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SYNTHESIS OF NOVEL BIOPOLYMER BASED SUSTAINABLE COMPOSITE FOR FOOD PACKAGING MATERIAL AND IT'S APPLICATIONS

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ABSTRACT

Food packaging has a vital role in protecting foodstuffs from extrinsic factors such as oxidation, heat and light . In today's circumstance synthetic polymers are widely used, which causes environmental and chemical pollution.A bio-degradable and eco-friendly plastic have been synthesized in this study which is used for food wrapping. Active antioxidant film was fabricated by using polyvinyl alcohol (PVA) and Chitosan and incorporated withcitric acid. The microstructure and physical properties of prepared films were examined by the FT-IR analysis , SEM analysis ,Film thickness , Contact Angle measurement and Antimicrobial activity .The resultshows that addition of citric acid to PVA improved the elongation break and water vapor permeability increased with the addition of citric acid. In addition to citric acid in films, the antioxidant activity properties of the films were enhanced by up to 80%. Further, increasing the amount of citric acid slightly affected the color of the active films. The thermal properties of the films were enhanced with the addition of citric acid and chitosan. The dispersion of chitosan in the PVA matrix was affected by an increase in citric acid concentration in the PVA matrix. The resultssuggest that PVA-chitosan film containing citric can be utilized as a novel antioxidant packaging material in the food processing industry.

INTRODUCTION

Natural and synthetic polymer composites are used to prepare a biodegradable polymeric film. These films are used in food packaging to make it stronger, lighter or perform better. Polymeric composite films have effective antibacterial activity and, so they are used to control the food spoilage. Polyvinyl alcohol (PVA) is one of the most important polymers. It is a colorless, water-soluble, nontoxic, biocompatible, extremely hydrophilic and fully degradable semi- crystalline polymer. The main reason is due to its easy processability, high optical precision and biocompatibility and has excellent thermal stability these properties make PVA as an applicant in several applications. Chitosan (CS) is a linear harmless polycationic polysaccharide containing of β-(1→4)-linked d- glucosamine (2-amino-2-deoxy-d-glucose) and N-acetyl d- glucosamine (2-acetamido- 2-deoxy-d-glucose) units. Commercially, it is produced by chemical N-deacetylation of chitin, which is a component of shells from aquatic crustaceans (oysters, shrimp, lobsters, Antarctic krill and crabs,). The degree of deacetylation and the molar weight of the polymer is one of its most significant chemical characteristics, which might influence the method of its use. Furthermore, it also has antimicrobial/antibacterial activity and can therefore be used to increase the shelf life of food and as a constituent of biodegradable edible films for food. Storage atmospheres have a high influence on the properties of the film. Stress on the film increases with the increase the temperature from 4°C to 30°C and may cause it to breakdown It could control the viscosity during the film production, prevent from absorbing too much oil. Citric acid is a weak organic acid found in citrus fruits. It is a natural preservative and is also used to add an acidic (sour) taste to foods and soft drinks. In biochemistry, it is important as an intermediate in the citric acid cycle and therefore occurs in the metabolism of almost all living things. It also serves as an environmentally benign cleaning agent and acts as an antioxidant. Citric acid is blended with composite mixture of PVA/chitosan. These composites are dried in Petri dish at room temperature for 7-10 days. This film could afford food safety, increased the shelf life of food and quality conservation of food

In the present study, the PVA/chitosan was crosslinked with CA (1 wt. % and 2 wt. %) by solution casting technique. The synthesized PVA/Chitosan /CA blend films were characterized by Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), contact angle measurements and thickness measurements. Of crosslinker have a profound influence on physicochemical properties of PVA/Chitosan/CA and it will produce a positive effect on bactericidal activity. The main objectives of the present investigation are

To prepare the polyvinyl alcohol (PVA) / Chitosan/Citric acid (CA) polymeric film by solution casting method.

- To analyze the functional groups by Fourier, transform infrared spectroscopy.
- To investigate the antibacterial activity of biopolymer against gram- positive and gram-negative bacteria.
- To analyze surface morphology and thickness of the polymer by scanning electron spectroscopy.
- To investigate the hydrophobic or hydrophilic nature of the film, by contact angle measurement.

METHODOLOY

2.1. MATERIALS:

Chitosan (85% deacetylated) was commercially purchased from Indian Sea Foods, Cochin, India and polyvinyl alcohol (PVA) with average molecular weight of approximately 1,25,000 were obtained from HI Media Laboratories Pvt. Ltd. (Mumbai, India). Citric acid (CA) was purchased

from Lobechemie PVT, Ltd. Mumbai. Deionized water was used in all experiments. All the chemicals were used as received from the supplier.

Poly vinyl alcohol (PVA):

polyvinyl alcohol (PVA) polymer, with the hydrophilicity, good film forming ability, emulsifying and adhesive quality and outstanding physical and chemical stability, is a kind of excellent materials or the preparation of hydrophilic membranes. To form stable membranes with good mechanical properties, and to improve the selective permeability, PVA must be solubilized by modification methods due to its solubility. PVA is colorless, odorless, non- toxic, water soluble and is resistant to grease, oils and solvents. They exhibit many worth able characteristics' such as transparency, softness, heat seal ability, ductile but strong flexible and good strength to weight ratio. In addition of their polymers are low cost, show efficient mechanical properties such as tear and tensile strength, they are good barrier to oxygen and heat. This means that PVA is thermodynamically immiscible with collagen. In the case of PVA the polymer chain is very flexible due to either intra or inters associations. This flexibility of the chain in PVA varies monotonically with temperature.

Chitin and Chitosan:

Chitin is the second most abundant agro- polymer produced in nature. It appears naturally in the exoskeleton of arthropods and in the cell walls of fungi and yeasts. It is an acetylated polysaccharide composed of N- acetyl-D-glucosamine and is produced commercially by chemical extraction processes from prawns and crabs wastes. Chitin can also be produced using enzyme hydrolysis or fermentation process, but these processes are not economically feasible yet on industrial scale [36].

Chitosan is obtained from deacetylation of chitin, and different factors (e.g., alkali concentration, incubation time, ratio chitin to alkali, temperature and chitin source) can affect its properties. Chitosan is usually insoluble in water, but may be easily dissolved in acidic solutions. Its distinct characteristics from other polysaccharides rely on its cationic groups along the backbone and its antimicrobial properties against bacteria, yeasts and fungi [37-39]. The good film-forming properties allow the production of membranes (thickness > 30 μm) and coatings (<30 μm) to act as food preservative. Chitosan membranes are biodegradable, biocompatible, non-toxic, renewable and commercially available. Furthermore, chitosan membranes are reported as being semipermeable to gases presenting low oxygen permeability, essential for some food products preservation, and moderate water vapor barrier [40].

Despite these unique properties of chitosan membranes, much research has been done focused on their improvement. Adding glycerol to chitosan membranes, and applying thermo-mechanical treatment (mechanical kneading), it is possible to obtain a kind of thermoplastic material that grants good mechanical properties [41].

The functional properties of chitosan-based membranes may also be improved by combination with other hydrocolloids. Blends of chitosan and anionic polymers have been reported to have improved mechanical and barrier properties when compared to those made of chitosan only. This fact is attributed to the formation of polyelectrolyte complexes through electrostatic interactions between the protonated amino groups of chitosan and the negatively charged side-chain groups in the other biopolymer at the operating pH Improvements in mechanical properties, better performance in terms of water vapor permeability and lower water solubility have been reported for combinations of chitosan with other polysaccharides, such as starch, pectin or alginate [38-39] and proteins, like gelatin and whey proteins, compared to chitosan membranes.

Citric acid

Citric acid is found naturally in citrus fruits, especially lemons and limes. It's what gives them their tart, sour taste. A manufactured form of citric acid is commonly used as an additive in food, cleaning agents, and nutritional supplements. However, this manufactured form differs from what's

found naturally in citrus fruits. Manufactured citric acid is one of the most common food additives in the world. It's used to boost acidity, enhance flavor, and preserve ingredients. Sodas, juices, powdered beverages, candies, frozen foods, and some dairy products often contain manufactured citric acid. It's also added to canned fruits and vegetables to protect against botulism, a rare but serious illness caused by the toxin- producing Clostridium botulinum bacteria.

2.2. METHODS:

2.2.1. preparation of chitosan:

For chitosan to be extracted from fish scales it is necessary to convert it first to chitin. Generally, extraction of chitin from raw fish scales consists of three steps including demineralization for removal of calcium carbonate/phosphate, deproteinisation for Removal of protein and then, chitin can be converted into chitosan by N-deacetylation which partially removes the acetyl group From the polymers chain composition. Fish scales was washed to remove the muscles residue attached to it and then dried in intense sunlight and left for Autolysis for 24 hours at room temperature which improve the quality of chitosan.

STEP 1: Demineralization

Demineralization is carried out with 2% HCl at room temperature with a solid to solvent ratio of 1: 5 (w/v) for 16 hr for eliminating the organic matter specifically calcium carbonate (CaCO3) in dilute acidic medium. The residue was then washed till neutral pH and then dried in sunlight.

STEP 2: Deproteinization

The Deproteinization was carried out with 4% NaOH at room temperature with a solid to solvent ratio of 1:5 (w/v) for 20 hr. For removal of protein content of fish scales. The residue was washed until neutral pH and then dried in sunlight.

STEP 3: Deacetylation

Deacetylation was carried out with 4% NaOH at 60 ± 50C with solid to solvent ratio of 1:10 (w/v) 20 hr. This Process involve the partial removal of acetyl groups from chitin structure to convert chitin to form chitosan.

The residue was washed and dried at oven for 4 hour at 40±50C [1].

2.2.2. PVA/ Chitosan/CA Film preparation:

PVA/ Chitosan/CA films were prepared by solution-casting technique. Solution casting method is based on the principle of Stokes' law. In this method, polymer and prepolymer are equally merged and make soluble in the suitable solution. The polymer being the matrix phase dissolved easily soluble in the solution, whereas the nanoparticles dispersed in same solution or different solution. Finally, both got intermixed [2].

In brief, 50 mL of 1 wt. % PVA solution was prepared by dissolving the required amount of PVA in deionized water at 90°C followed by mechanical stirring until a clear solution was obtained. Chitosan solution 1 wt. % was prepared by dissolving in 1% acetic acid at room temperature with stirring. PVA and chitosan solutions were blended by a mechanical stirrer at room temperature to give a PVA/chitosan solution,1 wt. % and 2 wt. % (w/v) of Citric acid (CA) are blended with composite of PVA/Chitosan/CA and CA act as a cross linker followed by the addition of a drop of sulfuric acid to catalyze the reaction.

The mixture was allowed to stir at room temperature for 1 h to complete the cross-linking reaction. These viscous composite solutions were cast on Petri dish. Are dried at room temperature. The dried films were peeled from the casting surface. These films have uniform thickness. Film characteristics were determined after all sample films were preconditioned a constant temperature.

PVA/Chitosan/CA combination occurs by hydrogen binding and Ionic cross-linking of the amino and hydroxyl groups of chitosan and PVA respectively.

2.2.3. Synthesis of PVA/Chitosan/CA:

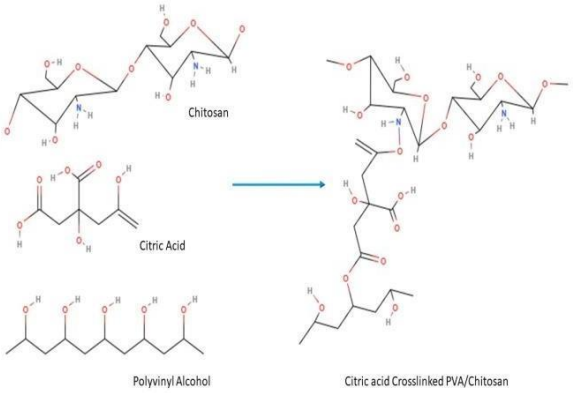

Fig.1 Synthesis of PVA/Chitosan/CA

4.3..CHARACTERIZATION:

4.3.1. Film thickness measurements:

Film thickness was measured using a screw gauge. Measurements were taken at five different locations of each film sample and the average film thickness was calculated.

4.3.2. Fourier transform infrared (FTIR) analysis:

The FTIR spectrum of the PVA/ Chitosan/CA (1 wt. % and 2 wt. %) samples were recorded using a Fourier transform infrared Spectroscope (Perkin Elmer Spectrum RX I, USA). A small quantity of samples mixed with KBr was powdered and compressed to pellets. Spectra were recorded in the range of wavenumber 400– 4000 cm−1 with a resolution of 4 cm−1.

4.3.3. Scanning Electron Microscope (SEM):

The morphology of PVA/STPP biodegradable film was examined by scanning electron microscopy (SEM; S- 4700, Hitachi Group Corp. ltd, Japan). Randomly selected areas of the PVA/ Chitosan/CA film were cut into squares and the usual diameter of the films were analyzed by randomly calculating the diameters of the film at different points from SEM images using the image analysis software.

4.3.4. Contact angle measurement:

Static water contact angle measurements were made by placing the membranes at room temperature on a sample stage and recording the contact angles using a Digi drop goniometer. A typical experiment started with the positioning of 2 µL Millipore water droplet on the membrane surface, using a micro syringe with a 20- gauge needle. Images were captured using a camera to measure the angle formed at the liquid-solid interface. To minimize the experimental errors, the contact angles were measured at three different positions for each sample.

4.3.5 Antibacterial activity:

PVA/ Chitosan and PVA/ Chitosan/CA (1 wt. % and 2 wt. %) polymeric solution and fabricated polymeric film were tested against gram-positive bacteria (Staphylococcus aureus and Bacillus subtilis) and gram-negative bacteria (Escherichia coli and Pseudomonas aeruginosa) using well diffusion method and to determine their antibacterial activity. Then the plates prepared for agar wells by scooping out the media with a sterile cork borer (8mm in diameter). Each well was

loaded with 100 µl of PVA/ Chitosan and PVA/ Chitosan/CA (1 wt. % and 2 wt. %) polymeric solution and it was incubated at
37 °C for 24 h. After incubation, the inhibitory effect was measured based on the
clear zone in the solution. If there is no clear zone around the well, that assumed the no inhibitory activity of given polymeric composite solution.

RESULTS AND DISCUSSION 3.1.
3.1. FTIR Spectral Analyses:

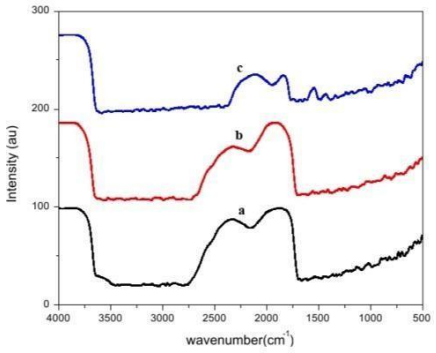

Fig.2 FTIR Spectra of (a) PVA/ Chitosan,
(b) PVA/ Chitosan/CA 1 wt. % and (c) PVA/ Chitosan/CA 2 wt. % films.

Cross-linking of PVA/Chitosan chains with Citric acid has been substantiated through comparison of FTIR spectra of non-cross linked PVA/ Chitosan and cross-linked PVA/Chitosan/CA acid. The results are depicted in Fig 2. To prove possible intermolecular interactions between different components in the prepared composites system [3], FT-IR spectra of PVA/ Chitosan blend and PVA/Chitosan/CA composites containing different concentrations of CA (1 wt. % and 2 wt. %) were recorded in the range 500-4000 cm−1. Comparing the IR spectra of the prepared PVA/Chitosan as well as the fabricated PVA/Chitosan/CA composites films, it could be observed that the exact peaks of PVA/Chitosan and PVA/Chitosan/CA blend, all peaks seemed in the spectrum suggests that there is no variation of the structure after compounding. PVA/Chitosan blend shows FTIR absorption bands at 3285 and 2928 cm−1, associated to the hydroxyl group (OH) stretching and group of (CH2) asymmetric stretching. Furthermore, the absorption bands concerning to amide I, amide II of C=O stretching vibrations, and N -H bending vibrations of NH2 as well as and CH2 flapping joined with OH group, this peaks at 1642 cm−1, 1581 cm−1 and 1345 cm−1 respectively. The bands corresponding to OH groups shifted to 3310 cm−1 and changed into weaker signals for PVA/Chitosan/CA composite films compared to PVA/Chitosan blend. The promising intermolecular interactions concerning these groups influence the differences in the characteristic absorption bands [4,5].

3.2. Scanning electronic microscopy (SEM):

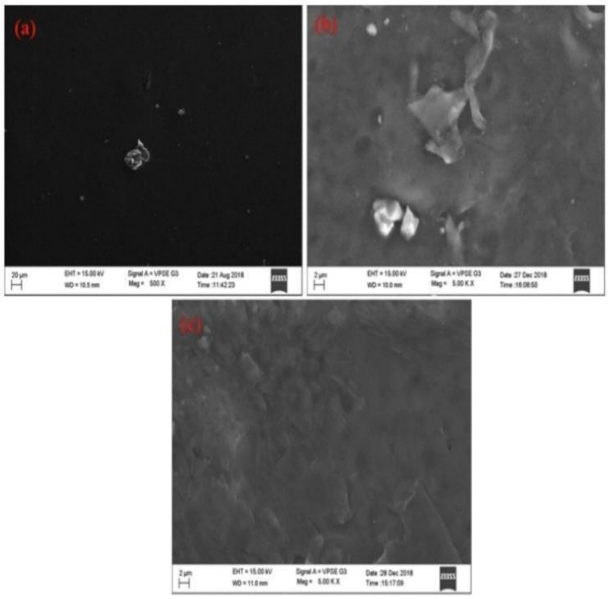

Fig.3. SEM images of (a) PVA/ Chitosan,
(b) PVA/ Chitosan/CA 1 wt. % and (c) PVA/ Chitosan/CA 2 wt. % films.

For further investigating the surface morphological structures, the resulting Nano composite films were investigated by SEM analysis. Fig.3. (A) shows the SEM images for PVA/Chitosan (Control) film. The (PVA/Chitosan) film exhibit a relatively smooth and homogeneous surface. Fig.3. (B) shows the SEM images for PVA/ Chitosan/CA 1 wt. % film, there exhibits a rough surface with several micron-sized particles inside the matrix was observed for the blend films owing to the cross-linking of (Citric acid) [6-7]. Fig.3. (c) shows PVA/Chitosan/CA 2 wt. % films display the flake like structure with perfect arrangement structure, CA crosslinking is showing some flake like structure surface.

3.3. Film Thickness

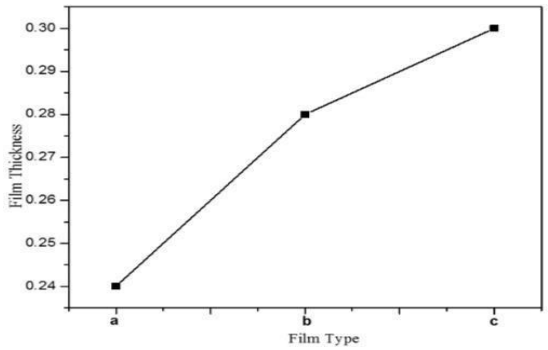

Fig.4 Film thickness of (a) PVA/ Chitosan,
(b) PVA/ Chitosan/CA 1 wt. % and (c) PVA/ Chitosan/CA 2 wt. % films.

The thickness of prepared PVA/Chitosan composite film was restrained by micrometer and it is presented in Fig.4. The means were calculated and used to determination of mechanical and physical belongings in the thickness of film depends upon the volume of the solution we take [18]. Five thickness capacities were reserved into each film, hence one in the centre besides four around

the perimeter. Thus, an average thickness value was used in the calculations as the increases of citric acid concentration respectively. Besides, the 1 and 2 Wt.% for the film thickness also increases, particularly, the PVA/Chitosan specify the particular patrician name of film thickness is 0.24 mm. In CA incorporated films, were the thickness increases to 0.28 and 0.30 mm respectively, since the CA present in it react with the molecular chain of the polymer by expanding their network so this would probably lead to increase the thickness of films. Uniformity in this thickness also plays a vital role in film quality. In addition to this might also influence the mechanical and barrier property[8-9].

3.4. Contact Angle measurements:

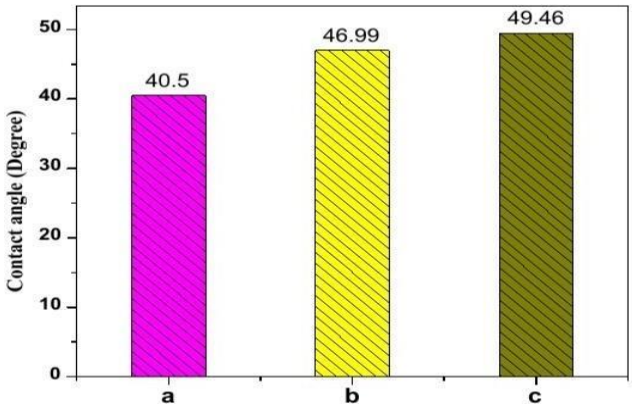

Fig.5. Water contact angle values of (a) PVA/Chitosan (b) PVA/Chitosan/CA 1 wt. % and (c) PVA/Chitosan/CA 2 wt. % films.

Fig.5. shows the contact angle measurements of pristine PVA/Chitosan and crosslinked PVA/Chitosan/CA (1 wt. % and 2 wt. %) films. Water contact angle reflects hydrophobicity/hydrophilicity of a surface[10-12].Crosslinking by CA removed a large number of hydroxyl groups from the polymer chain. PVA/Chitosan/CA (1 wt. % and 2 wt. %) maximum observed contact angle reading of 40.5°, 46.9° and 49.4° respectively, on modification of CA crosslinked film becomes moderately hydrophobic when compared to the highly hydrophilic nature of PVA and the addition CA crosslinked film shows moderately hydrophobic nature. From these results exhibit PVA/Chitosan/CA has the highest contact angle[13].

3.5. Antimicrobial activity:

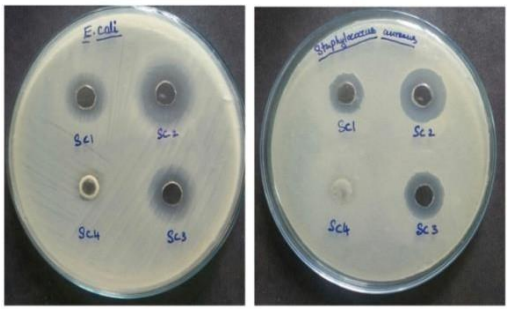

Fig.6 Images of antibacterial activity of (SC1 PVA/Chitosan (SC2) PVA/Chitosan/CA 1 wt. % and (SC3) PVA/Chitosan/CA 2 wt. % films against

E. coli and S. aureus.

Inhibitory effect of PVA/Chitosanand PVA/Chitosan/CA solutions against *E. coli* and *S. aureus* are shown as in Fig. 6. Antimicrobial activity was determined by the diameter of the growth inhibition zone. It is notable that PVA/Chitosan solution show a small microbial inhibitory zone, but CA crosslinked solution display distinctive microbial inhibitory regions against all four tested bacteria by disk method proving that tuning microstate soft polymers could have a profound influence on its antibacterial properties. Since there is no clear zone surrounding, we assumed that there is no inhibitory zone, and furthermore, the diameter was valued as zero. In terms of surrounding clearing zone, PVA/Chitosan solution show a little inhibitory effect against all tested microorganisms [14]. The schematic representation of comparative study of antibacterial activity of PVA/Chitosan blend solution and PVA/Chitosan/CA crosslinked film with 1 wt. % and 2 wt. % CA are shown in the scheme 1. In general, the antibacterial action is exhibited by two kinds of a mechanism including bactericidal and anti- adhesion way. It is well-documented in literature that bacterial proliferation involves four conservative steps as listed as (i) adhesion of cells on material surface (ii) accumulation and aggregation of cells (iii) biofilm formation and maturation and (iv) proliferation of bacteria for a new cycle after detaching form biofilm, of which first and significant step is attachment of bacterium upon material surface is foremost impotent [15]. Cell adhesion to the implant surfaces is the critical starting point of the biological functions at the interface influencing the cellular responses of the organism. Therefore, cell adhesion to the implant surfaces represents the initial interaction, and it is influenced by the surface chemical and topographical characteristics [16]. The diffusion itself is dependent on the size, shape, and polarity of the diffusion material. The chemical structure and the crosslinking level of the films also affect this phenomenon.

To this end, it is desirable to tune material surface to unfavorable bacterial attachment rather than attempting to kill bacteria after entering into the system. Crosslinking with CA tunes microstate of PVA/Chitosan to create a surface wherein adhesion of bacteria is not favored. Besides, CA functional group is capable of flowing through bacterial cell membranes to lower intercellular pH. Destruction of bacteria is accomplished by damaging enzymatic activity, proteins, DNA and extracellular membranes due to low pH within the cells. Also, it is proposed that organic acids are able to suppress NADH oxidation leading to bacterial death.

The inhibitory effect is predominant when CA is used as crosslinker used in this study suggesting that presence of CA is beneficial for antibacterial activity. The reason for the observation is multi-faceted.

(i) CA reconstructs the micro-domain structure of PVA/Chitosan in such a way that PVA/Chitosan/CA possesses desirable surface characteristics which repel bacterium when it comes into contact with the surface (ii) CA itself act as an antibacterial agent. CA modifies local pH and /or involve in chelation bond with metal ion present in the bacterial cell wall, that inhibits absorption of essential nutrients and eventually causing the death of bacteria. The zone of inhibition against E-coli is 14 mm, 23 mm and 17 mm, S. aureus is 13 mm, 18 mm, and 15 mm according to SC1, SC2, SC3.Similar results are noticed by Fu et al when CA is used as a cross-linker for chitosan derivative, 99 % S. aureus was killed. Furthermore, it has been found that the PVA/Chitosan/CA 2 wt. % has higher zone of inhibition and also it can be used to extend food shelf-life [17].

CONCLUSION

In this investigation, various concentrations of Citric Acid (CA) have been utilized for crosslinking PVA/Chitosan and were characterized for their physicochemical and bactericidal properties. Functionalities of crosslinker have a profound influence on physicochemical properties of PVA/Chitosan and produce a positive effect on bactericidal activity. Crosslinking with CA 2 wt. % substantially enhance film properties through establishing an appropriate balance between

hydrophobic/hydrophilic microstructure. CA itself could act as an antimicrobial agent and it depresses internal pH of bacteria and kills it by altering the permeability of membrane indicating the unique benefit of using CA crosslinker. This is first report to comparatively evaluate the antimicrobial properties of PVA/Chitosan without incorporating additional antibiotics or inorganic materials, that should reiterate enormous research interest in utilizing PVA/Chitosan based active food packaging. Increase in crosslinking density decrease in free volume between surface topography, electrostatic, and hydrophilic/hydrophobic interactions in the bacterium-substrate system were studied to gain insights into the
E. coli adhesion process.

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