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DEVELOPMENT AND CHARACTERIZATION OF A NOVEL EDIBLE FILM BASED ON GUAR GUM AND CARBOXYMETHYL GUAR GUM

Anuradha Saha[1], Rajinder K. Gupta[2] and Yogesh K. Tyagi[1*]

[1]University School of Basic and Applied Sciences,
[2]University School of Biotechnology, Guru Gobind Singh Indraprastha University, Dwarka, Sector 16C, New Delhi - 110078, India.

***Corresponding Author: Dr. Yogesh K. Tyagi**
University School of Basic & Applied Sciences, Guru Gobind Singh Indraprastha University, Dwarka, Sector 16C, New Delhi - 110078, India.

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ABSTRACT
The growth in demand of fresh vegetables and fruits has propelled food industry to establish safer storage methods for prolonging shelf life and improving quality. Recently, edible coatings have been extensively explored for extending shelf life of fruits and vegetables. Edible and biodegradable films have several benefits like biodegradability, non-toxic, economical and readily available. On the other hand, its synthetic counterparts cause environmental pollution which is the greatest concern in today's world. Edible films and coatings represent a barrier to oxygen, moisture, which results in a better preservation of food quality. The purpose of this study is to evaluate the physico-chemical properties of guar gum, carboxymethyl guar gum, cinnamon oil and potassium sorbate based composite coatings which had been used to extend the shelf life of vegetable like cucumber and tomato. Carboxymethyl guar gum is a novel material used for edible coating. Mechanical, barrier, structural, thermal and light transmission properties were obtained along with water activity and contact angle were also evaluated.

KEYWORDS: Edible films, Fruits, Coatings, Shelf life, physico-chemical properties.

1. INTRODUCTION
The increasing growth of human population leads to increase demand for food production due to which preserving and maintaining the food storage becomes a great challenge. One of the ways is to increase shelf life of food by using healthy packaging materials.[1] Synthetic packagings used generally in food industry are non biodegradable and causes environmental pollution.[2] Therefore, the focus is now on biopolymer based edible films and coatings which are biodegradable and environmentally friendly materials.[3] Various natural polysaccharides are used in the preparation of edible films such as chitosan[4,5], psyllium gum[1], cellulose and cellulose derivatives[2], alginate, carragennan[6], starch[7] and many others. The combinations in the form of blends of these natural polysaccharides in addition with various plasticizers are used in the preparation of edible films.[8] Chitosan is also known for its antifungal activity[9] which is popularly used for edible coatings throughout the world.

Plant derived gums such as guar gum is less utilized as edible coating material. It is readily available, economical, non-toxic, and biodegradable with its added advantage of acting as a fibre in human body system (GRAS approved). Guar gum is a high molecular weight galactomannan that belongs to the *Leguminosae* family and derived from the seed of *Cyamopsis tetragonolobu*.[10] Guar gum has recently been employed as an edible coating to prolong the shelf life of cucumber[11], tomatoes[12], Japanese persimmon.[13] Mehyar et al.[14] and Mehyar et al.[15] reported that natural polymers like guar gum when used as edible coating is a suitable substrate to carry food preservatives like potassium sorbate and essential oil, therefore enhancing the antifungal activity of edible coatings and potassium sorbate as a preservative agent. They further reported that guar gum edible coatings when combined with potassium sorbate retained potassium sorbate concentration on the surface of produce, which proves effective against moulds isolated from selected vegetables and protect potassium sorbate from disappearance during storage. The high viscosity of the guar gum solution [concentration of 1.0% (w/v)] may be responsible for producing a film on the surface of food commodity[16] which helps in extending the shelf life of the produce. Carboxymethyl guar is modified form of guar gum consisting of 1, 4-β-D-mannose backbone with 1, 6-α-D-galactose side groups. It was modified by adding a carboxymethyl group on galactose side chain of each guar unit.[10] Essential oil of cinnamon and food preservative such as potassium sorbate were incorporated

to provide antimicrobial property. Cinnamon oil is considered as "Generally Recognized as Safe" by the FDA. It has better antimicrobial activity than other essential oils [17]. The decreasing order of antimicrobial potency of essential oil incorporated in the food system as reported by[17] is as follows: oregano/clove/coriander/cinnamon>thyme>mint>rosemary>mustard>sage. The aim of this study was the preparation and characterization of natural polysaccharide based biodegradable films using guar gum and its anionic derivative carboxy-methyl guar gum and used it as an approach for the development of edible film to extend the shelf life of fruits and vegetables.

2. MATERIALS AND METHODS

2.1. Preparation of film forming solution

Film was prepared at controlled room temperature and relative humidity by solvent casting method. Guar gum and carboxymethyl guar gum composite solutions were prepared by mixing 1g of guar gum with 100 mL of distilled water. 1g of carboxy-methyl guar gum was mixed with 100 mL distilled water and both were stirred continuously and uniformly on a magnetic stirrer. Glycerol (35% w/w) as a plasticizer and tween-80 (0.1% w/w) as surfactant was added into the solution. The other variation of guar gum coating solution was prepared similarly with the extra addition of 0.1% w/v cinnamon oil and 0.4% w/v potassium sorbate (compositions given below). All the solutions were stabilized and conditioned at room temperature to remove any bubbles and air particles. The solutions were air-dried for 24 hours in the ventilated oven at controlled humidity and temperature to obtain films by casting method.[4,5] Dried films were conditioned under desiccator at (25+2)˚C, 50±5% R.H. for 48 h or until its further evaluation for testing. Following were the composition of the edible coating solutions used to prepare films: Coating A_1: Carboxymethyl guar gum only (1% w/v), Coating A_2: Carboxymethyl guar gum (1% w/v) + potassium sorbate (0.4% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v), Coating B: Carboxymethyl guar gum (1% w/v) + cinnamon oil (0.1% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v), Coating C: Carboxymethyl guar gum (1% w/v) + potassium sorbate (0.4% w/v) + cinnamon oil (0.1% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v), Coating D_1: Guar gum only (1% w/v), Coating D_2: Guar gum (1% w/v) + potassium sorbate (0.4% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v), Coating E: Guar gum (1% w/v) + cinnamon oil (0.1% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v), Coating F: Guar gum (1% w/v) + potassium sorbate (0.4% w/v) + cinnamon oil (0.1% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v).

2.2. Mechanical Properties

Tensile strength (TS) and elongation at break (EB) were measured by the Universal Testing machine (Lloyd Instrument CF Plus, UK) according to the standard method of ASTM D882 method. The films were cut with a dimension of (5×2.5) cm subjected to a speed of 100 mm/min and 10N load cell. The tensile strength (TS) was expressed as mega pascal (MPa) and elongation at break (EB) was expressed as percentage (%). Observation of each sample was taken three times. Thickness of the film was analyzed using a digital micrometer (Mitutoyo, Japan) (least count: 0.001 mm) at 3 random positions on the films.

2.3. Barrier Properties

2.3.1. Water vapour permeability

The permeation cell was filled with 50 mL of distilled water in order to generate 100% R.H. which was sealed by the film to be analyzed. Then, the cells were weighed using an analytical balance and placed inside the desiccators at 30-40% R.H. and 25˚C. The changes in weight of the cells were recorded at intervals of 24 hours. Water vapour transmission rate was measured as gm/m^2/day at 37.8˚C, 90% RH by standard test method ASTM F1249 and testing instrument Permetran-W (Mocon Inc., USA).

2.3.2. Oxygen Permeability

Oxygen Transmission rate was measured as cc/m^2/day at 23˚C and 0% RH by standard method ASTM D3985 (isostatic method) using test instrument Mocon Ox-Tran Model 2/21. The film sample was kept in sample holder having an exposed area of 50 cm^2. The nitrogen and oxygen cylinders were properly connected, and then the pressure gauge along the tree-regulator pressure of 740 mm Hg was set. The sample was cut with the template provided for Mocon instruments with the help of rubber support padding provided.

2.4. Thermal properties

2.4.1. Thermo-gravimetric analysis (TGA)

TGA tests were carried out by NETZSCH T4209F1 Libra. Samples (10 mg) were heated at rate of 10˚C min^{-1} from 25˚C to 300˚C under nitrogen (inert) atmosphere (purging gas flow rate 40 mL/min) to determine the different degradation processes of the developed materials. The gradual change in mass was recorded at y-axis.

2.4.2. Differential Scanning Calorimetry (DSC)

DSC analysis of the films were carried out by a NETZSCH DSC 200 F3, (US) at a rate of 10˚C/minute at 25˚C heated to 250˚C in nitrogen atmosphere. Approximately 5 mg of each sample was placed in an aluminium pan. An empty pan was taken as a reference.

2.5. Light transmission properties

2.5.1. Opacity

Opacity of the developed film was measured by Elcometer 6014 Shade and opacity meter, USA (dual function refractometer measuring opacity using 45/0˚ geometry) on the black standard and white standard according to the standard method of ASTM E1347. Three replicates of each film sample were determined. The results were expressed as a percentage.

2.5.2. Colour

The colour analysis was performed by a Minolta CIE colorimeter, (model Chroma Meter CR400, Osaka, Japan). The colorimeter was standardised using a standard white plate (L*= 97.10, a*= 0.13, b*=1.88, c*=1.88). After standardization, the colour measurement was performed by placing the film sample over colorimeter. Luminosity L* [0 (black) to 100 (white)], Chroma a* [red-green chromaticity (-60) to red (+60)] and Chroma b* [yellow-blue chromaticity (-60) to (+60)] were obtained. Three spots were chosen randomly to measure colour properties of prepared edible films. The total colour difference (ΔE) and whiteness indexes (WI) of the samples were evaluated according to Ahmadi et al., (2012).

$\Delta E = [(L^*-L)^2+ (a^*-a)^2 + (b-b^*)^2]^{0.5}$

$WI = 100 - [(100-L)^2 + a^2 + b^2]^{0.5}$

2.5.3. Haze

Haze was measured by spherical Haze meter M57D model B52782 Diffusion system by standard test methods of ASTM D1003.

2.6. FT-IR spectroscopy

FT-IR spectra from (Bruker Alpha spectrometer) were obtained in a range from 4000 to 500 cm^{-1} with a resolution of 2 cm^{-1} and 64 scans. The IR spectra were reported in % transmittance mode.

2.7. SEM

The surface morphology of the dry edible film was evaluated by placing a cut film sample in copper stubs. Samples were gold coated to make them conducting and visualized under scanning electron microscope (Hitachi S-3700N, Japan) at different magnifications by applying an accelerating voltage exposure of 15kV.

2.8. Contact angle

Contact angle was obtained by DSA25 KRUSS GmbH (Goniometer) using sessile drop method. In this method, a syringe was filled with 5 mL of a coating solution to be tested after it had been cleaned a few times with the same solution, and a droplet was placed on top of the horizontal surface. All measurements were conducted in ambient conditions. Contact angle measurements were conducted for 60s to prevent changes in the surface. Experiments were done in triplicate.

2.9. Water activity

Water activities of the developed edible films were evaluated by Aqualab Dew point water activity meter (hygrometer, USA) according to [18] method.

2.10. Statistical analysis

All data were reported as mean ± standard error. The mean values obtained were based on the data calculated from three independent experiments. Differences at $p<0.05$ were considered significant.

3. RESULTS AND DISCUSSION

3.1. Water vapour transmission rate

The water vapour permeability of guar gum films was higher than carboxymethyl guar gum films as replacement of hydroxyl group with bigger functional group such as carboxy-methyl increased the barrier property. Further, carboxy-methyl group also provides anionic characteristic to guar gum polymer which increases its solution clarity and solubility in aqueous system [19]. Presence of lipid such as cinnamon essential oil also provides better barrier to the coating films. Water present in the biopolymer films also acts as plasticizer which increased the transmission rate [20]. Addition of cinnamon essential oil to guar gum and carboxymethyl guar gum-based films decreased water vapour permeability of the films due to the hydrophobic nature of cinnamon essential oil (lipid) which could affect hydrophilic/hydrophobic balance of the films [21,22]. The WVTR ranged from 1287-4023 $gm/m^2/24h$ and did not change significantly ($p>0.05$) in the presence of potassium sorbate, cinnamon essential, modified guar gum in place of guar gum (Table 1). Glycerol due to its plasticizing action, changes the polymer network by creating mobile regions with large inter-chain distances, promoting water clustering by competing with water at active sites of the polymer matrix. The absorbed water plasticizes the film matrix, leading to a less dense structure, making the chain ends more mobile, thus increasing water transmission rate.[20,23] Rao et al.,[23] reported 4000-4141 ($gm/m^2/day$) in chitosan and guar gum films with different compositions. Although the WVTR of biodegradable polymers were much higher than those of synthetic materials, it was sufficient for short-term (hours to days) protection of food against moisture.[24]

3.2. Oxygen Transmission Rate (OTR)

OTR of developed edible films was found to be in the range of 2000-3056 $cc/m^2/day$ (Table 1). There was no significant difference ($p>0.05$) among the coatings. Guar gum is a hydrocolloid due to which its oxygen barrier capacity was on the lower side; however, if we keep this fresh produce in a high gas barrier atmosphere, then the shelf life of produce might decrease due to increase in concentration of carbon dioxide. This can lead to anaerobic conditions that may further increase the ripening rate and production of anaerobic microorganism.[25,26] Low or optimum permeability such as that of polysaccharide coatings helps to release the excess carbon dioxide, so the balance of oxygen and carbon dioxide is maintained, which could be helpful to extend the shelf life of fresh produce.

3.3. Mechanical properties

Guar gum films and carboxy-methyl guar gum films with and without blending have a thickness ranged from (0.025 to 0.100) mm (Table 1) but the values did not differ significantly ($p<0.05$). Thickness has been increased in those films, where cinnamon essential oil was added. Mechanical properties were expressed in

terms of tensile strength, % elongation at break. The results of mechanical property of the guar gum and modified gum films have been shown in Table 1. It was found that the addition of plasticizer in carboxy-methyl guar gum (Coating A_1 and A_2) and guar gum films (coating D_1 and D_2) led to increase in elongation and decrease in tensile strength (Table 1). Addition of cinnamon essential oil (lipid) led to increase in elongation and decrease in tensile strength of the films indicating that they become little weaker and non-homogeneous.[27] There was no significant difference ($p>0.05$) among the coatings but it was significantly different ($p<0.05$) from standard chitosan coatings. Tensile strength showed that lipid may function as plasticizer, increasing the softness and flexibility of the composite films. Increase of tensile strength with the addition of potassium sorbate preservative in both coatings A, C, D, F as compared to coating B, E showed that potassium sorbate added in composite films increased the tensile strength of the film, thereby, improving the mechanical property of the films. Our outcomes were in agreement with [27] in wheat gluten films combined with lipid. The less value of mechanical strength may be a disadvantage for films in some applications, but it was not considered as a drawback if the supporting material used for coatings is fruits and vegetables. Mikkonen et al., [28] reported that galactomannans with lower galactose content such as carboxymethyl guar gum produced films with higher elongation at break and tensile strength.

Table 1: Mechanical properties, water vapour transmission rate (WVTR) and oxygen transmission rate (OTR) of developed edible films prepared from edible coating for fruits and vegetables

S. No.	Film sample	Tensile strength (MPa)	Elongation at break (%)	Average thickness (mm)	Water vapour transmission rate (gm/m^2/day)	Oxygen transmission rate (cc/m^2/day)
1	Coating A_1	14.00 ± 0.50	01.10 ± 0.88	0.050 ± 0.002	2000.89 ± 2.65	2403.54 ± 3.9
2	Coating A_2	13.38 ± 1.12	12.82 ± 1.54	0.048 ± 0.002	1887.04 ± 3.33	2000.05 ± 7.8
3	Coating B	16.60 ± 1.25	19.72 ± 1.25	0.025 ± 0.003	1456.67 ± 5.50	2241.90 ± 5.6
4	Coating C	11.03 ± 0.41	36.73 ± 2.00	0.035 ± 0.003	1287.92 ± 3.50	2123.00 ± 9.8
5	Coating D_1	13.63 ± 1.49	18.15 ± 0.50	0.042 ± 0.001	3579.00 ± 0.00	2456.00 ± 8.7
6	Coating D_2	13.15 ± 0.66	21.95 ± 1.75	0.050 ± 0.004	4023.56 ± 7.60	2354.87 ± 9.8
7	Coating E	09.47 ± 0.33	39.40 ± 1.83	0.049 ± 0.006	3112.78 ± 4.40	3056.00 ± 0.0
8	Coating F	10.28 ± 0.63	36.73 ± 1.15	0.055 ± 0.002	3003.00 ± 1.50	2481.21 ± 0.5

[(where, each value = means ± standard error of the three replicates, and Coating A_1: Carboxymethyl guar gum only (1% w/v), Coating A_2: Carboxymethyl guar gum (1% w/v) + potassium sorbate (0.4% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v), Coating B: Carboxymethyl guar gum (1% w/v) + cinnamon oil (0.1% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v), Coating C: Carboxymethyl guar gum (1% w/v) + potassium sorbate (0.4% w/v) + cinnamon oil (0.1% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v), Coating D_1: Guar gum only (1% w/v), Coating D_2: Guar gum (1% w/v) + potassium sorbate (0.4% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v), Coating E: Guar gum (1% w/v) + cinnamon oil (0.1% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v), Coating F: Guar gum (1% w/v) + potassium sorbate (0.4% w/v) + cinnamon oil (0.1% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v)].

3.4. FT-IR

Fig. 1a and 1b represents the spectral data of guar gum and carboxymethyl guar gum films. A guar gum spectrum was characterized at 1024 cm^{-1} that represents CH_2-O-CH_2 in FT-IR scans. Both the spectra were corroborated well with other reported literature. The stretching vibration for hydroxyl group (OH bond) was at 3296 cm^{-1} and that of CH groups (asymmetric stretching) were at 2934 cm^{-1} (sharp). The absorption band located at 1644 cm^{-1} was due to the OH (hydroxyl) bond belonging to water molecules. CH_2 group bending (broad band) was assigned to an absorption band located at 1419 cm^{-1} frequency region. Figure 1b is characterized by the appearance of an added peak at 1534 cm^{-1} due to the presence of potassium sorbate, ester carboxyl bond stretching frequency appearing at 1639 cm^{-1} and reduced intensity of CH_2 bending vibration was appearing at 1384 cm^{-1}, asymmetric stretching at 2934 cm^{-1} showed good interaction of guar gum and potassium sorbate. In FT-IR spectrum (Fig. 2a), the absorption from 3500-3200 cm^{-1} broad band represents a hydroxyl group of reduced intensity due to the presence of cinnamon oil in guar gum films. The absorption band at 2923 cm^{-1} indicates CH stretch of alkanes which appeared common for both guar gum and cinnamon essential oil. (Fig. 2b) coating F corresponds to the spectra of the guar gum films incorporated with two kinds of antimicrobial agent, cinnamon essential oil and potassium sorbate. The IR spectra indicated an overlap of each absorption spectrum of various components of essential oil. The IR characteristic fingerprint peaks were mostly in the range of 1800–600 cm^{-1}. Two or more substances, when mixed together, their physical blends and chemical interactions were reflected by changes in their characteristic spectral peaks. [29] Presence of cinnamon essential oil in guar gum film has been characterized by the addition of absorbance band at 1643 cm^{-1} corresponding to stretching vibration of C=O bond for aldehyde (carbonyl stretch) and 1727 cm^{-1} corresponding to aldehyde group of a saturated fat which was absent in the guar gum spectra (Fig. 2a and 2b). These peaks were less broad due to the presence of conjugation of cinnamic acid and aromatic ring. Another characteristic band found at 1650-1550 cm^{-1} was due to the presence of alkene (C=C)

stretch which showed the presence of cinnamon oil functional group component in the film structure. [30] The peak at 1450 cm^{-1} (bending vibration) was a characteristic band for an alcohol C-OH group. The peak at 1377 cm^{-1} (bending vibration) represents the CH_2 alkanes and the peak at 1269 $cm^{-1}$and 1285 cm^{-1} correspond to the characteristic absorptions of esters and eugenol in volatile oil that is the stretching vibration of phenolic C-OH groups and aromatic acid ester C-O-C symmetric vibration. The peak at 1070 cm^{-1} and 1084 cm^{-1} attributed to the stretching vibration of C-OH deformation vibration. Strong absorption band between 1018-668 cm^{-1} indicates the presence of aromatic C=C bond [30,31] (Fig. 2a, 2b; 4a, 4b). (Fig. 3b) is characterized by the appearance of added peak at 1535 cm^{-1}, ester carboxyl bond stretching appearing at 1626 cm^{-1} and reduced intensity of CH_2 bending vibration was appearing at 1384.43 cm^{-1} asymmetric stretching at 2929 cm^{-1} due to the presence of potassium sorbate which indicated good interaction of carboxymethyl guar gum and potassium sorbate. The spectrum showed a reduced intensity of the OH stretching absorption band appearing at 3299 cm^{-1} indicating that OH groups were carboxymethylated (Fig. 3a, 3b; 4a, 4b). The band due to presence of OH bending vibrations at 1644 cm^{-1} in guar gum was absent indicating the carboxy-methylation of guar gum (involvement of OH group). 1000-1024.76 cm^{-1} (here 1024.13 cm^{-1}) indicated the presence of aromatic C=C stretch. In (Fig. 4a and Fig. 4b), the presence of the cinnamon essential oil in the film has been characterized by the addition of the absorbance band at 1700-1621cm^{-1} corresponding to stretching vibration of C=O bond for aldehyde (carbonyl stretch) and 1743 cm^{-1} corresponding to the aldehyde of a saturated fat which was absent in the guar gum spectra. The peaks were less broad due to conjugation of cinnamic acid and aromatic ring.

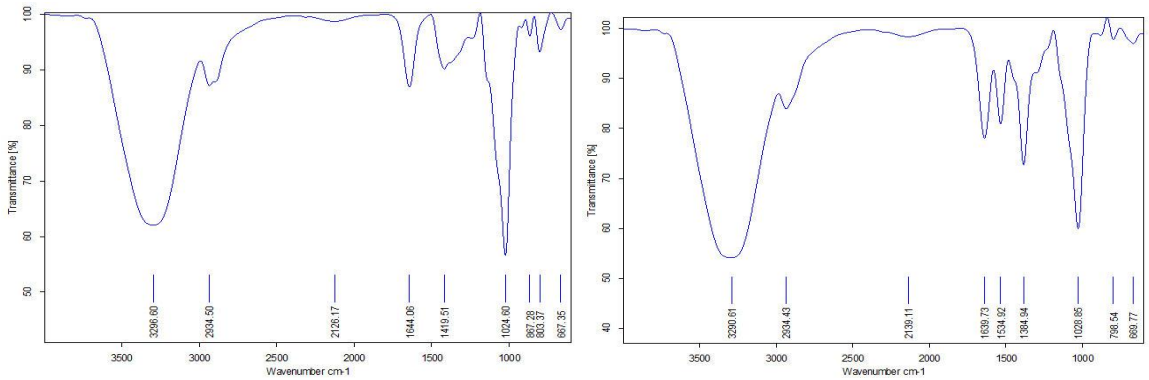

Fig.1. a) FT-IR spectra of coating D_1. b) FT-IR spectra of Coating D_2.

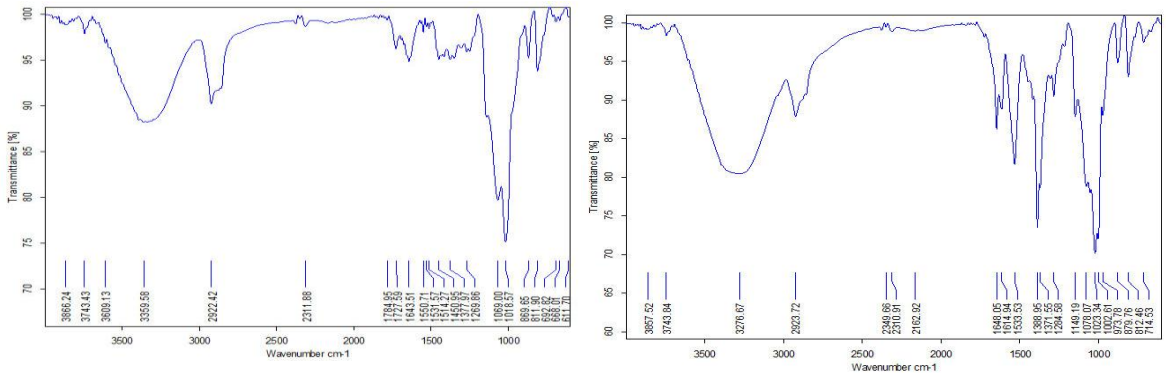

Fig. 2. a) FT-IR spectra of Coating E. b) FT-IR spectra of Coating F.

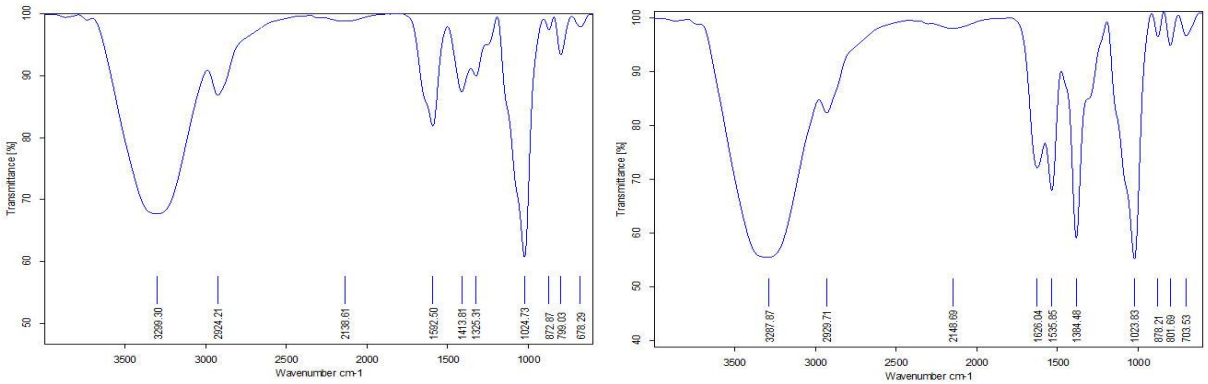

Fig. 3. a) FT-IR spectra of Coating A_1. b) FT-IR Spectra of Coating A_2.

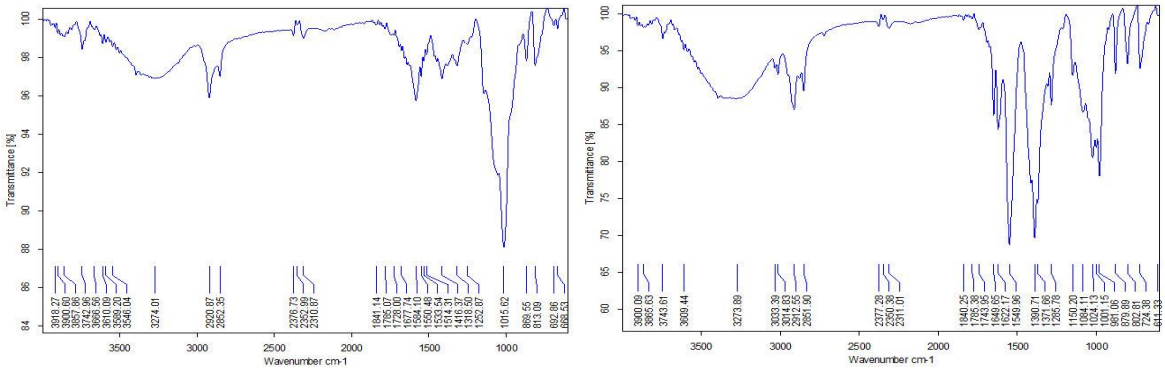

Fig.: 4. a) FT-IR Spectra of coating B. b) FT-IR spectra of Coating C.

Film colour

Table 2 illustrates the measured colour parameters according to CIELAB l*, a* and b* values of edible coating films. Plasticizer addition in all the edible coating films resulted in an increase in lightness (L*) values. Total colour difference ΔE values from the standard colour plate showed that edible films were transparent, which was a desirable characteristic in edible film packaging and coatings. Incorporating essential oil revealed significantly ($p<0.05$) higher ΔE values than that of the standard values, but it does not affect the appearance of coated fruits and vegetables. Addition of cinnamon essential oil reduced the transparency, but the reduction was not significant ($p>0.05$). Similar observations were reported by [22] in chitosan based films containing cinnamon essential oil and Mehdizadeh et al.,[32] in starch-chitosan films containing thyme essential oil. The values of colour parameter b* of films incorporated with cinnamon essential oil were higher than other films. Pranato et al. [33] also reported that addition of garlic essential oil increased the yellowness of the alginate based film as indicated by increase of b* value and decrease of L* value. These results agreed with our observations.

Table 2: Hunter colour values (L*, a* and b*), whiteness index (WI), total colour difference (ΔE) of the developed edible film.

S. No.	Edible film	L*	a*	b*	ΔE	WI
1.	Coating A_1	87.05 ± 0.29	-1.99 ± 0.37	3.74 ± 0.83	9.55 ± 0.25	83.42 ± 0.25
2.	Coating A_2	87.07 ± 0.30	-1.64 ± 0.25	2.99 ± 0.50	9.80 ± 0.20	83.56 ± 0.15
3.	Coating B	87.09 ± 0.71	-0.87 ± 0.09	0.81 ± 0.15	10.17 ± 0.86	89.51 ± 0.03
4.	Coating C	87.30 ± 1.49	-0.48 ± 0.00	0.23 ± 0.08	10.13 ± 1.71	91.33 ± 0.66
5.	Coating D_1	86.51 ± 0.25	-0.13 ± 0.03	0.81 ± 0.09	10.84 ± 0.27	82.83 ± 0.96
6.	Coating D_2	86.31 ± 0.20	-0.10 ± 0.04	0.72 ± 0.10	11.11 ± 0.25	91.66 ± 0.30
7.	Coating E	86.64 ± 1.00	0.09 ± 0.04	-0.68 ± 0.07	11.25±1.33	89.17 ± 2.29
8.	Coating F	87.64 ± 0.08	0.59 ± 0.07	1.39 ± 0.32	9.37 ± 0.02	84.58 ± 0.50

[(where, each value = means ± standard error of the three replicates, and Coating A_1: Carboxymethyl guar gum only (1% w/v), Coating A_2: Carboxymethyl guar gum (1% w/v) + potassium sorbate (0.4% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v), Coating B: Carboxymethyl guar gum (1% w/v) + cinnamon oil (0.1% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v), Coating C: Carboxymethyl guar gum (1% w/v) + potassium sorbate (0.4% w/v) + cinnamon oil (0.1% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v), Coating D_1: Guar gum only (1% w/v), Coating D_2: Guar gum (1% w/v) + potassium sorbate (0.4% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v), Coating E: Guar gum (1% w/v) + cinnamon oil (0.1% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v), Coating F: Guar gum (1% w/v) + potassium sorbate (0.4% w/v) + cinnamon oil (0.1% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v)].

3.5. SEM

The scanning electron micrograph images for the guar gum films revealed that the film was without any visible pores and the texture was uniform, homogenous and non-porous. Carboxymethyl guar gum films were found to be more smooth, even, uniform and homogenous (Fig. 5a, b) than guar gum films (Fig. 7a, b). Potassium sorbate addition did not affect the surface morphology of the films (Fig. 5b, 6a). There were small pores observed in cinnamon oil containing films (Fig. 6a, b and Fig. 8a, b). The image of the composite film (guar gum, cinnamon essential oil, potassium sorbate) revealed some minor cracks and pores on its surface which indicated the blending of the component added in the polymer matrix and homogenous dispersion of lipid within the film matrix (Fig. 8a). Some rough aggregates have been seen in film forming solution which could have been caused by aggregation of oil droplets in composite films, which may affect the homogenous distribution of polysaccharides.[34] This could explain the lower value of tensile strength and elongation at break of essential oil containing composite films. However, in totality, all the films tested were found to be uniform, smooth, little non-porous and homogenous (no phase separation) which is essential for the structural integrity, semi permeability property and uniform surface coating over the food

commodity. Similar results have been reported by Perdones et al.,[35] in the structure of edible films containing chitosan which was found to be smoother and more homogenous than that of films formed by mixing the polymer with pure essential oils. These results were in accord with the results of barrier property and mechanical property.

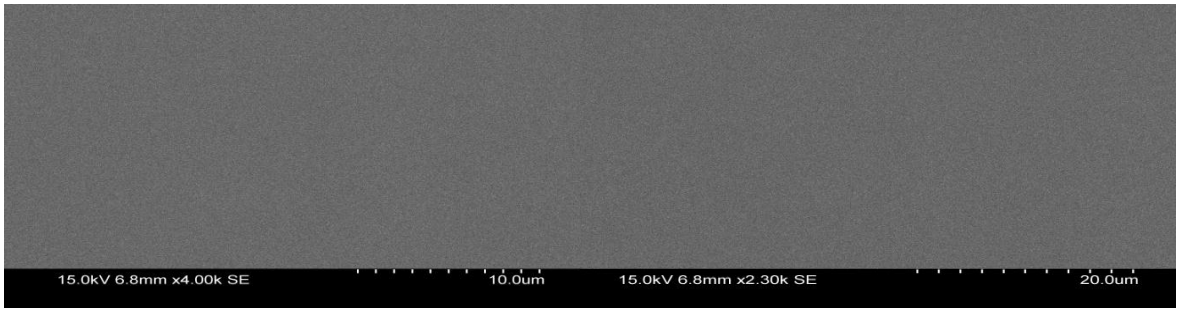

Fig. 5. a) SEM micrographs of coating A_1 film. b) Coating A_2 film surface.

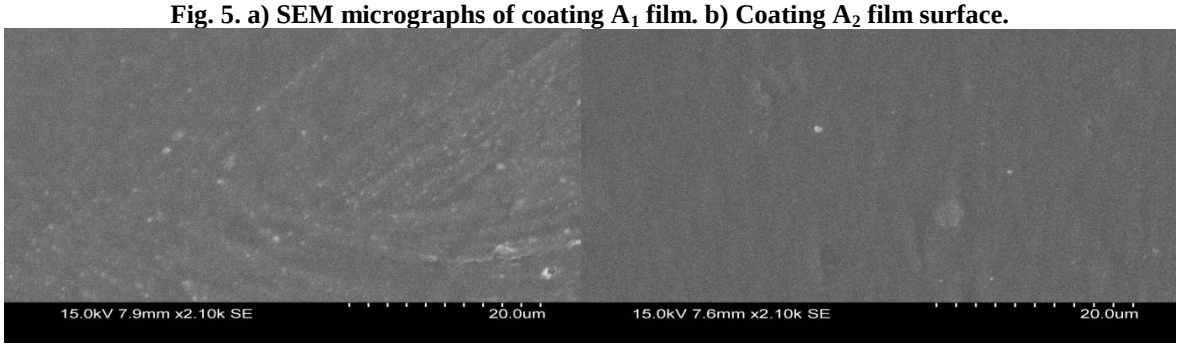

Fig. 6. a) SEM micrographs of coating B film surface. b) Coating C film surface.

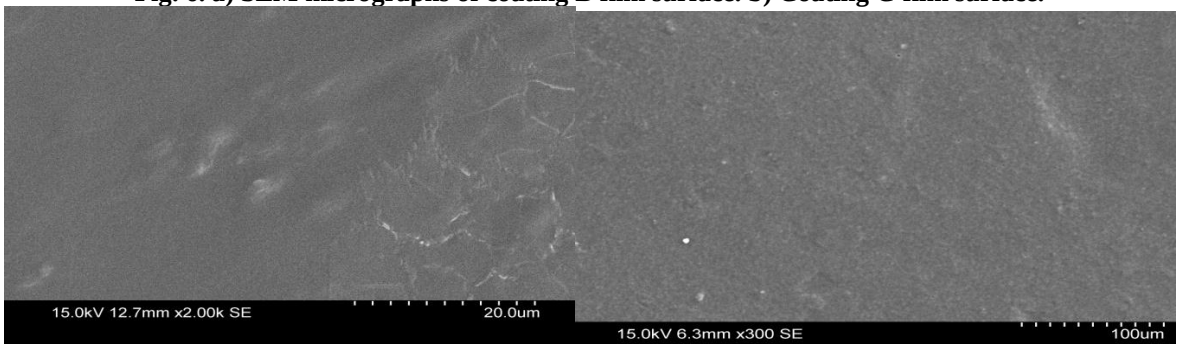

Fig. 7 a) SEM micrographs of coating D_2 film surface. b) Coating D_1 film surface.

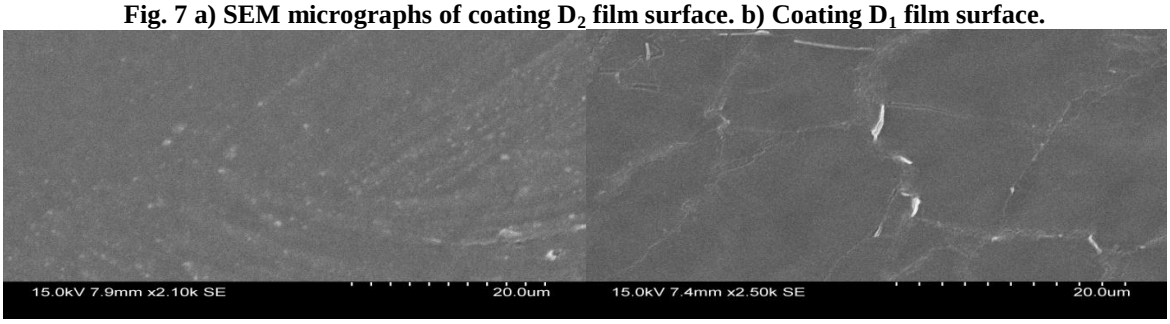

Fig. 8 a) SEM micrographs of coating E film. b) Coating F film surface

3.6. Light transmission properties

3.6.1. Opacity

The results of opacity are shown in Table 3. Opacity was found to be dependent on the presence of cinnamon essential oil in the film. All the developed films were transparent as indicated by film colour values. Carboxymethyl guar gum films were more transparent than native guar gum films. Therefore, low opacity value indicated that films were more transparent and light could effectively pass through the films. Addition of potassium sorbate and cinnamon essential oil in the films increased the opacity values but the increase was not significant (Table 3). Increased value in case of lipid addition may be attributed to the dispersion of small oil droplets throughout the polysaccharide network.[27] Similar results were reported by [32] in starch chitosan films containing thyme essential oil and [21,22] in chitosan films containing cinnamon essential oil. Pure films (coatings A_1, D_1) showed lower values as compared to other coatings. Chitosan films were the most transparent

among all the coatings which has been confirmed by its lowest opacity values.

3.6.2. Haze

As correlated with other results such as colour, opacity, and surface properties, addition of cinnamon essential oil increased the haze value which was related to decrease of transparency and lightness (L*) values (Table 3). Moreover, as carboxy-methyl guar gum films were more transparent than guar gum films, haze values of carboxy-methyl guar gum were lesser than that of guar gum films.

3.6.3. Contact angle

Contact angle of the edible coating solution was in the range of 59.0˚-79.6˚ on the fruit skin. Since the angle was less than 90˚, it showed that the coating solution covers the fruit surface skin effectively. In other research studies, it was found that the contact angles of semperfresh, beeswax and carnauba wax (commercial coatings) were 61.6º, 45.3º and 56.0º, respectively [36]. Therefore, our coatings under study had similar efficacy. Lower contact angle was attributed to higher hydrophilicity of the film that was due to the water binding capacity of glycerol (plasticizer) and functional groups of galactomannan. Addition of cinnamon essential oil decreased the hydrophilicity due to the loss of free hydroxyl groups in lipid-polymer interaction [21,22] which resulted in increased contact angle (Table 3). There was no significant difference in values among the coatings.

3.7. Water activity

Coated food commodity itself does not lose significant moisture until the coating material loses moisture. Hence, lower water activity of the coated material protects the food inside due to changes in environmental condition. Water activities are presented in Table 3. There was no significant difference ($p>0.05$) among the water activities of the developed edible films. However, addition of cinnamon essential oil increased the water activity, but did not exceed 0.7 which is optimal for fungal growth. It remained between (0.5-0.65) which was desirable for food packaging.

Table 3: Opacity, haze, water activity and contact angle at 25˚C of the developed edible film.

S. No.	Edible films	Haze (%)	Opacity (%)	Contact angle (˚)	Water activity (a_w)
1	Coating A_1	03.00 ± 0.18	0.8 ± 0.05	67.8 ± 0.81	0.59 ± 0.01
2	Coating A_2	03.70 ± 0.03	0.7 ± 0.04	68.4 ± 2.25	0.61 ± 0.01
3	Coating B	06.90 ± 0.20	2.6 ± 0.03	69.0 ± 1.00	0.64 ± 0.02
4	Coating C	08.90 ± 0.31	9.6 ± 0.18	59.0 ± 0.50	0.59 ± 0.01
5	Coating D_1	28.60 ± 2.14	4.4 ± 0.15	66.8 ± 0.31	0.58 ± 0.05
6	Coating D_2	13.00 ± 0.57	4.4 ± 0.01	78.6 ± 0.85	0.62 ± 0.00
7	Coating E	30.00 ± 1.61	4.0 ± 0.00	62.3 ± 1.50	0.62 ± 0.04
8	Coating F	26.00 ± 0.50	4.2 ± 0.10	63.5 ± 0.65	0.58 ± 0.01

[(where, each value = means ± standard error of the three replicates, and Coating A_1: Carboxymethyl guar gum only (1% w/v), Coating A_2: Carboxymethyl guar gum (1% w/v) + potassium sorbate (0.4% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v), Coating B: Carboxymethyl guar gum (1% w/v) + cinnamon oil (0.1% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v), Coating C: Carboxymethyl guar gum (1% w/v) + potassium sorbate (0.4% w/v) + cinnamon oil (0.1% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v), Coating D_1: Guar gum only (1% w/v), Coating D_2: Guar gum (1% w/v) + potassium sorbate (0.4% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v), Coating E: Guar gum (1% w/v) + cinnamon oil (0.1% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v), Coating F: Guar gum (1% w/v) + potassium sorbate (0.4% w/v) + cinnamon oil (0.1% w/v) + glycerol (35% w/w) + tween-80 (0.1% w/v)].

3.8. Thermal properties

3.8.1. Differential Scanning Colorimetry (DSC)

3.8.2. All DSC curves indicated major endothermic peaks that were observed over a temperature range of 60˚C - 80˚C (Fig. 9a-12b) which indicated that the prepared edible coatings were thermally stable till this temperature range. Generally during transport and mechanical handling, temperature of the surrounding environment of the fruit changes due to which edible coating that act as protective coatings should be stable under ambient conditions for large range of temperatures.[37] Cinnamon essential oil and potassium sorbate addition does not affect the thermal stability of carboxymethyl guar gum and guar gum films. Changes were found after 50˚C - 69.4˚C which was related to water evaporation associated with hydrophilic groups from the polymeric structure as described in study reported by [38], [28] and [39]. Guar gum films showed better thermal behaviour than carboxymethyl guar gum as changes were seen after 66˚C in guar gum thermogram (Fig. 10a-12b). Phase changes were found (glass transition temperature) after 65˚C in guar gum enriched with potassium sorbate and cinnamon essential oil indicating that it was thermally stable till 65˚C and displayed better thermal behaviour among all the coatings (Figure 12b). FT-IR results and the DSC thermogram indicate that both cinnamon oil and potassium sorbate showed synergistic interaction with guar gum and carboxymethyl guar gum.

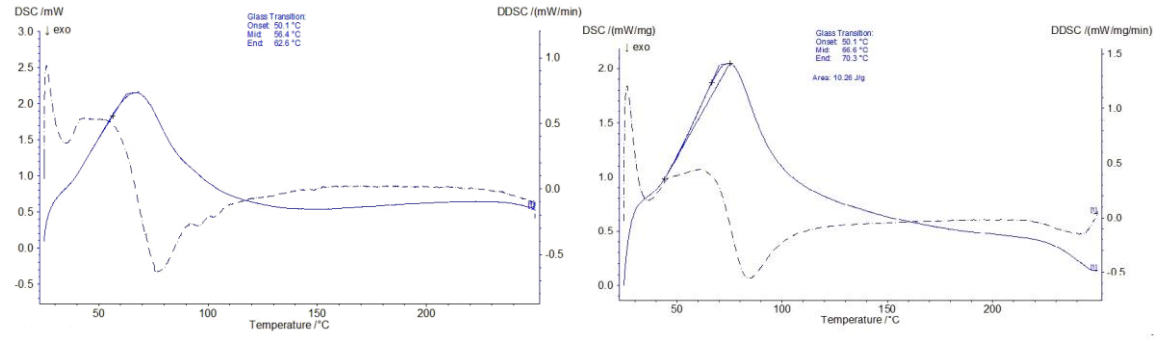

Fig. 9 a). DSC thermogram of coating A_1 b). DSC thermogram of coating A_2.

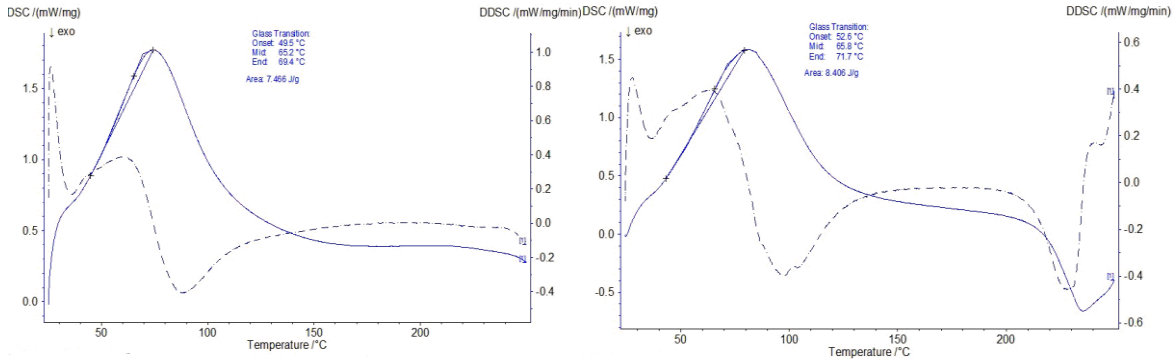

Fig. 10 a). DSC thermogram of Coating B. b). DSC thermogram of Coating C.

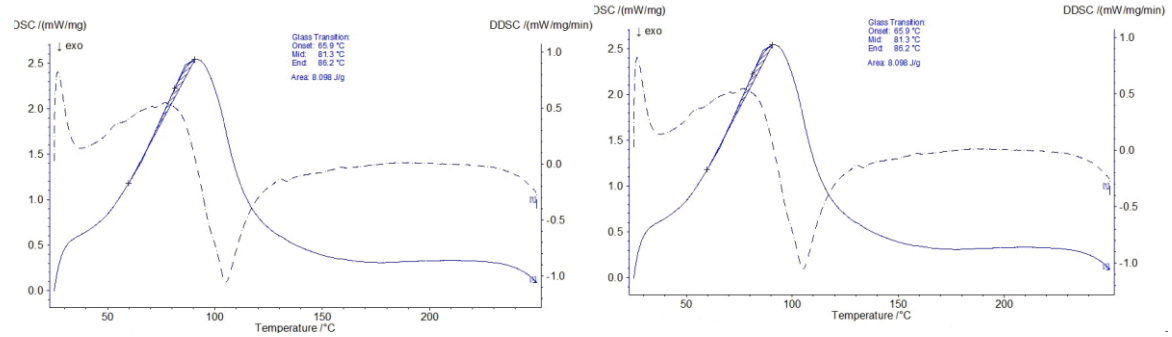

Fig. 11 a). DSC thermogram of coating D_1. b). DSC thermogram of coating D_2

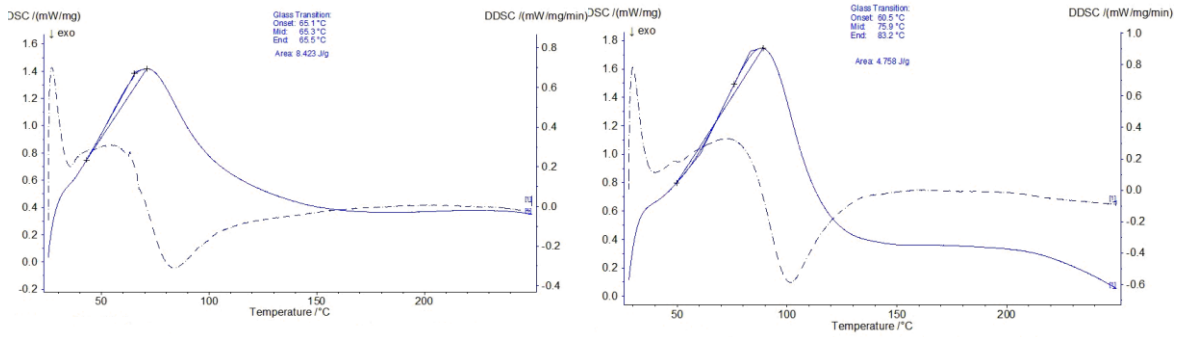

Fig. 12 a). DSC Thermogram of Coating E. b). DSC thermogram of coating F.

3.8.3. Thermogravimetric analysis (TGA)

DSC and TGA were combined in order to gain a better understanding of the thermal characteristics of a sample. TGA (changes of mass with respect to temperature) curves of carboxy-methyl guar gum (Fig. 13 a) showed several different zones. The initial weight loss (8.79%) at 100˚C, second at 170˚C due to polymer degradation, third at 250˚C, fourth at 325˚C and last at 350˚C – 450˚C due to degradation of carboxy-methyl group of the polymer. This weight loss was absent in guar gum polymers confirming the absence of carboxy-methyl group in the guar gum matrices (Fig. 15 a). The major

endothermic peak indicates complete decomposition from 250˚C - 300˚C (highest weight loss). Also, there was a difference between residual mass (ash content) of the two polymers. Incorporation of cinnamon oil and potassium sorbate into edible coating film resulted in a minor difference in the thermal zones in the spectra. Fig. 13 b and 14 a show similar thermal behaviour as that of carboxy-methyl guar gum, where the first mass loss (17.85%) occurred at 100˚C, while in case of only carboxy-methyl guar gum, first mass loss occurred at 90˚C. The major endothermic peak similar to guar gum found at 325˚C indicating 66.65% loss of the initial mass.[38,40] Relatively better thermal stability has been found in the (coating C and coating F) composite films. The rate of weight loss of guar gum increased with increasing temperature, attaining its maximum at 300˚C and decreasing thereafter, a broad endothermic peak obtained at 325˚C which was accounted for 79.18% mass loss. This loss can be attributed to the complete structural degradation and loss of total volatile component from the polysaccharide backbone such as carbon dioxide and water molecules.[28,40] The major endothermic degradation has found from 280˚C - 320˚C. In (Fig. 15 b), addition of potassium sorbate (coating D) did not affect the thermal stability of guar gum films significantly; only little temperature difference was found. From the (Fig. 16 a) and (Fig. 16 b), we can say that addition of cinnamon essential oil to the guar gum films (coating E and F) improved its thermal stability as less thermal degradation was found with relatively greater residual mass (31.30% and 31.50% respectively) than guar gum only edible films.[28,37] reported thermal degradation of polysaccharides occurs through random scission of glycosidic bonds, followed by further decomposition and degradation by a sequence of cleavages of galactose and mannose from the guar gum backbone.

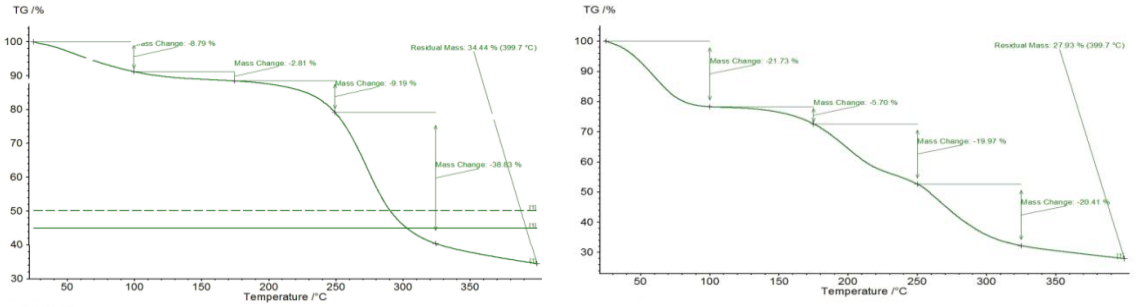

Fig. 13 a). TGA curve of Coating A_1. b) TGA curve of coating A_2.

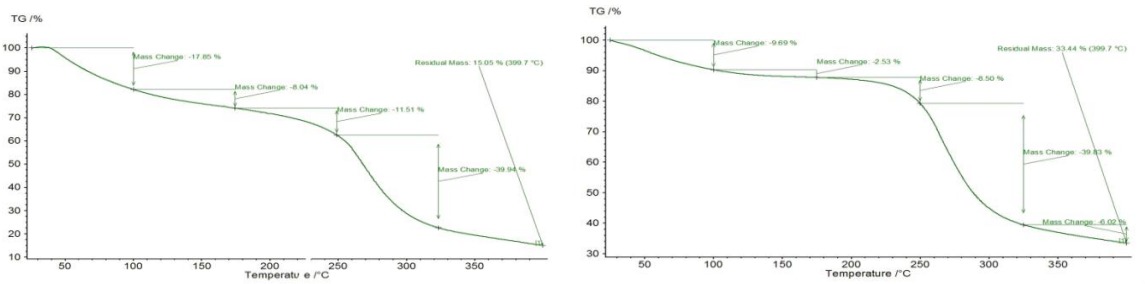

Fig. 14 a). TGA curve of coating B. b). TGA curve of coating C.

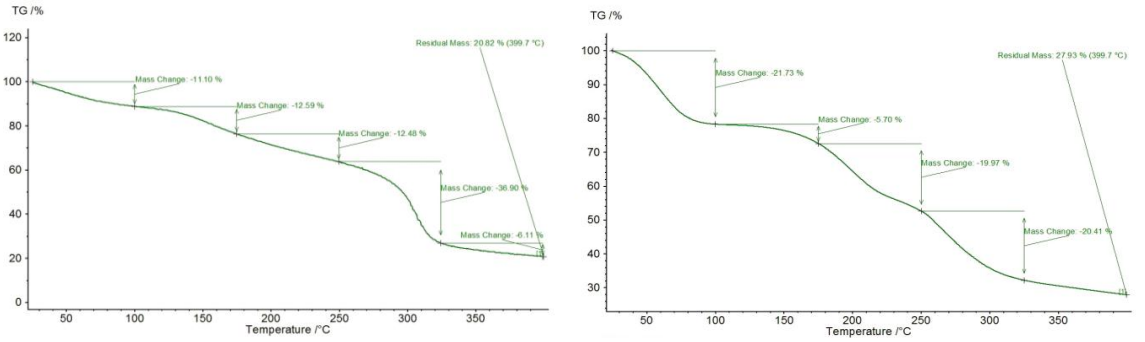

Fig. 15 a). TGA curve of coating D_1. b). TGA curve of coating D_2.

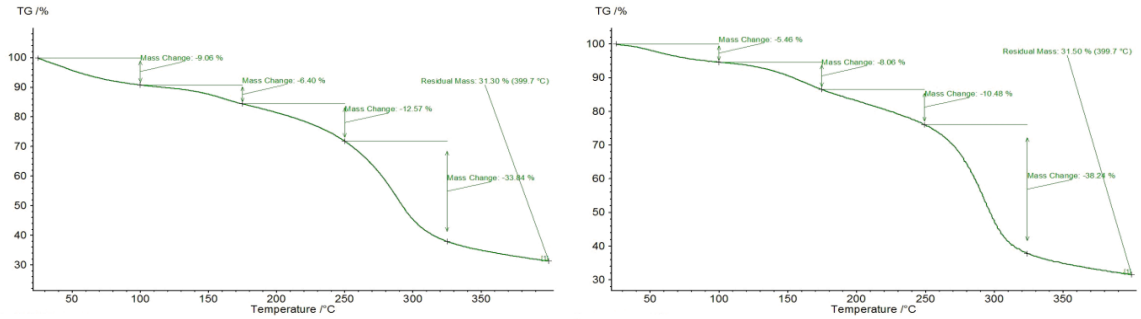

Fig. 16 a). TGA curve of coating E. b). TGA curve of coating F

4. CONCLUSIONS

The present study revealed that that guar gum and carboxymethyl guar gum had a good potential to make novel edible films. Guar gum and carboxymethyl guar gum based composite edible films are biodegradable, stable, safe, transparent, non toxic and odourless which are the desirable attributes of edible packaging and films. The contact angle, opacity and water activity of the film indicates that the physico-chemical properties of edible films depend on the nature of polymers used. FT-IR analyses suggest different synergistic chemical interaction occurring between functional groups and no adverse reaction occurred among the components. SEM micrographs analysis suggests smooth, non porous and compatible appearance of the film. Improved thermal stability of these composite films indicates stability of edible coating material towards weather change during transport and storage. Plasticizer addition improved the flexibility and addition of cinnamon essential oil and potassium sorbate imparts antibacterial property to edible coating which preserves the food better against microbial damage during storage. We found that guar gum and carboxymethyl guar gum based composite coating has successfully enhanced the shelf life of vegetable like cucumber by 5 days as compared to uncoated cucumber.

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