SYNTHESIS AND CHARACTERIZATION OF ECO-FRIENDLY SMART PACKAGING MATERIALS FOR EDIBLES

A Thesis submitted in the partial fulfilment of the requirements for the award of the degree

of

DOCTOR OF PHILOSOPHY

by

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(2K13/PhD/AC/02)

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JUNE 2020

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DECLARATION

I hereby certify that the thesis entitled **"SYNTHESIS AND CHARACTERIZATION OF ECO-FRIENDLY SMART PACKAGING MATERIALS FOR EDIBLES"** is an original work carried out by me under the supervision of **Dr. Raminder Kaur**, Faculty of Polymer Science and Chemical Technology, Department of Applied Chemistry, Delhi Technological University, Delhi. This thesis has been prepared in conformity with the rules and regulations of the Delhi Technological University, Delhi. The research work reported and results presented in the thesis have neither partially nor fully submitted to any other university or institute for the award of any other degree or diploma.

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CERTIFICATE

This is to certify that the thesis entitled **"SYNTHESIS AND CHARACTERIZATION OF ECO-FRIENDLY SMART PACKAGING MATERIALS FOR EDIBLES"** by **Ms. Neelam Yadav (Roll No: 2K13/PhD/AC/02)** in the fulfilment of requirements for the award of the degree of **Doctor Of Philosophy**, is an authentic record of student's own work carried by her under the supervision of **Dr. Raminder Kaur**, Assistant Professor, in the discipline of Polymer Science and Chemical Technology, Department of Applied Chemistry, Delhi Technological University, Delhi.

This is also certified that the work embodied in this thesis neither partially nor fully submitted to any other Institute or University for the award of any other diploma or degree.

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ACKNOWLEDGEMENTS

It gives me immense pleasure to express my deep sense of gratitude and sincere thanks to my supervisor ***Dr. Raminder Kaur****, Department of Applied Chemistry, Delhi Technological University, Delhi,* for her consistent guidance and encouragement from inception to completion of this thesis work. It has been an honour to be her Ph.D. student. She is an excellent supervisor and continuously encouraged and helped me for the achievement of goals of the research work. I am grateful for all her contributions in terms of time, suggestions, and constructive criticism and facilities to make my Ph.D. experience productive and stimulating.

I owe my heartfelt gratitude to the ***Prof. Yogesh Singh****, Honourable Vice Chancellor, Delhi Technological University* for his kind permission and ***Prof. S. G. Warkar****, Head, Department of Applied Chemistry, DTU* for providing me the necessary facilities to carry out this research work. I wish to express my sincere thanks to the ***faculty members*** *of DTU* for their help and support during this research work.

I would like to thank all technical and non-technical staff of the department and my friends, seniors and fellow researchers ***Dr. Mukesh Kumar, Dr. Manjeet Malik, Dr. Anuja Agrawal, Dr. Monika Duhan, Mr. Surya Tanwar, Dr. Nidhi, Dr. Chandra Mohan****,* for providing me endless encouragement, and support during the period of research work. I would also like to thank to all those who directly and indirectly supported me in carrying out this thesis work successfully.

Furthermore, I am indebted to ***my parents*** and ***my family*** for their endless encouragement, moral support and guidance throughout my whole life, I wholeheartedly thank my *daughter* ***Manya*** for her selfless love and care, that has always been a driving force for the completion of my research work.

Above all, I owe to ***Almighty God*** for granting me wisdom, health and strength to accept and overcome the challenges of the life.

Yadav

Date: 16-06-2020 (***Neelam Yadav)***

ABSTRACT

In today's world, new food packaging technologies are developing as a response to the consumer demands or industrial production trends towards mildly preserved, fresh and convenient food products with prolonged shelf-life and controlled quality. In addition, the changes in retailing practices, or consumer's busy lifestyles present major challenges to the food packaging industry, and act as driving forces for the development of new and improved packaging concept, that extend the shelf-life of the packaged foodstuff, while maintaining and monitoring its safety and quality. Unfortunately, all sort of packaging ends-up in garbage and dumping sites, hence, resulting in the piling up of the non-recyclable waste. The food packaging films that show post-consumer biodegradability are rarely explored by the researchers. The present study was carried out with an aim to develop an environment friendly qualitatively responsive film for the food packaging. The ethyl cellulose (EC) was used as the base material for the development of these food packaging films. Ethyl cellulose films were plasticized with different percentage of polyethylene glycol (PEG) and the samples of standard dimensions were subjected to different testing, such as, soluble matter content, moisture content, oil permeability, surface morphology, mechanical testing etc. The films with EC to PEG ratio of 4:2 had shown the best properties among all formulations tested, with total soluble matter percentage equal to 56. 26 and the moisture content percentage equal to 50. Tensile stress analysis had shown an increase in tensile properties with increase in coalescence temperature from 30°C to 60°C, and was found maximum for EC: PEG ratio 4:2 film, equal to 0.017Mpa in the range of 50°C to 60°C. The mean value of the load carrying capacity for a varying time period was maximum for EC: PEG ratio 4:2 while minimum for the EC: PEG ratio 4:1.

Further, the qualitatively responsive smart films were developed, using the best formulation of the EC films i.e. EC: PEG ratio 4:2, with an emphasis on the change in pH of the packed food stuff. These pH responsive ethyl cellulose films were developed by incorporating the azo indicators such as

Methyl Red (MR) and Methyl Orange (MO) in the EC film formulation, by casting method. After activation in different pH range, the color variation was measured for each film, with the CIE Lab methodology. A significant L∗ [the parameter L∗ represents the lightness of color from 0 (dark) to 100 (light), in CIELAB units] variation of EC-MO was seen ranging from 59 (at 0% acid) to 32 (at 60% acid) while for EC-MR, the variation in L∗ parameter was seen ranging from 89 (at 0% acid) to 32 (at 50% acid). As evident from the results obtained, the developed bio-degradable smart films had shown remarkable sensitivity towards the pH variation, Further, these qualitatively responsive films were tested for their water absorption capacity and mechanical properties. The water absorption capacity of the EC film incorporated with indicators were observed to be low as compared to the EC-standard film. The incorporation of MO resulted in a regular increase in water absorption capacity range from 34.08–47.11 while the MR incorporated films showed an irregular increase from 41.13–42.13, during a 24 hrs interval. The film with MO also showed a good mechanical property when tested by a micro UTM. The peak load was observed at around 2.7 N. Necking was more observant in the EC film incorporated with MO as compared to other samples, thus showing good plasticity. The water vapour permeability (WVP) of the ethyl cellulose films found to be affected by the incorporation of indicators. As reported, the WVP for EC-standard film increased during initial 2 hrs from 2.29407 x10^{-9} $gm^{-1}s^{-1}Pa^{-1}$to 3.44111 x10^{-9} $gm^{-1}s^{-1}Pa^{-1}$, and then noted to be decreased upto 8.60277x10^{-10} $gm^{-1}s^{-1}Pa^{-1}$ during the test duration of 24 hrs, Similar trends were show by EC-MO and EC-MR films respectively, with an initial (first 2 hrs) increase of WVP from 3.44451 x10^{-9} $gm^{-1}s^{-1}Pa^{-1}$ to 4.99454 x10^{-9} $gm^{-1}s^{-1}Pa^{-1}$ and from 4.57908 x10^{-9} $gm^{-1}s^{-1}Pa^{-1}$ to 4.97975 x10^{-9} $gm^{-1}s^{-1}Pa^{-1}$, and then, a decrease upto 1.07640 x10^{-9} $gm^{-1}s^{-1}Pa^{-1}$and 1.23062 x10^{-9} $gm^{-1}s^{-1}Pa^{-1}$respectively, within next 24 hrs The WVP of the film was also influenced by the temperature variation and are found to be increased, when the temperature was raised from 20°C-50°C. As ethyl cellulose is biodegradable in nature, the resulted films are also biodegradable and environment friendly. These qualitatively responsive ethyl cellulose films can be utilized as conventional food wrappings or as a small patch within the conventional transparent packaging.

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LIST OF ABBREVIATIONS

Symbol	**Notation**
AP	Active Packaging
BHA	Butylated Hydroxy Anisole
BHT	Butylated Hydroxy Toluene
CMC	Carboxy Methyl Cellulose
E	Modulus of Elasticity
EAB	Elongation at Break
EC	Ethyl cellulose
EC-MO	Ethyl cellulose film with Methyl Orange Indicator
EC-MR	Ethyl cellulose film with Methyl Red Indicator
EC-standard	Ethyl cellulose film without Indicator
GRAS	Generally Recognized as Safe
HDPE	High Density Polyethylene
IP	Intelligent Packaging
LDPE	Low Density Polyethylene
MAP	Modified Atmosphere Packaging
MO	Methyl Orange
MR	Methyl Red
ORC	Oxidized regenerated cellulose
PE	Polyethylene
PEG	Polyethylene Glycol
PET	Polyethylene terephthalate
RFID	Radio Frequency Identification
TS	Tensile Strength
TTI	Time Temperature Indicator
WVP	Water Vapour Permeability
WVTR	Water Vapour Transmission Rate

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1. INTRODUCTION

A package is a vehicle of protection and, accomplishes the objective of supplying safe, wholesome, and quality product to the consumer. Packaging is an art and technology that has been evolved for enfolding and guarding various products for circulation, storage and trading. It is a process of designing, assessing and creating synchronized arrangement of goods for transportation; storage; sale; and end usage by providing preservation, containment, protection and information. The connection between packaging and consumer protection is of high significance. The fundamental safety objective for the packaging is to make the content inside totally passive and to ensure its minimum exposure. The long mean life of the packed product is the basic necessity for the modern society. We need packaging, for convenience and to protect items from the outside environment.

Foods are the constituents consumed for giving nutritional support to the living beings. Generally, the food supplies are stored to be used within weeks to months after harvest; and this storage is done both traditionally as well as commercially. The main purpose of food storage is providing healthier balanced diet, all through the year, readiness for disasters, crises, food shortage or famine. Storage is also done for subsequent cooking, mainly for spice and dry constituents, also, the harvested and processed foods are stowed, for timely and hygienic distribution to the consumers. Food packaging makes our lives easier.

Traditional food packaging was meant only for the mechanical support, of the otherwise non-solid food and protecting it from the external influences, like, microorganisms, oxygen, off-odours, light etc. Consumer’s inclination towards the convenience in transportation and upsurge the shelf life of the foodstuffs, against the deteriorative reactions had brought significant improvements in the traditional packaging technology. In addition to delivering the food product conveniently, the food packaging was assigned an additional role as an advertising tool that helped in communicating with the buyers.

1.1 ANTIQUITY IN FOOD PACKAGING TECHNIQUES

Food packaging technique was initiated by Nicholas Appert in the 19th century by developing canning. Further, it was analogue with different packaging techniques, as paperboard cartons by Robert Gair, glass bottle packaging, by Michael Owens. The commencement of 20th century witnessed packaging with tin coated steel cans, glass containers & wooden crates, and invention of cellophane. Subsequently, most of the innovations in packaging, such as, plastic packaging (PE, Polyvinylidene chloride), aseptic packaging, metal packaging, flexible packaging, and aluminium packaging occurred between World War I and World War II.

1.2 DIFFERENT FOOD PACKING MATERIALS

Packing means putting all the packages in a big box, container, chest, crate etc. for the purposes of storage, transportation, handling etc. The commonly used packaging materials are:

Foliage: Generally grilled, broiled, baked and steamed doughs are wrapped in banana vine or bamboo leaves; crude sugar is wrapped in corn husk, are the superb way to pack the products that are to be consumed momentarily after the purchase. Also, the bamboo, cotton, jute and coconut etc. were converted into strings or yarns and used as packaging materials. These materials showed tearing resistance, flexibility, and are bio-degradable, cheap and easily available, but they hardly provide any protection from oxygen, microbes, insects and moisture to the packed products.

Logs: Wooden barrels and containers has been used to store beer, fruits and vegetables offering good protection, strength and stacking feature. Though, the low cost plastics have replaced the wood containers, but still some of the wines and spirits are stored in wooden containers, or to transfer some of the flavoured compounds, to increase the aroma.

Paper: Paper is a cheap packaging material obtained from the wood pulp, but it is extremely absorptive, and can easily be torned. To overcome some of these properties, the paper is treated either with wax or resins, to strengthen to some level, but its reuse greatly depends on its initial use.

Ceramic: These products are used for containment of solid and fluid products, and show significant porous capacity to keep the product cool. They are also, quite suitable, for resisting the microbial growth and insect infestation.

Glass: Glass is quite prevalent due to its numerous good packaging properties, like, it can be pasteurized, sterilized and its rigidity protects the food from crushing, resist moisture, microbes and above all, it is reusable. However, its transportation cost is high, it is quite heavy and is easily breakable.

Plastics: Plastics can be used in the form of sheets as well as containers of varying thickness. Plastic provide good resistance against different gases and moisture, and due to its light weight and relatively low cost, it is very commonly used, e.g. polythene, cellulose and polypropylene etc.

1.3 PROBLEMS WITH CONVENTIONAL FOOD PACKAGING

Though, traditional packaging provides mechanical support, containment, communication, tampering resistance, protection from external environment, handling convenience and showed inertness between food material and packaging. However, these cconventional packaging are generally inadequate in the capability to the extend shelf life of foodstuffs. Maximum number of foods, from the time they are reaped, trounced or factory-made, experience progressive decline in quality, depending upon the food and become sluggish or spoil and become practically unusable. During storage, the foods may experience deterioration to variable grades in their sensory features, nutritive value, protection and tempting appeal, depending upon the time and the conditions of storage. The different characteristic of spoiled food may be any one (or more) among, as given in Table 1.1. The reason of food spoilage may be pitiable cleanliness, microbial growth, enzymatic and chemical reactions, inappropriate temperature control and physical abuse. This presents a great problem in the market, because, the food materials have to be acquired, stored, transported and further supplied in a healthy form, and well in advance of estimated usage.

Table 1.1: General Characteristic of Spoiled Food

Food	**Quality Factors**	**Faults**
Fruits and Vegetables	Overall Appearance	Fungal growth, Slime development, Production of gas (compartments of gas, fizzes)
	Color	Discoloration (often pink, red, grey or green)
	Texture	Damage of texture (soft, syrupy)
	Odour	Rottenness odours (putrid, sulphur, sweet, alcoholic)
	Aroma	Off aromas (bitter, yeasty, rancid)
Meat	Overall Appearance	Putrefaction, Breakdown of proteins (slime)
	Color	Sourness, Production of lactic acid, Discoloration
	Flavor	Rancidity (breakdown of fats)
Fish	Odour	Production of Ammonia, Trimethylamine, Hydrogen Sulphide

1.4 CHANGING TRENDS IN FOOD PACKAGING TECHNOLOGY

The changing trend of industrial production, and increasing demands of the consumers for slightly preserved convenient foodstuffs, having better fresh like potentials, has led to the introduction of many new concepts in food packaging. In addition, the modifications in the retail and circulation practices, such as: internet shopping, internationalization of the market, increased distance distribution, increased storage time and different temperature requirements are leading to huge changes in packaging technology [1]. Innovative packaging technology is surfacing because of rising concerns of regulations, world-wide markets, extended shelf life, safer and healthier foodstuff, lowering synthetic preservatives, environmental concerns, genuineness, and reduction in wastage of foodstuffs, which was lacking in conventional passive packaging systems [2]. As Innovative packaging involves the interaction amid the foodstuff and packing material, it becomes quite necessary to check the safety aspects of the materials used in making the packages, and the reaction of migrating substance from the food to packaging material or vice versa. The changes caused in food packaging skills is owed to the combined efforts of the food scientist, microbiologists, engineers, regulators, chemists and other specialists. These days, the multifaceted society is more engrossed on the packing, that shields the food from chemical reactions, light, microbial contamination, water vapor, oxygen and physical abuse, hence, improving its shelf life and, resulting in the development of the active packaging and the intelligent packaging. Most of the industry professionals have used the term ‘smart’ and ‘intelligent’ packaging for the functional packing systems. The smart or active packaging is any kind of packing that offers definite functionality, along with the generalized part of the packaging i.e. containment, physical barrier and communication. These smart packaging can be regarded as an augmentation of three main functions of packaging i.e. preservation, containment, protection and information [3]. In the recent decades, the consumers are focusing more on the safety concern of the packaging, along with a demand for slightly or non-processed food, with zero preservatives and high quality [4]. All these factors have headed to the advancement in packaging technology, thus, improving the protective action of the package, including active packaging [3, 5], intelligent packaging [3, 6], modified atmosphere packaging [7], and addition of nanoparticles [8, 9] in packaging materials. The various techniques by which packaging can be improved is presented in the Figure 1.1.

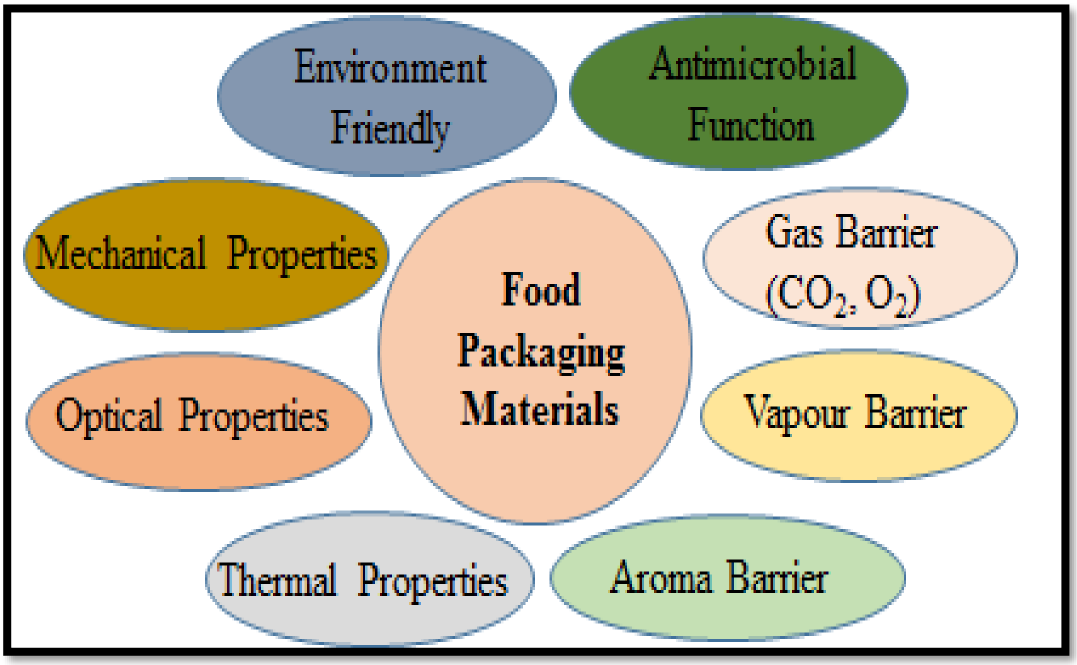


Figure 1.1: Emerging Inclinations in the Polymer Packaging

In addition to this, the growing awareness amid consumers, about the damages caused to the ecosystem, due to the excessive use of conventional plastic packaging, resulted in a stimulation in the development of biodegradable packaging. It has also been resolute in many researches that the biodegradable packaging is a fast-upcoming trend in the food industry. A number of aspects including strategy and legislative variations, improved properties of biodegradable packaging, world's demand for food and energy resources, and partly due to the decrease of its price, will certainly affect the fabrication and demand for this packaging [10].

The changing trend of industrial production, and consumer demand has commanded the expansion of novel packaging technology, which increases the mean life of foodstuff, along with sustaining and monitoring the safety and value of the foods. In the last decade, the innovative packaging has achieved a pinnacle by the development of active & intelligent packaging, which, revealed, deliberate interactions between the packing material and the foodstuff/headspace. The active packaging increases the shelf life of the packed food, with the preservation (or even enhancement) of its quality, whereas the intelligent packaging aims to monitor the freshness of packed foods. The innovation of active, as well as, intelligent packaging is responsible for delaying the deterioration in packaged food, and has refined the superiority of food products.

1.5 ACTIVE PACKAGING

Active packaging is an interface between the packed food, packing material, headspace within the package and the outer environment (if it interacts with the packaged product). Contrary to the conventional packaging, instead of using preservatives in foodstuff, for intensifying its shelf life, in active packaging, some active agent are added to the packing material itself, thus increasing the shelf life of the packaged foodstuff, by changing the condition (such as microbiological changes, physiological processes, chemical processes, and sensory property) inside the package [11]. The active agent in the packaging can either be in the form of coating; in-situ in the polymer matrix; or in the form of sachets, instead of contacting directly with foodstuff. For example, sachets are used in the packaging of meat and poultry foods, baked goods, pizzas, coffee and dried foodstuffs, for the absorption of either oxygen or carbon dioxide. Some sachets also prolong the shelf life of high moisture bakery goods by emitting ethanol as an antimicrobial agent, but, these sachets are not convenient for liquid foods and they have the danger of accidental consumption by consumers. In-situ active agent containing packaging include: plastic containers, PET bottles and closures. Active agents in packaging materials can be incorporated by co-extruding it with the polymer matrix.

A graphical illustration of different concepts of active packaging materials is as given in Figure 1.2.

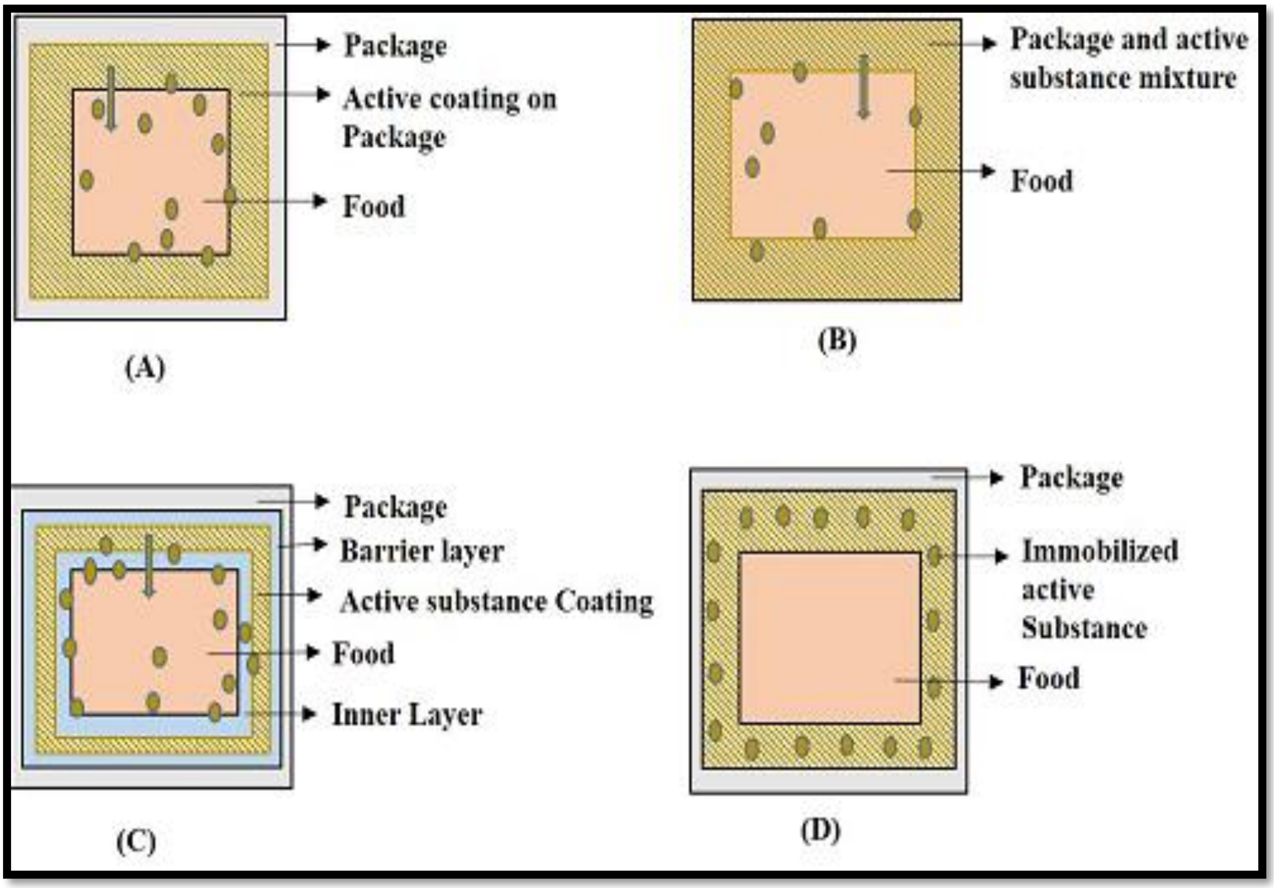


Figure 1.2: A Graphical Illustration of Different Concepts of Active Packaging Materials

Active package is a pioneering idea of packaging for broadening the shelf life of foodstuff. As demarcated by the European Regulation Number 450/2009, "the active packaging is a packaging system having intentionally added substances that are either emitted or absorbed into or from the packed food or the headspace of the package" [12]. The categories of the active agents that can be included is very diverse i.e. natural extracts, organic acids, ethanol enzymes, bacteriocins, ions, fungicides etc. Also, the nature of the matrix material, into which they are incorporated, can vary too, thus including plastics, papers, metals or blends of these. The active packaging substances work on the basis of either the absorption (scavenging system) or release (emitting systems) of gases or steam within the package, which may significantly influence the material within.

Accordingly, active packaging can be categorized as:

1.5.1 Active packaging system with absorbing substance or Scavengers

1.5.2 Active packaging system with releasing substance or Emitters

1.5.1 Active Packaging System with Absorbing Substance or Scavengers

These packaging systems eliminate the unwanted compounds, from the foodstuff, that may cause undesirable chemical reactions or catalyze the rate of a particular reaction, which, could causes the deterioration of the food at a faster rate e.g. oxygen, carbon dioxide, moisture, odour and ethylene etc. This has steered to the expansion of a big range of active packaging, containing different active substances for improving the value of the packed food and also increases its shelf life. In addition to these, the materials that absorb flavour are also being used in active packaging to captivate undesirable aromas from foods such as fruit juices. Table 1.2 gives a detail of active absorbing substance that can be used in the packaging systems for reducing the undesirable constituents present inside the packaging.

Table 1.2: Active Packaging System with Absorbing Substance or Scavengers

Active Absorbing Substance	Causes	Affect	Active Substance	Benefit	References
Moisture	The excellence of foods depends on its moisture and water activity.	Lower relative humidity, increased moisture content worsens the food quality.	$CaCl_2$, NaCl and glucitol	Helps in lowering the moisture content, relative humidity and browning index.	[13,14]
Oxygen	The quantity of oxygen causes oxidation reactions and the microbial growth in the package.	Affecting the color, nutritive value and the physical appearance of the foodstuff.	Fe-based absorbers	Presence of moisture affects the oxygen absorption resulting in oxidation of ferrous to stable ferric oxide trihydrate complex.	[15]
			Cobalt as oxygen scavenger	It catalyses the oxidation reaction of polymers	[15]
			Palladium	Helps in catalysing the oxidation of hydrogen to H_2O, lowers the mold growth.	[16,17]
			UV sensitive dyes	Removal of initial dissolved O_2 can improve the oxidative stability and viability of bacteria.	[18]
			Vitamin C	Increases the shelf life of food.	[19]
			Trihydroxy benzoic acid		[20]
			Unsaturated fatty acids	Ascorbic acid retention, lowering in browning.	[20,21]
Ethylene	Accelerates chlorophyll degradation, respiration rate and ripening.	Declines the shelf life and upsurges the softening of fruits.	Charcoal with $PdCl_2$	Lowers the softening of fruits and chlorophyll loss.	[22-26]
			Nanoparticles of Ag, TiO_2 and china clay	Decreases the decay rate of postharvest storage.	[27]
			Zeolite based minerals	Improves the shelf life of fruits.	[28-30]

1.5.1.1 Moisture Absorbers

Packaging, used as moisture scavengers is basically useful to the products, which are very much affected by the relative humidity in the headspace of the packaged food. The relative humidity having percentage below 86% increases the moisture, thus, causing weight loss and change in texture of the foodstuff. Thus, the high relative humidity in a controlled level is good for averting the drying of the foods, like: fresh fruits, vegetables, fish and meat [31]. Conflicting to this, the relative humidity of 100 %, cause staining of the food products, by making the food more prone to the microbial growth. The approaches of the moisture regulation in the packing can be discussed under three sections: 1. Moisture reduction; 2. Moisture prevention and, 3. Moisture elimination.

The first two categories are considered to be quite passive and can be used without the inclusion of any active constituents. The materials used for these passive interactions, may be micro perforated films [32], hygroscopic materials (e g. 100% cellulose) or other suitable packaging materials which provides good barrier to water vapours. The third category of moisture regulation, i.e. moisture eliminator is further divided into two categories i.e. relative humidity controllers and moisture removers. The materials that absorb the humidity existing in the environment of the packed foods (amount being absorbed depends on the water vapor sorption isotherm), are called 'Relative Humidity Controllers' or 'Desiccants' e.g. sodium, potassium calcium alumina silicate, zeolite, bentonite, sorbitol, calcium chloride, sodium chloride, silica gel and clay [33]. These moisture absorbers/removers are the materials, used to absorb the moisture present in the foods having greater water activity e.g. poultry, fish, meat, fruits and vegetables [34]. The moisture removers, applied to packaged food, are generally used in the form of sheet (made of porous polystyrene, cellulose), blankets or pads (made of porous polypropylene or polyethylene). The activity of these moisture remover components can be increased by adding super absorbent minerals and salts or even polymers e.g. CMC, polyacrylate salt, starch, silica etc. [35]. Further, the activity of the moisture remover can also be enhanced by adding antimicrobial, antioxidant or carbon dioxide control agents. Various moisture absorbing materials used in food packaging are given in Table 1.3.

Commonly used Desiccants are:

Zeolites

The moisture present in the packaged products can easily be absorbed by the zeolite, and additionally, can also be discharged according to the requirement of the packaged environment. This activity does not affect the crystalline structure, or even the moisture absorption properties of the zeolites [36].

Bentonite/Sorbitol/Calcium Chloride

For the foods like, fresh mushrooms (Agaricus bisporus), the optimum value of relative humidity inside the package is very high i.e. approximately 96%, thus, they have a shorter shelf life. Studies shows that, the packaging formulation for mushrooms was reconstituted by using the mixture of fast absorbing (Calcium chloride, Sorbitol, and KCl, with moisture absorbing capability 0.91 ± 0.02 [g H2O/g] in 5 days) and slow absorbing (Bentonite/ Sorbitol, with moisture-holding capability 0.34 ± 0.02 [g H2O/g] in 5 days) moisture components [37]. The effect of these formulations are as reported in the Table 1.3.

Poly (Acrylic Acid) Sodium Salt

The polymers, such as, cross-linked poly (acrylic acid) sodium salt powder (SAP), show a positive result as an absorber and used as a super absorbent to inhibit the mold growth and decrease the content of aflatoxin [38]. The application of SAP was done for maize and the result is discussed in Table 1.3.

Sodium Chloride and Hygroscopic Ionomers

The active packaging has been developed in the form of 3 layers, consisting of barrier component, active particle component of sodium chloride and a sealing component, for absorbing moisture, and maintaining the humidity in the packaged foods [39, 40].

Table 1.3: Various Moisture Absorbing Materials used in Food Packaging

Moisture Absorbing Materials	Matrix	Application	Inferences Drawn	Drawback	References
Zeolites	Films of either paper, pulp or plastic incorporated with nano zeolite.	Packaging is used for non- edible materials. .	It helps in standardization of moisture in the packaged product.	-	[36, 41]
Bentonite/ Sorbitol/ Calcium Chloride	It is used in the form of powder spread in trays or in bags.	Storage of mushrooms.	There was increase in the relative humidity from 76% to 96%. The moisture absorbing capacity of the desiccant amplified from 0.51 to 0.94g per g of desiccant in the ratio of bentonite/sorbitol/$CaCl_2$, 0.55:0.25:0.2 g/g. The temperature change (from 4 to 16°C) caused no influence on moisture absorption capability of the desiccant. The lower amount (approx. 5g/250g mushroom) of desiccant worked more efficiently in lowering the browning index than 10 g of desiccant for 250 g of mushroom. The storage condition was 10 °C for 5 days.	-	[37]
Calcium Oxide/ Calcium Chloride/ Sorbitol		Food application is not studied.	The combination of calcium oxide/ $CaCl_2$ /sorbitol in a proportion of 0.5:0.26:0.24 worked as desiccant and showed 0.81 water /g holding capacity.	-	[13]
Poly (acrylic acid) sodium salt	The desiccant was used in the form of fine particles placed in the porous tea bags.	Storage of fresh maize (moisture content 32%).	The use of SAP-maize ratio of 1:5 and 1:1 lowered the aflatoxin contamination and also helped in drying of grains in a cheaper way.	-	[38]
Sodium Chloride and Hygroscopic ionomers	Thermo formed multilayer trays: Polyethylene/foamed hygroscopic ionomer-NaCl/PE.	Packaging of strawberries and tomatoes.	The film comprising of 0% and 12% sodium chloride absorbed about 7.6 ± 0.01 and 13.2 ± 0.01 g water respectively. For the packaging containing tomatoes and strawberries the tray with 12 % NaCl, effectively monitored the relative humidity to below 97 %.	-	[14]
	Thermo formed multilayer trays: Polypropylene/foamed and stretched PP-NaCl/EVOH/PE.	Packaging of mushrooms.	For mushrooms the trays containing 18% NaCl was reported to absorb around 11.4 g of water as compared to the control packaging. Also, the relative humidity was also maintained upto 93%.	-	[42]
			The increase in the percentage of NaCl content from 6 to 18% helped in the absorption of water, thus resulting in bulk loss in the range of 1.3 ± 0.02 to 4.5 ± 0.02 g mushroom stored at 5 ± 0.05 °C.	-	[43, 44]

1.5.1.2 Oxygen Absorbers

Most of the packed foodstuffs are highly reactive to oxygen that cause undesirable effect on their shelf life, due to the oxidation [45, 46]. The presence of oxygen also stimulates the increase of aerobic microbes [47, 48], causes changes in sensory quality [49-51], color variations [17, 52-54] and nutritional loses [55-58]. The packaging industries thus face special challenge for providing packaged products with long shelf life when stored without refrigeration in such conditions, and also for the products which have high lipid component and undergo oxidation reaction at very high rate. This has led to investigation of various packing which involves components that can inhibit such reaction or slow down the rate of these reactions.

The oxygen scavengers are used in the food packaging to eliminate the existing residual oxygen in the packaged foodstuff [11, 48, 59-60], or to mend the barrier capability of the packaging, by working as an active barrier [61].This target is attained either by Modified Atmosphere Packaging (MAP) process or by gas flushing, thus, resulting in approximately 0.5%-5% oxygen in the packaged food [48, 53, 62], which keeps on increasing during the storage. The oxygen absorbing systems were initially used as self-adhesive labels and loose sachets, included in the food packaging. Later, the in-situ packaging material was developed, that included the active component in the packaging stuff itself, using single layer or multilayer materials, or as responsive closures linings. Mechanisms for oxygen scavenging can either be chemical or bio-chemical.

Chemical Oxygen Scavengers

Most commonly used chemical based oxygen scavengers is iron [52, 63-66], which becomes active in the presence of moisture. The other metals used in oxygen scavenging activity, for example cobalt [67, 68], and palladium [16], act as catalysts. In addition, ascorbic acid, [19, 62], photosensitive dyes [18, 69-71], gallic acid [72, 73], and unsaturated fatty acids [60, 62] also acts as oxygen scavengers. Ascorbic acid has reported to work as reducing agent in the oxidation reaction with transition elements as a catalyst [74]. Oxygen scavenging films have been reported with the combination of zinc (as transition metal) and ascorbic acid (Zn /AA) ; iron (as transition metal) and ascorbic acid (Fe /AA), which increased the oxygen scavenging routine of 47.5 ± 0.1 and 37.4 ± 0.1 mL, respectively, for a duration of about a month. The ethyl cellulose films containing polyether poly-furyloxirane and organic dyes (eosin and curcumin) showed that in the presence of light, these films transforms triplet oxygen to very sensitive singlet oxygen which is captivated by the PFO [75]. Studies have reported the reaction of polyester linked unsaturated hydrocarbons with the oxygen in the presence of transition metals (e.g. cobalt) as catalyst [76].

Biochemical Oxygen Scavengers

These includes the spores of many bacteria [77] or yeast [78] and few enzymes that are used for the process of oxygen scavenging. [79-83].

Various oxygen absorbing materials used in food packaging are given in Table 1.4.

Table 1.4: Various Oxygen Absorbing Materials used in Food Packaging

Oxygen Absorbing Material	Matrix	Application	Inference Drawn	Drawback	References
Iron	Multilayer trays made of PP containing oxygen absorbing materials in the middle layer in the percentage as given (40%, 80% and 100% w/w).	Packaging of processed meats.	OS packaging considerably decreased the oxidative reactions causing variation in the flavour and color of the packed product in comparison to the control packaging. Also, the lower phospholipid peroxidation was supported by the TBA values.	-	[15]
	Iron containing oxygen scavenging laminates.	Storage of hot filled ready to eat cheese spreads.	The iron containing oxygen scavenging laminate decreased about 67.44 vol % of the oxygen existing in the pouches within 24hrs of storage. It was further decreased to about 1 vol % during 11-day storage and this percentage of oxygen was maintained for about 1 year of storage period. Since, the oxygen shows a significant role in the degradation of the vitamin C, thus, the O_2 scavenging laminates were found useful in maintaining the vitamin C content of the packaged food.	-	[84]
	Oxygen scavengers with Nano particles of Fe combined with sodium chloride, calcium chloride, and activated carbon.	Foods with high amount of lipids.	The comparison of the nano-sized and micro-sized particles of the iron-based oxygen scavengers showed about 1.4 time's higher activity, in case of nano- sized particles.	-	[85]
	Nanoscale oxygen scavengers based on zero valent Fe particles with Si matrix.		The nano-scale Fe particles showed an oxygen scavenging (OS) rate, at least 10 times greater, at 100% RH, compared to that of commercially available Fe-based OS fused in PE or PP polymer matrices.	-	[86]
	A fast OS-system was developed by depositing palladium on a PET/SiOx film using magnetron sputtering technology.	Food such as cooked ham.	The Palladium-based OS-system effectively stopped discoloration of an O_2-sensitive foods. This catalytic system based on Pd (with a high O_2 scavenging activity) was able to eliminate 2 vol% of the headspace O_2 concentration within 35 min, and no discoloration was spotted for 21 days of storage at 4 °C under illumination.	The shortcoming of this catalytic system is the poisoning (inactivation) by volatile S compounds existing in the headspace of packed foods, like roast beef, ham, cheese, peanuts and par-baked buns, etc.	[87, 88]

	An OS-system centred on TiO_2 nanotubes (TONT).		The TONT OS- system showed higher oxygen uptake rate as compared to iron-based scavengers. The aforementioned OS-systems were moisture triggered, but they give a great performance in dry environments.	-	[89]
	An OS system using activated carbon and sodium L-ascorbate.	For the storage of raw meat loaves.	As compared to commercial iron-based oxygen scavenger, this OS system showed 2.2 times greater oxygen scavenging capacity. Also, ascorbic acid helped in resisting the lipid oxidation and decreased microbial growth.	-	[90]
	Films based on LDPE/pyrogallol.	Used in soybean oil packaging.	These films showed high oxygen scavenging capacity in alkaline medium under high temperature and humidity.	-	[91, 92]
	The film based on LDPE/Gallic acid.	Packaging of foodstuffs with high water activity.	These films showed oxygen scavenging capacity of about 0.70 ml/cm for 7 days which is almost equivalent to commercial OS-films. Multi-layered (LDPE and PLA) biobased film with gallic acid has also been developed for foodstuffs having great water activity.	-	[73, 93]
Ascorbic acid	LLDPE films blended with (Fe/AA) or (Zn/AA) used in as sealed bags.	Storage of bakery goods (eg. Buns and bread slices).	LLDPE film blended with (Fe/AA) or (Zn/AA) used as an active packaging for bun and bread slices showed a lower rate of water vapor transmission and oxygen diffusion, through the active packaging as related to control LLDPE, thus, lengthened the storage life of packed product up to 5 to 6 days.	The study was not focused on the size and volume of the package which limited the idea of exact quantity of scavengers required to prolong the mean life of the foodstuffs.	[19]
Photosensitive dyes	Ethyl cellulose film blended with polyether polyfuryloxirane and organic dyes (eosin and curcumin).	Storage of sunflower oil.	The storage of sunflower oil in light at 23°C in the OS package showed higher oxidation stability, as calculated by its peroxide value and gas chromatography measuring headspace hexanal. PV was found to be 20 meq/kg for active packaging as compared to 75 meq/kg for control.	Oxygen content in the headspace is dependent on the initial irradiation, which is a challenge for industrial applications of such films.	[18]
	Vacuum-sealed OS pouches.	Packaging of orange juice.	In OS packaging the initial dissolved oxygen was reduced to 0.04 ppm within 3 and 7 d at 25 °C and 4°C respectively. The ascorbic acid in the packaged juice was also considered by calculating the browning index, which was reported as, at 4°C was below 0.15 and at 25°C, was around 0.34, both being low as compared to the control sample, having browning index of about 0.44.	Industrial application needs additional process of UV illumination in the production line.	[70]

	Oxygen scavenging films containing substituted anthraquinone (reducible organic compound).	Packaging of dairy product eg. Probiotic yoghurt.	The dissolved oxygen content was reduced to about 1.7 ppm in an OS active package, containing reducible organic compound as a component. This film required the UV light for the initiation of scavenging reaction.	-	[69, 93]
	Oxygen scavenging laminates with prototype ZerO2 TM.	Packaging of ultra-high temperature (UHT) milk.	The development of stale flavors of methyl ketones and aldehydes in milk can be prevented by the use of OS active films that helped in the lowering of oxygen from 7- 3.8 mg/L in 14 weeks of storage, at about 26°C. Stale flavors are also reduced to 23% and the free fatty acid level was maintained below threshold value of lipid oxidation.	Sensory evaluation was not done for the film.	[71]
Unsaturated hydrocarbon dienes	Oxygen scavenging co-polyester based polymer in pet bottles.	Packaging of citrus juices.	As compared to conventional packaging, the vitamin C loss in active packaging containing oxygen scavenging component was reduced to half at 35°C and upto 3 to4 times lowered at a temperature of 5°C.	Testing sample used should be of commercial juices or beverages instead of model system.	[76]
	PET films containing oxygen scavenging components (cast-extruded, monolayer).	Packaging of bananas.	The application of OS PET film in the packing of banana slices had maintained the color of the packaged product in comparison to the one that are packed in control film.	-	[20, 21]

1.5.1.3 Ethylene Absorbers

Ethylene is one of the plant-growth stimulating hormone that help in accelerating the process of maturing and increasing the rate of respiration of the climacteric products. The increase in respiration rate for fresh and marginally processed products, result in lowering the shelf life of the climacteric produce during the post-harvest storage. The rate of respiration of different vegetables and fruits are as given in Table 1.5. The basic reaction involved in the process of decay is:

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6\,CO_2 + 6\,H_2O + \text{energy}$$

Glucose is a carbohydrate found in plants in the form of starch. The above reaction shows that, with increased respiration rate, all the molecules of glucose are oxidized to CO_2 and H_2O with some amount of energy, and further, no more energy will be generated, thus, resulting in the onset of decay of the fruit and vegetables. The ethylene also hastens the degradation rate of chlorophyll of green vegetables and boosts the softening of fruits [94, 95]. This is the major reason for absorbing the ethylene content from the food products. The classification of different fruits with their rate of ethylene production is as shown in Table 1.6.

Table 1.5: Respiration Rate of Various Food Products

Food Products	**Respiration Rate at 5˚C ($mg\ CO_2\ kg^{-1}h^{-1}$)**
Dried fruits and vegetables, nuts and dates	Very slow (<5)
Apple, grape, onion, potato, garlic and citrus	Slow 5-10
Apricot, carrot, cherry, cabbage, plum, lettuce, tomato, pepper, peach, banana, pear and fig	Moderate 10-20
Black berry cauliflower raspberry strawberry and avocado	Fast 20-40
Brussels sprouts, snap bean, spring onion and artichoke	Very fast 40-60
Asparagus, sweet corn, mushroom, broccoli, spinach and pea	Extremely fast >60

Table 1.6: Classification of Different Fruits with their Rate of Ethylene Production

Fruits	**Rate of Ethylene Production (µL/Kg hr. at 20°C)**
Citrus fruits, grapes, cherry, strawberry leafy vegetables, cauliflower, root vegetables and potato	Very low: 0.01-0.1
Watermelon, pumpkin, cucumber, cranberry, black berry, blueberry, raspberry and pineapple	Low: 0.1-1.0
Tomato, mango, fig and banana	Moderate: 1.0-10
Apricot, plum, apple, peach and kiwifruit (ripe)	High: 10-100
Cherimoya and exotic fruit	Very high: > 100

The ethylene produced is in very less amount and can be easily absorbed by the small quantity of the scavengers. The absorption of ethylene is necessary for raising the post-harvest shelf life of the vegetables and fruits. The ethylene released by the ripening of fruits and vegetables is trapped by chemicals incorporated in packaging films. Some commonly used ethylene scavengers are:

Potassium permanganate

Potassium permanganate plays a significant part in the process of ethylene scavenging. The conversion of ethylene to CO_2 and water results in color change of potassium permanganate from purple to brown, thus, showing its residual ethylene absorption capacity [25]. The $KMnO_4$ oxidizes ethane in a chain of reactions, thus, convert it into acetaldehyde, acetic acid and lastly to CO_2 and H_2O. It is an irreversible reaction, as given below:

$$3\ C_2H_4 + 2\ KMnO_4 + H_2O \longrightarrow 2\ MnO_2 + CH_3CHO + 2\ KOH$$

$$CH_3CHO + 2\ KMnO_4 + H_2O \longrightarrow 3\ CH_3COOH + 2\ KOH + 2\ MnO_2$$

$$3\ CH_3COOH + 8\ KMnO_4 \longrightarrow 6\ CO_2 + 8\ MnO_2 + H_2O$$

Overall reaction: $3\ C_2H_4 + 12\ KMnO_4 \longrightarrow 12\ MnO_2 + 12\ KOH + 6\ CO_2$

Minerals

Researchers have reported the use of minerals as ethylene scavengers, in the form of layers in the packaging, embedded in solids or distributed in plastic matrix or in the form of sachets. Thus, in active packaging system, the main focus is given to incorporation of these minerals in the packaging films itself [94]. It has been stated that the mean life of climacteric fruits and vegetables (e.g. bananas, apricot, kiwifruit, cucumber, carrots, and asparagus) are extended by the use of ethylene scavenging packages [29] as given in Table 1.7.

Metal Nanoparticles

Many compounds are able to regulate the propagation of microorganism and upsurge the shelf life of the packaged product when incorporated into packing materials. The most popular active agents among these are the metal nanoparticles, as they are very effective against most of the food spoilage strains. They also enhance the property of ethylene oxidation or oxygen absorption. Some of the metal composites for example; copper, magnesium, zinc, silver, gold and titanium nanoparticles are active in numerous food packaging applications. The various nanoparticles used in food packaging with the limitations are discussed in the Table 1.7.

Zeolites

Ethylene absorbers based on zeolite are of good commercial use. Zeolite has the best characteristic property of its porosity and three-dimensional arrangement that exhibits adsorption property, molecular sieving ability and cation exchange capability. Therefore, zeolites have been incorporated as an ethylene scavenger into the packaging films, and are functional in many industrial, agricultural and commercial uses. It has also been reported that the reduction of the particles to nano-sized zeolite have improved its properties to greater extent. Many researches have been reported, which include zeolites as an active ingredient in the packaging film and improved its permeability.

Various ethylene absorbing materials used in food packaging are given in Table 1.7.

Table 1.7: Various Ethylene Absorbing Materials used in Food Packaging

Ethylene Absorbing Material	Matrix	Application	Inference Drawn	Drawback	References
Potassium permanganate	Small sachet containing scavenger is absorbed in the film.	Beneficial for preserving fruits and vegetables e.g. apples, bananas, mangoes, carrots, tomatoes and onions.	Matrix used for incorporation of potassium permanganate should be extremely permeable to ethylene.	Permanganate in direct contact of food is reported to be toxic.	[96-98]
	Inert matrix of Silica (SiO_2) and alumina (Al_2O_3) nanoparticles infused with $KMnO_4$.	Refrigerated tomato	The packaging containing $KMnO_4$ oxidizes ethylene and indicates its removal through color change from purple to brown.	The high toxicity of $KMnO_4$ and restricted durability in high-moisture environments resist its direct contact with food products	[99]
Minerals	Nano particles of Active carbon, Zeolite etc. are distributed in plastic film.	It is used in packaging of fresh commodities.	The minerals incorporated in polymer matrix rises the permeability of the film. The equilibrium inside the package is maintained by increased diffusion rate of CO_2 and allowing the entry of O_2.	-	[28, 29]
	Photoactive TiO_2.	Climacteric fruits and vegetables.	The reaction is the oxidation of ethylene into CO_2 and H_2O.	The exposure of metal oxide to UV light for its activation, can cause negative effect on food quality.	
	Metal Organic Frameworks (MOF) containing Cu and Al.	Banana	This can absorb ethylene thus resisting the impact on the plant physiology.	-	[100]
	Nano-composite films of LDPE and Halloysite nanotubes (HNTs)	Banana, tomato and strawberry	These films show high capability of ethylene adsorption thus reducing the process of softening and aging of fruits.	-	[27]
	Nano Ag pads placed in trays	Used for fresh-cut melon	This system also works as a barrier to ethylene.	It is not applicable in the packaged structures.	[101,102]

	Palladium as scavenging packaging is used in the form of sachets or in the storage rooms.	Used in packaged food.	These packages have high ethylene adsorption capability.	Could not be used in the form of packing films, industrial application of palladium is restricted due to its high cost.	[22-26]
	Charcoal/ palladium chloride in the form of absorbent or in the form of sachets	Lowers the softening of garden-fresh kiwifruits and bananas, loss of chlorophyll in green leafy vegetables as spinach.	Checks build-up of ethylene. It effectively absorbs the ethylene produced by slices of kiwifruits and bananas (for 3 days at 20°C)	Could not be used in the form of packaging films, Not used for broccoli pieces.	[25]
	Ethylene absorbent in the paper packets placed in trays covered with glass.	Broccoli and spinach	Ethylene absorbent efficiently absorbed 0.4 ppm ethylene from the trays.	This type of packing is not effective for foodstuffs with high respiration rate.	
	Activated carbon (30%)/ polysaccharide glucomannan (0.3 %) in rice straw paper	Can be applied to mango, tomato and bananas	The calculated adsorption capacity of the ethylene/ surface area was 34.2 μL/L/m. so, a separate bag inside the carton was suggested.	Food application was not evaluated	[103]
	Ethylene scavengers are also used in the form of coatings (eg. sepiolite, and sepiolite permanganate) on cardboards along with polylactic acids.	Fresh fruits and vegetables.	Worked as an active packaging.	Systems for food applications were not reported.	[104]
Nanoparticles	PE/Nano Ag/TiO_2/Kaolin	Storage of fresh strawberries (For 12 days at 4°C)	Polyethylene packaging containing nano particles lowered the rate of strawberry deterioration from 26.8% to 16.7%, it also sustained the amount of TSS, ascorbic acid and the activity of different enzymes (pyrogallol peroxidase and polyphenol oxidase)	There was no monitoring for the headspace gases and no clue for shelf life.	[105]

	PE containing 30% nano-Ag powder, Kaolin-clay or PE and TiO_2 cured with warm air or blend of both nano-packaging and warm air treatment.	Used for Chinese bayberries packaging	This packaging maintained the rate of respiration, production of ethylene and firmness of fruits, the blend of warm air and nano-packaging showed best results as compared to these working individually (during storage period of 8 days.)	-	[106]
	Blended form of nano Ag//kaolin in polyethylene/ nano TiO_2	Conservation of Chinese jujube	It is reported that the packaging actively reduced the browning reaction, softening of fruits during 12day storage. Also, initially the rate of ethylene production increased and then subsequently decreased.	No indication for shelf life of packaged product	[107]
	Blended form of PE with nano-Ag, nano- TiO_2, mont morillonite	Kiwifruits storage at 4 °C for 42 days.	Ethylene concentration, color difference, softening and degree brix is reduced significantly, preventing any type of physiological change.	-	[108]
	Nanoparticle of ZnO coated with PVC	Freshly cut Fuji apple maintained at a temperature of 4 °C for 12 d.	These packages have higher content of O_2 as compared to CO_2 thereby lowering the respiration rate. These packages also reduce the decay of fruits, reduce enzyme activity and maintains degree brix.	-	[109]
	Films made of chitosan and nanoparticles of TiO_2	Cherry tomatoes	These films delay the ripening of vegetable crops and extended its storage life by the process of ethylene photodegradation	-	[110]
Zeolite-based minerals	LDPE bags containing 50% of alumina silicate (zeolite)	Broccoli	Chlorophyll degradation, stem hardening and quality loss was considerably decreased by using LDPE packaging with zeolite. The decrease in ethylene concentration was reported to be from 61.8 ppm under control condition to 0.33 ppm in case of storage in active LDPE packaging.	-	[28]

	HDPE bags containing sachet with zeolite and $KMnO_4$ at 4°C for 31 days.	Used in the storage of kiwi fruit	This packaging helped in keeping the high content of Vitamin C and also the firmness of the fruit. 60.67mg/100mL of Vitamin C was reported for the active packaging while it was lower for control packaging 47.37 mg/100mL.	No result was given for ethylene measurement or shelf life.	[111]
	Ethylene absorbing non-perforated film with gas permeability.	Storage of mango at 12°C.	Ethylene absorbing non-perforated film reduced weight loss with no sign of decay. This film lowered the rate of ethylene production and also postponed the rate of ripening.	-	[112]
	LDPE bags with Zeolite.	Ripening of kiwifruits	These active packaging containing LDPE and zeolite established the equilibrium in the headspace (i.e. Steady state of O_2 and CO_2 gas) and reported 20 days of storage.	No report for ethylene calculation was done.	[30]
	LDPE pouches containing sachets, LDPE films containing hydroscopic minerals.	Storage of fresh broccoli	LDPE films with hydroscopic minerals maintained the chlorophyll content, color as well as texture of the product and also provided the highest shelf life.	No ethylene measurement was reported	[113]
	Nano-zeolite with palladium and $KMnO_4$.	Tomatoes	These films maintain the characteristics and extends the shelf life of the tomatoes under storage conditions.	-	[114]

1.5.2 Active Packaging System with Releasing Substance or Emitters

These packaging systems incorporate some active compounds, like, antioxidants, antimicrobial agents, flavors, carbon dioxide and ethylene etc., that interact with the packed food or the headspace of the packaged foods to decrease the growth of microbes, or decrease the rate of the reactions that decrease the shelf life of the foodstuffs. The sachets that release water vapour are one of the key examples of effective innovative packaging used for the ready-to-cook fresh vegetables.

Some of the major constituents that can be used as an active emitter in the packaging materials are given in Table 1.8.

Table 1.8: Active Packaging System with Releasing Substance or Emitters

Active Releasing Systems	Causes	Affect	Active substance	Benefit	References
Antimicrobial compounds	Excessive development of pathogenic microbes in the presence of moisture causes increase in food borne illness	Extension of lag phase of microbes and their inactivation, reduction in surface contamination	Essential oils	Resisting the growth of pathogenic microorganisms	[115, 116]
			Enzymes and Bacteriocins	Regulates the microbial development on the foodstuffs.	[117, 118]
Carbon dioxide	Excessive development of pathogenic microbes in the presence of moisture, decreases the quality of food	Highly permeable polymers are used to maintain the content of CO_2	MAP (60% CO_2 and 40% O_2), (60% CO_2 and 40% N_2) and vacuum	Upkeeping of the shelf-life, maintenance of freshness	[119-122]
Antioxidants (synthetic and natural)	Lipid oxidation and protein denaturation can cause adverse effect on the quality of foodstuffs.	Reduction in lipid oxidation	BHT	Decreases lipid oxidation and protein denaturation	[123, 124]
			α- Tocopherol, BHT, BHA	Maintains the oxidation reaction	[125, 126]
			Ellagic acid or buriti oil, proteins nanofibers	Helps in improving the oxidative stability	[127-130]

1.5.2.1 Carbon dioxide Releasers

The amount of carbon dioxide, and its solubility rate in the aqueous or fatty phase of the foodstuff plays a significant part in the antimicrobial activity of the CO_2. However, the solubility of the CO_2 is dependent on the temperature and shows inverse relation (i.e. as the temperature is increased the solubility decreases) [131, 132]. Along with temperature, the rate of solubility of CO_2 also depends on the properties of the food, such as, its compositions (percentage of protein, lipid and water), surface occupied by it and its pH value [45].The partial pressure of the CO_2 gas present in the environment of the packaged food, shows proportional outcome for its antimicrobial activity. Table 1.9 includes the various CO_2 emitters with their application in different food packaging.

1.5.2.2 Antimicrobial Releasers

Antimicrobial packing is an active packaging, which extend the shelf life of the foodstuff by inhibiting bacterial growth and decay. Antimicrobial food packaging is aimed to constrain the propagation of the pathogenic microbes and the spoilage of packed food. In one system, branded as “Bio Switch”, an antimicrobial component is released on command, when the bacterial growth occurs. With a change in the environs, for example, occurrence of UV light, change in pH and temperature, the antimicrobial component responds accordingly. Thus, the external stimulus marks the release of an antimicrobial component of the package. The antimicrobial packaging system, potentially increase the specificity and stability of preservation and lessen the quantity of chemicals required in foods. The commonly used active releasing agents or emitters in antimicrobial food packaging include essential oils, enzymes and bacteriocins, antimicrobial polymers, etc., the details of which have been given in Table 1.10.

Essential Oils

Several plant-essential oils, when used in food packaging, increase the product quality and shelf life. Most of the essential oils are generally recognized as safe (GRAS) [135] and so has been used as bio-based films and coatings. Being, of plant source, these are a better replacement for petroleum-based additives and beneficial for both the individuals and the environment [136]. Several researches have used essential oils as active packaging ingredients, but real food application is not studied so far. Thus, the safety of these compounds should be tested before their incorporation in the industrial use.

Enzymes and Bacteriocins

Researchers have focused on the application of proteins, especially enzymes and bacteriocins, on the foodstuff packaging to regulate the microbial development in the foodstuffs [117,118].

Antimicrobial Polymers

The food packaging films made up of polymers such as chitosan and ε-polylysine show antimicrobial properties, biodegradability, nontoxicity, edibility and good barrier properties. However, while evaluating the sensory quality of the packaged foods, biopolymers, ε-polylysine very active contrary to the propagation of Gram-negative and Gram-positive bacteria; chitosan along with its derivatives, actively work as antifungal and antimicrobial agent in the food packaging. Though, the antimicrobial polymers target a wide range of microbes and proven to be beneficial in food packaging, however, the commercialization of these biopolymers as food packaging is to be upgraded under real storage conditions of the food products.

Table 1.9: Various Carbon dioxide Releasing Materials used in Food Packaging

Carbon di oxide Releasing Systems	Matrix	Application	Inference Drawn	Drawback	References
	MAP (60% CO_2, 40% O_2) incorporated along with CO_2 emitter	Packing of cod fillets	The gas to product ratio of 1.3: 1.0, caused an addition to the storage life, from about 14 days to 21 days (In sensory property (flavour, odour and appearance, as well as in bacterial growth) in comparison to the vacuum-packing (7d to 14 d) storage life. The amount of the gases in the headspace increased for the MAP with emitter in comparison to MAP without emitter.	-	[119-120]
	MAP (60% CO_2, 40% N_2) with CO_2 emitter	Fresh reindeer meat.	MAP with CO_2 emitter reduced the TVC. Initially the decrease was 56% for day1 and then reached 67% on day 21. It also resulted in significant lowering of drip loss; it was 1% for modified atmosphere packaging with CO_2 emitter as compared to 3% for MAP without emitter.	-	[121]
	MAP (100% CO_2)	Storage of chicken and fillets	The active packaging showed a great reduction in the drip loss. The active packaging, displayed a weight loss of about 2.5% contrary to 7.5% in the fillets packed. The packaging with emitters maintained the level of CO_2 upto 100% during storage time. The storage of chicken in 100% CO_2 showed inhibition in the growth of bacteria while for fillets no response for microbial growth was reported.	-	[133]
	Sachets with combination of O_2 scavenging and CO_2 releasing concept	Storage of lamb cuts	The percentage of CO_2 released in the active packaging and the control packaging was almost same about 45% for a duration of 17 day. Thus, an effective result was not shown by this work.	The technology is not much clear	[134]
	Vacuum packaged–CO_2 releasing structure	Ready-to-eat meat product	The packaging of ready- to- eat meat has controlled the propagation of Listeria monocytogenes, TVC and Enterobacteriaceae at various temperatures for a duration of 4 weeks.	No ddata was available for the sampling	[122]

Table 1.10: Various Antimicrobial Releasing Materials used in Food Packaging

Antimicrobial Releasing Systems	Matrix	Application	Inference Drawn	Drawback	References
Essential Oils	Chitosan films coated with thyme essential oil in different percentage.	Storage of ready to eat cooked pork.	The film containing different percentage of thyme EO with chitosan has decreased the yeast count as a function of EO amount for the duration of 21day storage.	-	[115]
	Fish gelatin is merged with basil leaf essential oil.	Packaging of sea bass slices.	The film was used to examine the sensory and microbiological state of the packaged foodstuff, it increased the shelf life of the foodstuff upto 12 days.	-	[137]
		Storage of Lettuce.	This film also showed effectiveness against mold growth for a duration of 7 days storage.	-	[138]
	Films made from the gelatin of starfish with 0.05% vanillin.	Packaging of crab sticks.	The film is reported to show antimicrobial action against *L. monocytogenes* in the packaged foods.	-	[139]
	Carvacrol (volatile compound) of oregano EO.	Storage of tomatoes.	Tomatoes packed in a packaging film of pectin coated with oregano EO inhibited the growth of *Alternaria alternate.* The amount of EO used for inhibiting the microbial growth is about 25.9 g/L.	-	[140]
	Composite film of gelatin, clove oil and nanorods of ZnO_2.	Refrigerated storage of shrimp.	The packaging film showed great antibacterial activity against S. typhimurium and L. monocytogenes.	-	[141]
	Nanocomposite films composed of essential oil of clove, isolates of soy protein and montmorillonite.	Refrigerated storage of fillets of Tuna.	The packaging film stimulated a decrease of the final amount of microbes up to 12 days, while the count of enterobacteria and lactic acid bacteria the amount continued to be close to detection limit all through the storage.	-	[116]
Enzymes and Bacteriocins	Whey protein films with lysozyme.	Packaging of smoked salmon.	This film prolonged the shelf life of packed foodstuffs by obstructing the propagation of *Listeria monocytogenes* upto 4.4 log CFU/cm^2.	-	[142]
	Carboxymethyl cellulose along with lactoferrin and lysozyme were used as packaging material.	Packaging of sliced meat.	Coating of paper with lysozyme suppressed the propagation of aerobic bacteria to roughly 1 log cycle in comparison to the control packing.	-	[143]
	Coating films with solution of cellulose and nisin.	Refrigerated storage of hot dogs.	This film showed the lowering of *Listeria monocytogenes* upto 2 logs CFU during 60day storage.	-	[144]

	Films containing LDPE with nisin.	Storage of raw and pasteurized milk.	This film lowered the propagation of bacterial microbes' upto 0.9 log in raw milk and 1.3 log for pasteurized milk. Nisin is lawfully used as food additive.	-	[57]
	Coating of nisin into PE/Polyethylene oxide or polyamide.	Storage of beef and fresh oysters.	This film reduced the growth of *Brochothrix thermosphacta* and coliform bacteria.	-	[145, 146]
	Coating of chitosan or cellulose nanocrystal with nisin and EDTA.	Packaging of fresh pork meat.	The study reported that the coatings on the films controlled the propagation of psychrotrophs, mesophiles and *Lactobacillus spp.*	-	[147]
	Polymeric films (PVC, LLDPE or polyamides) coated with citric acid, nisin, EDTA (ethylene diamine tetra acetic acid) and PEG (polyethylene glycol) sorbitan monoleate.	Cold storage of broiler drumsticks.	The film prolonged the shelf life of packaged product by 0.6 to 2.2 day.	-	[148]
	Interleaves containing nisin, potassium lactate, enterocins and sakacin.	Storage of cooked ham.	The film was suitable for inhibiting the propagation of *Salmonella* spp. and *L. monocytogenes.*	-	[149, 150]
	Nisin stimulated poly (hydroxybutyrate)/poly (caprolactone) (PHB/PCL) nanocomposite films.	Vacuum-packed ham (sliced and cooked).	The efficiency of the film as shelf-life extender was confirmed by inoculation of ham with Lactobacillus plantarum CRL691 (bacterium model for spoilage of processed meat).	-	[151]
	Bacterial cellulose lactoferrin edible films.	Packaging of fresh sausages.	The film showed a great antimicrobial activity against S. aureus and E. coli.	-	[152]
	PET-coated film comprising of lactoferrin and lysozyme.	Fresh salmon.	The combination of lactoferrin and lysozyme made the films effective in declining H_2S-producing bacteria during storage and at higher temperature.	-	[153]
	Pullulan films with Lysozyme nanofibers.		The multifunctional material with antimicrobial activity against S. aureus.	-	[130]
	Chitosan (cationic polysaccharide) prepared through N-deacetylation.	Pork slices.	This film shows antimicrobial activity against excess of Gram-positive bacteria (e.g., Listeria innocua, S. aureus, and lactic acid bacteria) and Gram-negative bacteria (e.g., Pseudomonas spp., E. coli, and Salmonella spp.) and fungus (e.g., Aspergillus niger and Candida albicans).	-	[154]

Antimicrobial Polymers	Packaging films containing ε-polylysine and whey protein.	Packaging for fresh pieces of beef.	The film was suitable for preventing the propagation of lactic acid bacteria, and lowering the rate of growth of total flora in fresh cut beef products.	-	[155]
	Chitosan as an antimicrobial agent is added to LDPE or carboxymethylcellulose or as coatings on plastic films.	Packaging of fresh red meats.	Although the chitosan/LDPE films did not prevent the growth of microbes on the surface of red meat but it helped in maintain the red color of the product in the course of cold storage.	-	[156-158]
	Films made of bio nanocomposites and chitosan.	Packaging of white cheese.	These films considerably decreased the entire bacterial count and also prevented the development of mold, yeast and coliform organisms all through the 30 days storage at 7°C.	-	[157]
	Coating of ethylene copolymer with chitosan.	Turkey breast.	The study reported the effect of the packing in contradiction of the development of *Listeria monocytogenes Scott A*. The film decreases the log from 1.7 in 10 days to 1.2 in 15 days at a temperature of about 4 °C storage.	-	[158]
	Plastic films coated with chitosan and antimicrobial components (nisin, sodium lactate, Na-acetate, Na-sorbate and Na-benzoate).	Ham steaks, cold-smoked salmon.	The chitosan coated plastic film showed no resistance to the propagation of *L. monocytogenes*, however the incorporation of other antimicrobial components exhibited the inhibition of propagation of *L. monocytogenes*, with the best antilisterial result was shown by the sodium lactate component. This film also lowered the propagation of microbes on cold-smoked salmon.	-	[159, 160]
	PLA films with a coating of different ratio of antimicrobial agents varying from 5-10% of lauric arginate ester (LAE), 2-20% of sodium lactate, and 0.3-0.6% of sorbic acid.	Turkey slices, ready to eat meat.	The films of PLA with the ratio 5:5:2:0.3 of chitosan: LAE: sodium lactate: sorbic acid and 5:5 of chitosan: LAE totally controlled the growth of *Salmonella typhimurium* and also inhibited the growth of *Listeria innocua* to a considerable level. This film also reduced the log count of microbes in ready to eat meat.	-	[161]
	LDPE film containing chitosan, nisin, potassium sorbate or Ag substituted zeolite.	Storage of chicken drumsticks.	The study reported the positive effect on physiochemical and microbial quality of the packed foodstuff. The total microbial count was reduced and had lower TBARS value.	-	[162]
	Films containing chitosan and lauric arginate ester (LAE).	Chicken breast fillets.	The chitosan film inhibited the growth of mesophilic, psychrophilic, lactic acid, H_2S-producing and coliform bacteria's, yeast and fungi upto a log reduction of 0.47 to 2.96. Addition of 5% LAE to chitosan film also showed the log reduction from 1.78 to 5.81.	-	[163]

1.5.2.3 Organic Acids/ Organic Compounds Releasers

Different organic compounds used in active packaging include citric acid, sorbic acid, potassium sorbate, potassium metabisulfite, oxidized regenerated cellulose, allyl isothiocyanate etc.

Citric Acid

Naturally citric acid occurs in most of the citrus fruits and, is used as flavouring agent and preservatives in foods.

Sorbic Acid

The application of sorbic acid containing films is limited to meat products and jelly coatings, where the lowering of microbial count is seen. The sorbic acid containing films are applicable only at lower temperature, as, at high temperature, the activity of sorbic acid is significantly influenced.

Potassium Sorbate

Potassium sorbate is a derivative of sorbic acid that naturally occurs in some berries. It is also synthetically manufactured using sorbic acid and potassium and used as preservative, which help in resisting the growth of molds, yeast and other microbes in various foods.

Potassium Metabisulfite

Most of the fruits and vegetables are extremely viable to the enzymatic reactions. The addition of potassium metabisulfite in packaging can offer additional properties to it, in order to resolve this problem.

Oxidized Regenerated Cellulose (ORC)

The cellulose is a plentiful and universally existing biopolymer, which is renewable, biodegradable, low in cost, have low toxicity and good mechanical properties [164], but it has a limitation of low solubility, which hinders its applications [165]. However, this property can easily be corrected by converting it to oxidized regenerated cellulose (ORC), which contains 3-25% of carboxylic group. The antimicrobial effect of this ORC depends on the amount of the carboxylic groups present in it. ORC mixed with PCL is used for imparting the bacterial barrier and mechanical properties.

Allyl Isothiocyanate

In some researches, the use of the allyl isothiocyanate has been testified, against a varied range of bacteria. Its use has been given a GRAS status and used in wide range of foodstuffs [166].

Nanoparticles

The increasing usage of nano-materials having antimicrobial properties, as active ingredient in the active packaging, for various food products has been reported by the researchers [167]. The reported particle size for these antimicrobial nanoparticles, ranges between 1nm-100nm. These nanoparticles can be amalgamated with the polymer matrix to upsurge the shelf life of the packed foodstuffs. These antimicrobial emitters nanoparticles showed higher surface to volume ratios, which resulted in greater surface activity and, thereby, prompted better inhibition of microbial growth, as compared to its micro and macro counterparts [168]. The nano-particles of some metal oxides (e.g. MgO, ZnO and TiO_2), metal ions (e.g. platinum, gold, silver, copper) and organic nano-clays have been reported as active ingredients of active packaging systems. Although silver had shown the antimicrobial activity since long, but the activity of the silver in the form of nanoparticles has shown a many time increase in the shelf life of the packed foods [169 -171]. Different organic compounds incorporated in active packaging are discussed in Table 1.11.

Table 1.11: Various Organic Acid/ Organic Compounds Releasing Materials used in Food Packaging

Organic Acids/ Organic Compounds Releasing Systems	Matrix	Application	Inference Drawn	Drawback	References
Citric acid	Corn starch /LLDPE films containing 30% of (citric acid /glycerol/corn- starch) in the ratio 1.5:30:68.5).	Package used for minced beef.	The study reported the lowering in the entire bacterial count upto 1 log CFU/g.	More work is required to establish antimicrobial effect.	[172]
Sorbic acid	PLA film containing sorbic acid and algal extract.	Packaging of flat fish megrim (*Lepidor hombus whiffiago nis*).	The film showed a reduction in the antimicrobial content (0.9 log CFU/g) and also enhanced its sensory properties.	No substantial antimicrobial was seen after 11 days of storage	[173]
	Poly (vinylidene chloride) (PVDC) film with 1.5% or 3 % sorbic acid.	Packaging of Cheddar cheese and beef bologna.	The films showed lower count of mesophilic aerobic bacteria and also lower the count of inoculated *L. monocytogenes* at storage condition of 4 °C for 28 days for the packaging of beef bologna. This film did not show any positive effect for the storage of cheddar cheese.	Prohibition of sorbic acid in meats by Commission Regulation (EU) No 1129/2011 [175].	[174]
Potassium sorbate	PBAT films blended with 5% potassium sorbate.	Frozen storage for chicken steaks.	The results showed negligible amount of E. coli for a duration of 30 days (initial count being 1.94 log CFU/g).	-	[176]
	3% K- sorbate / 3% Na-lactate or combination of both with 1.5% each.	For protection of smoked rainbow trout fillets (*Oncorhy nchus mykiss*).	Among the three (3% potassium sorbate alone, 3% sodium lactate alone and combination of both with 1.5% each), the bacterial count was found to be lowest for the combination of both, i. e. 1.7 log CFU/g for duration of 4 weeks, at a temperature of 6± 1 °C and was very much lower as compared to control (bacterial count about 8.2 log CFU/g).	-	[177]
Potassium metabisulfite	Films made of PVC and potassium metabisulfite in 1:1 ratio.	Packaging of sliced gala apples (*Malus domestica*).	PVC film consisting of 2% potassium metabisulfite lowered the browning index to about 50% as compared to 90% for control, Also, it maintained the shelf life of the apple till 20 days at 8-12°C observing the microbial infection to 6 logs CFU/g.	-	[178]

Oxidized regenerated cellulose	Films containing mixture of microparticles oxidized regenerated cellulose in poly (Ɛ- caprolactone).	Used in packaging of sliced salami.	The films lowered the propagation of *S. aureus* and *E. coli*, it also lowered the oxygen and water permeability.	-	[179]
Allyl isothiocyanate	Vapour phase of AITC alone can be used or in blend with MAP (50.5% N_2/49% CO_2/0.5% O_2).	Shelf life of catfish fillets.	Amount of AITC used alone or in a blend with modified atmospheric packaging proved beneficial as an antimicrobial agent against *Pseudomonas aeruginosa*. It increased the storage time of catfish fillets from 5 days upto 23 days.	The pungent smell of AITC, that can be controlled by adding low concentration of AITC in foods	[180]
Nanoparticles	Nano-composite based LDPE with Ag/TiO_2.	Mildew condition of rice.	Rice packed in LDPE containing nanoparticles of Ag/TiO_2 showed low Total Plate Count (TPC) of about 5.48 log cfu/g.	-	[92]
		Microbiological safety of bread.	Packaging containing Ag/TiO_2 subdued the propagation of yeast (B. subtilis and B. cereus). It increased the shelf life of the bread by lowering the percentage of degradation of key components present	-	[181]
	PVC/Ag nanoparticles.	Triglyceride oxidation (fillets of chicken breast).	This type of packaging results in either lowering or increase of lipid oxidation which prolonged the shelf life of chicken breast and lowered the propagation of microorganism respectively.	-	[170]
	LDPE/nano Ag/ZnO.	Orange juice packaging.	This packaging helped in extending the storage life of orange juice upto 28 days.	-	[182]
	Active packaging films with ZnO as an antimicrobial agent.	Poultry, meat.	The initial bacterial count (S. aureus and S. typhimarium) in the packed fresh poultry meat was reduced by 2 log phases (condition 24 h of incubation at a temperature of 8 ± 1°C).	-	[183]
	LDPE/ Titanium dioxide (TiO_2).	Packaging of fresh pears.	Packaging (involving LDPE with nanoparticles of TiO_2) of fresh pears reduced the count of mesophilic bacteria from 3.14 to < 2 log CFU/gm and that of yeast from 2.45 to < 2 log CFU/gm (17d.).	-	[184]
	Copper (Cu)/PLA.	Packaging of Fiordilatte cheese.	PLA film with Cu incorporated in it hindered the proliferation rate of microbes (*Pseudomonas* spp.).	-	[185]

1.5.2.4 Antioxidant Releasers

Traditionally, the lipid oxidation in the packaged food was reduced by directly adding the antioxidants to the foodstuff, but the problem arises, when the quantity of antioxidant added got totally consumed up, thereby, ceasing the protection of the packaged foods. Thus, an alternative packaging technology was adopted, where the antioxidants were incorporated into the packages itself. The details of the different antioxidant releasers incorporated in the food packaging is as given in the Table 1.12. Initially, the synthetic antioxidants such as BHT and BHA were used to reduce the lipid oxidation reactions. But nowadays, the main focus is towards the natural materials, and thus, the synthetic antioxidants are being replaced by natural ones e.g. tocopherol, essential oils, polyphenols and other natural extracts [186-190].

1.5.3 Commercial Active Packaging

Enormous literature in the form of review papers, research articles and patents are available on the application of active packaging for the foodstuffs. These studies offer an advanced understanding and exploitation of these technologies at commercial level [197]. The Table 1.13 highlights the commercialized active packaging explored for various foodstuffs.

Table 1.12: Various Antioxidant Releasing Materials used in Food Packaging

Antioxidant Releasing System	Matrix	Application	Inference Drawn	Drawback	References
BHA/BHT	LDPE combined with BHT packaging.	Fillets of fresh Sierra fish were packed.	LDPE/ BHT packaging helped in lowering of lipid oxidation as well as protein denaturation and was expressed in terms of TBARS, peroxide value, and free fatty acid contents. This packaging is also helpful in maintaining the firmness.	The synthetic anti-oxidant used, which is considered to be not suitable for edibles.	[191]
α- Tocopherol	Films containing polylactide-co-lycolide and 2% α- tocopherol or films containing 1% BHT and 1% BHA.	Used in packaging of dry buttermilk and dry whole milk.	Although the volatility of BHT and BHA is higher than the α-tocopherol, but the study showed better antioxidant performance of the α-tocopherol. Further the sealable films (HDPE/ LDPE /EVOH) with inner coating of LDPE and 4% α- tocopherol also reduced the lipid oxidation at 40°C.	-	.[123-124]
	LDPE films with 1.9% and 3% of α- tocopherol.	Corn oil packaging.	The stability of oxidation was maintained at 30°C.	-	[192]
	Films containing PLA and 2.58% α- tocopherol.	Packaging of soybean oil.	The film helped in delaying the initiation of lipid oxidation at temperature range of 20°C – 40°C.	-	[125]
	Combined use of LDPE/ α- tocopherol with MAP.	Packaging of fresh Bluefin tuna fillets.	Packaging with combine application of modified atmospheric packaging and LDPE incorporated with α-tocopherol tremendously reduced the lipid oxidation in bluefin tuna fillets, it was also reported that use of natural antioxidants into LDPE also helped in prolonging the storage life of salmon.	-	[126, 193]
Flavonoid/ Catechin	EVOH films containing 4.6% natural antioxidants (flavonoid quercetin).	Fresh products packaging.	The lower value of peroxide index (12meq/kg) and TBARS (25%) exhibited the improved stability of lipid oxidation.	-	[127]

	Catechin an extract from green tea is used as an antioxidant.	Sunflower oil and fried peanuts.	The oxidation stability of the oil was studied. The hexanol content in the headspace initially reduced upto 25 days of storage, after that, it increased in the same ratio similar to the control packaging. Comparing activity of catechin and quercetin, quercetin showed more effectiveness.	-	[194]
	Films made of cassava starch with rosemary extracts.	Aqueous and fatty food products.	The packaging focuses on sustaining the quality and nourishment of packaged products. The antioxidants decrease the oxidative degradations.	-	[195]
	The composite film containing hydroxypropyl-methylcellulose nanoparticles of PLA and extracts of green tea.	Foodstuffs containing high fat content.	The packaging focuses on sustaining the quality and nourishment of packaged products. The antioxidants decrease the oxidative degradations.	-	[196]
	Films composed of chitosan containing ellagic acid or buriti oil.	Fatty food products.	The packaging focuses on sustaining the quality and nourishment of packaged products. The antioxidants decrease the oxidative degradations.	-	[128, 129]
	Film composed of pullulan comprising of proteins nanofibers.	Food products with high fat content.	The packaging focuses on sustaining the quality and nourishment of packaged products. The antioxidants decrease the oxidative degradations.	-	[130]

Table 1.13: Commercially Available Active Packaging Films

Types	Trademark	Applications	Functions	Form of Packaging	References
Moisture Scavengers	Moist Catch (absorbing films); Linpac, TenderPac®, Nor®Absorbit Fresh-R-Pax® (in the form of trays); MeatGuard (as absorbing pads); Dri-Loc® (as absorbing pads); Onyx Desiccant Paper (absorbing paper).	Fruits (strawberries), vegetables (mushrooms, tomatoes), snack foods (sandwiches), fresh fish, meats, poultry, cereals (maize, grains) seeds, dried foods.	Regulates excess moisture in packages, controls humidity.	Films suitable for microwave, absorbent pads and trays, sachets and dual compartment systems.	[14, 32]
Oxygen Scavengers	ATCO® (oxygen scavenging as high as 100-200 cm^3); Cryovac® OS2000 FreshPax® (oxygen absorber containing palladium metal and hydrogen gas); OxyCatch® (oxygen is captivated by cerium oxide units); Ageless® (Iron based); Celox™ FreshMax® OxyGuard® Shelfplus® O2 OxyRx® OMAC®; Enzyme-based Bioka ActiTUF™.	*High moisture foods*- Fruits and vegetables, sliced cooked meat products, fish. *Intermediate moisture foods*- cooked rice, bakery products, bread, cakes, biscuits, pizza, pasta, cheese. *Low moisture foods*- dried beef, dried fruits, cured meats, coffee and dried foods. *Lipid containing foods*- Seeds, nuts, oils, fats, fat-containing instant powders. *Refrigerated and frozen foods*- snack foods.	Controls enzymatic discoloration, lipid oxidation, and growth of aerobic microbes, unsuitable oxidation and growth of molds.	High temperature films, films used as labels, bottles crown, sachets.	[20, 84, 198]
Ethylene Scavengers	Profresh Retarder® Ethysorb Ethylene Control Ethylene PEAK fresh® Evert Fresh Green Bags® Power Pellet Bio-fresh.	Horticultural products-Climacteric fruits and vegetables eg. Apples, bananas, melons, apricots, and tomatoes.	Controls ripening of fruits and vegetables.	Films in the form of sachets.	[199]
Flavour/ Odour Emitters and Absorbers Film	Compel Aroma® Anico™ Aroma-Can BMH™.	Fruits- flavour of fruit juices; Animal products- fishes, poultry; Dried products- cereals; Fried snack foods; Dairy products.	Aroma maintenance.	In the form of films.	[199]

Carbon Dioxide Emitters	Ultra-Zap® Xtenda Pak pads SUPERFRESH CO_2 ® Fresh Pads	Animal food- fatty fish, meat; Lipid products- instant powders (with fat), oils, nuts and fried foodstuffs; bakery goods.	Slows down the metabolic rate of microorganisms, checks bulging up of packaging.	CO_2 releaser in the form of pads and box.	[170]
Antimicrobial Emitters	AgIon® Surfacine® d2p® Biomaster® Sanic Films Wasaouro® Biomaster® Irgaguard® IonPure® Bactiblock® Food-touch® SANICO®.	Animal product-Seafood, processed meat fresh meat and, fresh- smoked fish; cereals and bakery goods; processed and fresh vegetables and fruits, Ready-to-eat meals.	Lowers post- harvest decay.	Trays and films with silver, Sheets and films having antibacterial and antifungal coatings.	[166]
Antioxidants Emitters	ATOX (containing oregano essential oils).	Instant powders (with fat), fried products, fresh fish and meat.	Prevention of oxidation.	Used as coatings on film, Incorporated in polymer matrix.	[126]

1.6 INTELLIGENT PACKAGING

The intelligent packaging involves the incorporation of the preservatives within the foodstuffs, which give the information about the quality of the product, through the packaging [200]., Intelligent packaging assists in detecting, recognising and recording the disparities in the food or in the headspace of the packaging, and help it to communicate to the users, via a marker indicator, that is attached as label, fused into, or printed on the food packaging material itself [59, 201]. The description of the intelligent materials, according to EC/450/2009 [12] is "the material which observes the quality of the packed foodstuff or the headspace (temperature, pH, moisture, humidity etc.)".

Intelligent packaging systems are categorized into:

1.6.1 Indicators
1.6.2 Sensors
1.6.3 Radio Frequency Identification Systems

1.6.1 Indicators

Indicators usually respond through changing the color or some other measurable physical property due to the variation in the concentration of the constituents, when the chemical reactions undergo in the packaged goods. Different types of the indicators include:

Freshness Indicators

The freeze-chilled foodstuffs, during the storage undergo variations either due to microbial development or oxidation reactions. The microbiological development, as well as, the metabolic reactions cause the pH change; growth of the toxic substances, off-odours/flavours, release of gas and the development of slime. The oxidation of phospholipids and dyes cause successive release of objectionable flavours, in terms of rancidity, formation of the compounds, which result in adverse biochemical reactions, or the discoloration in the food products. The emphasis of the intelligent packaging is thus, on the freshness indicators, which, simply indicates the variations caused, by different reactions. The freshness indicators gather the information from the by-products released by different reactions, and propose the state of the packaged food stuff.

Time-Temperature Indicator (TTI)

The TTI enriches the labelling of the packaged goods by giving the information of the deviation and past temperature profile, during the transportation and stowage. It delivers the information about the change in temperature above the threshold value of the packaged food, or the duration for which the packed food had undergone temperature variations. All the physical, chemical and microbiological activities occurring in the food stuff is mainly dependent on the temperature, so it is quite necessary to keep a record of the variation in the temperature of the packaged products, quite closely and, this is accomplished by via labels which visually specifies the history of the temperature and its variations. Various time temperature indicators that are commercially accessible, are based on different reactions like, polymerization, diffusion and enzymatic. A time temperature indicator can be located on the shipping containers or the distinct packages as a small self-adhesive label, which undergo an irreversible change, like, a color change, when experiences altered temperature (low or high) conditions. TTIs are predominantly useful for the chilled or frozen food products, where the cold storage is chiefly required during transportation and distribution for maintain the quality and safety of the foodstuff.

Integrity Indicators

The package reliability of the food products during the sequence of manufacture, processing, transportation and stowage is extremely dependent on its leak indicator. The amount of oxygen and the carbon dioxide in the perishable packed products distresses the activity of the aerobic microorganisms, and thus, the quality of the food stuff. The amounts of these gases are examined by the leakage indicators, commonly termed as ‘Integrity Intigators’.

Table 1.14 illustrates the various kinds of indicators used in intelligent packaging systems.

Table 1.14: Intelligent Packaging Systems with Different Types of Indicators

Types of Indicators	Matrix	Application	Functions	Drawbacks	References
Freshness Indicators	colorimetric responsive labels	Storage of seafood's.	The volatile amines released during storage of seafood's interacted with the colorimetric labels to display the freshness of the food.	It also showed color change for the products with no significant deterioration.	[59, 202]
	Bio based pH colorimetric indicator		Detection of compounds released due microbial growth eg. D-lactate, L-lactic acid, n-butyrate and acetic acid.	-	[203]
	Chitosan as a CO_2 indicator (aqu. Solution)	Packaging of meat products	Alteration in the transparency detects the presence of CO_2 in the packaged meat causing its deterioration.	-	[204, 205]
Time Temperature Indicator (TTI)	Commercialized diffusion-based TTIs.	These indicators are used either as CTTI (Critical temperature ie equivalent to the melting temperatures of esters) or TTI (where melting temperature is lesser than the temperature of storage)	These indicators are centred on the diffusion of blue dyed ester which is a combination of blue dye (butyl stearate, melting temperature=12°C) and fatty acid ester (octyl octonoate, melting temperature = -17°C).	-	[202]
	Commercialized diffusion-based TTIs (eg. Check Point® III)	pH-sensitive chemical (dependent in diffusive reaction.)	The diffusion reaction causes change in pH and changes the color of the indicator which is matched with the different color shown by the indicator based on the quality of the product. Color change indicates different percentage of the expiry, i.e. 20%, 60%and 100%.	-	[202]

	Commercialized enzymatic TTI (eg. VITSAB® and Check Point® I)	Used for products undergoing enzymatic hydrolysis of the phospholipid substrates.	Enzymes based TTI contains two compartments, one comprising of aqueous lipolytic enzyme and second comprising of phospholipid substrate added in PVC carrier, having suspended aqu pH indicators.	-	[202]
	Commercialized TTI polymer	It includes solid state polymerization.	It includes 1, 4 – addition polymerization generating highly colored polymer. The decrease in reflectance detects the color response.	-	[202]
	TTI based on Photochrome (eg. OnVu™)	It involves photochromic solid state reaction.	It involves organic pigments which show two stages where rate of color change is temperature dependent: stage 1 is colorless and unchanging and stage 2 is colored and metastable.	-	[206, 207]
	Commercialized bacteria based TTI (Eg. TRACEO®)	Transparent labels containing particular strains of lactic acid microbes.	The two responses given are: change in color from colorless to pink (irreversible reaction) and secondly opacification response i.e. once the packaged foodstuff undergoes the mishandling (critical temperature misuse)	-	[208, 209]
Integrity indicator	Tablets that are reactive to O_2 (Ageless Eye®)	Color changing for O_2	It indicates pink color for the O_2 content < 0.01%, and turns blue for higher O_2 content >0.5%.	-	[210]

1.6.2 Sensors

Photosensitive and electrical signals are generally sensed and responded by the devices called sensors. Sensors transmute the physical or chemical factors such as temperature, humidity and pressure etc. into an electrically computable signals [211]. The vital functional parts of the sensors are, a receptor and a transducer.

Biosensors

The sensors that help in detecting, recording and transmitting the data associated with the biochemical reactions and fluctuations, are called biosensors [212]. Biosensors have two main components that are bio-receptors and transducers. The bio-receptors assist in targeting and to analyte the biochemical signals, and comprises of the organic materials as antigens, hormones, genetic materials and micro-organisms etc, and, the transducers assist in interpreting biochemical signals into quantifiable electronic response. These are system dependent and are either colorimetric, optical or acoustic materials.

Gas Sensors

The intelligent packaging systems that show response to the existence of different gaseous constituents in the packaged foodstuffs are called gas sensors. Gas Sensors monitor the configuration of gases inside a packaged product by changing the color of the indicator, through an enzymatic or chemical reaction. These devices give response when the indicators are in direct contact with the gaseous environment adjoining the food in a package. Different types of gas sensors include: oxygen sensors, ethanol sensors, water vapour sensors, organic polymers (conducting), carbon dioxide sensors, crystalline piezoelectric sensor and transistors with metallic oxide semiconductor field effect [211, 213].

Printed Electronics

Printed electronics are the flexible chemical sensors consisting of printed receptors, located on the top of the printed transducers. This technique depends on the application of inks, that are coated on the flexible substrate, and function electrically. Another form of printed electronics are intelligent packaging devices that are molecular specific. In these devices, the definite molecular printing is done on a pre-polymeric blend, where, the analyte molecule is bonded with the pre-polymer. Once, the development of polymer is over, the analyte molecule is detached, thus, leaving a cavity, where, the targeted molecule of that specific shape is recognized [59, 214].

Chemical Sensors

The device which detects a specific gas or chemical and translate it into signal, with the aid of transducer, are called chemical sensors. Chemical sensors are capable of sensing the existence of a particular gas or chemical along with its composition, concentration and activity. The transducer in a chemical sensor is very particular and, it may be an active or passive component subjected to the requirement of an external power supply [215]. An improvement in the receptors of the chemical sensors is the development of an optical transducer, which is designed using silicon incorporated into silicon semiconductor material. Its significant feature is that it can work in the absence of power supply and, can even detect from a distance by the using infrared, ultraviolet and visible lights [216].

Electronic Nose

The intelligent packaging system that imitates the mammal’s olfactory system is termed as electronic nose. This device can detect the aroma mixtures present in the odour, by giving response to each flavour, odour and taste. It consists of an arrangement of biosensors or chemical sensors [215, 217].

Table 1.15 illustrates various types of sensors for food packaging.

Table 1.15: Intelligent Packaging Systems with Different Types of Sensors

Types of Sensors	Matrix	Application	Function	Drawback	References
Biosensors	PE printed with antibodies (based on visual system) (Toxin Guard®).	Packed foodstuffs.	Identifies pathogens such as E coli. Salmonella species.	-	[218]
			Detects the amines generated either by the course of decarboxylation of amino acids or by amination of aldehydes caused by microorganisms.	-	[219]
	Smearing of xanthine oxide to graphite, platinum or silver.		Detects the production of xanthine due to the degradation of animal tissue.	-	[220]
			Detects the amines generated either by the course of decarboxylation of amino acids or by amination of aldehydes and ketones caused by microorganisms.	-	[219]
Gas Sensors/ Optical Oxygen Sensors		Detects the quality of packed foodstuff.	The direct interaction of the sensor with the gaseous constituents existing in the packaged food, show the results on the basis of luminescence quenching and changes in absorbance.	-	[221]
Opto-chemical Sensors	They detect gaseous component such as volatile amines, CO_2 and H_2S.	Detects volatile amines in, poultry, meat and fish.	Three main forms of this sensors is: 1. pH sensing indicator (fluorescence system)-having ph sensitive dyes for sensing volatile amines. 2. Colorimetric sensing (absorption system)-have methyl red/cellulose membrane etc. for sensing volatile amines by visible color change. 3. Phase fluorimetric sensing device (energy transfer system).	-	[222-225]

Printed Electronics	Flexible substrate having electrically functional inks.	Products which are molecular specific	They are lightweight, flexible, foldable and portable, and based on varied forms of substrates that are exclusively tailored.	-	[215]
Chemical Sensor	Nano materials of carbon such as graphite, nanotubes, nano fibres, graphene.	Detect deterioration, presence of pathogens, contamination and tampering during the course of manufacturing, processing and supply.	Use of nanoparticles of carbon in the chemical sensors shows good results due to the great specific surface area along with their exceptional mechanical and electrical properties.	-	[215, 226, 227]
Electronic Nose		Fresh yellow fin tuna, vacuum packed beef.	Satisfactory quality evaluation is reported.	-	[228, 229]
		Fruits and vegetables.	They detect the quality of the vegetables and fruits by sensing aroma released by them.	-	
	PEN 2 E nose.	Ripening phases in tomatoes.	The ripeness of tomatoes detected by sensing volatile compounds produced by them.	-	[230]
		MAP packaged cut pieces of broiler chicken.	The comparison obtained from electronic nose and those from sensory and headspace gases were quite equivalent.	-	[231]

1.6.3 Radio Frequency Identification (RFID)

In present food packaging technology, RFID tags are gaining popularity as, an essential criterion for carrying data of the packed food, and tracking of the product during the course of processing, supply and storage chain. RFID is an automatic identification technology and works with radio waves. At a rudimentary level, RFID comprises of three major parts: RFID label, RFID reader and RFID antenna. RFID tags includes of an integrated circuit, containing of a silicon microchip, along with small antenna connected on a substrate, and is seized in different elements like plastic or glass. This RFID labels can transfer data to the RFID reader which, captures the data by producing radio signals, and subsequently passes it to the computer for further scrutiny [232]. An RFID antenna aids in reading the labels from a distance of about 15 ft to 100 ft. There are two categories of RFID tags depending on the power supply; *Active RFID Tags,* which are power-driven, by using an internal battery or, external power supply unit, and are operative for large range transmission [215]; and *Passive RFID Tags,* which depend on the power given by the reader, and are operative in short range transmission.

1.6.3.1 Advantages of RFID over the Conventional Barcodes

1. The RFID is not necessary to be in the straight line of the vision of the scanner.
2. Numerous RFID tags can be read at exactly the same time, and in a faster way.
3. Maximum number of the RFID tags are used to store data e.g. nutritive facts, temperature and cooking directives.
4. The RFID tags can also be pooled with the time temperature indicators or biosensors, for additional improvement in the technology [212].

The usage of Radio Frequency Identification (RFID) in food packaging systems is given in Table 1.16.

Tables 1.16: Intelligent Packaging Systems with Radio Frequency Identification (RFID)

Types of RFID	**Matrix**	**Application**	**Function**	**Drawback**	**References**
Radio Frequency Identification	RFID system operates with radio waves (comprising of three parts: RFID tags or label, RFID reader and RFID antenna.)	RFID tags are can also store data e.g. nutritive facts, temperature and cooking directives.	**Active RFID tag** (effective for large range transmission) **Passive RFID tag** (effective in short range transmission)	-	[232]

1.6.4 Commercial Intelligent Packaging

Commercial intelligent packaging facilities are the primary manufacturer, service providers of flexible packaging material, specialty packaging materials, food packaging products, exporters and more. The commercial intelligent packaging facilities are dedicated to the finest manufacturing practices, reliability, quality and economical pricing, and moreover in the continuous planning and creation of innovative products, and committed to provide an obdurate support and solutions to the trades in the packaging technology.

Table 1.17 gives an overview of the commercially available intelligent packaging systems.

Table 1.17: Commercially Available Intelligent Packaging Systems

Intelligent Packagings	Trade Name	Application	Function	Company	References
Biosensors	Toxin Guard®	It senses the targeted pathogens e.g. *Listeria sp*, *Salmonella sp*, *E. coli*.	The system depends on visual diagnosis of antibodies printed polyethylene packaging.	Toxin Alert Incorporated, Toronto, Canada.	[218]
Freshness Indicators	Fresh Tag	Detects amine formation in deterioration fishery products.	Increased pH due to decomposition of volatile amines shows response based on methyl red.	COX Technologies Incorporated, Belmont, North Carolina.	[202]
	Sensor Q®	Checks the freshness of fishes.	Quantity of amines shows the change in color of pH sensitive bromocresol dye.	Food Quality Sensor International Incorporated (FQSI), Lexington, Massachusetts.	[233]
	Ripe Sense	Change in color indicates ripeness of fruits.	Works by detecting the aroma of the ripening fruits and display color change from red to orange and then to yellow depending on the maturity state of the fruit.	Ripe sense Limited, Auckland, New Zealand.	[234]
Time Temperature Indicator (TTI)	VITSAB®	Checks the packed seafood or other perishable goods.	The enzymatic hydrolysis of lipid reduces the pH which is indicated by color change of the labels.	Vitsabs International AB, Sweden.	[235]
	Freshness Monitor®, Fresh-Check®	Used in packaging of meat, seafood and poultry.	Based on the solid state polymerization reactions.	Lifelines Technology Incorporated, USA.	[211, 236]
	MonitorMark™	Used for highly perishable foodstuffs.	It is based on the molecular diffusion criteria. The indicator is dependent on the temperature of the packed food.	3M™ Company, St. Paul, Minnesota.	[237, 238]

	OnVu^{TM}	Packaging of frozen foodstuffs.	The indicator is created on solid state reaction and displays color variation at changed wavelength of lights and at variable temperatures.	Ciba Specialty Chemicals, Incorporated, Switzerland.	[238]
Integrity Indicators	Novas® Timestrip Best-by^{TM}	Indicates freshness of packed foodstuff.	Variation in O_2 and CO_2 content of the packed product due to tampering is displayed by color change.	Insignia Technologies Limited., Newhouse Lanarkshire; Timestrip Limited., Cambridge, United Kingdom; Fresh Point Lab, Nesher Haifa Israel.	[239-241]
	O2 Sense^{TM}	Packaging of perishable foodstuffs.	These are luminescence-based indicators.	FreshPoint Lab, Nesher Haifa, Israel.	[241]
	Ageless Eye ®	Packaging of meat products.	Works by detecting both CO_2 and O_2 scavengers in the packed foods.	Mitsubishi Gas Chemical Incorporated, Tokyo.	[210]
Passive and Semi Passive RFID	Easy2log®	Packaging of seafood's, frozen products and milk-based goods.	The assemblage of a great resolving sensors, and enormous memory size with a standard RFID interface approves the operational tracking for the frozen products.	CAEN RFID Srl, 55049 Viareggio (LU), Italia.	[242, 243]
	Corrugated box packaging with RFID tag.	Used for grocery products.	Tracing of grocery products during manufacturing, stowage and transportation chain.	Mondi, 1030 Vienna, Austria.	[244]
	CS8304	Finds application in cold storage rooms.	It is used as a passive RFID for locating frozen goods during transportation and stowage.	Convergence Systems Limited, Hong Kong.	[245]
Active RFID	TempTRIP	Used in various food packagings.	It mechanism is based on time temperature checking aspect and contains a RFID reader, scanner with internet.	TempTRIP LLC, WA 98230 United States.	[246]

1.7 SAFETY CONSIDERATIONS ASSOCIATED WITH THE USAGE OF ACTIVE AND INTELLIGENT PACKAGING

Materials used in food-contact applications are rested open to the pre-market monitoring approval, by the Food and Drug Administration, if they are deemed ‘‘food additives”, under the Federal Food, Drug, and Cosmetic Act [247]. According to the Federal Food, Drug, and Cosmetic Act. Section 201(s), ‘‘Food additive” are substances that are reasonably expected to become a component of food under the intended conditions of use”. In a broader way, the solution to the safety issues, in connection with the active and the intelligent packaging should be grounded on three main pillars:

Labelling:

Labelling should be the essential component of all packaging. The labels should be designed with the goal to avert misuse and misinterpretation by the downstream handlers or consumers, e.g. to avoid sachets from being swallowed.

Migration

The migration of the active and the intelligent agents should be sensibly considered, along with their breakdown products, as a function of their toxicity. The compliance of the releasing active packaging with the food legislation shall be closely related. The migration of the active components should be assessed by developing the migration tests, and mass transfer modelling tools, as those already existing or suggested for conventional packaging, might not be attuned to active and intelligent systems.

Efficacy of the Packaging

The efficiency of the developed packaging should be tested for the purpose, it was designed for, as, in some very definite cases, the capability of the packaging to achieve the claimed function can elevate the safety issues. For instance, as for any food preservation technology, e.g. delivering a preservative, or absorbing oxygen for preventing microbial growth, without studying, its antimicrobial resistance or pathogen over growth may even risk the lives of end users.

A legislative framework and suitable testing methods are, thus, required for assisting such a highly innovative field. Though active and intelligent packaging, is not subjected to any exceptional regulatory concern in the United States, the directives of such packaging material in Europe is still progressing. The EU methodology to establish a new cataloguing between the active and intelligent packaging, and the rest of the food-contact materials has been critically remarked by Heckman in 2007 [248]. Regulation 1935/2004/EC withdraws this legislation, in order to allow packaging to benefit from technological innovation [249]. This framework regulation authorises the usage of intelligent and active packaging, provided the packaging can be exposed to enhance the safety, quality and shelf-life of the packed foods.

1.8 RESEARCH GAPS

Though, a lot many literature studies exist on the different types of food packaging material, available in the market, but most of them are based on the conventional packaging trends, utilizing the petroleum product as the base material. The trailing research in the smart packaging is the lesser utilization of the biopolymer, and environmentally friendly packaging materials [250], which is the demand of today’s environment. So, in order to minimize the use of petroleum products, the packaging technology is now focusing more on the biopolymers for the advancement. In addition to this, the demand for the smart packaging is forcing the researchers to develop a packaging that shows the additional property of increased shelf life of the packaged food, as well as, the facility to detect the quality of the food enclosed in the package, without opening it. Most of the research work on smart packaging till date is very much based on the concept of active packaging and modified atmosphere packaging, whereas, the intelligent packaging still needs to be explored at various levels of its utilization, in the market. Most of the intelligent packaging idea are based on the electronic sensors and some are based on the indicators which include freshness, temperature and integrity indicators [251], and is still lacking behind the major concept of food deterioration, which includes the change in the pH of the packaged food, due to the formation of the acid inside the package.

1.9 ORIGIN OF THE RESEARCH PROBLEM

The packaging technology is now taking a sharp increase, especially in the food sector. The increasing demand for the partially processed foods for easy and quick consumption is promoting the packaging of a variety of foodstuffs. And, to be sure of the quality of the packed food, the smart packaging is covering the market at a faster pace. To fulfill the needs of the fast-growing packaging technology, and a focus on providing degradable packaging to the food products, attempts are being made to identify a smart biodegradable polymeric film to be used. The biodegradation of the bio polymers reduces the CO_2 and greenhouse gas emission level as, these can be easily broken down by naturally occurring bacteria and, thus, release less dangerous components upon decomposition. At the commencement of the food deterioration process, the change of the pH occurs, due to the decomposition of various constituents of the food, such as proteins, fats, carbohydrates etc. into different carboxylic acids and aldehydes, which can be easily detected by the color change, using the acid indicator dyes. Thus, the biopolymers incorporated with pH sensitive indicators can be of great use in detecting the quality of the foodstuff, at the time of procurement or, before consumption, thus, making it safer for the consumers.

1.10 OBJECTIVE OF THE RESEARCH WORK

During this PhD programme, the aim of my research was the "**Synthesis and Characterization of Eco-friendly Smart Packaging Materials for Edibles".** For the synthesis and design of ecofriendly and safe smart packaging material, the main focus of the study was to develop a qualitatively responsive polymeric film using a biopolymer. Broadly, this research aims to accomplish the subsequent specific objectives:

1. Selection of a suitable biopolymer, solvent and plasticizer for the synthesis of ecofriendly film for food packaging.

2. Synthesis of ethyl cellulose polymeric film with different ratio of plasticizers.

3. Study of the physico-mechanical properties of the resulted ethyl cellulose polymeric films.

4. Incorporation of suitable indicators to the ethyl cellulose polymeric film, with an aim to develop qualitatively responsive smart films.

5. Study of the physico-mechanical properties and biocompatibility of the ethyl cellulose film incorporated with pH responsive indicators.

6. Study on the water vapor permeability of the developed smart film.

1.11 OVERVIEW OF THE THESIS

The increasing demands of the consumers for preserved foodstuffs along with the modifications in the retail and circulation practices has steered to the introduction of smart packaging. To fulfill the needs of the fast-growing packaging technology, and a focus on providing the degradable packaging to the food products, the present studies have been conducted with an objective to develop an ecofriendly qualitatively responsive smart packaging material. The entire thesis is structured in six chapters. The **Chapter 1** of the thesis offers an outline of the packaging materials used in conventional packaging and the requirement of smart packaging in the modernized society. A comprehensive review on different types of active and intelligent packaging and their responses for altering the shelf life of the food products have also been presented here. The gaps in the already available literature have been discussed and the specific objectives to carry out this research work have been highlighted. The **Chapter 2** elaborates the experimental part, which includes, the methodology adopted for the development of the smart films, with different percentage of plasticizer, and indicators. A brief outline of the various characterization techniques used, to study and characterize, the developed biodegradable smart polymeric film has also been included in this chapter. The **Chapter 3** deals with the synthesis of the ethyl cellulose films and to study of the effect of various polymer to plasticizer ratios on the properties of the biopolymer films. The **Chapter 4** includes the studies on the development of the qualitatively responsive, pH sensing ethyl cellulose films, as smart food packaging material. The studies on the water absorption capacity, colorimetry and mechanical behaviour of these films have also been incorporated in this chapter. The **Chapter 5** provides the investigations on the water vapor permeability of the pH responsive smart films. Lastly, the conclusion and the future prospect of the study are encompassed in the **Chapter 6,** which is followed by the **References.**

CHAPTER 2

MATERIALS AND METHODS

2.1 RAW MATERIALS/CHEMICALS

In this study, the following raw materials/chemicals were used for the preparation of the eco-friendly smart food packaging materials:

1. Cellulose powder
2. Starch soluble
3. Methyl cellulose
4. Carboxy methyl cellulose
5. Ethyl cellulose
6. Ethanol
7. Acetone
8. Toluene
9. Glycerol
10. Ethylene glycol
11. Diethylene glycol
12. Triethylene glycol
13. Tetraethylene glycol
14. Polyethylene glycol
15. Propylene glycol
16. Methyl orange indicator
17. Methyl red indicator
18. Phenolphthalein indicator
19. Bromophenol blue indicator

2.1.1 Specification and Sources of Raw Materials/ Chemicals

Specification and sources of the raw materials and chemicals used to prepare eco-friendly smart food packaging materials and their characterization is given in Table 2.1.

Table 2.1: Specification and Sources of the Raw Materials and Chemicals

Sr. No.	Raw Materials/ Chemicals	Sources	Specification
1	Cellulose powder	Sigma-Aldrich Chemical Pvt Limited, Bangalore	ACS reagent Particle dimensions: 20µm (No components considered to be either (PBT), or (vPvB) at levels of 0.1% or higher).
2	Starch soluble	Sigma-Aldrich Chemical Pvt Limited, Bangalore	ACS reagent pH: 5-7 (25°C, 2% in solution) Not hazardous, Regulation (EC) No.1272/2008.
3	Methyl cellulose	Sigma-Aldrich Chemical Pvt Limited, Bangalore	Viscosity:4,000cP
4	Carboxy methyl cellulose	Sigma-Aldrich Chemical Pvt Limited, Bangalore	Average M_w ~ 90,000 Viscosity: 50-200cP
5	Ethyl cellulose	Sigma-Aldrich Chemical Pvt Limited, Bangalore	Viscosity 4cP, c=5%,80:20 Toluene: Ethanol
6	Ethanol	Chang Yu Hi-Tech Chemicals, China	Analytical Reagent Grade
7	Acetone	Central Drug House (P) Ltd, Delhi	Analytical Reagent Grade
8	Toluene	Hi Media Laboratories, Mumbai	Analytical Reagent Grade
9	Glycerol	Sigma-Aldrich Chemical Pvt Limited, Bangalore	ACS reagent
10	Ethylene glycol	Sigma-Aldrich Chemical Pvt Limited, Bangalore	Anhydrous, 99.8% Water (by Karl Fischer) ≤0.003%
11	Diethylene glycol	Sigma-Aldrich Chemical Pvt Limited, Bangalore	Analytical Standard
12	Triethylene glycol	Sigma-Aldrich Chemical Pvt Limited, Bangalore	ReagentPlus®,99%

13	Tetraethylene glycol	Sigma-Aldrich Chemical Pvt Limited, Bangalore	ReagentPlus®,99%
14	Polyethylene glycol	Sigma-Aldrich Chemical Pvt Limited, Bangalore	Analytical Standard
15	Propylene glycol	Sigma-Aldrich Chemical Pvt Limited, Bangalore	Food Chemical Codex (FCC), FG
16	Methyl orange indicator	Sigma-Aldrich Chemical Pvt Limited, Bangalore	ACS reagent
17	Methyl red indicator	Sigma-Aldrich Chemical Pvt Limited, Bangalore	ACS reagent
18	Phenolphthalein indicator	Central Drug House (P) Ltd, Delhi	1% (w/v)
19	Bromophenol blue indicator	Hi Media Laboratories, Mumbai	0.1% (w/v)

2.1.2 Purity of Raw Materials/Chemicals

The reliability and accuracy of the results is influenced not only by the precision of the instrument used or uniformity of the experiment performed but also on the quality and purity of the raw material used. The percentage purity of the raw materials/chemicals used during the experimental work is as given in the Table 2.2. All the chemicals were used as received without doing any further treatment.

Table 2.2: Purity of Raw Materials/Chemicals

Sr. No.	Raw Materials/Chemicals	Percentage Purity
1	Cellulose powder	Quality level: 200
2	Starch soluble	Quality level: 200
3	Methyl cellulose	Quality level: 200
4	Carboxy methyl cellulose	Quality level:100
5	Ethyl cellulose	Ethoxy content of about 48-49.5%
6	Ethanol	99.9%
7	Acetone	99.5%

8	Toluene	≥ 99.5%
9	Glycerol	≥ 99.5%
10	Ethylene glycol	≥ 99.75%
11	Diethylene glycol	≥ 99.5% (GC)
12	Triethylene glycol	≥ 98.5% (GC)
13	Tetraethylene glycol	≥ 98.5% (GC)
14	Polyethylene glycol	Quality level: 100
15	Propylene glycol	≥ 99.5%
16	Methyl orange indicator	Dye content 85%
17	Methyl red indicator	Quality level :200 Solubility: Ethanol:1mg/ml
18	Phenolphthalein indicator	Quality level :200 Solubility: Acetone: soluble
19	Bromophenol blue indicator	Quality level :200 Solubility: Methanol: 10mg/ml

2.2 RESEARCH METHODOLOGY

The methodology adopted to accomplish the desired objective of the research is apportioned into the following subdivisions:

- Preparation of the eco-friendly films, using a variety of available biopolymers, solvents and plasticizers, by casting method.
- Selection of the best combination of bio-polymer, solvent and plasticizer by examining the texture, uniformity and structure of the resulted films.
- Standardizing the formulation of the polymeric film by using different polymer to plasticizer ratios in order to achieve the best properties.

- Study of the physico-mechanical properties of the selected polymeric film.
- Incorporation of suitable indicators in the selected formulation to prepare qualitatively responsive smart films.
- Study of the physico-mechanical properties of the prepared eco-friendly polymeric films incorporated with pH responsive indicators.
- Study on the water vapour permeability of the developed smart film.

2.2.1 Preparation of the eco-friendly films, using a variety of available biopolymers, solvent and plasticizers, by casting method

A set of polymeric films were developed by using different bio-polymers, solvents and plasticizer combinations. For this, the homogenized solutions (2.5% w/v) of different cellulosic derivatives (cellulose, starch, methyl cellulose, carboxy methyl cellulose and ethyl cellulose) were prepared, by varying organic solvents (ethanol, acetone, toluene and water), with constant stirring at 100 rpm for 20-25 minutes, using a magnetic stirrer, at room temperature. To these solutions, different plasticizers (glycerol (GLY), ethylene glycol (EG), propylene glycol (PG), diethylene glycol (DEG), triethylene glycol (TEG), tetraethylene glycol and polyethylene glycol (PEG), fatty acids ; monosaccharides (glucose, fructose, mannose, sucrose) ; and water as plasticizers of edible and/or biodegradable films) were added, in order to reduce the brittleness, enhance toughness and impart flexibility. These different formulations were casted in Petri dishes and dried overnight on levelled surface, at room temperature, to prepare a set of polymeric films. A schematic representation of the film preparation by casting method is as shown in Figure 2.1. The appearances of the films were assessed by their texture and uniformity. Further the films were acclimatised at 24°C ± 2°C, 75% relative humidity for 24 hrs and the thickness was determined using micro-meter. The microstructural examination of all the films was done using a scanning electron microscope (SEM; S-3700N; Hitachi, Japan) at 10 kV as accelerating voltage.

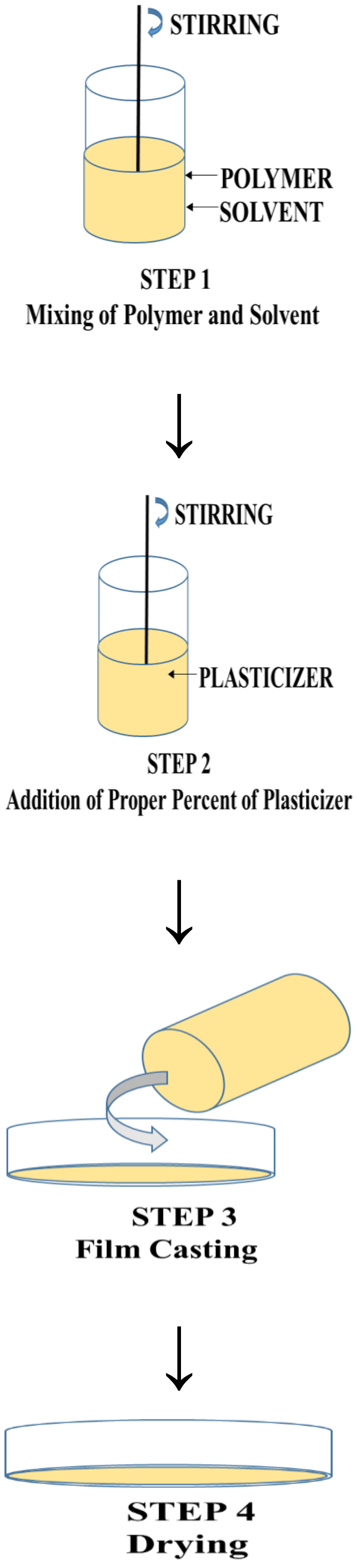


Figure 2.1: A Schematic Representation of the Film Preparation by Casting Method

2.2.2 Selection of the best combination of bio-polymer, solvent and plasticizer by examining their texture, uniformity and structure

The polymeric films formed from biopolymers were examined for their texture, uniformity and structure. The resulted films were found to vary significantly due to the variation of solvent and the percentage of the polymers used. The cellulose derivatives, like methyl cellulose and carboxy methyl cellulose are readily soluble in water (hot or cold) and the films formed by these cellulose derivatives showed inferior characteristics, with respect to the packaging materials. In contrary, the ethyl cellulose shows limited solubility in water (either hot or cold) so, ethyl cellulose was considered better, for the purpose of food packaging. Moreover, pure ethanol is also been suitable to an extent of food grade material, so it was taken as the best suitable solvent for the preparation of films. Polyethylene glycol (MW 400) was observed as suitable plasticizers for ethyl cellulose, in ethanol. The ethyl cellulose was testified as the most suitable biodegradable polymer for film preparation, due to its ease in casting and perfectly smooth film, in the laboratory conditions and, thus, selected for carrying out the further studies.

2.2.3 Standardizing the formulation of the polymeric film by using different polymer to plasticizer ratios in order to achieve the best properties

A homogenized solution of ethyl cellulose and ethanol was prepared (2.5% w/v) at room temperature, by constant stirring at 100 rpm for 20-25 minutes. To this solution, the plasticizer, polyethylene glycol (PEG) was added. The ethyl cellulose to polyethylene glycol ratios were taken as 4:1, 4:2 and 4:3, respectively, for different formulations. The samples i.e. sample1 (EC: PEG = 4:1), sample 2 (EC: PEG = 4:2) and sample 3 (EC: PEG = 4:3) respectively were casted from these formulations, in petri dishes (diameter = 14 cm), avoiding any bubble formation. The contents of the petri dishes were then, dried overnight at room temperature on a levelled surface, thus, resulting in the spotless films that was manually peeled, unbroken from the casting surface. A schematic representation of the film preparation by casting method, using different formulations of ethyl cellulose and polyethylene glycol i.e. respectively 4:1, 4:2 and 4:3 is as shown in Figure 2.2. The samples of ethyl cellulose films containing different ratio of PEG (five replicates of each sample were taken) were assessed for their physical and chemical properties.

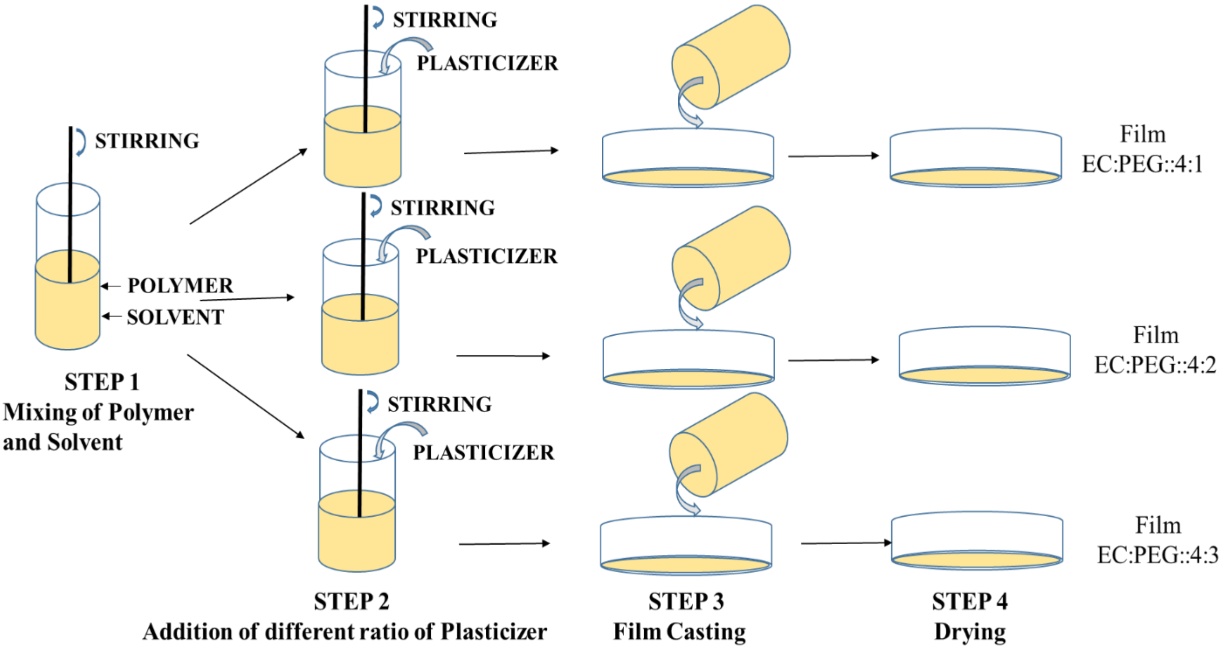


Figure 2.2: A Schematic Representation of the Film Preparation Using Different Formulations of Ethyl Cellulose and Polyethylene Glycol

2.2.4 Incorporation of suitable indicators in the selected formulation to prepare qualitatively responsive smart films

The pH indicator-based ethyl cellulose films were prepared by casting method. For this, a 2.5% (w/v) homogenized solution of ethyl cellulose in ethanol was prepared by constant stirring at 100 rpm for 20-25 minutes using a magnetic stirrer, at room temperature. The polyethylene glycol as a plasticizer, was added to it, using the ratio of EC: polyethylene glycol as 4:2. Further, 0.1 wt % of the indicator solution in water was added into the cast solution, and the stirring was continued for 1-2 minutes. The cast solution was then gently transferred into a petri dish (diameter = 14 cm), avoiding any bubble formation. The content of the petri dish was, then, dried overnight at room temperature, on a levelled surface. The spotless film, thus resulting, was manually peeled unbroken, from the casting surface. The different indicator incorporated EC films were prepared in the similar manner, and were stored in plastic bags to check the moisture absorption prior to the testing. A schematic demonstration of the preparation of smart films with different indicators is presented in the Figure 2.3.

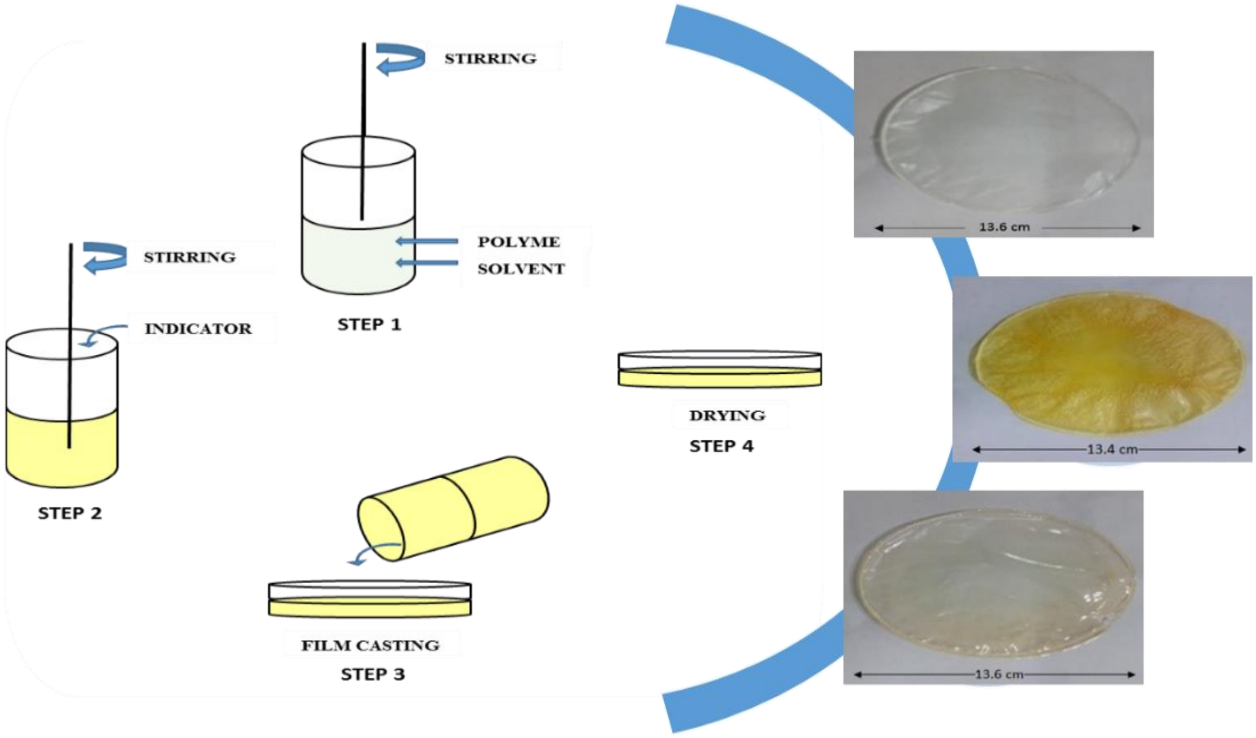


Figure 2.3: A Schematic Representation of the Preparation of Smart Films with Different Indicators

2.3 Characterization of the Prepared Eco-friendly Polymeric Films

The synthesised eco-friendly polymeric films, with or without indicators, were assessed for their suitability as food packaging materials. For this, they were characterized for their physical, structural and mechanical properties, along with the colorimetric analysis.

2.3.1 Study of the Morphology of the Polymeric Films

2.3.1.1 Film Appearance

The appearance of the films was assessed visually by their color, texture and uniformity.

2.3.1.2 Scanning Electron Microscopy (SEM)

The structure of the film is affected by the organization of various constituents in the film making solution and the interaction taking place between the constituents during drying. The microstructural examination of the film is also helpful to know the mechanism of water vapour permeability across the films and the arrangement of components in the film and, their consequence on mechanical properties of the film [252]. The microstructural examination of all the films was done using a scanning electron microscope (SEM; S-3700N; Hitachi, Japan) at 10 kV as accelerating voltage (Figure 2.4). Prior to testing, the films were set aside in the desiccators with P_2O_5 for 2 weeks, to ensure the absence of water. Further, the films were frozen using liquid nitrogen and then cryo-fractured cross section of these films were gold sputtered coated to render them electrically conductive (*placing gold layer of about 100 A° so as to escape charging up of the films under electron beam*), and observed under scanning electron microscope. The image processing was conducted by using in-built software SEM data manager of Hitachi PC-SEMs.

Figure 2.4: Scanning Electron Microscope (Hitachi S-3700N, Japan)

2.3.2 Study of the Physico-mechanical Properties of the Polymeric Films

2.3.2.1 Film Thickness

The thickness of the films was measured using the ASTM standard (ASTM D6988). The polymeric films were acclimatised at 24°C ± 2°C and 75% relative humidity for 24 hrs and the thickness was determined using micro-meter (Figure 2.5), which recorded up to exactness of ± 0.001mm. Thickness measurements was done at 6 diverse points of the each films (centre of each film, at centre of each quarter of the film and edges of the film) and the mean value was used to report the estimated thickness.

Figure 2.5: Micrometer Measurement of th Thickness of the Plastic Film

2.3.2.2 Yield of the Film

Yield is the measure of the film coverage. Usually the films are sold by the kilogram; yet the film area determines, exactly how many packages can be wrapped, or how many labels can be produced. So, yield is a critical property for determining the correct amount of film to be purchased, and it impacts the finances of the application. The yield of the EC films formed was calculated on the basis of the composite film obtained after drying at room temperature for 24 hrs Thus, the yield of each film was calculated from the mass of the ethyl cellulose, ethanol, plasticizer and indicators used in the formation of the film. The mass fraction of ethyl cellulose film was calculated using the following equation [253]:

$$\textbf{Yeild of EC film}(\%) = \frac{M_{Film}}{(M_{EC}+M_{ethanol}+M_{indicator}+M_{plasticizer})}\textbf{X 100} \qquad \textbf{(3.1)}$$

Where, M_{film} is the mass of films, after drying at room temperature for 24 hrs and M_{EC}, M_{ethanol}, $M_{\text{indicators}}$ and $M_{\text{plasticizer}}$ are respectively, the initial mass of ethyl cellulose, ethanol, indicators and plasticizer used for the film casting.

2.3.2.3 Soluble Matter Percentage (SM %)

The soluble matter of the films was checked by water immersion technique. The percentage of the soluble matter of the resulted films were estimated by immersing the samples (2.0 cm×2.0 cm each) in 50 ml of distilled water, which was slowly stirred, for a duration of 24 hrs The samples were then removed, and dried in oven for 24 hrs The equation (3.2) was used to calculate the amount of the soluble matter in the resulted films [254, 255].

$$\textbf{Soluble Matter Percentage}(\textbf{SM}\ \%) = \frac{\textbf{Initial dry weight} - \textbf{Final dry weight}}{\textbf{Initial dry weight}}\ \textbf{X100} \qquad \textbf{(3.2)}$$

2.3.2.4 Moisture Content Percentage (MC %)

The moisture content of the polymeric films was calculated by calculating the weight loss of films by drying it in a furnace at 105 °C ± 3 °C, for approximately 12 hrs, till a constant weight had been achieved (dry sample weight). Moisture content was determined as the percentage loss in mass during the drying of the films using equation (3.3) [256-258].

$$\textbf{Moisture Content Percentage}\ (\textbf{MC}\%)\frac{\textbf{Initial mass} - \textbf{Final mass}}{\textbf{Initial mass}}\ \textbf{X100} \qquad \textbf{(3.3)}$$

2.3.2.5 Mechanical Properties

The mechanical properties of the bio-polymers are important for the integrity of packaged products and to ensure their physical protection [259, 260]. The characteristic features of the load-time or typical stress-strain profiles are generally used to characterize the polymer properties. Toughness is directly proportional to the area under a load time or load-displacement curve, which is quantitated as energy. The higher the amount of energy a polymeric film can absorb, prior to break under load, the higher is its toughness. Elastic modulus indicates the elasticity of the film, with lower values corresponding to higher elasticity. On the other hand, the tensile strength indicates the film strength, with larger values corresponding to the stronger films. Ideally a film coating must be both elastic and strong and, therefore, must yield a higher tensile strength-to-elastic modulus ratio, which, thus indicates the better mechanical quality of the films. The mechanical properties like tensile strength (σ_{ut}), elongation at break (EAB %), elastic modulus (E), and work of failure, for the ethyl cellulose films were determined by ASTM method (ASTM D882 - 09) using the Universal Testing Machine (Micro UTM KLA Tencor T150 UTM with a gauge length of 2 mm to 10 mm, with a load variable of 50 mN to 20 kN (Figure 2.6)). For the testing of all the films, the load limit used was taken as 2 kg, with a start from 0 kg and a travel limit of 35 mm.

The wet film was dried in a levelled forced air-drying oven, pre-set at a desired coalescence temperature (the temperature at which the components of a miscible solution attract each other) for 24hrs [257]. The samples of ethyl cellulose film were cut into dimensions of 60 mm×60 mm, with an average thickness of 1 mm. For testing, the sample was griped on the device, with a gap of 1 mm and, pulled away from both ends, at a speed of 0.1 mm/s and load of 1 N [261,262]. The curves plotted between load vs time and stress (tension force / cross sectional area) and strain (change in length /original length) was used to determine the tensile properties [261, 262].

Ultimate tensile strength (MPa), of the films was determined by taking the ratio of the maximum force exerted on the film to the cross-sectional area and calculated by using the equation (3.4) below:

$$\sigma_{ut} = F/S \qquad (3.4)$$

The percentage change in the strain, is represented by the equation (3.5), as:

$$\text{EAB}\ (\%) = \Delta L/L_0 \ \text{X}\ 100 \qquad (3.5)$$

Equation (3.6) was used to calculate the elastic modulus that is the, ratio of stress and strain at the elastic limit.

$$E = \sigma/\epsilon \qquad (3.6)$$

Where, σ denotes stress and ϵ denotes strain at the elastic limit.

The work of failure, represented by the Equation (3.7) is a function of work done in breaking the film specimen and, is the representative of the film thickness.

$$\text{Work of Failure} = \frac{\text{Area under the curve x Cross head speed}}{\text{Film thickness x Film width}} \qquad (3.7)$$

The applied load is an important parameter to be measured, especially when comparing the results of two studies, since the strain or the percent elongation of a polymeric film is normally inversely proportional to the rate of strain and, the parameter changes due to the various reasons, namely, sample preparation method, coalescence temperature and, also the coating process variables.

Figure 2.6: Micro UTM (KLA Tencor T150 UTM with a gauge length of 2 mm to 10mm and a load variable of 50mN to 20 kN)

2.3.2.6 Water Absorption Capacity

The water absorption capacity of the polymeric films is used to calculate the amount of the water absorbed by them under definite conditions, hence, to ensure their performance in water or humid environments. The water absorption capacity of the ethyl cellulose films (with and without indicators) was determined in accordance with the ASTM standards (ASTM D 570). The equation (3.8) was used to calculate the water absorption capacity of the ethyl cellulose films [263]:

$$\textbf{Water Absorption Capacity (in wt\%)} = \frac{\textbf{Wet weight} - \textbf{Conditioned weight}}{\textbf{Conditioned weight}}\textbf{x100} \qquad (\mathbf{3.8})$$

Where, the conditioned weight was taken by drying the samples in an oven for 24 hrs at 50 °C ± 2 °C, cooled in a desiccator and instantaneously weighed to 0.001 g. The wet weight is taken by placing the conditioned sample into the distilled water, keeping it fully immersed for different durations (varying from 1 hr to 24 hrs), wiping the surface water and, immediately weighing to the nearest 0.001 g. the reproducibility of the result was confirmed by using five replicas for each sample.

2.3.2.7 Colorimetric Analysis

The colorimetric measurements were executed by the CIE L^*a^* b^*system. The color parameters of the ethyl cellulose films, with different indicators were measured by varying the pH values of the acid used for the assessment. The resulted pH indicator-based ethyl cellulose films showed significant color changes at different acidic concentrations. For colorimetric characterization, Chroma Meter CR 400 colorimeter (Konica Minolta, Japan) was used (Figure 2.7). For the standardisation purpose, a white calibration plate was used. The colorimetric measurements were accomplished using the CIE L^* a^* b^* system, where, the parameter L^* denotes the lightness of color from 0 (dark) to 100 (light); a^* is the grade of greenness/redness (negative value of a^* is green and positive value of a^* is red) and, b^* is the grade of blueness/yellowness (negative value of b^* is blue and positive value of b^* is yellow); both a^* and b^* extend in the two axes forming a plane orthogonal to L^*, and show no specific numerical limits [263]. A schematic representation of the CIELAB color space is as shown in Figure 2.8.

Figure 2.7: Chroma Meter CR 400 Colorimeter (Konica Minolta, Japan)

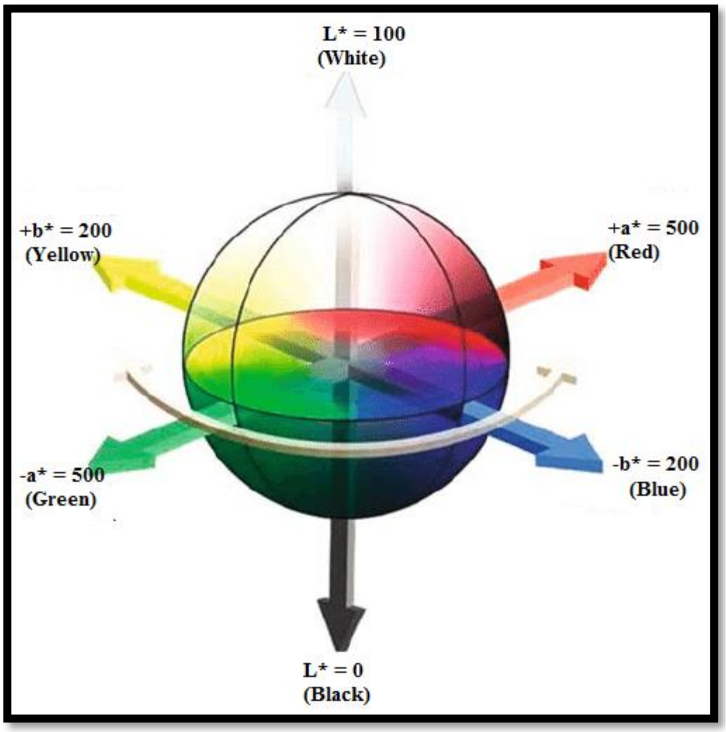


Figure 2.8: A Schematic Representation of the CIELAB Color Space

2.3.2.8 Water Vapour Permeability

Vapour permeability is the capability of a substance to allow the vapour (of water, gas, volatile liquid) to pass through it. To be more specific, water vapor permeability is a measure of the amount of vapour that is transmitted through a substance, under a specified set of conditions. The greater the value of the permeability of the substance, the more quickly the vapour can pass through it. The water vapour permeability (WVP) of the ethyl cellulose films was calculated by the cup method, as per the ASTM E96-95 standard, under a set of temperature conditions. The weighing's at prescribed time duration, determine the rate of vapour movement through the specimen. An illustration of cup method of water vapour permeability testing is as shown in Figure 2.9. The water vapour transmission rate (in g $m^{-2}s^{-1}$) is estimated by plotting the graph between, the weight loss (Δw) and the time (Δt), which is rectilinear in nature.

The ratio of the gradient (Δw/Δt) to that of the test area (A) gives the values of the rate of water vapour transmission as per the equation (3.9) below:

$$\mathbf{WVTR} = \frac{(\Delta w/\Delta t)}{A} \qquad \textbf{(3.9)}$$

Where, Δw/Δt is the vapour loss per unit of time (*g* s^{-1}) and A is area exposed to vapour transfer (m^2). Further, the water vapour permeability WVP ($g\ m^{-1}\ s^{-1}\ Pa^{-1}$) is determined by equation (3.10) [261], as:

$$\mathbf{WVP} = \frac{\mathbf{WVTR\ x\ L}}{\Delta p} \qquad \textbf{(3.10)}$$

Where, L denotes the thickness of the ethyl cellulose film (*mm*) and Δp is the variation of the partial water vapour pressure across the film, which is calculated by equation (3.11), as:

$$\Delta p = p(RH_2 - RH_1) = 2081.325\ Pa \qquad \textbf{(3.11)}$$

Where, p is the saturation vapour pressure of water at 25°C±2°C and RH_1 and RH_2 are the values of relative humidity where RH_1= 0%, RH_2 = 75%) (*Pa*) respectively.

For each formulation of ethyl cellulose film, at least five replicates were executed.

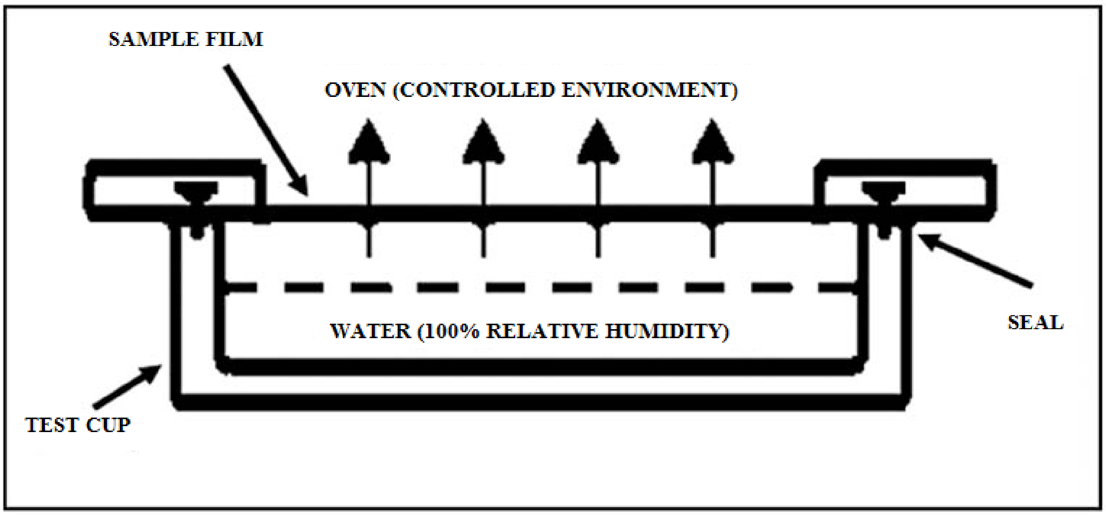


Figure 2.9: An Illustration of Cup Method Water Vapour Permeability Testing

2.3.2.9 Anti-permeability for Oils

The bio-polymeric films used for the food packaging, especially, for the oily foods or the oil containing edibles, should be anti-permeable for the oils, otherwise the leakage of oil from the packaging films may result into the decline in their appearance, flavor and shelf life [264]. To test the anti-permeability of ethyl cellulose films for oils (and oily foods), the samples with dimensions 2 cm x 2 cm, from each film, was firmly pressed on an open end of the test tube containing soya bean oil. Further, the test tube was placed inverted on the filter paper and was observed for the permeability of the oil, through the ethyl cellulose film with respect to time. The procedure was conducted on 5 samples of similar composition each, for a duration of 3 days, under normal conditions of temperature, pressure and relative humidity [265].

2.3.2.10 Reliability and Collapsibility of Films

The samples of the ethyl cellulose films were considered reliable, as they maintained the integrity of the appearance when peeled from the petri dish. Further, to test the plasticity or collapsibility, the samples of ethyl cellulose films were creased for 20 times at the same line [266].

2.3.2.11 Biocompatibility

Biocompatibility of a material is needed to be ensured, so that, the material remains stable and non-toxic to the body, and not affected by the conditions of application and storage [267]. The biocompatibility of the ethyl cellulose films was checked by their toxicity contents, stability and processing effects.

CHAPTER 3

SYNTHESIS OF ETHYL CELLULOSE FILMS: EFFECT OF DIFFERENT POLYMER TO PLASTICIZER RATIOS

3.1 INTRODUCTION

Packaging protects the food from the outside environment and ensures to supply safe, wholesome and healthy food to the consumers. Commonly used food packaging includes plastics materials, such as, polyethylene (both HDPE and LDPE), polypropylene, polyvinyl chloride, polyethylene terephthalate and polystyrene [268]. During the storage, they may also interact with the packaged food and may release toxic chemicals into it [269]. In addition, the quality of the packaged food is likely to deteriorate due to the change in its natural ingredients, which may include, the loss in the moisture content or the volatile odour. The plastics used in food packaging are derived from petroleum and, generate greenhouse gases, thus, cause a huge impact on the environment. Ending into garbage, the food packaging accounts for almost two-thirds of the total packaging waste by volume, hence, leading to both environmental and health hazard [270, 271]. With the advancement of new technologies, the manufacturers are getting innovative with their eco-friendly efforts to reduce the plastic wastes, however, the food packaging films, which show post-consumer biodegradability, and thus, not causing much burden on the environment, are not been explored [272]. Due to the different environmental concerns and rising awareness among the customers, regarding the harmful outcomes of the plastic food packaging, the latest researches are more focused on the development of bio-based performance end products for food packaging. Most widely used bio-based polymers are the cellulose derivatives, such as, methyl cellulose, cellulose acetate, hydroxy-propyl cellulose and ethyl cellulose, that, have a backbone of cellulose, with repeating structure of anhydrous glucose units, each having three reactive -OH (hydroxyl) sites [273]. Ample of work has been done in the past, for the preparation and investigation of modified atmosphere packaging films based on protein, lipid and polysaccharide, which provide barrier to the volatile component of food as well as its moisture content [274, 275]. However, the main concern is that, these bio-degradable packaging films lack many desirable characteristics of packaging materials, to be used at a commercial scale. These problems can easily be overcome by improving the film characteristics, using different approaches, like, the modification of raw material or, the incorporation of plasticizers. As per the previous studies, the type of plasticizer and its concentration can modify the different physical properties of the films [276]. The present study has been conducted with an aim to synthesize the ethyl cellulose-based bio-degradable films, using polyethylene glycol, as plasticizer. In order to achieve the improved physical properties, the studies have been conducted by taking different polymer to plasticizer ratios, and the various properties of the resulted films were determined. The ethyl cellulose (EC) and polyethylene glycol (PEG) used were in the ratio 4:1, 4:2 and 4:3, for different formulations. The samples i.e. sample 1 (EC: PEG = 4:1), sample 2 (EC: PEG = 4:2) and sample 3 (EC: PEG = 4:3) respectively, were casted from these formulations, in petri dishes (diameter = 14 cm), avoiding any bubble formation.

3.2 RESULTS AND DISCUSSION

3.2.1 Film Appearance

The samples of ethyl cellulose films, formed on flattened surface, were peeled off unspoiled from the petri dish. The appearance of the sample 1 was hazy, and, that of sample 3 was translucent, while, the sample 2 was opaque, as seen in Figure 3.1. However, the texture of all the samples was smooth and homogeneous and showed no breakage while peeling from the surface as reported in Table 3.1.

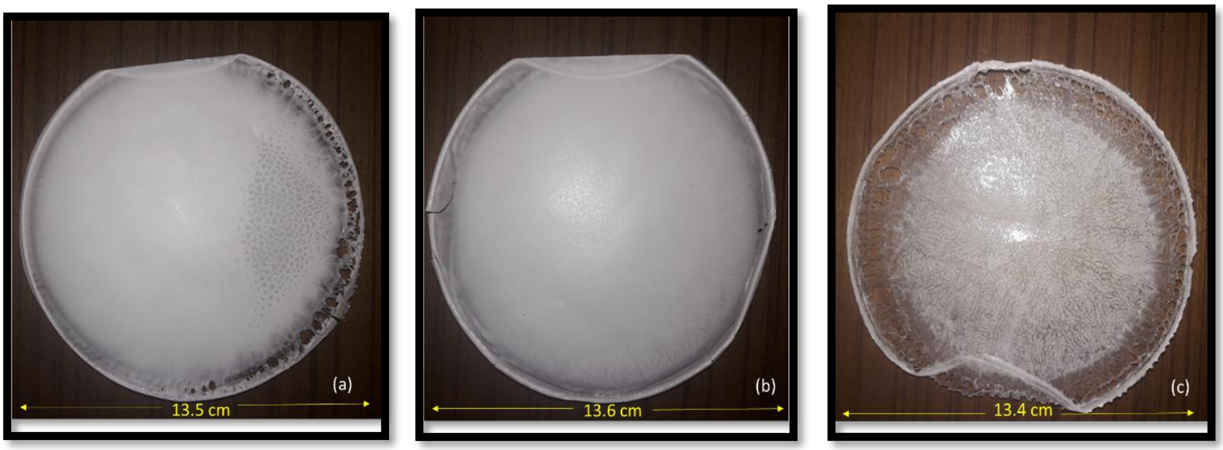


Figure 3.1: Ethyl Cellulose Films with Different Ethyl Cellulose (EC) to Polyethylene Glycol (PEG) Ratio (a) EC: PEG = 4:1 (b) EC: PEG = 4:2 (c) EC: PEG = 4:3

Table 3.1: Appearance of Ethyl Cellulose Film with Different EC: PEG Ratios

Sample	EC: PEG	Color	Texture	Appearance
1	4:1	White	Homogeneous	Hazy
2	4:2	White	Homogeneous	Opaque
3	4:3	White	Homogeneous	Translucent

3.2.2 Films Thickness

The thickness of the ethyl cellulose films was calculated by using micro-meter. The thickness of each film was measured at 6 different points (centre of each film, at centre of each quarter of the film and edges of the film), and an average of the all values was calculated. The mean thickness of the various samples is reported in Table 3.2. Mean thickness, for sample 1 (EC: PEG = 4:1), was equal to 1.010 mm with a standard deviation of 0.01; for sample 2 (EC: PEG = 4:2) was equal to1.017 mm with standard deviation of 0.04; and for sample 3 (EC: PEG = 4:3) was equal to 1.014 mm with a standard deviation of 0.02 respectively.

Table 3.2: Thickness of Ethyl Cellulose Film with Different EC: PEG Ratios

Sample	EC: PEG	Thickness (mm)
1	4:1	1.010
2	4:2	1.017
3	4:3	1.014

3.2.3 Soluble Matter Percentage (SM %)

The samples of the ethyl cellulose films, immersed in the distilled water for 24 hrs maintained their structures, and did not showed any swelling. The results of the soluble matter contents, for different ethyl cellulose films, revealed the maximum percentage i.e. approximately 75.00 %, for the film containing EC to PEG ratio 4:3, and the minimum for the film with EC to PEG ratio equal to 4:2, having approximately 56.25% of total soluble matter. However, the soluble matter for ethyl cellulose film containing EC: PEG ratio 4:1, showed the total soluble matter of about 60.97 %. The mean values of percentage of soluble matter content for ethyl cellulose films, with different EC to PEG ratios is given in Table 3.3 and shown in Figure 3.2.

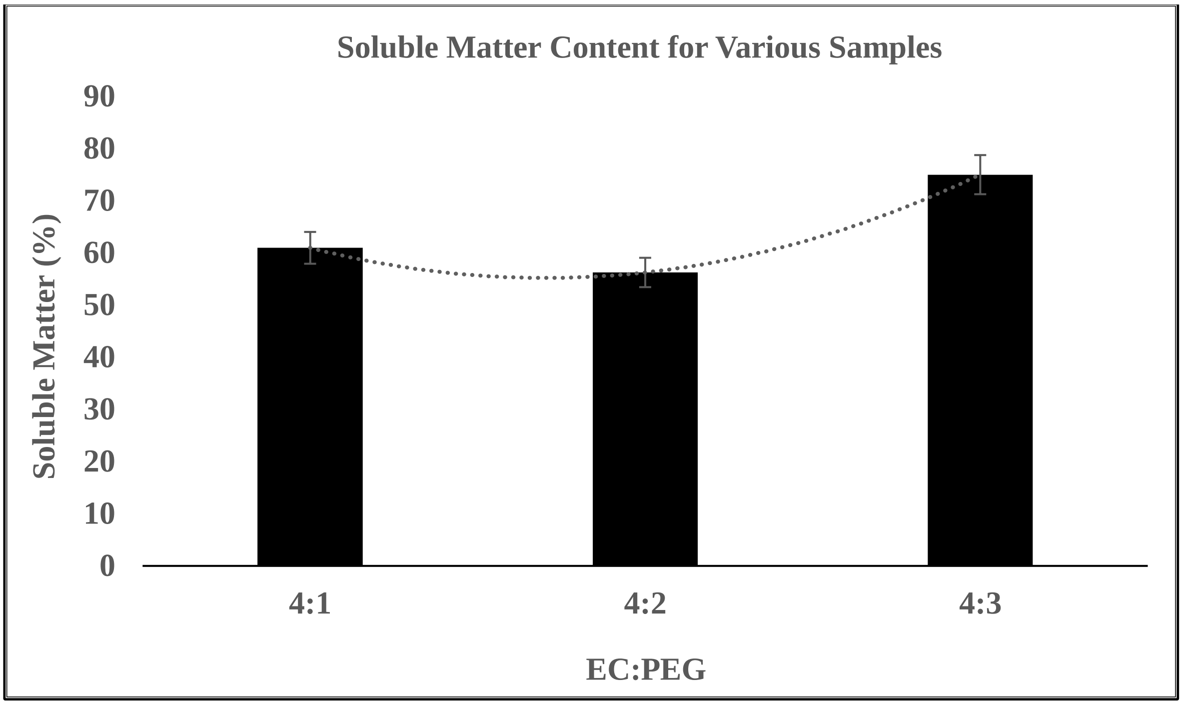


Figure 3.2: Soluble Matter Content for Ethyl Cellulose Films with Different EC: PEG Ratios

Table 3.3: The Mean Values of Percentage of Soluble Matter Content and Moisture Content for Ethyl Cellulose Films with Different EC: PEG Ratios

Sample	EC: PEG	Soluble Matter (%)	Moisture Content (%)
1	4:1	60.97 (0.00023)	62.79 (0.23)
2	4:2	56.25 (0.00032)	50 (0.34)
3	4:3	75 (0.00039)	68.18 (1.2)

3.2.4 Moisture Content Percentage (MC %)

The sample of ethyl cellulose film, with EC: PEG ratio equal to 4:2, showed a slight lower moisture percentage (about 10% decrease), as compared with the sample having EC: PEG ratio equal to 4:1, while the ethyl cellulose film having EC: PEG ratio equal to 4:3 showed an increase in moisture content. The mean values of the percentage moisture content, for ethyl cellulose films with different EC: PEG ratios, is given in Table 3.3 and shown in Figure 3.3. The low moisture percentage of sample 2 (EC: PEG = 4:2) can be explained as a result of interference of water structure in the binding condition.

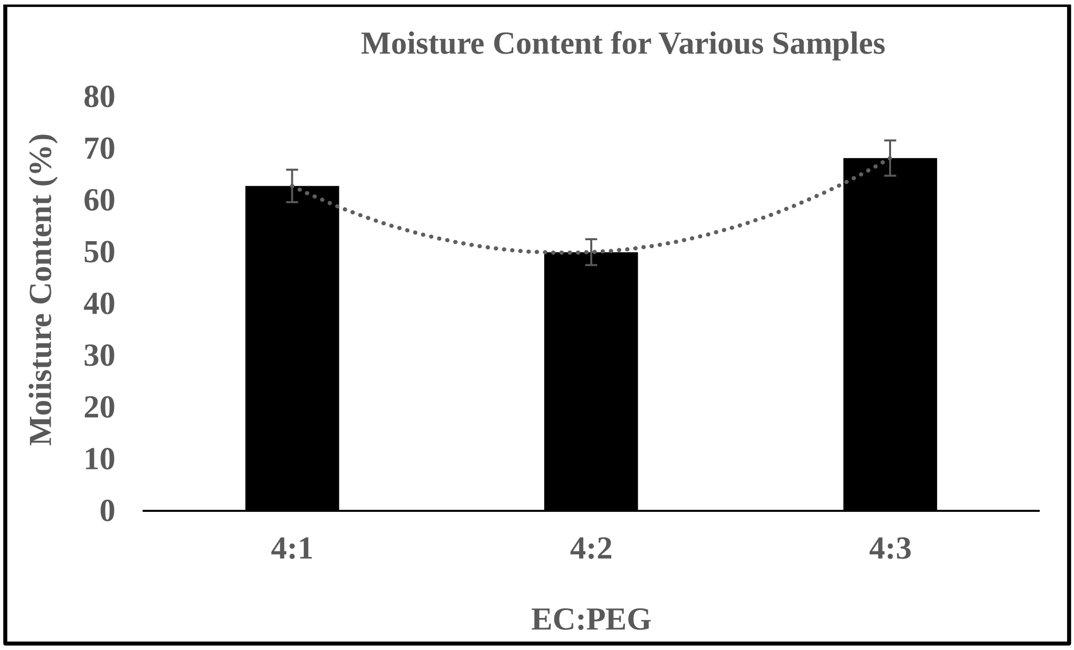


Figure 3.3: Moisture Content for Ethyl Cellulose Films with Different EC: PEG Ratio

3.2.5 Scanning Electron Microscopy (SEM)

The microstructural examination of the ethyl cellulose films was qualitatively studied, using scanning electron microscopy (SEM). The images of the surface and the cross sections of the EC films revealed the effects of the addition of different percentage of PEG. Figure 3.4 show the SEM images of PEG plasticized ethyl cellulose films with EC: PEG ratio 4:1, EC: PEG ratio 4:2 and EC: PEG ratio 4:3 respectively. The surface images of both, ethyl cellulose films with EC: PEG ratio 4:1 and 4:2 showed unbroken, compact and smooth traits without any micro-cracks. However, the EC film with ratio 4:3 showed few cracks, and its surface was not apparently smooth, which might be due to decreased polymer-polymer cohesiveness, with increased content of plasticizer, hence, leading to the deterioration of the quality of the film. After observing, it was found that, both the films, with EC: PEG ratio of 4:2 and EC: PEG ratio of 4:1 are uniform and exhibit good quality.

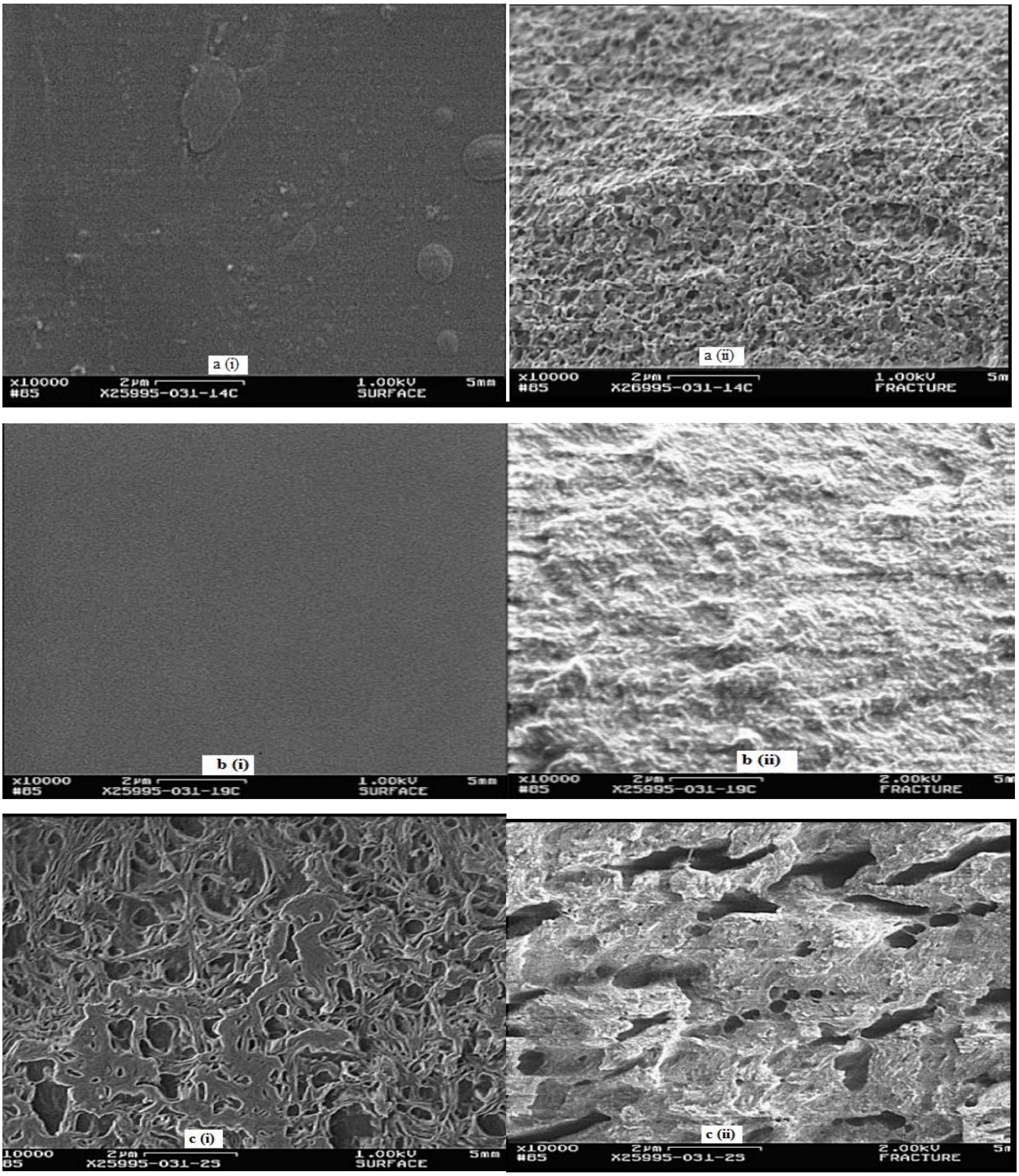


Figure 3.4: SEM Images of PEG 400 Plasticized Ethyl Cellulose Films (a) EC: PEG ratio: 4:1; (i) Surface of the Film, (ii) Cross Section of the Film (b) EC: PEG ratio: 4:2; (i) Surface of the Film, (ii) Cross Section of the Film (c) EC: PEG ratio: 4:3; (i) Surface of the Film, (ii) Cross Section of the Film

3.2.6 Mechanical Properties

Figure 3.5 depicts the plot of tensile strength as a function of coalescence temperature, for the ethyl cellulose films. As seen from the figure, the tensile strength of the films increased with a corresponding increase in coalescence temperature, In addition, it was observed that, the sample 2 was relatively stronger, in comparison to the other samples but however its strength decreased as the temperature was raised above 60°C. Also, at 70°C, no appreciable differences were observed in the tensile strengths of the films, casted from all formulations. This could possibly be due to evaporation of the plasticizers from the films, at elevated temperatures. Mean values of tensile strength of various samples at different coalescence temperatures is as given in Table 3.4.

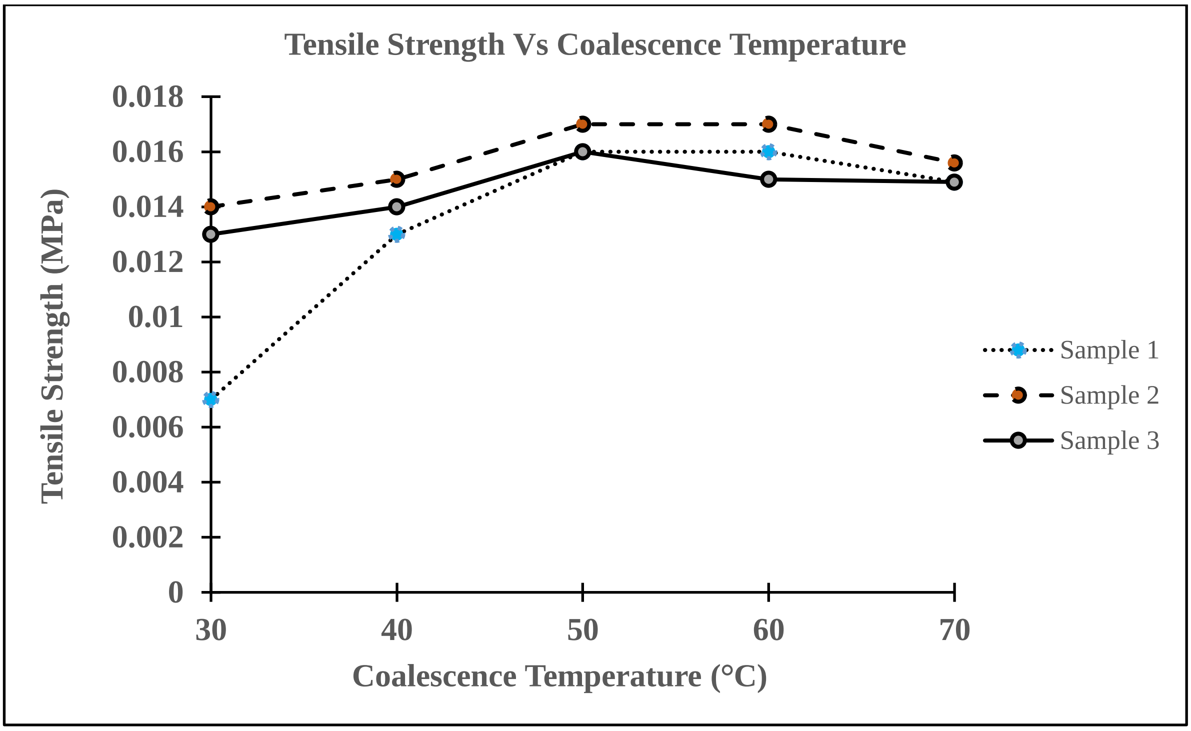


Figure 3.5: Plot of Tensile Strength Vs Coalescence Temperature of Different Ethyl Cellulose Films (Sample1-EC: PEG = 4:1; Sample 2- EC: PEG = 4:2; Sample 3- EC: PEG = 4:3)

Table 3.4: The Mean Values of Tensile Strength of Various Samples at Different Coalescence Temperature

Coalescence Temperature (ºC)	Tensile Strength (Mpa)		
	Sample 1 (sd)	Sample 2 (sd)	Sample 3 (sd)
30	0.007(0.00015)	0.014(0.001)	0.013(0.00125)
40	0.013(0.0017)	0.015(0.00146)	0.014(0.00115)
50	0.016(0.00114)	0.017(0.00126)	0.016(0.00321)
60	0.016(0.00125)	0.017(0.00111)	0.015(0.00167)
70	0.0149(0.00143)	0.0156(0.00129)	0.0149(0.00125)

Mean values of the work of failure of various samples at different coalescence temperatures are given in Table 3.5. The values of work of failure plotted as a function of coalescence temperature for all the three samples in Figure 3.6. As seen from figure there is no significant difference in the work of failure for the films casted from the formulation EC: PEG ratios 4:1 and 4:2 and was approximately equal at initial temperature i.e. 5 Nm/sec. While the work of failure value for the formulation with EC: PEG ratio 4:3, is almost approaching zero at lower coalescence temperature i.e. at 30°C. At higher coalescence temperatures, the higher values of the work of failure depict a significantly higher absorption of energy, possibly due to the complete penetrate of plasticizer molecules into the polymeric network. From the load-time profiles, it was observed that the films, at and above 50°C, exhibited distinct and prolonged plastic deformation, with the resultant increase in the area under the curve. This could be due to strong interaction between the neighbouring polymer particles at and above the coalescence temperature.

Table 3.5: The Mean Values of Work of Failure of Various Samples at Different Coalescence Temperature

Coalescence Temperature (ºC)	Work of Failure (Nm/sec)		
	Sample 1 (sd)	**Sample 2 (sd)**	**Sample 3 (sd)**
30	5(0.67)	5.4(0.78)	0.1(0.0124)
40	4(0.45)	5.9(0.64)	3(0.21)
50	5.5(0.167)	6.1(0.51)	5(0.14)
60	15(0.253)	19(0.92)	13(1.5)
70	30(1.67)	32(1.12)	17(2.1)

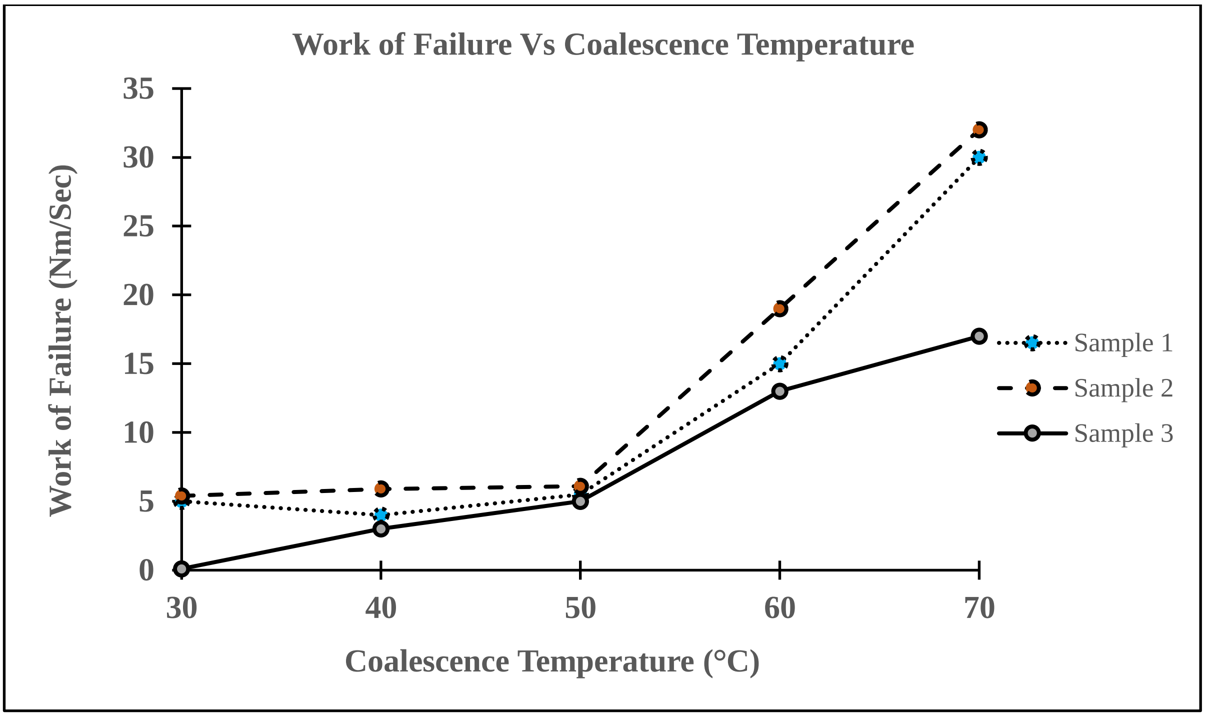


Figure 3.6: Plot of Work of Failure Vs Coalescence Temperature of Different Ethyl Cellulose Films (Sample1-EC: PEG = 4:1; Sample 2- EC: PEG = 4:2; Sample 3 – EC: PEG = 4:3)

The effect of the coalescence temperature on the elastic modulus values of the films is shown in Figure 3.7. The plot of the applied load with time is used to calculate the value of elastic modulus. In general, higher value of load carrying ability indicates a high value of elastic modulus, thus, reflects the elasticity of the film. It was detected that, as the coalescence temperature get increased, the elastic modulus of the films increased almost linearly, for all the samples of the polymeric films, until they achieved a peak value. A decline in the values of elastic modulus was further observed, at elevated coalescence temperatures, which is due to the softening of the film, at elevated temperature.

Mean values of load carrying capacities for different ethyl cellulose films, at various time periods is as given in Table 3.6.

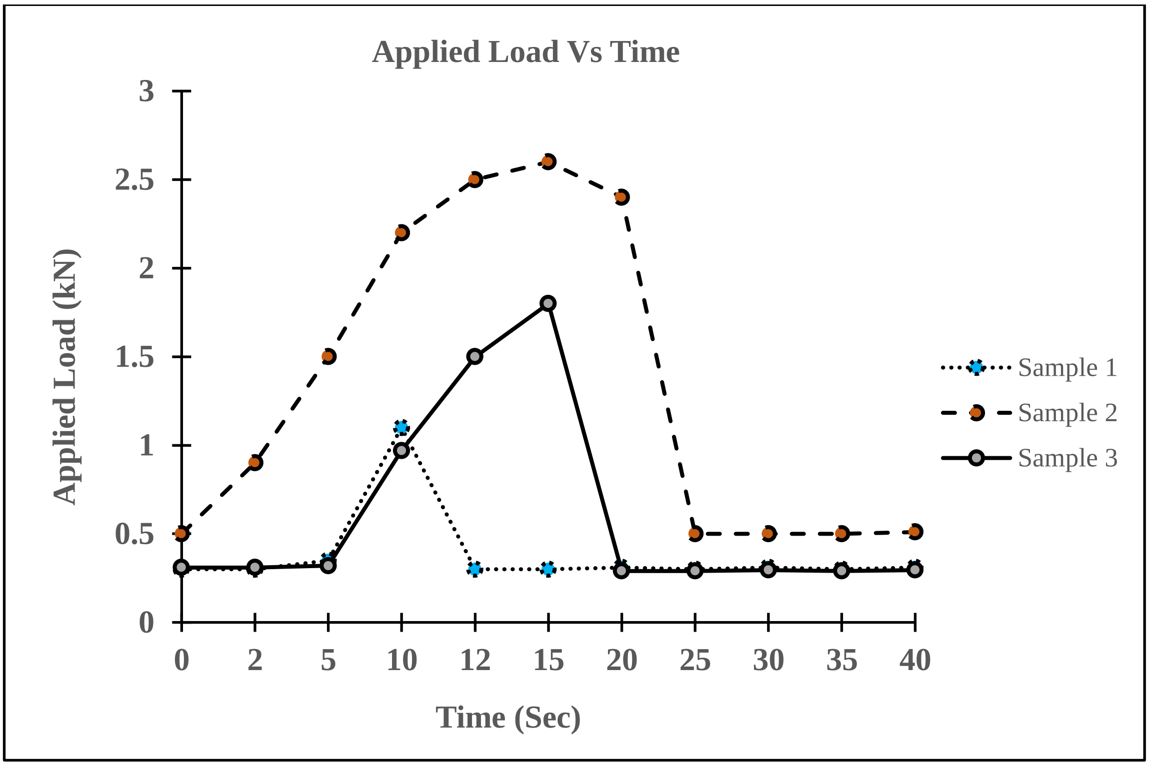


Figure 3.7: Plot of Applied Load Vs Time Profile of Different Ethyl Cellulose Films (Sample1- EC: PEG = 4:1; Sample 2- EC: PEG = 4:2; Sample 3 – EC: PEG = 4:3) at a Temperature of 50°C

Table 3.6: The Mean Values of Load Carrying Capacities for Various Time Periods

Time (Sec)	Applied Load (Elastic Modulas in Mpa)		
	Sample 1(sd)	**Sample 2(sd)**	**Sample 3(sd)**
0	0.3(91.52)	0.5(152.54)	0.31(94.57)
2	0.3(91.52)	0.9(274.57)	0.31(94.57
5	0.35(106.78)	1.5(457.62)	0.32(97.62)
10	1.1(335.58)	2.2(671.17)	0.97(295.92)
12	0.3(91.52)	2.5(762.69)	1.5(457.62)
15	0.3(91.52)	2.6(793.2)	1.8(549.42)
20	0.31(94.57)	2.4(732.18)	0.29(88.47)
25	0.3(91.52)	0.5(152.54)	0.29(88.47)
30	0.31(94.57)	0.5(152.54)	0.295(90)
35	0.3(91.52)	0.5(152.54)	0.29(88.47)
40	0.31(94.57)	0.51(155.59)	0.295(90)

The independent interpretation of these three parameters, i.e., tensile strength, work of failure, and elastic modulus may not always lead to meaningful conclusions with respect to the in-situ performance of the films. The mechanical properties of the films were observed to be dependent on the type and amount of the plasticizer as well the coalescence temperature. With an increase in the coalescence temperature, the films exhibited a characteristic transition in their mechanical properties, i.e., from a soft and weak system (as evident from lower values of tensile strength, strain at break and elastic modulus) to a hard and tough system (as evident from higher values of tensile strength, strain at break, and elastic modulus). Thus it can be assumed that the films coalesced at or around the coalescence temperature i.e. 45°C-50°C may be less susceptible to physical defects.

3.2.7 Anti-permeability for Oil

The anti-permeability test of different sample of ethyl cellulose films showed no traces of oil leakage through them, thus, offering good anti-permeability for oil.

3.2.8 Reliability, Collapsibility and Water-solubility of Ethyl Cellulose Films

The samples of the ethyl cellulose films, formed by casting method, showed complete integrity while peeling off from the surface of the petri dish. The thickness of the resulted films is as reported in Table 3.1. The folding test performed for finding the collapsibility of ethyl cellulose films showed that 20 times folding of film at a particular trace did not showed any fissure in sample1 and sample 2 but, in sample 3 slight marking was observed. The visual test showed that the sample 2 had a good flexibility of all the films. Further, the water solubility of the samples of ethyl cellulose films with different EC: PEG ratios indicated a delayed water solubility in sample 2, in comparison to sample 1 and sample 3. The comparison of the properties, i.e. reliability and collapsibility of the ethyl cellulose films with different EC: PEG ratios is as given in Table 3.7.

Table 3.7: Comparison of Reliability and Collapsibility of Ethyl Cellulose Film with Different EC: PEG Ratios

Sample	EC: PEG	Reliability	Collapsibility
1	4:1	Easy Peeling (From Casting Surface)	No Fissure
2	4:2	Easy Peeling (From Casting Surface)	No Fissure
3	4:3	Easy Peeling (From Casting Surface)	Slight Fissure

3.3 SIGNIFICANT FINDINGS

The ethyl cellulose films with different amount of polyethylene glycol, as plasticizer, had been casted to be used as a bio-degradable food packaging material. The casted films were hazy, opaque and translucent in appearance and their texture was smooth and homogeneous. The SEM images of the surface and cross section of EC: PEG films with 4:1 and 4:2 ratio showed unbroken, compact and smooth traits, while the film with 4:3 ratio showed few cracks, and the surface was not apparently smooth. The resulted ethyl cellulose films showed complete integrity while, peeling. The folding test showed no fissure in the sample1 (EC: PEG = 4:1) and sample 2 (EC: PEG = 4:2), but in sample 3 (EC: PEG = 4:3), slight crack was observed on folding, thus showing less flexibility. Among the different EC: PEG ratios used, the film with EC: PEG ratio 2:1 was found to have better suitability for food packaging applications and showed a very good flexibility and collapsibility. The soluble matter and moisture content of the film with EC: PEG ratio 4:2 was found to be minimum, among all the films tested. The film with EC:PEG = 4:2 showed a maximum tensile strength of 0.0175 MPa, at a coalescence temperature of 50^{o}C and, a maximum work of failure of magnitude 32 Nm/sec was observed, at temperature of 70^{o}C. The film also exhibited, a maximum load in the range of 2.2 – 2.6 kN for a substantially good amount of time. The film with EC to PEG ratio 4:2, was hence found to be mechanically stable and able to handle sufficient amount of load. The three parameters, characterizing the mechanical strength of the film, namely, tensile strength, work of failure, and elastic modulus were found to be satisfactory for all the ethyl cellulose films.

CHAPTER 4
DEVELOPMENT OF QUALITATIVELY RESPONSIVE SMART FILMS BY ENCOMPASSING INDICATORS

4.1 INTRODUCTION

Packaging of the food stuff is a major requirement since the olden days. Though, traditional packaging provides mechanical support, containment, communication, tampering resistance, protection from external environment, handling convenience and shows inertness between the food material and the packaging, however, these are generally inadequate, in the capability to lengthen the shelf life of the foodstuffs. The shelf life of the packaged food is influenced by many intrinsic (like water activity, nutrient content, pH, respiratory rate and biological structure) and extrinsic (relative humidity and temperature) factors. To overcome the adverse effect caused by these factors, many significant innovations in the food packing technologies have taken place over a period of time. The application of active and smart/intelligent packaging in food industry is a comparatively new innovative concept, which has been developed in order to meet the new demands of consumers, in the direction of processed foodstuffs with improved shelf life [251, 277-278]. The intelligent or smart packaging includes the monitoring of the superiority of the packed food, by giving its information to the customer, without even opening the package. Intelligent package contains indicators which may notify the pH of the packaged food; time temperature conditions; biosensors; ripeness monitors or radio frequency regulators to assess the quality and integrity of the food within the package [230]. Likewise, the active packaging modifies the conditions within, which, restores the sensory properties of the packaged food and thus, increase its shelf life by the release of antimicrobial or antioxidant compounds or oxygen or ethanol scavengers [279, 280]. Many researchers have reported the different criteria for the enrichment of the packaging films to enhance their utility. TT indicators were applied in the study of pasteurization and sterilization [281, 282]; Freshness indicators were use, to monitor the changes due to the chemical, or microbial reactions

[283, 284]; and, Oxygen and carbon dioxide indicator were used as the leakage detector, as well as for any chemical or enzymatic changes occurring in the packed food [285]. An innovative approach towards the anthraquinone indicator based intelligent packaging showed response to the oxygen barrier [286]. The use of the triphenylmethane indicator has been reported, in the intelligent packaging, for detecting the spoilage of the fish [287]. In addition, the indicators have also been used by the researchers that respond by change in color, when in contact with the volatile compounds, released by the spoiled foods [255, 288]. Further, the linear low-density polyethylene film containing pH sensitive indicator, in the form of label was reported in the literature [258].

Polymers generally used in the packaging of food products include polyolefin, substituted olefins, polyesters, polyamides and polycarbonates etc. [289]. Though, most of these polymers used in food packaging show a great performance in terms of their gas penetrability, water vapor diffusion rate, chemical & abrasion resistance and mechanical strength, but these are not environment friendly. With the progression of innovative technologies, the latest investigations in food packaging are motivated by the environment friendly and performance-based end products with enhanced post-consumer biodegradability. Though, lot many studies are available on the different types of food freshness indicators [2, 251] and environmentally friendly packaging films [250], but no study has reported the development and/or utilization of the environment friendly smart responsive packaging for food, using biopolymers. There are only a few reports on the pH responsive packaging based on the acid–base reactions or polymerization, but the basic packaging materials used were derived from the petroleum products, and thus, suffer from the drawbacks of the conventional packaging; including a bad impact on the environment.

The present study has been piloted with an aim to develop environment friendly qualitatively responsive films for the food packaging, with an emphasis on the change in pH of the packed food stuff. For this purpose, pH responsive ethyl cellulose films have been prepared, by incorporating azo- indicators in them, such as, Methyl Red (MR) and Methyl Orange (MO), by casting method. The ethyl cellulose itself is biocompatible, biodegradable and inert. Moreover, the azo linkage in azo indicators used, may easily undergo enzymatic breakdown in the liver and kidney, and the aromatic amines, so produced are excreted in the urine. The resulted films are, thus, also biodegradable and environment friendly and there is no major concern to evaluate their food safety. These qualitatively responsive ethyl cellulose films, can substitute the conventional food wrappings or can be used as a small patch within the conventional transparent packaging.

4.2 RESULTS AND DISCUSSION

4.2.1 Visual Inspection

All the ethyl cellulose films, formed by casting method, were found to be consistent, smooth and intact when peeled from the casting surface. Figure 4.1 (a) shows the ethyl cellulose film without indicator, which, is homogeneous, transparent and clear in appearance. The film containing methyl orange (MO) indicator as shown in Figure 4.1 (b), is characterized by a homogeneous texture and yellowish color. The Figure 4. 1(c) represents the ethyl cellulose film containing methyl red (MR) indicator, which is slightly pinkish in tint. The results of the visual inspection made on ethyl cellulose films, with and without indicators are also reported in Table 4.1.

(a) (b) (c)

Figure 4.1: (a) Ethyl Cellulose Film Without Indicator; (b) Ethyl Cellulose Film Containing MO Indicator; (c) Ethyl Cellulose Film Containing MR Indicator

Table 4.1: Appearance of the Ethyl Cellulose Films with Different Indicators

Sample	Color	Texture	Appearance
EC- standard	Colorless	Homogeneous	Transparent
EC-MO	Yellow	Homogeneous	Opaque
EC-MR	Pink	Homogeneous	Transparent

4.2.2 Film Thickness

The mean thickness of various ethyl cellulose films is reported in Table 4.2, and were measured as: 1.012 mm with a standard deviation of 0.011 for EC-standard; 1.013 mm with standard deviation of 0.02 for EC-MO; and 1.010 mm with a standard deviation of 0.01 for EC-MR respectively.

Table 4.2: Thickness of Ethyl Cellulose Films with Different Indicators

Sample	Thickness (mm)
EC- standard	1.012
EC-MO	1.013
EC-MR	1.010

4.2.3 Yield of Ethyl Cellulose Films

The results for the yield of ethyl cellulose films, with and without indicators are given in Table 4.3. It was observed that, there is slight increase in the yield of the EC film on the addition of the indicators. The yield was found to be maximum in case of ethyl cellulose film incorporated with MR indicator i.e., 5.65%, whereas the yield of ethyl cellulose films incorporated with MO indicator was observed as 4.69%.

Table 4.3: The Yield of Ethyl Cellulose Film Incorporated with Indicators

Sample	Yield (%)
EC-standard	3.44
EC- MO	4.69
EC-MR	5.65

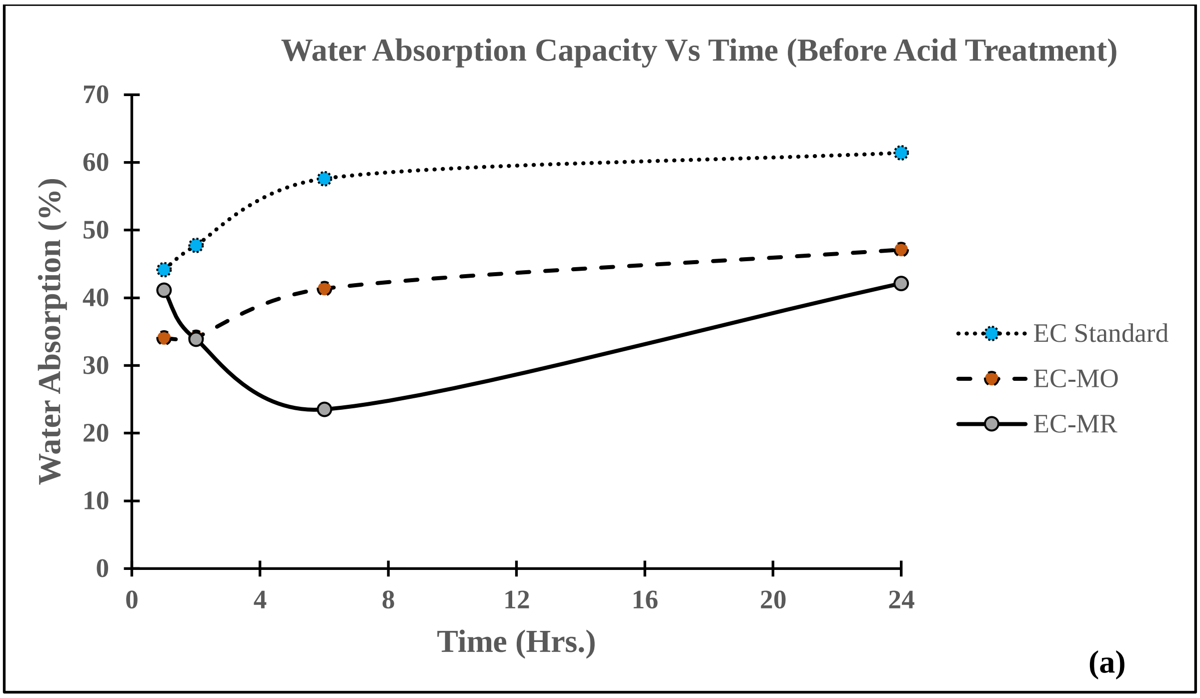
4.2.4 Water Absorption Capacity

Due to the hydrophilic character of the polymer itself, the water absorption capacity of the resulted EC films showed highest percentage for the EC-standard film among all the samples, showing similarity with the water absorption capacity of chitosan [253]. However, the water absorption capacity of EC film changed significantly, by the addition of the indicators. This is due to the reason that, the azo-indicators themselves are sparingly soluble in water. The variation in water absorption capacity for all three samples is reported in Table 4.4 and shown in Figure 4.2 (a). As evident from figure, for EC-standard film, the water absorption capacity increased significantly, and was the highest among all the three samples, while the EC-MO film absorbed the least water, when the duration of immersion was one hr However, after two hrs, the water absorption, in case of EC-MR film was less, as compared to that of the EC-MO film. Further after 6 hrs of immersion, the water absorption capacity of EC-standard and EC-MO films were observed to have been increased significantly but, the water absorption of EC-MR film was apparently decreased. The probable reason for this decrease in water absorption of the indicator loaded ethyl cellulose film might be due to the ability of the azo dyes to gain close contiguity to the ethyl cellulose due to the intermolecular interactions, such as, H-bonding, which resist the water molecules to form bonds with the ethyl cellulose. The results obtained at 24 hrs immersion had shown a highest percentage of water absorption i.e. about 61.42% in the EC-standard film, among all the samples. However, the water absorption in EC-MO and EC-MR films was relatively less i.e. 47.11% and 42.13%

respectively. After 24 hrs of immersion, the water absorption of all ethyl cellulose film samples showed insignificant increase.

Table 4.4: Percentage of Water Absorption Capacity of the Ethyl Cellulose Films (Before Acid Treatment)

Sample	**Water Absorption Capacity (Wt %)**
After 1 Hr.	
EC-standard	44.15
EC- MO	34.08
EC-MR	41.13
After 2 Hrs.	
EC-standard	47.74
EC- MO	34.15
EC-MR	33.89
After 6 Hrs.	
EC-standard	57.61
EC- MO	41.35
EC-MR	23.52
After 24 Hrs.	
EC-standard	61.42
EC- MO	47.11
EC-MR	42.13



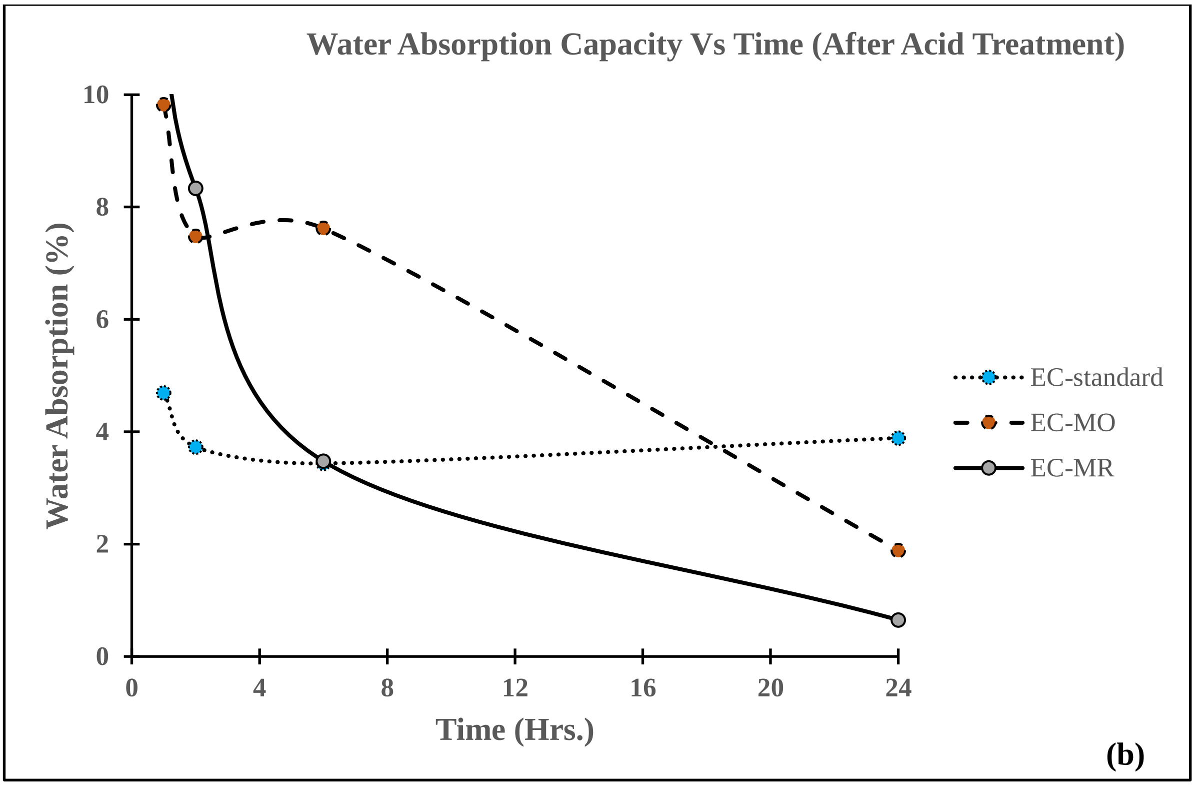


Figure 4.2. Water Absorption Capacity of Ethyl Cellulose Films Incorporated with Azo Indicators at Different Time Interval (a) Before Acid Treatment (b) After Acid Treatment

The water absorption capacity of the all the samples of EC films were also studied post treatment with the acid (Table 4.5), which had shown an inordinate decrease in all the samples, compared to without acid treatment. As seen from Figure 4.2 (b), the water absorption capacity declined at a lower rate, till 24 hrs and then became negligible, for all the films after 24 hrs.The EC-standard film (without indicator) showed 3.89%, EC-MO film showed 1.89% and EC-MR showed 0.68% decrease in the water absorption, respectively, with 24hrs of water immersion, as compared to the films without acid treatment. This response of the films might be due to the unavailability of the reactive site in the EC films, due to the interaction with acid, at an early stage.

Table 4.5: Percentage of Water Absorption Capacity of Ethyl Cellulose Films (After Acid Treatment)

Sample	**Water Absorption Capacity (Wt %)**
After 1 Hr.	
EC-standard	4.69
EC- MO	9.82
EC-MR	10.85
After 2 Hrs.	
EC-standard	3.73
EC- MO	7.48
EC-MR	8.33
After 6 Hrs.	
EC-standard	3.44
EC- MO	7.62
EC-MR	3.48
After 24 Hrs.	
EC-standard	3.89
EC- MO	1.89
EC-MR	0.65

4.2.5 Colorimetric Analysis

When the ethyl cellulose films, containing azo indicators, were exposed to different concentrations of the acidic solution (pH ranging from 2.76–1.78), the EC-MO film showed a significant reversible and gradual change in color, while, only mild change in color was observed for EC-MR film (Figure 4.3). A more pronounced color change was observed with luminosity, when the color parameters ($L*$, $a*$, $b*$) of the EC-indicator film were measured. The color parameters ($L*$, $a*$, $b*$) of the ethyl cellulose films with different indicators were measured, that revealed pronounced changes in the parameters $L*$, $a*$ and $b*$ respectively, at different acid concentrations. The $L*$ value (lightness) of the acid treated EC-indicator films showed an irregular decrease. In case of EC-MO film, the value of $L*$ ranged from 59 to 35 and, for EC-MR film the value of $L*$ ranged from 90 to 39, with increase in the concentration of acid from 1 percent to 90 percent (pH ranged between 2.76 to 1.78). The EC-MO film, without any acid treatment, had found to had reflected maximum light, thus, had maximum lightness value ($L* = 59$). Further, on treatment with varying concentrations of acid (Table 4.6), the EC-MO film treated with 60% acid (pH = 1.87), showed the darkest color ($L* = 32$) among all the other EC-MO samples. All the EC-MO films treated with different percentages of acid showed a negative value of $a*$ and $b*$, corresponding to the green and blue color respectively. Similarly, the EC-MR film, without any acid treatment showed the maximum reflection of the light, thus indicating the high lightness value ($L* = 89$), as compared to EC-MR films, treated with acid (Table 4.7). Among all the EC-MR films, treated with different percentages of acid, the darkest color ($L* = 32$) was observed for 50% acid (pH= 1.91). The color value of the EC-MR film, without acid treatment showed the positive value of $a*$ and $b*$; while on treatment with different percentages of acid, it showed a negative value of $a*$ and $b*$, corresponding to green and blue color value. The comparison of the pH response of EC-MO and EC-MR film on the basis of colorimetric value shows the similar performance of both the films, but visually, the color variation was better for the EC-MO film.

The contact of films with different concentration of acid, resulted in the severity of color change, thus, indicating their response to the pH variation of the medium. As the concentration of the acid was increased, its pH value lowered from 2.76 to 1.78. Thus, the films showed a sharp color change at lower pH; with EC-MO film showing distinct color difference at 60% acid concentration, and EC-MR film showing a noticeable color change at 50% acid concentration. However, visually the response of EC-MO film was significantly better than that of EC-MR film, as evident from the Figure 4.3. The color variations of the indicator encompassed ethyl cellulose films is associated with the change in the chemical structures of the indicator molecules, during their interaction with the H^+ ions present in the acidic medium.

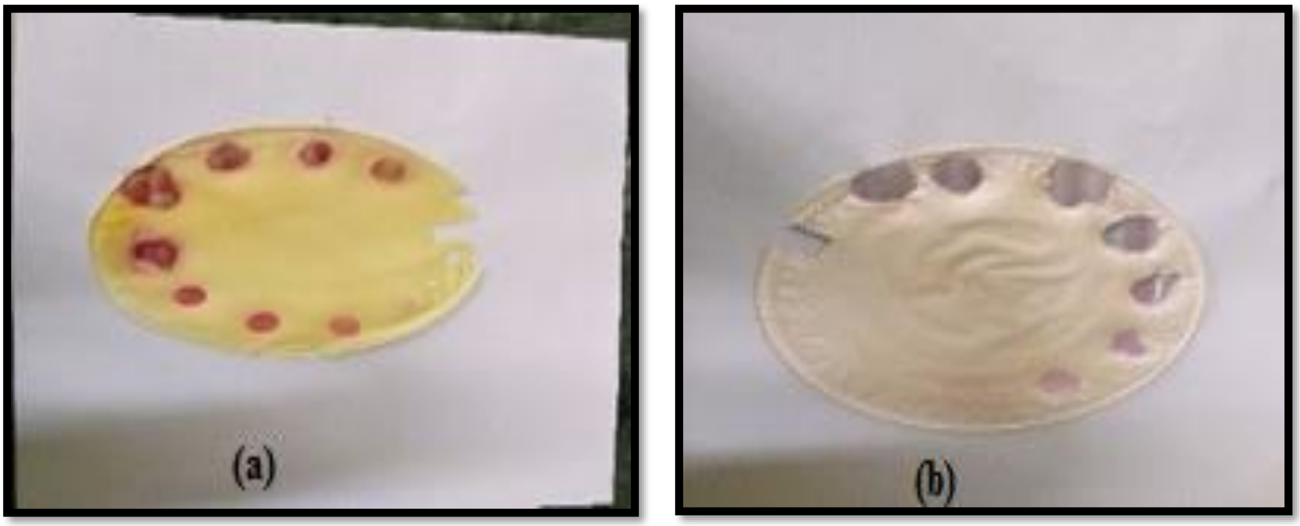


Figure 4.3: Color Parameters of (a) EC- MO Film (b) EC- MR Film, with Varying Percentage of Acid

Table 4.6: Color Parameters of EC-MO Film with Varying Percentage of Acid

Acid %	pH	Colorimetric Value CIE D65		
		L*	a*	b*
0%		58.7179	-1.4658	-4.1823
1%	2.76	58.9817	-1.6781	-2.9081
2%	2.61	59.1956	-1.9467	-1.6502
3%	2.52	51.2371	-1.2387	-1.1551
4%	2.46	49.1567	-2.0212	-2.2317
5%	2.41	48.1298	-2.156	-2.1167
6%	2.37	45.2378	-2.2149	-2.0164
7%	2.34	44.2136	-1.981	-1.7164
8%	2.31	44.3289	-2.0056	-2.1834
9%	2.28	39.9125	-2.1371	-1.9651
10%	2.26	35.1119	-2.0528	-2.319
20%	2.11	36.3369	-1.4348	-1.7545
30%	2.02	36.4989	-1.9731	-2.1738
40%	1.96	35.1006	-2.0718	-2.3242
50%	1.91	34.2933	-2.119	-2.4897
60%	1.87	31.844	-2.5027	-2.8777
70%	1.83	34.2013	-2.0448	-2.52
80%	1.81	33.6231	-2.2819	-2.6312
90%	1.78	35.0393	-2.0738	-2.3659

Table 4.7: Color Parameters of EC-MR Film with Varying Percentage of Acid

Acid %	pH	Colorimetric Value CIE D65		
		L*	a*	b*
0%		89.3598	1.4011	2.9762
1%	2.76	89.7542	1.2123	2.7976
2%	2.61	89.8951	1.2333	2.5576
3%	2.52	65.2348	-1.0131	-1.2161
4%	2.46	66.2371	-1.2161	-1.1637
5%	2.41	64.5621	-1.0089	-1.7812
6%	2.37	53.2149	-1.8214	-1.7215
7%	2.34	48.2314	-2.0131	-2.2561
8%	2.31	45.2861	-2.0041	-2.1581
9%	2.28	43.2914	-1.6598	-1.7123
10%	2.26	38.6919	-1.9762	-1.4614
20%	2.11	36.3859	-2.005	-2.017
30%	2.02	36.5391	-1.6566	-1.4676
40%	1.96	35.5335	-2.0576	-2.2125
50%	1.91	32.3331	-2.4548	-2.7541
60%	1.87	34.9448	-2.1383	-2.2092
70%	1.83	39.9617	-1.7431	-1.2627
80%	1.81	34.364	-1.4112	-2.2434
90%	1.78	38.6783	-1.9597	-1.7541

4.2.6 Scanning Electron Microscopy (SEM)

The scanning electron microscopy (SEM) results of the pH responsive ethyl cellulose films revealed the effect of indicators on their structures. The surface images of ethyl cellulose films, with and without indicators showed unbroken, compact and smooth traits without any micro-cracks, thus, indicating the complete merger of the indicators in ethyl cellulose matrix.

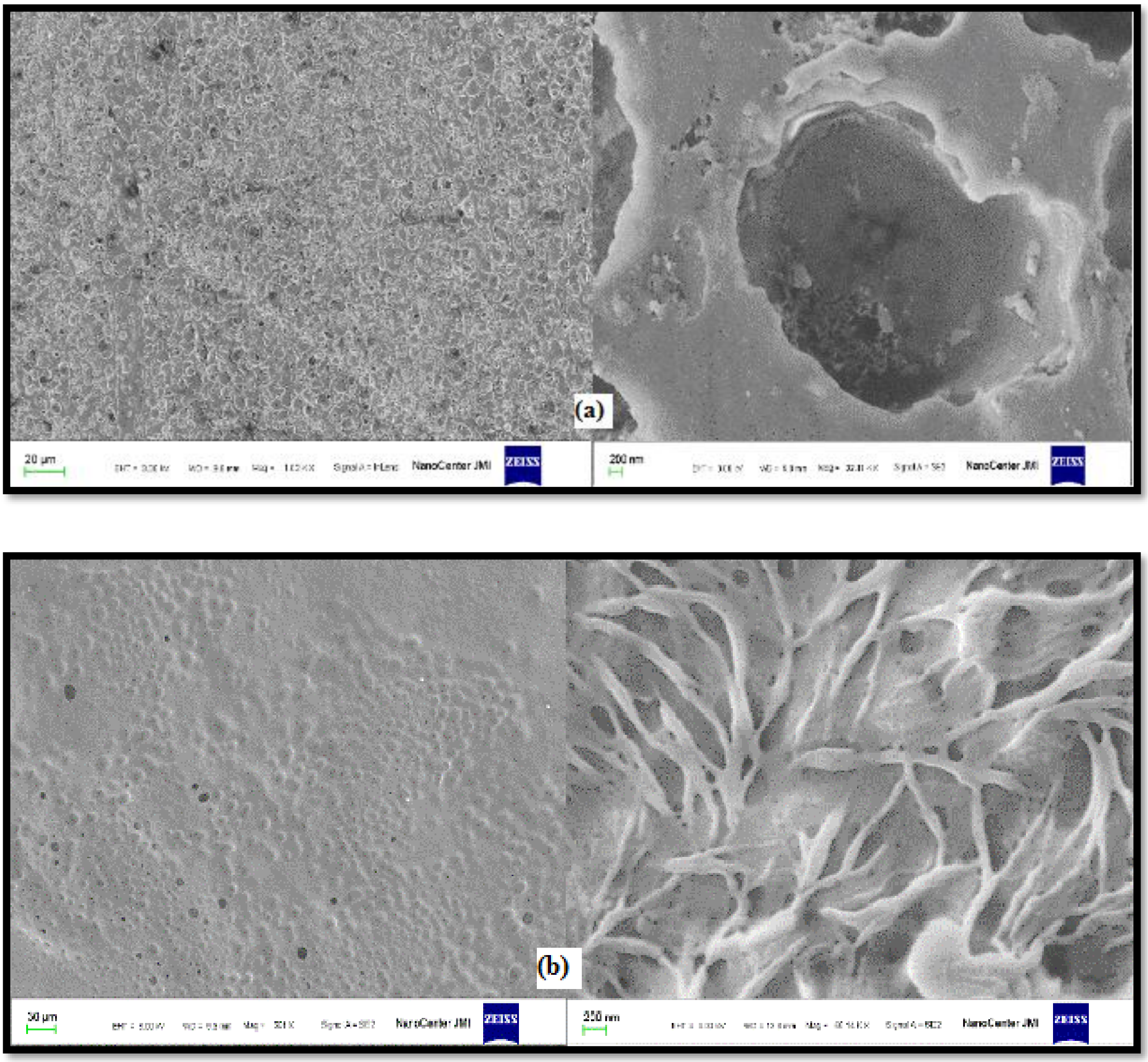
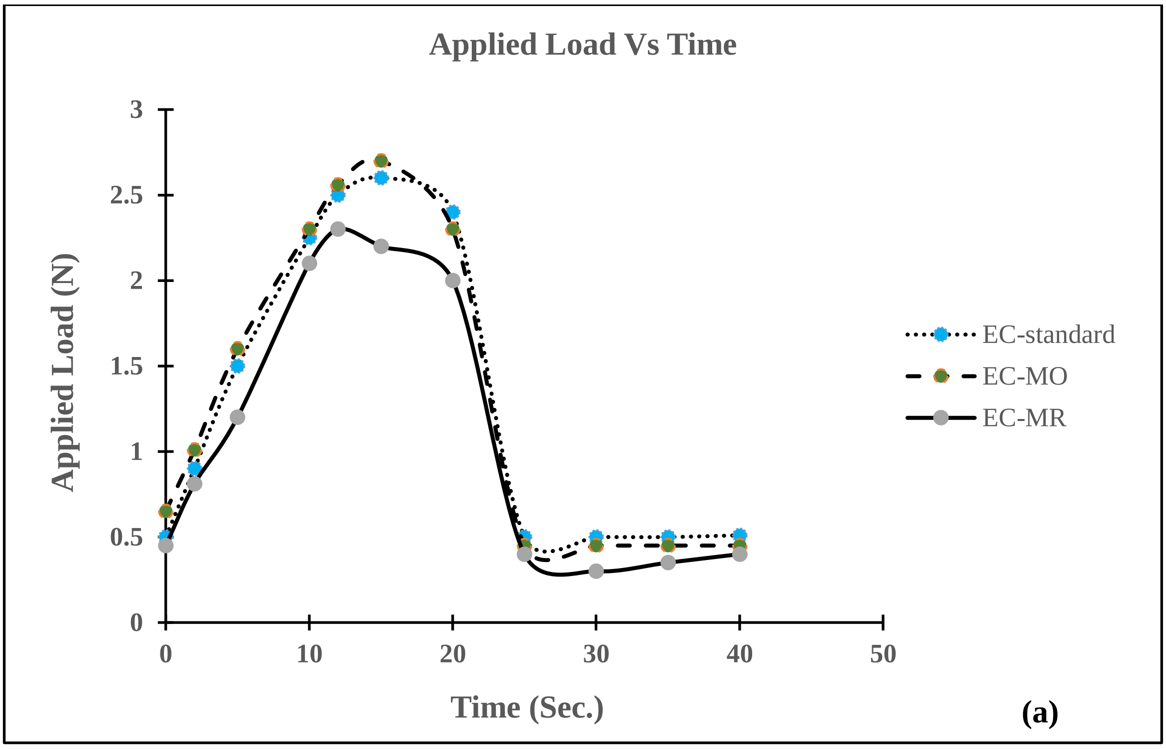


Figure 4.4 (a) Appearance of Surface of Ethyl Cellulose Film Prepared from EC and PEG Ratio 2:1 in Ethanol; (b) Appearance of Surface of Ethyl Cellulose Films Prepared from EC and PEG in Ratio 2:1 in Ethanol and 0.1 wt% Methyl Orange

Figures 4.4 (a) and (b) respectively, show the appearance of ethyl cellulose film, without and with indicator. It is evident from the figures, that, the films obtained are dense, continuous and smooth, devoid of any micro cracks. However, the structure of ethyl cellulose film without indicator shows good hexagonal pores, while the film with the indicator shows a more homogeneous and dense structure, with few and very small hexagonal pores, as a result of strong interface between the ethyl cellulose and the azo-indicator [252].

4.2.7 Mechanical Properties

The mechanical properties of the ethyl cellulose films with and without indicators were reported by plotting Load vs. Time and Load vs Displacement curves (Figure 4.5 (a) and (b)), respectively.



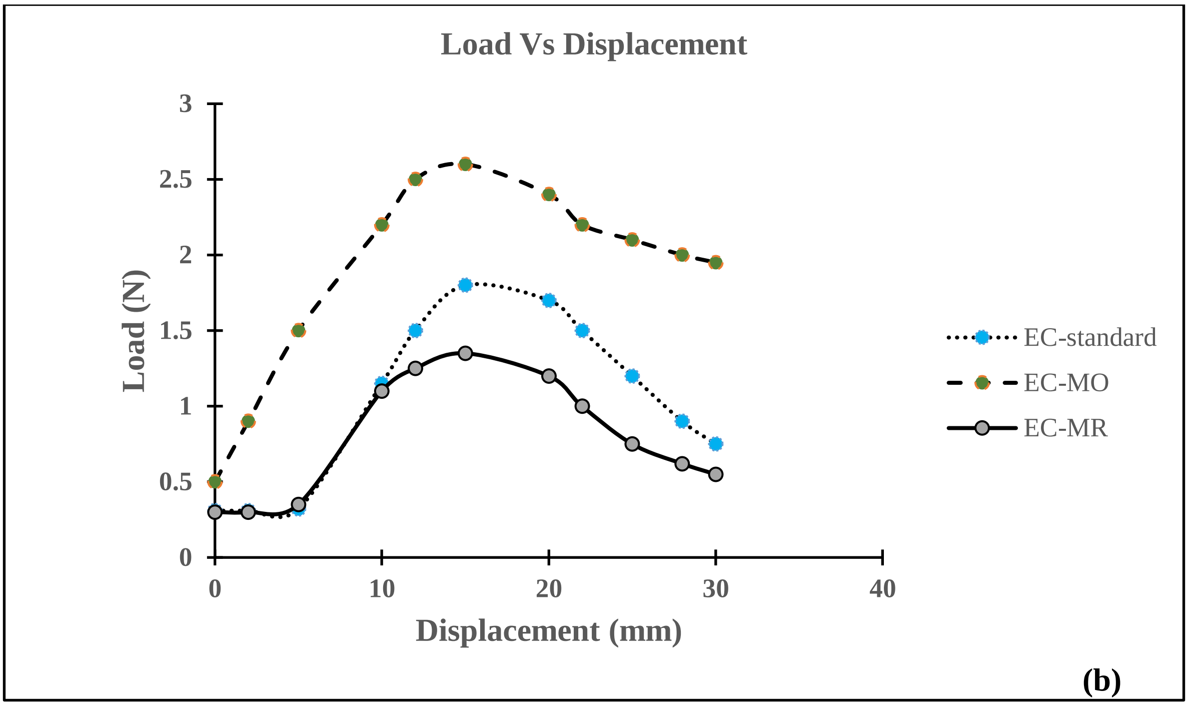


Figure 4.5: (a) Load Vs Time Curve for Different Ethyl Cellulose Films; (b) Load Vs Displacement Curve for Different Ethyl Cellulose Films

As observed from the Figure 4.5 (a) and (b), the EC films incorporated with indicators, showed slight variations in trends as compared to the EC-standard film. The EC-MO film had shown the highest elasticity with a variation of the strain with respect to the increase in the load i.e. around 15 mm, at a load of about 2.7 N, beyond which, the strain remained constant due to the neck formation. The EC standard film demonstrated a tensile strength, elongation at break and young's modulus of 0.07475 MPa, 11.661% and 21.4475 MPa respectively as given in Table 4.8. The tensile strength of EC-MO and EC-MR films were measured as 0.1127 MPa and 0.0612375 MPa respectively, which were very close to the EC standard film. The EC-MO and EC-MR films showed respectively lesser elongation at break i.e. 4.761 and 4.225%. These declined values suggest a lower flexibility of these films as compared to the standard EC film. For EC-MO film, it was observed that, the deformation of a higher magnitude had taken place, and was found to increase without any significant increase in the load. The peak of the curve occurred at around 2.7 N, which, further, came down to a breaking load of 0.4 N. Since, the presence of necking in more evident, it indicates that, the sample is more sustainable to the tensile load. However, the EC-MR film had shown an abrupt behaviour, after undergoing displacement, at even minor load. Further, with increase in a slight amount of load, it showed an increase in stresses at various displacements, even fluctuates abnormally. The modulus of elasticity of EC-MO and EC-MR films were estimated as 26.325 and 17.8273 MPa respectively, which also suggests its closeness to the EC standard film. In the nutshell, the comparisons of the values of the tensile strength, elongation at break and young's modulus of EC-MO and EC-MR films with that of EC standard film make them more applicable for the packaging purposes. The plot of stress-strain curve is shown in Figure 4.6

Table 4.8: Mechanical Properties of Ethyl Cellulose Films (With and Without Indicators)

Sample	Tensile Strength (TS)(Mpa)	Elongation at Break (EAB) (%)	Modulus of Elasticity (E)(Mpa)
EC-standard	0.07475	11.661	21.4475
EC-MO	0.1127	4.761	26.325
EC-MR	0.0612375	4.225	17.8273

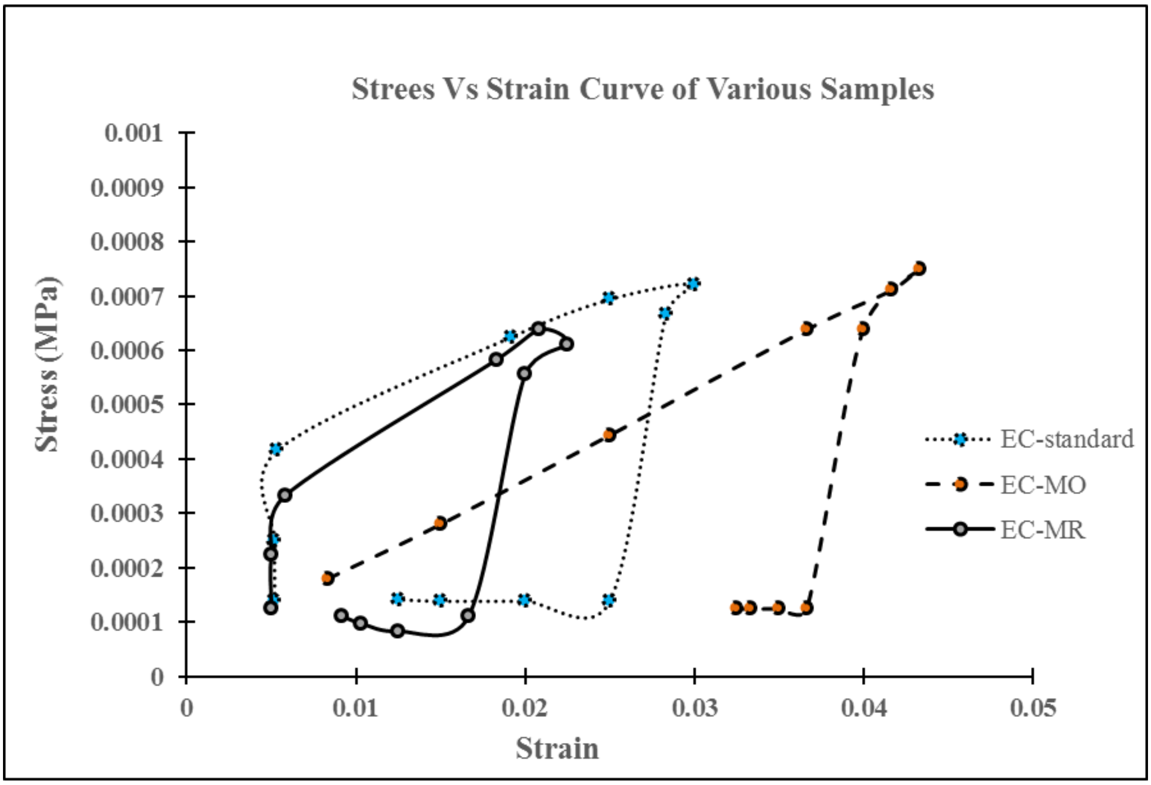


Figure 4.6: Stress- Strain Curve of Ethyl Cellulose Films (With and Without Indicators)

4.2.8 Soluble Matter Percentage (SM %)

The ethyl cellulose films, with and without indicators immersed in distilled water for 24 hrs, showed no swelling and maintained their structure well. The soluble matter percentage, among different pH responsive ethyl cellulose films, was more for the EC-MR film i.e., approximately 77%, and about 60% for the EC-MO film. However, the soluble matter for ethyl cellulose film without indicator, showed the total soluble matter of about 62.50%. The mean values of percentage soluble matter in different ethyl cellulose films are given in Table 4.9 and shown in Figure 4.7.

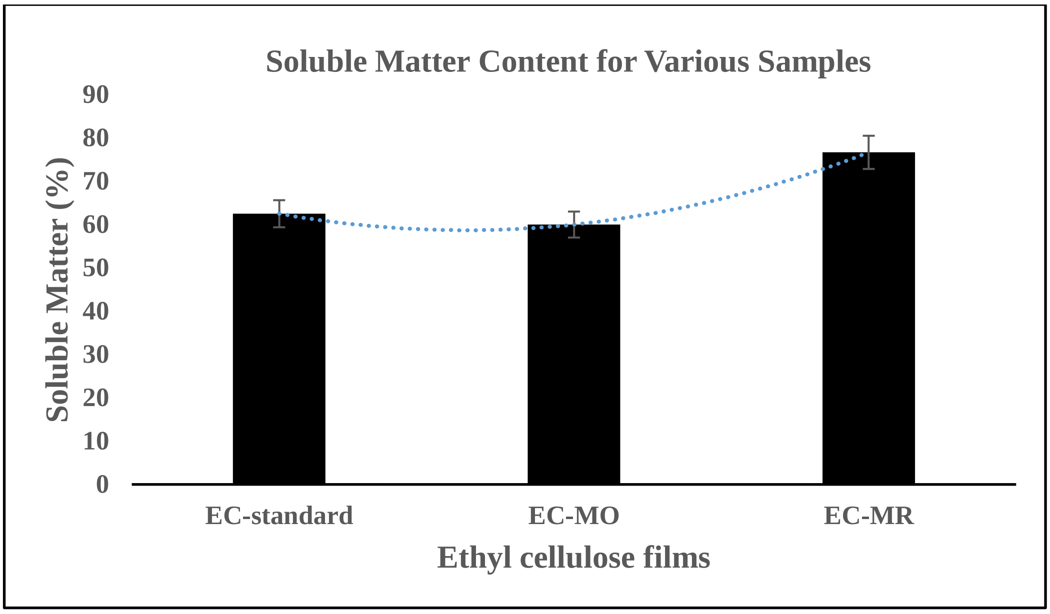


Figure 4.7: Soluble Matter Content of EC-standard and EC Films with Indicators

Table 4.9: The Mean Values of Percentage Soluble Matter and Moisture Content in Different Ethyl Cellulose Films

Sample	Soluble Matter (%)	Moisture Content (%)
EC-standard	62.50	58.82
EC-MO	60.00	47.62
EC-MR	76.67	77.78

4.2.9 Moisture Content Percentage (MC %)

The EC-MO showed approximately 10% lower moisture content as compared to the EC-standard film, while, the EC-MR film showed a large increase in the moisture content. The low moisture content of the EC-MO film might be due to the interference of the water structure in the binding condition. The mean values of percentage moisture content in different ethyl cellulose films are given in Table 4.9 and shown in Figure 4.8.

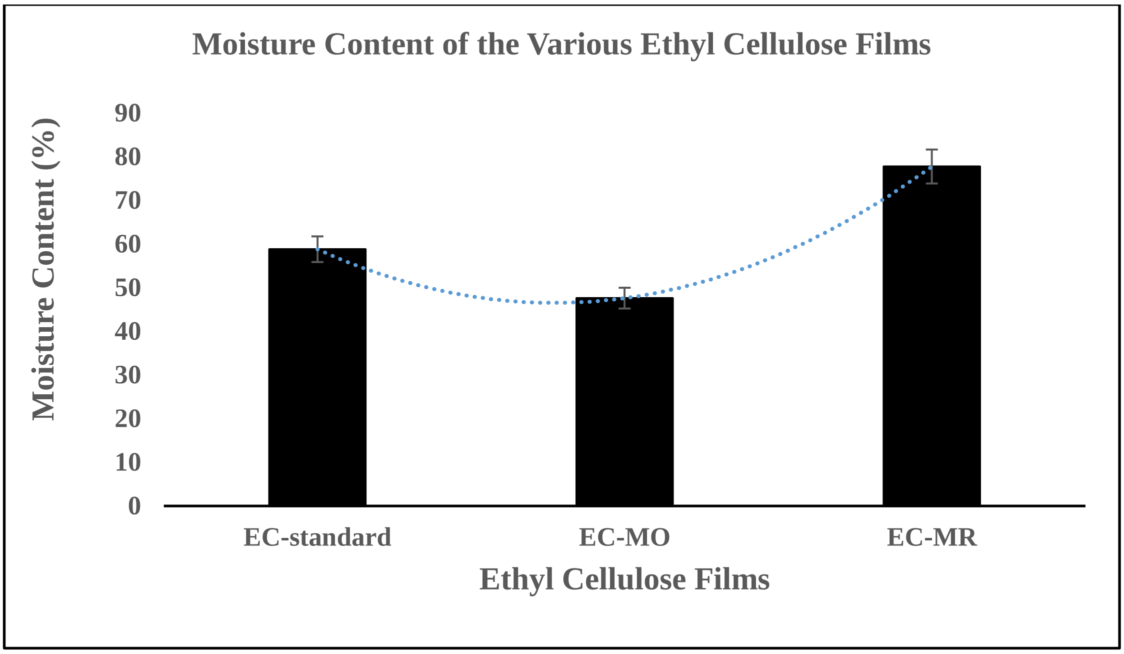


Figure 4.8: Moisture Content of Different Ethyl Cellulose Films (With and Without Indicators)

4.3 SIGNIFICANT FINDINGS

The pH responsive bio-degradable intelligent food packaging films have been developed by the incorporation of different pH sensitive azo indicators in bio-degradable ethyl cellulose. The resulted films were tested for their water absorption capacity, colorimetry and mechanical behaviour. The addition of the azo indicators decreased the water absorption capacity of the films upto 10%. The water absorption capacity of all the samples of EC films, post treatment with acid showed an inordinate decrease. The EC standard film demonstrated a tensile strength, elongation at break and young's modulus of 0.07475 MPa, 11.661% and 21.4475 MPa respectively, while for the other two films i.e. EC-MO and EC-MR the measured tensile strength was 0.1127 MPa and 0.0612375 MPa; and elongation at break was 4.761 and 4.225% respectively. The modulus of elasticity of EC-MO and EC-MR films were estimated as 26.325 and 17.8273 MPa respectively. The comparable strengths of EC-MO and EC-MR films with the EC standard film make them, very much applicable for the packaging purpose. CIELAB detected and correlated the color variations of ethyl cellulose films at different pH values. The films evidently responded well, with the change in pH and, are expected to response qualitatively with the acid, produced during the deterioration of the food stuff under real situation, and, might help to determine the deterioration of packaged food, without even opening. The percentage soluble content of the films is more than 60% that makes their bio-degradability realisable, post consumption. In fact, the ethyl cellulose is itself bio-degradable in nature, so the resulting pH sensitive films are biodegradable and environment friendly too. As, the azo linkage may easily undergo enzymatic breakdown in liver and kidney and the aromatic amines, so produced, are excreted in the urine, so there is no major concern to evaluate the food safety of these azo dyes incorporated ethyl cellulose films. Moreover, both, methyl red, as well as, methyl orange are very commonly used indicators in any laboratory set-up, and are not much expensive. Thus, the resulted pH responsive ethyl cellulose films will not much aid towards the increase in cost when produced in bulk, as commercial food packaging films.

CHAPTER 5

INVESTIGATIONS OF THE WATER VAPOUR PERMEABILITY OF THE pH RESPONSIVE SMART FILMS

5.1 INTRODUCTION

Universally used materials for food packaging comprise of plastics, paper, glass and metal, though, the plastic dominates the others (glass, paper and metal) in applications, owing to their low-cost production and exceptional material properties [268, 289]. Numerous biodegradable polymeric films are now gaining popularity among the researchers and manufacturers, to be used in food packaging, not to entirely substitute the synthetic plastics, but reasonably to advance their competence [250, 270, 272]. Food packaging is vital to evade deterioration of foodstuffs in the course of usage and storage, in addition to providing nutritional information and expiry date of the packaged food. The packing materials are responsible for the physical protection and give assistance in decreasing the rate of deterioration of foodstuffs, by impending moisture exchange with the surrounding atmosphere or amid food constituents, and thus, aid in prolonging their shelf life [290]. But, the interaction of the foodstuffs with the headspace of the package may induce various detrimental physical, chemical and microbial alterations in foodstuffs, therein reducing the safety and quality of the food.

Fresh vegetables and fruits show a high level of respiration and undergo rapid deterioration, due to the ongoing metabolisms, like, transpiration and respiration. These fresh produces are too liable to the contamination caused by fungi, bacteria and yeasts. The prerequisite of the packaging films used for the fresh produce is, high water vapor permeability and oxygen. Most of the polymeric films used in the existing modified atmosphere packaging (MAP) have shown too low water vapor permeability (WVP), in comparison to the moisture loss of the fresh products. Consequently, a high relative humidity (RH) forms in the headspace, thus, resulting in water vapor condensation and, leads to the microbial growth and deterioration of the foodstuffs. Further, at the time of storage, supply, and selling, the condensation in the headspace is amplified due to the temperature variations. Recent advancement in fresh produce packaging is thermoplastic polyurethane (PU), which offers a controllable gas permeability, with respect to temperature [291]. The present study has been conducted with an aim to investigate the water vapour permeability of the developed pH responsive smart films.

5.2 RESULTS AND DISCUSSION

5.2.1 Effects of Time and Indicator on the Water Vapour Permeability of Various Films

The water vapour transmission rate and water vapour permeability of the different ethyl cellulose films, with and without indicators, are given in Table 5.1. As evident from the table, the water vapour permeability of the ethyl cellulose films was affected by the incorporation of indicators. In the span of total 24hrs of the study, the WVP of the EC-standard film increased during the first 2hrs, from 2.29407 $x10^{-9}$ $gm^{-1}s^{-1}Pa^{-1}$ to 3.44111 $x10^{-9}$ $gm^{-1}s^{-1}Pa^{-1}$, and then started to decrease, upto $8.60277x10^{-10}$ $gm^{-1}s^{-1}Pa^{-1}$ in 24hrs. Similar was the case of EC-MO, where the WVP increased from 3.44451 $x10^{-9}$ $gm^{-1}s^{-1}Pa^{-1}$ to 4.99454 $x10^{-9}$ $gm^{-1}s^{-1}Pa^{-1}$ initially for 2hrs and then receded upto 1.07640 $x10^{-9}$ $gm^{-1}s^{-1}Pa^{-1}$, and for EC-MR film, the WVP increased from 4.57908 $x10^{-9}$ $gm^{-1}s^{-1}Pa^{-1}$ to 4.97975 $x10^{-9}$ $gm^{-1}s^{-1}Pa^{-1}$, for 2hrs, and then decreased upto 1.23062 $x10^{-9}$ $gm^{-1}s^{-1}Pa^{-1}$ respectively. In general, the water vapor transmission from a hydrophilic film is influenced by both, the solubility and diffusivity of the water molecules, in the film matrix. The high hydrophilicity of the indicator molecules favours the adsorption of water molecules, and, also contributed to the upsurge in the WVP of the film. Comparable results have been stated in literature for sodium caseinate and soluble starch, wheat gluten and whey protein [292].

Table 5.1: Effects of Time and Azo Indicator on the Water Vapour Permeability of Ethyl Cellulose Films

Sample	WVP (x $10^{-9}gm^{-1}s^{-1}Pa^{-1}$)			
	1 Hr.	**2 Hrs.**	**8 Hrs.**	**24 Hrs.**
EC- Standard	2.29407	3.44111	2.58083	8.60277x10^{-10}
EC-MO	3.44451	4.99454	3.61673	1.07641
EC-MR	4.57908	4.97975	4.03531	1.23063

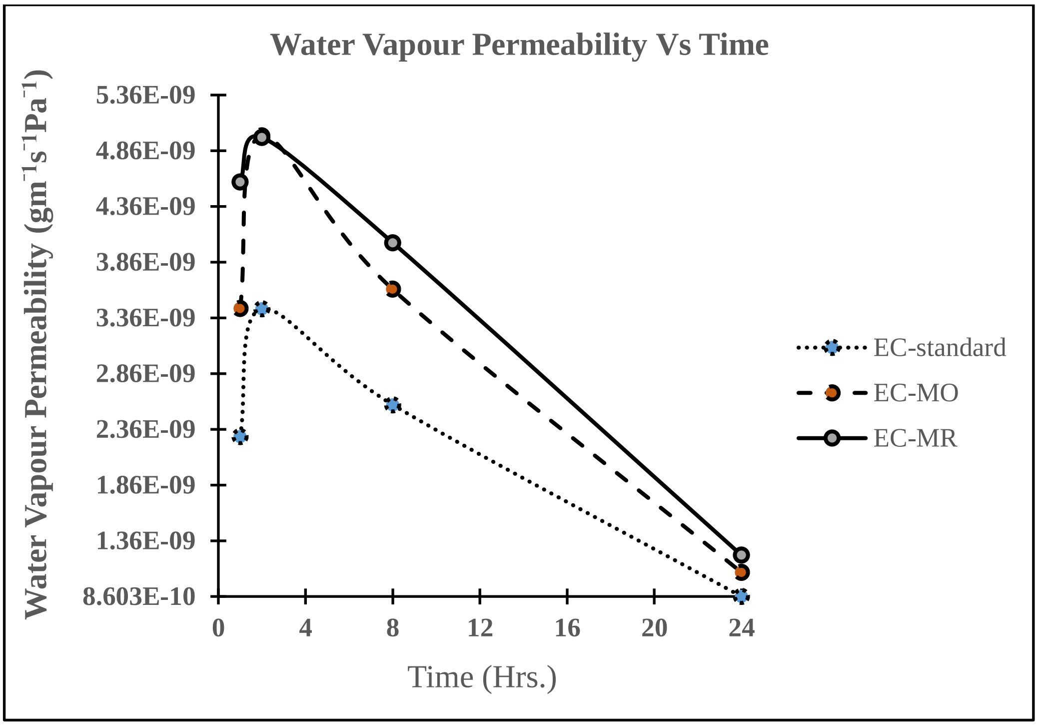


Figure 5.1: Time Dependence of Water Vapour Permeability of Ethyl Cellulose Films, With and Without Indicators

5.2.2 Effect of Temperature on Water Vapour Permeability

With the increase in the temperature, the water vapor permeability of the ethyl cellulose films was increased, as depicted by the Figure 5.2. The water vapour permeability of the EC films with and without indicators showed a great variation with rise in temperature from 20°C to 50°C, for initial 1hr of water exposure, which ranged from 1.92648 x10^{-9} $gm^{-1}s^{-1}Pa^{-1}$to 2.294073x$10^{-9}$$gm^{-1}s^{-1}Pa^{-1}$ for EC-standard film, 3.12157 x$10^{-9}$$gm^{-1}s^{-1}Pa^{-1}$ to 3.44450 x$10^{-9}$$gm^{-1}s^{-1}Pa^{-1}$ for EC-MO film and 4.13549 x$10^{-9}$$gm^{-1}s^{-1}Pa^{-1}$ to 4.57907 x$10^{-9}$$gm^{-1}s^{-1}Pa^{-1}$ for EC-MR film respectively. As asserted from the literature, for biopolymers [293], this upsurge in water vapour permeability of ethyl cellulose films, with increase in temperature can be credited to the enhanced motion of the polymeric fragments and amplified energy levels of the infusing molecules, as a consequence of raised temperature. Further, the increased moisture content in the films could have caused in swelling, thus, leading to the expansion of biopolymer matrix, which improved the diffusion of water vapour through, the ethyl cellulose films, as the temperature increased.

The maximum values of the WVP was recorded for all EC films for first 2hrs of water exposure, at raised temperature (from 20°C to 50°C). Among all samples, the EC- standard film showed minimum value of water vapor permeability and the values of WVP for EC-MO and EC-MR films were found nearly equivalent, as shown by Figure 5.3. The value of WVP, for all the ethyl cellulose films were recorded for a total duration of 24 hrs, under different temperatures i.e. from 20°C to 50°C, and are reported in Table 5.2. The EC-MR film showed the highest water vapor permeability among all samples, for entire times of exposures and tested temperature conditions.

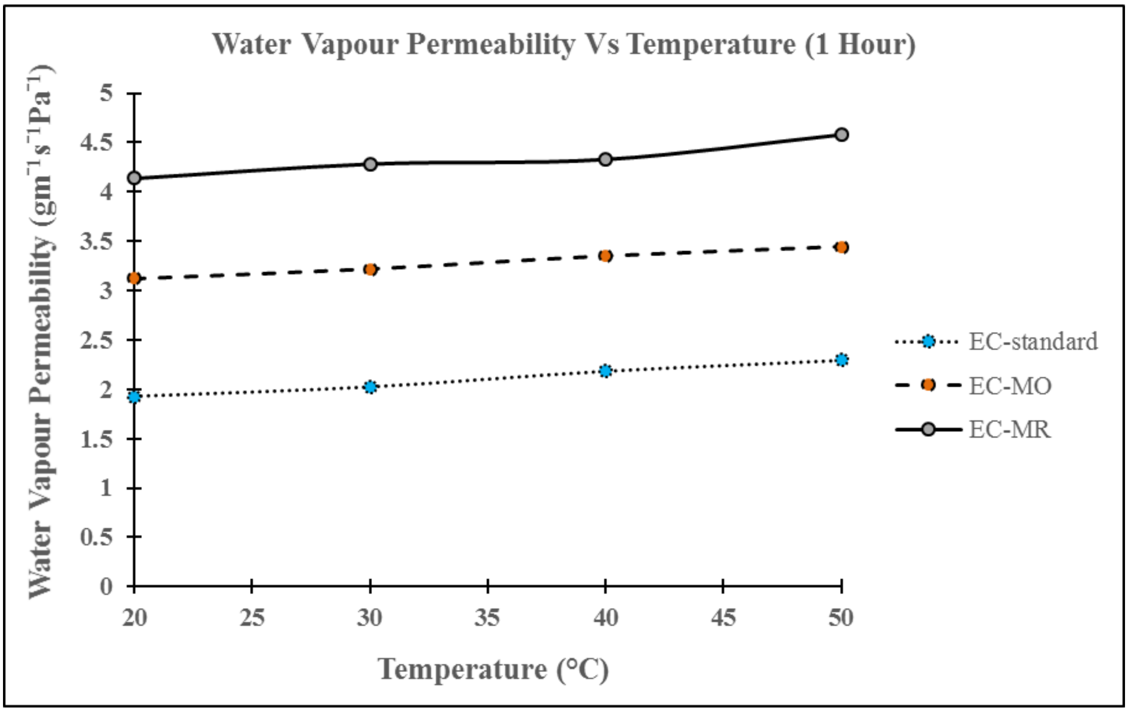


Figure 5.2: Effect of Temperature on the Water Vapor Permeability of Different Ethyl Cellulose Films, During 1Hr of Water Exposure

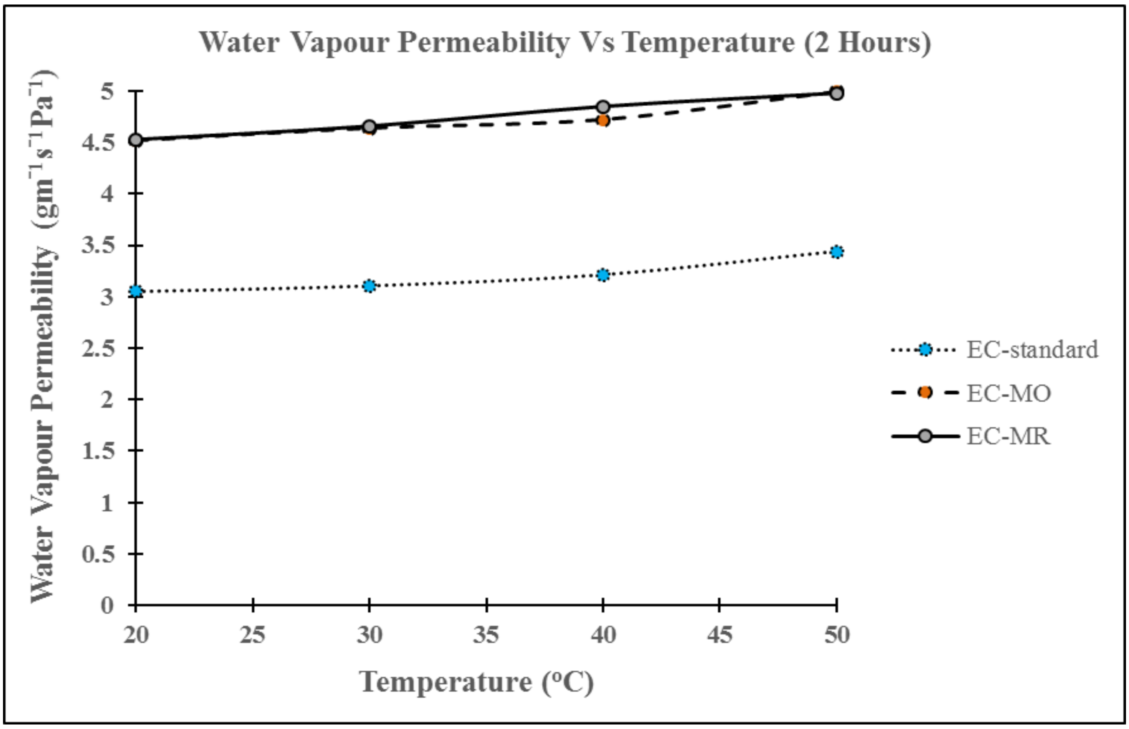


Figure 5.3: Effect of Temperature on the Water Vapor Permeability of Different Ethyl Cellulose Films, During 2Hrs of Water Exposure

Table 5.2: Effects of Temperature on the Water Vapour Permeability of Ethyl Cellulose Films With and Without Indicators

	Temperature (°C)															
	20				30				40				50			
Sample	Time Interval															
	1Hr.	2Hrs.	8Hrs.	24Hrs.	1Hr.	2Hrs.	8Hrs.	24Hrs.	1Hr.	2Hrs.	8Hrs.	24Hrs.	1Hr.	2Hrs.	8Hrs.	24Hrs.
EC-standard	1.92648	3.05438	2.10492	1.02751	2.02345	3.10891	2.37201	1.11059	2.18316	3.21601	2.49156	1.16189	2.29407	3.44111	2.58083	1.21451
EC-MO	3.12157	4.51394	3.31592	1.21005	3.21971	4.63701	3.41309	1.35973	3.35102	4.72057	3.52104	1.43846	3.44451	4.99454	3.61673	1.51964
EC-MR	4.13549	4.52918	3.75187	1.38516	4.28167	4.65924	3.95643	1.52601	4.32816	4.85067	4.01321	1.65983	4.57908	4.97975	4.03531	1.73736

5.3 SIGNIFICANT FINDINGS

The values of water vapour permeability of all ethyl cellulose films had shown the similar trends. Initially the WVP of the EC film increased, for a period of 2 hrs, and then showed a decline, till the minimum value is reached, in a total span of 24hrs. This trend is shown by all EC films, with or without indicators. With the increase in the temperature, the values of the water vapor permeability, of all ethyl cellulose films was reportedly increased. With a variation of temperature from 20°C to 50°C, for initial 1hr of water exposure, WVP ranged from 1.92648 x10^{-9} $gm^{-1}s^{-1}Pa^{-1}$ to 2.294073x$10^{-9}$$gm^{-1}s^{-1}Pa^{-1}$ for EC-standard film, 3.12157 x$10^{-9}$$gm^{-1}s^{-1}Pa^{-1}$ to 3.44450 x$10^{-9}$$gm^{-1}s^{-1}Pa^{-1}$ for EC-MO film and 4.13549x$10^{-9}$$gm^{-1}s^{-1}Pa^{-1}$ to 4.57907x$10^{-9}$$gm^{-1}s^{-1}Pa^{-1}$ for EC-MR film respectively. The presence of indicators has influenced the properties of the ethyl cellulose films. For all the EC films, the maximum values of the WVP was recorded, at 2 hrs of water exposure. Among all samples, the EC- standard film showed minimum value of water vapor permeability, and the values of WVP for EC-MO and EC-MR films were found nearly equivalent. With the increase in the duration of exposure, and varying temperature (from 20°C to 50°C), the water vapor permeability of all the films was reportedly increased, with a maximum value reached at an interval of 24 hrs, at each test condition of temperature. The EC-MR film showed the highest water vapor permeability among all samples, for entire times of exposures and tested temperature conditions.

CHAPTER 6

CONCLUSIONS AND FUTURE PROSPECTS

6.1 CONCLUSIONS

The changeover of the petroleum-based food packaging by the biopolymer food packaging is undeniably the demand of the market and ultimatum for the degrading environment. In addition to this, the intelligent biopolymers will be a boon to the market, as well as, the environment. Thus, the development of the intelligent polymeric films, from the biopolymers (mainly cellulose derivatives), were the main focus of this study. As, most of the cellulose derivatives are readily soluble in water as compared to the ethyl cellulose, so ethyl cellulose was considered as the utmost suitable biopolymer for this study. Since the ethyl cellulose itself is bio-degradable in nature, so the resulting film is also biodegradable and environment friendly. Moreover, the most appropriate solvent for the ethyl cellulose, i.e. pure ethanol, is also suitable to an extent of food grade materials. Polyethylene glycol (MW 400) was observed to be suitable plasticizer for ethyl cellulose in ethanol, thus, utilized in the development of biodegradable polymeric film by casting technique. In order to achieve the better-quality film, to be used for food packaging, the studies were extended to explore the effect of different polymer to plasticizer ratios on the properties of the resulted film. Further, the pH responsive biodegradable films were developed by incorporating the azo-indicators i.e. Methyl Orange (MO) and Methyl Red (MR) into this established formulation of the film, exhibiting the best properties. From the experimental studies conducted, the following significant conclusions have been drawn:

- The polymer to solvent ratio of 2.5% (w/v) was found most appropriate for all the polymeric films, as no phase separation was observed in the resulted films.
- The polymeric films formed from biopolymers varied significantly in the texture, due to the variation of solvent, as well as, the percentage of the polymer used.
- The ethyl cellulose (EC) was observed to be the most suitable biodegradable polymer for film

casting, due to its limited solubility in water (either hot or cold) in comparison to other cellulose derivatives. Moreover, the solvent used for casting the ethyl cellulose films, i.e. ethanol is also found suitable to an extent of food grade materials. Polyethylene glycol (MW 400) (PEG) was observed to be suitable plasticizer for ethyl cellulose in ethanol. The ease in casting and the realization of the perfectly smooth casted film, in the laboratory conditions, also strengthened this conclusion.

- All the casted films, obtained by varying the Polymer to Plasticizer (EC to PEG) ratio, were smooth and homogeneous but, hazy, opaque and translucent in the appearance, with mean thickness of 1.010 mm ± 0.001.
- Among all the formulations, the film with EC: PEG ratio equal to 4:2, was found the most suitable in terms of flexibility, solubility, moisture content and mechanical properties. The same formulation was used for conducting the further studies.
- The ethyl cellulose films incorporated with azo-indicators (MO and MR), were found consistent, smooth and intact when peeled from the casting surface, with transparent and clear appearance for EC standard, yellowish for EC-MO and slightly pinkish for EC-MR film.
- The yield of the bio-polymeric films showed a slight increase, on the addition of indicators and was found maximum for EC-MR film.
- The SEM images of the surface of the ethyl cellulose films with and without indicator had shown unbroken, compact and smooth traits, without any micro-cracks. However, the cross-section views of the ethyl cellulose film without indicator showed good hexagonal pores; while the film with indicators showed a dense structure with few and small hexagonal pores.
- The ethyl cellulose films containing azo-indicators were exposed to different concentrations of the acid solution (pH ranging from 2.76-1.78). A more pronounced color change was observed with luminosity, when the color parameters (L*, a*, b*) were checked. The EC-MO film treated with 60% acid concentration (pH=1.87), showed the darkest color (L*=32), among all the other EC-

MO samples with different percentages of acid. Among all the EC-MR films treated with different percentages of acid, the darkest color (L*=32) was observed for 50% acid (pH=1.91) concentration.

- The comparison of pH response of EC-MO and EC-MR films on the basis of colorimetric value had shown the similar performance for both the films, but visually, the color variation was better for the EC-MO film.
- The soluble matter among different pH responsive ethyl cellulose films was approximately 15% more for the EC-MR film as compared to EC-MO film. For the EC-standard film it was nearly equivalent to the EC-MO film.
- The moisture content of EC-MO film was approximately 10% lower as compared to the EC-standard film, while the EC-MR film showed a great increase in the moisture content.
- The water absorption capacity for the ethyl cellulose films (without acid treatment) showed great variation in the EC-standard film as compared to EC-MO and EC-MR films, within a span of 24 hrs. The results obtained at 24hrs water immersion had shown a highest percentage of water absorption i.e. about 61.42% in the EC-standard films. However, the water absorption in EC-MO and EC-MR films was relatively less i.e. 47.11% and 42.13% respectively. After 24hrs of immersion, the percentage variation of water absorption of all ethyl cellulose films with azo indicators was insignificant to be measured.
- The water absorption capacity of all ethyl cellulose films with azo indicator, post acid treatment, showed an inordinate decrease. The EC-standard film showed 3.89%, EC-MO film showed 1.89% and EC-MR showed 0.68% decrease in the water absorption respectively, with 24 hrs of water immersion as compared to the films without acid treatment.
- The EC-standard film demonstrated a tensile strength, young’s modulus and elongation at break of 0.07475 MPa, 21.4475 MPa and 11.661% respectively, while the other two films i.e. EC-MO and EC-MR films showed lesser elongation at break, equal to 4.761% and 4.225% respectively.

These declined values suggest a lower flexibility of these films as compared to the standard EC film. The tensile strength of EC-MO and EC-MR films were measured as 0.1127 MPa and 0.0612375 MPa respectively, which were very close to the EC standard film. The modulus of elasticity of EC-MO and EC-MR films were respectively estimated as 26.325 and 17.8273 Mpa. Comparison of the strengths of EC-MO and EC-MR films with the EC standard film makes them more applicable for the packaging purpose. Also, the mechanical property of the films suggests their convenient use upto a temperature of 60°C.

- The permeability of water vapor through the ethyl cellulose films without indicator during initial 2hrs ranged from 2.29407 x10^{-9} $gm^{-1}s^{-1}Pa^{-1}$to 3.44111 x10^{-9} $gm^{-1}s^{-1}Pa^{-1}$, and then started to decrease upto 8.60277x10^{-10} $gm^{-1}s^{-1}Pa^{-1}$ in total of 24hrs span. The water vapor permeability of EC-MO film was comparatively more than the EC-standard film, ranging from 3.44451 x10^{-9} $gm^{-1}s^{-1}Pa^{-1}$ to 4.99454 x10^{-9} $gm^{-1}s^{-1}Pa^{-1}$ initially for 2hrs and then receded upto 1.07640 x10^{-9} $gm^{-1}s^{-1}Pa^{-1}$ in next 24hrs The EC-MR film initially showed the high values of water vapor permeability, but it became comparable to that of EC-MO film at an interval of 24hrs The water vapor permeability of EC-MR film showed a range from 4.57908 x10^{-9} $gm^{-1}s^{-1}Pa^{-1}$ to 4.97975 x10^{-9} $gm^{-1}s^{-1}Pa^{-1}$, for first 2hrs and then decreased upto 1.23062 x10^{-9} $gm^{-1}s^{-1}Pa^{-1}$ in a span of 24 hrs
- With the increase in the temperature, the values of the water vapor permeability, of all ethyl cellulose films was reportedly increased. With a variation of temperature from 20°C to 50°C, for initial 1hr of water exposure, WVP ranged from 1.92648 x10^{-9} $gm^{-1}s^{-1}Pa^{-1}$ to 2.294073x10^{-9}$gm^{-1}s^{-1}Pa^{-1}$ for EC-standard film, 3.12157 x10^{-9}$gm^{-1}s^{-1}Pa^{-1}$ to 3.44450 x10^{-9}$gm^{-1}s^{-1}Pa^{-1}$ for EC-MO film and 4.13549x10^{-9}$gm^{-1}s^{-1}Pa^{-1}$ to 4.57907x10^{-9}$gm^{-1}s^{-1}Pa^{-1}$ for EC-MR film respectively.
- The ethyl cellulose is itself bio-degradable in nature, so the resulting pH sensitive films are biodegradable and environment friendly too. As, the azo linkage may easily undergo enzymatic breakdown in liver and kidney and the aromatic amines, so produced, are excreted in the urine, so there is no major concern to evaluate the food safety of these azo dyes incorporated ethyl cellulose

films.

- Both, methyl red, as well as, methyl orange are very commonly used indicators in any laboratory set-up, and are not much expensive. Thus, the resulted pH responsive ethyl cellulose films will not much aid towards the increase in cost when produced in bulk as commercial food packaging films.

6.2 FUTURE PROSPECTS

The ethyl cellulose films, being biodegradable, can be used as substitute for the existing petroleum-based food packaging films. These biodegradable films, when incorporated with azo-indicators, resulted in the development of pH responsive films. These indicator-based films had shown good response to the colorimetric analysis, at different pH range and also exhibits comparable mechanical properties and improved water absorption capacity, in comparison to ethyl cellulose film without indicator, so they can easily be used as qualitative responsive smart films in food packaging. Clinical trials can also be conducted on the synthesized smart films for using them as edible smart packaging films. In the current study the smart packaging films were developed with the prime focus on the food packaging applications. For commercial viability, the work can be done towards improving their mechanical properties by incorporating bio-based reinforcement fillers. The study can be augmented in the pharmaceutical sector too, for recording the responses of medicine under different service and storage conditions, wherein they would also guarantee an advanced level of product security in the medicinal and cosmetics businesses. If all these features can be accomplished, a more widespread use of these reported intelligent packaging systems would be possible.

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RESEARCH PUBLICATIONS

INTERNATIONAL JOURNAL PUBLICATIONS

- **Neelam Yadav** and Raminder Kaur, “Biodegradable Polymeric Film for Food Packaging” *Journal of Applied Packaging Research*, 11(2), 21-35, 2019.

- **Neelam Yadav** and Raminder Kaur, “Environment Friendly Qualitatively Responsive Ethyl Cellulose Films as Smart Food Packaging” *Materials Express*, 9(7), 792-800, 2019. (SCI Indexed).

- **Neelam Yadav** and Raminder Kaur, “The Potential Application of Different Materials for Active and Smart Packaging: A Review” *Food Engineering Reviews* (communicated).

- **Neelam Yadav** and Raminder Kaur, “An Overview of Intelligent Packaging: Concepts, Applications and Innovations in the Food Packaging” *International Journal of Polymer Science* (under revision).

- **Neelam Yadav** and Raminder Kaur, “Investigation of Permeation Properties of Ethyl cellulose Films Incorporated with Azo Indicators” *European Polymer Journal* (communicated).

CONFERENCE PUBLICATIONS

- **Neelam Yadav** and Raminder Kaur, “Effect of Percentage of Plasticizers in the Tensile Strength of Ethyl Cellulose Film”, International Conference on Future Learning Aspects of Mechanical Engineering organized by Amity University, Noida, India, October 3rd to 5th 2018.
- **Neelam Yadav** and Raminder Kaur**,** “Investigation of Physical and Mechanical properties of Ethyl cellulose Film”, International Conference on Computational and Experimental Methods in Mechanical Engineering organized by GLBITM, Greater Noida, India, December 8th to 9th 2017.
- **Neelam Yadav** and Raminder Kaur**,** “Development and characterization of food packaging film using ethyl cellulose”, International Conference on Advancements and Recent Innovations in Mechanical, Production and Industrial Engineering organized by ITS Engineering College, Greater Noida, India, April 21st to 22nd 2017.
- **Neelam Yadav** and Raminder Kaur**,** “Smart packaging for edible products: Improvement in packaging”, The Poster Presentation, International Conference on Advancements and Recent Innovations in Mechanical, Production and Industrial Engineering organized by ITS Engineering College, Greater Noida, India, April 10th to 11th 2015.

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1	SITM, Noida Extn	Assistant Professor	Aug'2014-June'2020	Chemical Engineering
2	VITS, Ghaziabad	Assistant Professor	Aug'2008-Dec'2010	Engineering Chemistry
3	IHBT(CSIR),Palampur	Scientist-B	May'2007-July'2008	Research
4	ITS, Greater Noida	Assistant Professor	Jan'2006- April'2007	Chemistry
5	HBTI, Kanpur	Lecturer	July'2004-Dec'2005	Chemical Technology
6	Jiwaji University	Lecturer	Jan'2004-June'2004	Food Chemistry

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