/cm² for CP 80/20 and decreased to 0.5 Kg/cm² in CP 10/90. The BS of CP films with glycerol showed comparatively lesser values than those of CP films without glycerol. The BS values of glycerol (10%) added CP films reduced from 5.9 Kg/cm² for C-100, to 0.2 Kg/cm² in CP 10/90. In the similar fashion, the BS values of glycerol (20%) added CP films decreased from 5.7

Kg/cm² for C-100, to 0.2 Kg/cm² in CP 10/90. This steady lessening in BS in both the blends with and without glycerol is undoubtedly due to the plasticizer effect that diminishes the intermolecular bonds between the polymer chains.

CP films without glycerol showed better tear strength of 12 g in C-100, and decreased to 3.0 g in CP 10/90. In case of glycerol added CP blends, no noteworthy observation was made with respect to tear strength.

Barrier Properties

The variation of water vapour transmission rate (WVTR) with different weight ratios of chitosan/PEO blends is reported in Table 3. The proportion of the polymers greatly influenced WVTR. It was observed (Table 3) that plain chitosan and chitosan with glycerol (10% and 20%) showed WVTR values of 4410.73, 4652.33 and 4895.52 (g/m²/day), correspondingly. With the addition of PEO, WVTR of blended chitosan/PEO films with or without glycerol decreases till CP 60/40 ratio and with the further addition of PEO, WVTR values increases up to

Table 3 — WVTR and Optical properties of CP films with and without glycerol

Material Films	WVTR g/m ² /days at 90%RH gradient at 38°C					
	Haze			WVTR g/m ² /days at 90%RH gradient at 38°C		
	With Glycerol			With Glycerol		
	0%	10 %	20 %	0%	10 %	20 %
CP-100/0	11	10.5	09.10	4410.73	4652.33	4895.52
CP-80/20	15	14.2	13.30	4236.12	3821.95	3467.76
CP-60/40	29.70	28.1	26.80	3694.89	3527.35	3433.80
CP-40/60	64.10	58.1	59.80	4277.63	5236.28	6264.92
CP-20/80	60.90	59.0	57.50	5495.35	8082.83	10586.31
CP-10/90	90.20	89.8	89.30	6209.10	8692.23	11069.54
CP-0/100	93.60	91.2	90.10	—	—	—

C = Chitosan, P=PEO

Table 4 — DSC Melt characteristics parameters of CP films with and without glycerol

Material Films	Endotherm				Endotherm				Endotherm			
	Without Glycerol (0%)				With Glycerol (10 %)				With Glycerol (20 %)			
	Tp (°C)	ΔH J/g	Tp* (°C)	ΔH* J/g	Tp (°C)	ΔH J/g	Tp* (°C)	ΔH* J/g	Tp (°C)	ΔH J/g	Tp* (°C)	ΔH* J/g
CP-100/0	—	—	129.36	295.1	—	—	130.09	200.8	—	—	137.46	407.9
CP-80/20	61.03	24.43	128.84	197.8	55.54	26.71	140.85	112.0	47.14	55.66	133.58	353.7
CP-60/40	62.30	73.55	137.23	122.5	57.05	76.14	128.46	102.5	50.27	91.84	131.93	163.1
CP-40/60	63.21	111.3	133.91	30.34	58.44	116.7	141.84	23.92	51.09	129.3	130.69	80.21
CP-20/80	64.73	158.8	143.17	4.251	59.39	129.0	144.69	3.356	53.54	149.8	132.97	12.81
CP-0/100	66.97	217.0	—	—	59.48	176.5	—	—	55.17	159.5	—	—

C = Chitosan, P=PEO

Tp (°C) & ΔH J/g = First endotherm peak and corresponding energy

Tp* (°C) & ΔH* J/g = Second endotherm peak and corresponding energy

6209.1 in plain chitosan, 8692.23, and 11069.54 in 10% and 20% glycerol blended films respectively where PEO concentration is 10% in the blends. With higher concentration of chitosan, there was low water vapour permeation, may be due to complete packing of chitosan matrices. But as PEO concentration increases, chitosan matrices are covered by PEO and PEO being hydrophilic results in increase in the water vapour permeation. On increasing the PEO concentration, the film became wet, thereby the barrier properties fall down. Gontard *et al.*¹⁷ has clearly demonstrated that water vapor transmission through a hydrophilic film depends on how much water molecules can diffuse in the film matrix. Films with these WVTR values can be used for fresh produce to control the moisture evaporation and increase their shelf life.

Optical Properties

Haze values of chitosan/PEO films with (10 and 20%) and without glycerol increased from 10.5 to 91.2, 9.10 to 90.10 and 11.0 to 93.60, respectively as the PEO concentration increased from 0-100% (Table 3). The increment in haze values subsequent to blending of PEO to the chitosan matrix could be

because of the scattering of light radiation by PEO.^{18,19} Because of the plasticized effect, haze values of chitosan/PEO blended films with glycerol (20%) diminished from 17.7% for C100 to 3.7% for unadulterated PEO bringing about an increase in transparency of the films as compared with chitosan /PEO blended films without glycerol.

Thermal Studies

Differential Scanning Calorimetric Analysis

As per the normalized DSC thermograms of chitosan/PEO (CP) blends without glycerol and with 20% glycerol, Tp (melting temperature), and area under DSC curve (ΔH) values of chitosan/PEO blends are given in Table 4. It is from the table, evident that Tp and ΔH of the chitosan /PEO blends increases from 61.03°C to 66.97°C and 24.43 J/g to 217 J/g as the concentration of PEO in the blends increases from 20 to 100%. Similar trends have been noted in chitosan /PEO blends with 10 and 20% glycerol. In case of chitosan/PEO blended films with 10% glycerol, the Tp increases from 55.54°C to 59.48°C and ΔH increases from 26.71 J/g to 176.5 J/g, respectively. In 20 % glycerol added CP blends, the Tp increases from 47.14°C to 55.17°C and ΔH

increases 55.66 J/g to 159.5 J/g respectively. Though, decrease in melt temperature was noted in all CP blends with 10 and 20% glycerol on comparing with corresponding CP blends without glycerol. The shift in T_p can be attributed to the interaction between ether oxygen of PEO and hydroxyl or amine group of chitosan. The broad endothermic peaks (T_p^*) seen in the region of 129 to 144°C in the CP blends with (10 and 20%) and without glycerol can be credited to the evaporation of residual water from the blends and corresponding (ΔH^*) values decreases as the concentration of PEO increases from 0 to 80%. From the Table 4, for glycerol a distinct endotherm peak appeared around 265°C, which is due to glycerol decomposition.²⁰

Surface Morphology Analysis

The SEM photomicrograph of unadulterated chitosan shows a homogeneous surface whereas PEO shows homogeneous and rough surface with cavities. In 80/20 and 60/40 of both CP blended films with and without glycerol, uniform surface of blended films supports the interaction between chitosan and PEO matrix (Fig. 2). The surface morphology is quite same

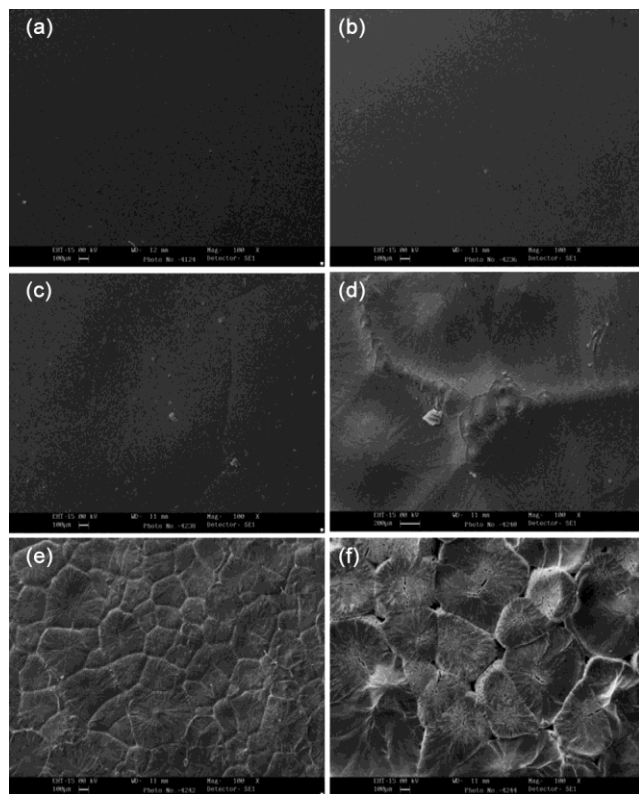


Fig. 2 — Surface morphology (SEM) of CP films with 20 % glycerol: (a) Chitosan-100; (b) CP 80/20; (c) CP60/40; (d) CP40/60; (e) CP80/20 (f) PEO-100

up to 60% of PEO in CP blends without glycerol whereas in case of CP blends with glycerol it was same only upto 40% of PEO. This may be due to the more flexibility of the films because of weakening of the polymer chains. Although, at higher percentage of PEO, the blends show a rougher surface with cavities and depressions revealing a phase separation. This phase separation at higher dosage of PEO may be due to the immiscible nature of blends.¹²

Biodegradation

Biodegradation usually takes place by microorganisms (in the soil or environment) which will utilize the films as a sole carbon source by degrading their polymer structure. The CP films with and without glycerol showed smooth surface initially and the films were fragmented into pieces in a short period of 3 weeks. Further, these films were completely biodegraded at the end of 5 weeks, as no pieces of films were left in the compost. Biodegradation may be attributed to the hydrophilic nature of polymer chains, that weakens them and thereby allowing soil microorganisms to attach and attack.^{12,21}

Conclusions

In summary, the CP films (with and without glycerol) displayed numerous intriguing features. Tensile strength of the CP films with glycerol reduced by 14% whereas % elongation augmented by more than 150% ensuing in flexibilized films. Haze values of CP films with glycerol decreased from 17% for chitosan to 3.7% for pure PEO because of the plasticized effect which increased the transparency of the films. The WVTR of CP films (with and without glycerol) showed a dual trend. For chitosan/PEO 60/40 ratio, it decreased up to 16.22% in chitosan/PEO, 24.18% and 29.85% in 10% and 20% glycerol added CP films. And then it increased further in CP blends with and without glycerol. The worth of these films is that, with high flexibility and high WVTR values, they can be utilized to pack fresh produce to control moisture evaporation along with enhancement of shelf life. These films biodegrade/disintegrate within five weeks.

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