Synthesis and evaluation of physical properties of Agar biopolymer film coating—an alternative for food packaging industry

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Abstract

The standard packaging material requirement is increasing proportionately with the increase in demand and consumption of packaged food. Indeed, it is challenging to design a perfect packaging material that can fall in line with international standards. It is a humongous task when it comes to handling conventionally and commercially available materials such as crude oil derivative polymers, as far as their recycling and degradability are concerned. In the present investigation, efforts were made to design a biopolymer-based film coating for the food packaging industry with adequate physical and mechanical properties. They can be used as a substitute for the conventionally available options till date. There is no shortage of biopolymers available for their application in food industry and they are already being used for similar purposes. However, still, there are some disadvantages associated with these materials. The present work is related to the synthesis, preparation of Agar based biopolymer film coating on a paper substrate, and their characterization according to specific standards prescribed by certifying agencies. It includes the study of Agar coated biopolymer film’s mechanical properties using nanoindentation technique, profilometry, and surface property such as hydrophobic nature of the coating and the gas barrier potential of the film as well. Apart from this, a new methodology (Image Processing Tools using MATLAB and Spectral Analysis) was used for studying the effect of moisture when these coatings were exposed to hot and moist environment.

1. Introduction

Now—a—days for modern society, there is a need for smooth transportation, storage, and distribution of commercially produced foods and beverages. According to a survey (WPO 2009) conducted by the World Packaging Organization, one-fourth of the food products are being wasted due to improper or lack of packaging. Over a period of time, the world has witnessed a significant improvement in packaging technology, and the use of new advanced materials by the packaging industry has increased with a speedy consumption of packaged food throughout the world. Generally, several types of materials are used in the packaging industries, however in the earlier days the majority of the materials used for packaging were metals and glass, and with the progress in technology, the focus was drastically moved towards the use of plastics/polymer, and later it shifted towards the use of paper [1]. In addition to these signs of progress in food packaging industry, there are other concerns, namely, material cost, environmental issues, regulation on pollutants and solid waste disposal, etc, that need to be adequately addressed. A survey data by the US Environmental Protection Agency (EPA 2005) shows that around 31% of the total solid waste generated is from food packaging industry. In another survey, it was explained that almost half of the complete waste generated from the packaging industry is from food packaging sector [2].

The petro-chemical based plastics are being widely used as a packaging material. According to the latest survey, the global consumption of polymer-based products is about 0.2 billion tonnes, with a growth rate of 0.5% annually. Plastics, the most commercially available crude oil derivatives such as polyethylene terephthalate
(PET), polyvinyl chloride (PVC), polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyamide (PA) are being popularly used for food packaging. They have all the desired properties, such as good mechanical properties (tensile and tear resistance), excellent gas barrier properties, and heat sensibility that are expected for any packaging material. The conventional packaging materials are losing their popularity due to environmental issues such as, their limited ability to biodegrade and most of the materials end up in land-filling instead of being recycled [3].

Biodegradation of most commonly available polymers, namely, polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC) can be explained by measuring the amount of CO₂ release due to decomposition of these polymers. Degradation of polymers that are made up of hydrocarbons is a measure of partial or complete conversion/combustion of these H-C in the presence of oxygen, and the amount of carbon dioxide release will give the rate of degradation of these materials. In addition to these, other factors such as residue weight and reduction in strength can be taken into consideration for defining the biodegradability of these polymers [4]. Few researchers have tried to study the degradation behaviour of commercially available polymer bags according to international standards such as the American Society of Material Testing (ASTM), International Standard of Organization (ISO) and European Committee for Standardization (ECN) in a composting atmosphere [5–7]. According to a study conducted by a group of researchers, the efforts were made to assess the biodegradability of biopolymer (PLA) based packages under real composting and ambient exposure conditions using visual inspection, GPC, and DSC-TGA technique [8].

To overcome these issues as mentioned earlier, researchers have developed some biodegradable polymers; namely, polyesters, poly-hydroxy-alkanoates (PHA), polylactide, polycaprolactone, polysaccharides, etc, whose are biodegradable under a microbial active atmospheric condition [9]. In addition to these, packaging products made up of cellulose and starch are supposed to be hydro-biodegradable. In aqueous conditions, these materials are prone to be hydrolyzed and bio-assimilate rapidly. Naturally, the cellulose and starch derivative products used for packaging material are hydrophilic, whereas some synthetic and natural polymers are hydrophobic. There are some hydro-biodegradable aliphatic polyesters such as poly-lactic acid (PLA) that possess better properties such as hydrophobic surface, wettability, and swellability compared to cellulose-based products. Studies show the use of polyactic acid as a coating material for the production of paper cups and packaging because the properties of such coated films are very promising compared to the existing packaging material [10]. However, some toxicological studies on PLA reveal that there might be instances of lactic acid release into the food [11]. Even though a release of a limited amount of lactic acid doesn’t create any damage to a healthy human body, it may create some health complications to certain individual those are intolerant to lactic acid [12].

Several studies were done on bio-degradable packaging materials prepared by polyactic acid-based biopolymers films. Still, it was not 100% degradable, and also there are issues of toxic effects with it. Few researchers have tried to study the use of a composite film consisting of sea-weed extract (Agarose) and nanocellulose for packaging applications [13]. The developed nano-composite film supposed to have sound mechanical properties along with a better hydrophobic surface and good gas barrier potential property [14]. Agarose, a neutral polysaccharide, is the prime component of Agar (sea-weed extract) whose rheological properties can be controlled by adding glycerin or ethylene glycol. It can also be used as a biopolymer coating on cellulose extract paper substrate for food packaging applications [15]. The prime goal of the present investigation is to study the physical and chemical properties of the Agar-coated biopolymer film on the paper substrate and to draw a comparison of their properties with commercially available PE-coated film.

2. Materials and method

Commercially available Agar powder was used for the preparation of biopolymer film coating. The procured Agar is having a mesh size of 80 and whose gel strength is greater than 11 g.cm⁻² with a gelation point in the range of 35 °C–42 °C. For this biofilm coating, a commercially available paper sheet of 120 GSM was procured and cut into smaller pieces of dimension 5 cm long and 4 cm wide.

The Agar–water solution was prepared in the glass beaker before its coating on the paper substrate. The water of volume 25 ml was taken in a glass beaker (50 ml) to which 0.25 g of Agar powder (1% of the total solution) was added. The solution was continuously stirred (750 rpm) and heated (100 °C) for 1 h under a hot plate with a stirring magnetic facility. After continuous heating and stirring, a pale yellow appearance of the solution was observed (as shown in figure 1). In this condition, glycerol was added to the solution to increase the elastic properties of the gel-like solution. The solution was stirred under the hot plate until a clear solution is achieved. The amount of glycerol varied from 0.5% to 1% of the total solution to study the effect on the mechanical properties of Agar-coated biofilm.
3. Characterization of coated polymer films

3.1. Bio-film coating process

After the completion of solution preparation, the coating was done on the paper substrate with the help of a painting brush. The paper substrate was being coated for several layers (5—Layers), and after the completion of coating, the coated surface was allowed to dry under a hot air flow (as shown in figure 2). Generally, it takes 5–10 min for complete drying of a single coating, and after each successive coating and drying, the Agar-coated paper sample was kept under a flat steel plate. Such practice was followed to avoid the bending of coated film that aroused due to a difference in elastic modulus of substrate and coating.

3.2. Water contact angle

The water-repellent nature of the coated surface was studied using a contact angle goniometer (Holmarch). Small, square samples having a dimension of 1 cm² were cut from both Agar-coated and PE-coated film, and the water contact angle was measured using de-ionized water. Several readings were taken from randomly selected regions to ensure the repeatability of the measurement data. After the test, images were collected to measure the accurate contact angle using image analysis software (ImageJ) to understand the film’s hydrophobic/hydrophilic nature.

3.3. Moisture exposure analysis

This analysis was done on the coated sample in several steps while following different techniques to characterize the effect of moisture exposure on the sample. The samples were exposed to a moist atmosphere such as hot water, cold water, and acetic acid, and later the analysis was done using suitable tools. For the present investigation, three techniques were used; namely, (i) Image Processing Tool using MATLAB; (ii) Spectroscopy analysis; (iii) by measuring the volume loss using Stylus Probe Profilometer. For this study, before the coating, the Agar gel was blended with blue color dye for the detection of a variation in contrast due to volume loss from the coated film substrate, and the difference in contrast due to this can be analyzed by detecting the change contrast after post-processing the image of both treated and untreated sample.

\[
\text{Contrast}_{\text{image}} = \text{Intensity}_{\text{Max}} - \text{Intensity}_{\text{Min}}
\]  

The image of both moister treated and untreated samples were uploaded in the software, and the color image was then converted to a histogram for further processing using MATLAB Image Analysis Tool. For the
present investigation, images of three samples for each moisture treated Agar-coated film (10 s, 30 s, 1 min, 3 min and 5 min) were taken for the analysis of contrast effect. The primary colors such as Red, Green, and Blue pertaining to the original image were segregated into a separate array to calculate the maximum and minimum count of each bin location. The entire algorithm was explained in figure 3, and the contrast can be calculated with the help of equation (1). This is a qualitative study to understand the extent of volume loss when the coated sample was exposed to hot water for distinct time interval such as, 10 s, 30 s, 1 min, 3 min and 5 min.

The purpose of studying the effect of acetic acid is to evaluate the performance of film coating during its exposure to fruit juices or beverages that contain some amount of acid in it. This quantitative study was performed by scanning the treated surface with the help of a Stylus Probe Profilometer (Bruker, DikstatXT). The scanning was conducted across a transition region within which the substrate, thickness of film coating, and reduced thickness due to moisture exposure lie within it. This technique was followed due to specific limitations (minimal scanning range) of the profilometer.

3.4. Film residual stress measurement

The residual stress measurement of the coated film for both Agar and PE film was done using a Stylus Probe Profilometer (Bruker, DikstatXT). The measured stress is a function of elastic modulus, Poisson’s ratio of the substrate, thickness of the substrate, and width of the film, known as Stoney’s equation (equation (2)) [16]. The elastic modulus and Poisson’s ratio of the paper substrate were chosen from previous work by a group of researchers [17, 18]. In contrast, the film thickness was taken as standard value (0.2 mm for 120 GSM), and the measured value of the film thickness using the profilometer was found to be 80 μm. As the film thickness is less than the substrate thickness (h_f ≪ h_s); therefore, it satisfies the pre-condition for the application of Stoney’s equation. During the stress measurement, the radius of curvature of the substrate before coating and after coating was measured by using the profilometer, and the film stress can be measured by using these values in equation (2).

For the present investigation, a standard scan rate was chosen for a range of 524 μm by following the hill and valley type scan pattern. The scanning was done for a resolution set at 0.555 μm/point for around 9000 points to scan with speed at 167 μm s⁻¹. The entire scanning was completed in 30 s, and the probe used for scanning was having a radius of 2 μm that uses 3 mg of force.
\[
\sigma = \frac{E_s}{6(1 - \nu_s)} h_f \left( \frac{1}{R} - \frac{1}{R_0} \right)
\]  
(2)

Where,  
\( E_s \) = Elastic modulous of substrate  
\( h_s \) = Thickness of substrate  
\( h_f \) = Thickness of film  
\( \nu_s \) = Poisson’s of substrate  
\( R \) = Radius of curvature after deposition  
\( R_0 \) = Radius of curvature before deposition

3.5. Nanoindentation test

This technique is suitable for studying mechanical properties such as elastic modulus and hardness of thin films. Nanoindentation technique is also known as instrumented indentation technique. An indenter is made to pierce the film up to a certain depth, and the response of the indenter (load in \( \mu N \)) is recorded or monitored by the instrument [19]. Nanoindentation is a unique technique to study the mechanical properties of these thin biofilms because due to certain limitations tensile study of these films is bit difficult. Therefore, instrumented indentation technique is used to find the reduced elastic modulus by using equation (3) [20]. Whereas, the measured hardness of the film is sensitive to the depth of indentation and can be provided by the ratio of peak load to the projected area of the indentation (shown in equation (4)). Numerous indenter tip such as Berkovich, Flat and circular type are being used for Nanoindentation studies; however, for the present investigation the Berkovich type indenters were used. This type of indenters are recommended for studying thin films. The modulus of the film coating on the paper substrate, obtained from this study is also known as reduced modulus (\( E_r \)), which is a function of elastic modulus of both the indenter and Agar biopolymer film. The elastic modulus and Poisson’s ratio value for the Berkovich indenter tip are given as 1140 GPa and 0.07 respectively.

\[
\frac{1}{E_r} = \frac{(1 - \nu^2)}{E} + \frac{(1 - \nu_i^2)}{E_i}
\]  
(3)

Where,  
\( E_r \) = Reduced modulus of the Agar-coated film (GPa)  
\( E \) = Elastic modulus of the Agar film (GPa)  
\( E_i \) = Elastic modulus of the indenter (GPa)  
\( \nu \) = Poisson’s ratio of the Agar film

Figure 4. (a) Water contact angle of Agar-coated film; (b) Water contact angle of PE coated film.
\[ \nu_i = \text{Poisson's ratio of the indenter} \]

\[ H = \frac{P_{\text{max}}}{A} \]  

(4)

Where, \( H = \text{Hardness of the film (GPa)} \)

\( A = \text{Projected area of the indentation} \)

3.6. Water vapor permeability

The Water Vapor Permeability tests were conducted by Hemshell Certified Lab as per the ASTM F—1249–13 standard. For the present investigation three random sample were collected from the bulk Agar-coated film with 1% glycerol and cut into standard dimension. Agar-coated sample (CAGAR_1% G) with an effective test area of
5 cm² was chosen for the permeability study under specific atmospheric conditions (Temp: 37.8 ± 0.5 °C, RH: 90% ± 3%). The uncertainty level of the measurement at 95% confidence level is ±3.17% @ 0.164 gm·m⁻²·day⁻¹ for WVTR. The Agar-coated film was placed in the middle of a chamber separating the dry compartment from wet compartment. In this test the coated film acts like a diffusion cell through which water vapor (maintained at standard humidity and temperature) present in the wet compartment were allowed to diffuse into the dry compartment. The diffused water vapor content in dry chamber were measured using infrared sensor that the energy absorbed by the water vapor into electrical signal.

4. Results and discussion

In this section results pertaining to water contact angle for the both Agar-coated and PE-coated surface were discussed, followed by a brief analysis on the effect of moisture exposure to the Agar-coated film surface. Besides these, results pertaining to the residual stress generation on both Agar-coated and PE-coated surface were also discussed, followed by a comprehensive study on elastic modulus of the coated film by using Nanoindentation technique. Later the WVTR result was discussed, in which a comparison on water vapor barrier potential of the Agar-coated was drawn with the existing packaging material [21].

The water contact angle for both Agar-coated and PE coated films were shown in figure 4, and it was found that the contact angles for both the films are acute angles. The water contact angle depicts that the surfaces are hydrophilic in nature due to their acute water contact angle with the surface. The surface coated with PE is found
to be less hydrophilic compared to the Agar-coated surface [22]. It can be concluded that the contact angle of the surface is a measure of surface energy, which is given by equation (5).

\[
1 + \cos \theta = 2 \sqrt{\gamma_s^d \gamma_l^d \gamma_{hv}} + 2 \sqrt{\gamma_s^h \gamma_l^h \gamma_{hv}}
\]  

Where,

- \( \theta \) = Contact angle of a liquid w.r.t. a solid surface
- \( \gamma_s^d \) = Component of the surface energy of the solid due to dipole-dipole interaction
- \( \gamma_s^h \) = Component of the surface energy of the solid due to hydrogen bonding
- \( \gamma_l^h \) = Component of the surface energy of the liquid due to hydrogen bonding
- \( \gamma_{hv} \) = Free energy of the liquid against their saturated vapor

Even though experimental studies were conducted on these coated polymer films, but it requires a quantitative approach to study the surface properties of the polymer coating. The technique involving Image Processing of surface-treated sample was only conducted on Agar-coated film, because it was a bit difficult to observe the changes that occurs in PE-coated films. It was believed that polyethylene coating does not degrade much compared to Agar-coated biopolymer film. The moisture exposure analysis results using the Image Processing Technique were given in figure 5, and the consolidated images used for the analysis were presented in figure 5(a). It is quite challenging to analyze the contrast variation of the picture by inspecting through visual observation; therefore, a qualitative approach was adopted to verify the difference in contrast to these images. The RGB image contrast for the individual case was presented (figures 5(b) to (f)) with two different sets of data: untreated and treated. Typically, an image can be represented by three primary colors, such as red, green, and blue; however, the difference in contrast of an image can be represented by analyzing the variation in these primary colors mention in the graph. For the moisture exposure test, the contrast value of green and red color can be neglected, because the Agar coating on the paper substrate was stained with blue ink, and blue is a dominating color over red and green. Therefore, it is logical to neglect other color those impact on contrast measurement is minimal. The difference in image contrast can be demonstrated by considering the blue color alone. For the contrast analysis using Image Processing Technique, triplicate of each sample (Agar-coating with blue color ink) were exposed to hot water and images were collected for contrast analysis. The degradation of film coating due to the exposure with various liquid was shown in figure 6(a), is given in the form of volume loss, and it was found that for the case of hot water exposure the volume loss is maximum compared to the case of cold water and acetic acid, and it is also analogous to the profilometry data shown in figure 6(b).

The residual stresses developed on the coated thin films were obtained by measuring the radius of curvature after coating (R) and radius of curvature before coating (R₀). The measured values using Stylus Probe Profilometer were fed into Stoney’s equation to obtain the residual stress developed in the film shown in figure 7. It can be noted that the surface appeared to be non-uniform after coating due to the formation of both concave

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**Figure 7.** Film stresses (Avg. Compressive Stress—Average of all compressive stresses developed throughout the coated film coating; Avg. Tensile Stress—Average of all tensile stresses developed throughout the film coating) developed due to Agar coating (CAGR) and PE coating (CPE) on the paper substrate.
and convex profile at various locations, and this led to the formation of compressive and tensile residual stresses on the sample surface. But, the overall picture depicts that the average stress on the film is compressive in nature for both Agar-coated and PE coated sample; however, the stresses developed due to Agar-coated film was found to be in the higher side, and a significant variation in stress level was noticed throughout the surface compared the PE coated sample.

The nanoindentation studies were conducted on two similar sets of samples of Agar-coated film with a variation of glycerol content. Two samples with different glycerol content were chosen, such as 0.5% and 1% of the total solution. The objective of studying the effect of glycerol content on the film coating’s elastic modulus was to verify the improvement of the film coating’s elastic property. The sample with 1% glycerol has shown improved elastic modulus compared to the sample with 0.5% glycerol, whereas the observation is different when it comes to the film’s hardness. The hardness of the film got reduced by doubling the glycerol content; on the other hand, the improvement is in good agreement with the modulus result (figure 8(a)). The load ~ displacement curve for both samples was shown in figure 8(b), where both loading and unloading curves shown in this curve were obtained by following a trapezoidal load ~ time pattern.

The Water Vapor Permeability test result for the Agar-coated sample was shown in figure 9, where a comparison was made with the gas barrier potential of a commercially available polymer. For the present
investigation, three random samples were cut into standard dimension from the Agar-coated film and WVTR test was conducted. Polymers indexed from a–e (figure 9) are categorized as Good barrier potential capability, whereas the polymers indexed from f–h (figure 9) are considered to be average barrier potential capability. The Agar-coated biopolymer film shows reduced gas barrier potential compared to other contemporary polymers with a WVTR value of 1246 gm.m$^{-2}$.day$^{-1}$. The observation mentioned above about the gas barrier potential of the Agar-coated film is not an encouraging result. Still, it can be improved by making specific changes in the chemistry of the film.

5. Conclusions

The comparison on the usability of Agar-coated film with the commercially available PE coated film on the paper substrate for their application in food packaging industry has been studied. Agar-coated polymer film and PE-coated film were evaluated regarding their physical properties and surface chemistry. It was found that the average film stress of these films possess both compressive and tensile stresses throughout their surfaces. The Agar-coated film shown high compressive and tensile stresses: $-1.0$ MPa and $0.75$ MPa, respectively, in comparison to PE-coated film, whose superficial compressive stresses were comparatively lower: $-0.07$ MPa and $0.1$ MPa, respectively. The high film stress values for the Agar-coated film over PE-coated film is likely due to two factors, namely: (i) high thickness of the coating; (ii) large variation in the modulus of substrate and coating. The high surface residual stress of the Agar-coated film may generate warping of the substrate and make it difficult to mold the coated film into any desired shape. The elastic modulus and hardness of the Agar-coated film with 1% glycerol and 0.5% glycerol were studied using nanoindentation technique and the results show that coated film with high glycerol content (1%) possess high elastic modulus (0.23 GPa).

From the water contact angle measurements, it was found that surface of Agar-coated film, was found to be more hydrophilic in nature than PE coated film. The volume loss for Agar-coated film, calculated using profilometry, after exposure to hot water found was higher (1 mm$^3$) than that found after exposure to cold water (0.97 mm$^3$) and acetic acid (0.29 mm$^3$). The effect of exposure time analysis on the surface degradation of Agar-coated film using Image Processing Technique showed coherent results, indicating the surface degradation with the increase in exposure time. The water vapor barrier potential of the Agar-coated film was experimentally calculated and the WVTR value was found to be higher (1246 gm.m$^{-2}$.day$^{-1}$) than that found for other coated films used in food packaging. Therefore, the physical proposed Agar coating studied in this paper are very promising compared to commercially available food packaging. However, the surface properties can be improved by making specific changes to their chemistry without compromising biodegradable tendencies. The volume loss of the Agar-coated film during moisture exposure analysis is not much of concern, because Agar is considered as an edible substance that does not cause any toxicity to the human body and could therefore substitute.
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