FABRICATION AND ANALYSIS OF BIOPOLYMER BASED MATERIALS FOR PACKAGING APPLICATIONS

A Thesis Submitted in Partial Fulfillment of the
Requirements for the Degree of

DOCTOR OF PHILOSOPHY

By

JUIKAR SUBODH KAMALAKAR
(Roll No. 2K17/PhD/AC/14)

Under the Supervision of
Prof. SUDHIR G WARKAR
Department of Applied Chemistry,
Delhi Technological University

To the
Department of Applied Chemistry
DELHI TECHNOLOGICAL UNIVERISITY
(Formerly Delhi College of Technology)
Shahbad, Daulatpur, Main Bawana Road, Delhi – 110042, India

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“A life that reflects value and satisfies souls is real success”

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Juikar Subodh Kamalakar

DELHI TECHNOLOGICAL UNIVERSITY
(Formerly Delhi College of Engineering)
Shahbad, Daulatpur, Bawana Road, Delhi-110042, India

CANDIDATE'S DECLARATION

I **Juikar Subodh Kamalakar** hereby certify that the work which is being presented in the thesis entitled "**Fabrication and analysis of biopolymer based materials for packaging applications"** in partial fulfillment of the requirement for the award of the **Degree of Doctor of Philosophy**, submitted in the **Department of Applied Chemistry, Delhi Technological University**, is an authentic record of my own work carried out during the period from **13th July 2017 to 24th June 2024** under the supervision of **Prof. Sudhir G. Warkar**.

The matter presented in the thesis has not been submitted by me for the award of any other degree of this or other institute.

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This is to certify that the student has incorporated all the corrections suggested by the examiners in the thesis and the statement made by the candidate is correct to the best of our knowledge.

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DELHI TECHNOLOGICAL UNIVERSITY
(Formerly Delhi College of Engineering)
Shahbad, Daulatpur, Bawana Road, Delhi-110042, India

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Certified that **Mr. Juikar Subodh Kamalakar (Roll No. 2K17/PhD/AC/14)** has carried out his search work presented in this thesis entitled **"Fabrication and analysis of biopolymer based materials for packaging applications"** for the award of **Doctor of Philosophy** from **Department of Applied Chemistry, Delhi Technological University**, **Delhi**, under my supervision. The thesis embodies results of original work, and studies are carried out by the student himself and the contents of the thesis do not from the basis for the award of any other degree to the candidate or to anybody else from this or any other University/Institution.

Prof. Sudhir G. Warkar
Professor,
Dept. of Applied Chemistry,
Delhi Technological University,
Shahbad, Daulatpur, Main Bawana Road,
Delhi-110042

Date:

FABRICATION AND ANALYSIS OF BIOPOLYMER BASED MATERIAL FOR PACKAGING APPLICATIONS

Juikar Subodh Kamalakar

ABSTRACT

Search Problem

Packaging is a process of preventing chemical and physical damage of the product, increasing shelf life of packaged product, preserving the product from contamination and helps in safe transportation. Various synthetic polymers are being used for packaging purposes, due to their excellent mechanical properties like tensile strength, tear strength, their barrier towards oxygen, carbon dioxide, water, aroma and so on, including easy processability and economy. However, these polymers pose various limitations due to their poor degradability and difficulty in recycling and so on.

Biopolymers are fourth generation packaging materials. Due to the shortcomings of the petrochemical-based polymers and their threat to the environment, biopolymers are seen as the sustainable substitute for traditional synthetic polymers and have attracted the researchers towards the development of biopolymer-based packaging materials.

Methodology Used

The study aimed towards the fabrication of packaging films using biopolymer Carboxymethyl guar gum (CMG) as the base material. Various ratios of glycerol (Gly) as a plasticizer and glutaraldehyde (Glu) as a cross-linker were employed in the fabrication of these biopolymer-based films through the solution casting technique. Comprehensive characterization, such as Attenuated Total Reflectance-Fourier Transform Infrared spectroscopy (ATR-FTIR), Differential Scanning Calorimetry (DSC), Thermo-Gravimetric Analysis (TGA), and Scanning Electron Microscopy (SEM), were conducted. The films were further examined for tensile strength, percent elongation, thickness, solubility in water, gloss, haze, and transparency.

Further after conducting these tests the films were also used to find out probable applications in packaging wherein, the cut potatoes were wrapped with CMG based films and observed visually for any color change (browning) and shrinkage.

Also, to explore the possibility of commercialization of the CMG-based packaging, by varying the percentage of CMG with low density polyethylene (LDPE), the CMG-LDPE blends were extruded and then injection molded as per requirement in different shapes and used for tensile strength, elongation at break, Izod impact, melt flow index, moisture content and water solubility test. Soil-degradation studies of the CMG-LDPE blends were also done through the soil burial method for a period of 84 days.

Research Gap

- In our literature survey it is found that the CMG based film has not yet been explored for packaging applications.
- CMG-LDPE blend also has not yet been explored.
- This underscored the potential novelty and unexplored possibilities in incorporating CMG into the realm of eco-friendly packaging solutions

Objective

The main objective of this research was to fabricate various biopolymer based films and to characterize and test them for suitability for packaging applications. The objectives of the research work were:

1. Fabrication and characterization of carboxymethyl guar gum (CMG) based material using suitable plasticizers and cross linkers for packaging applications.
2. Optimization of the process parameters for fabricated biopolymer material.
3. Assessing commercial-scale production and evaluation of properties by blending with synthetic polymers.
4. Testing of the fabricated films and blends for packaging applications.

Summary of chapters

The thesis is divided into six chapters and organized as follows:

Chapter 1: Introduction and Literature Review.

Chapter 2: Fabrication and Characterization of carboxymethyl guar gum-based (CMG) films

Chapter 3: Evaluation of CMG-based films for packaging applications

Chapter 4: Fabrication and testing of CMG-LDPE blends

Chapter 5: Soil-degradation studies on CMG-LDPE blends

Chapter 6: Conclusion and future scope of work

Chapter 1 describes about the introduction and classification of the various biopolymers developed in the recent past, modification methods for their processing and their packaging applications are also discussed.

Chapter 2 of the thesis aimed towards the fabrication of packaging films using carboxymethyl guar gum (CMG) as the base material. Various ratios of glycerol (Gly) as a plasticizer and glutaraldehyde (Glu) as a cross-linker were employed in the synthesis of these biopolymer-based films through the solution casting technique.

The series of a total of 64 variants of CMG-based films were fabricated by employing the different concentrations of glycerol as a plasticizer and glutaraldehyde as a cross-linker, via solvent casting technique.

Further the comprehensive characterization, such as attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), differential scanning calorimetry (DSC), thermo gravimetric analysis (TGA), and scanning electron microscopy (SEM), was conducted.

Chapter 3 In this chapter, the information on the evaluation of CMG based films for various parameters like tensile strength, percent elongation, thickness, solubility in water, gloss, haze, and transparency is provided for exploring the possibilities of using CMG films for packaging applications.

The maximum tensile strength of 37.82 MPa, maximum percent elongation of 124.20%, maximum gloss of 25.52% at a 20° angle, maximum haze of 41.93%, maximum transparency of 88.53%, and a minimum water solubility of 60.42% were observed for the developed films. This reveals that CMG-based films hold promising potential as a novel biomaterial for future applications in packaging, such as edible coatings and water-soluble packaging films.

After conducting these tests the films were also used to find out any probable applications in packaging. The Cut potatoes were wrapped with CMG based films and observed visually for Color change (browning) & shrinkage.

Chapter 4 highlights the fabrication of CMG-LDPE blends. To explore the possibility of commercialization of the CMG based packaging, the CMG-LDPE blends were fabricated by varying the percentage of CMG in the blends. The CMG powder in a varying percentage was mixed with LDPE granules using glycerol (1%) as a wetting agent. Then extruded, in a twin screw extruder, cooled and converted into small pieces. Further CMG-LDPE pieces were injection molded as per requirement in different shapes and used for the evaluation of tensile strength, elongation at break, Izod impact, melt flow index, moisture content and water solubility test.

Chapter 5 revels the soil-degradation studies conducted on the CMG-LDPE blends. To have the information on the degradation of the CMG-LDPE blends, soil degradation studies of the CMG-LDPE blends has been done through soil burial method for a period of 84 days.

Predetermined quantity of samples were buried 5-6 cm deep inside the soil while maintaining the moisture in the plantation soil for the period of 84 days. The samples were removed from the soil for every 7 days and tested for their soil degradability.

In Chapter 6, the conclusion and future scope of the present work has been summarized. CMG-based films were successfully fabricated by utilizing glycerol as a plasticizer and glutaraldehyde as a cross-linking agent by solution casting method.

Summary of findings

CMG-based films were successfully fabricated by utilizing glycerol as a plasticizer and glutaraldehyde as a cross-linking agent by solution casting method.

- Series of CMG-based films were successfully fabricated by utilizing glycerol as a plasticizer and glutaraldehyde as a cross-linking agent by solution casting method.

- The reaction temperature was optimized at 75 °C by using DSC and TGA. CMG Films indicated good film forming properties at 75 °C temp.
- SEM and FTIR studies indicated evidence of cross linking of CMG with glutaraldehyde.
- CMG-based films were evaluated for tensile strength, elongation@ break, gloss, haze, transparency, and water solubility.
- The maximum values observed for tensile strength 37.82 MPa, elongation at break 124.20%, gloss 25.52%, haze 41.93%, and transparency 88.53%.
- Solubility test results indicated a minimum water solubility of 60.42% by weight which indicates the potential applications of CMG-based films in areas such as edible coatings and water-soluble packaging.
- The potato wrapping study indicated the applications of CMG based films for cut fruits and vegetable packaging.
- All these properties suggests the possibility of fabricated CMG-based films for packaging applications.
- The CMG-LDPE blends were successfully fabricated with 10%, 20% and 30% CMG. This suggests that they can be processed on moulding machines.
- The water resistance of the CMG-LDPE blends is more in comparison with its films indicates its wider packaging applications.
- The CMG-LDPE blends were found to be biodegradable in soil. Soil degradability of the blends was 1.94%, 7.58% and 21.96% for 10% 20% and 30% blends respectively. This indicates environment friendliness of these blends.
- Further research might enable the use of flexible use of CMG-LDPE blends for flexible packaging and rigid blends for thermoformed containers.

LIST OF PUBLICATIONS

1. Subodh K. Juikar, and Sudhir G. Warkar*, 2023, Biopolymers for packaging applications: An overview, *Packaging Technology and Science-An International Journal, Wiley Online Library, Volume 36 (4), pages 229-251 (April 2023).*

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2. Subodh K. Juikar and Sudhir G. Warkar*, Fabrication and assessment of carboxymethyl guar gum-based sustainable films for packaging application, *Colloid and Polymer Science, Volume 302, pages 1137-1148 (April 2024).*

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LIST OF SYMBOLS, ABBREVIATIONS AND NOMENCLATURE

Abbreviation		Meaning
%	:	Percentage
AS	:	Australian Standards
ATR-FTIR	:	Attenuated Total Reflectance-Fourier Transform Infrared
^{14}C	:	a radioactive Isotope of Carbon.
C30B	:	Cloisite 30B
Ca^{2+}	:	Calcium ion
$CaCl_2$	:	Calcium chloride
CH/SC	:	Chitosan and Sodium Caseinate
CIPET	:	Central Institute of Petrochemicals Engineering & Technology
CMC	:	Carboxy Methyl Cellulose
CMCh	:	Carboxy Methyl Chitosan
CMG	:	Carboxy Methyl Guar Gum
CO_2	:	Carbon dioxide
COVID-19	:	Coronavirus Disease-2019
DIN	:	Deutsches Institut für Normung (German Institute for Standardization)
DOP	:	Dioctyl Phthalate
DSC	:	Differential Scanning Calorimetry
EAB	:	Elongation at Break
EBO	:	Epoxidized Broccoli Seed Oil
EN	:	European Standards
Eqn.	:	Equation
ESO	:	Epoxidized Soyabean Oil
EU	:	European Union
EVA	:	Ethylene Vinyl Acetate
EVOH	:	Ethyl Vinyl Alcohol
Glu	:	Glutaraldehyle
Gly	:	Glycerol

Abbreviation		**Meaning**
GMA	:	Glycidyl Methacrylate
H_2O	:	Water
HDI	:	Hexamethylene Di Isocyanate
HDPE	:	High Density Polyethylene
ICI	:	Imperial Chemical Industries
IR	:	Infra Red
ISO	:	International Organization for Standardization
JIS	:	Japanese Industrial Standards
k-Car	:	κ-Carrageenan
KCHK	:	Kementerian Lingkungan Hidup dan Kehutanan (Ministry of Environment and Forestry)
LAPOL 108	:	A Patented Bioplasticizer
LBG	:	Locust Bean Gum
LCA	:	Life Cycle Analysis
LDPE	:	Low Density Poly Ethylene
LLDPE	:	Linear Low Density Polyethylene
MA	:	Methyl Acrylate
MAH	:	Maleic Anhydride
MAP	:	Modified Atmosphere Packaging
MDI	:	Methylene Diphenyl DI Isocyanate
MDPE	:	Medium Density Polyethylene
MGST	:	MA-Grafted Starch
NaOH	:	Sodium Hydroxide
NPK	:	Nitrogen Phosphorus and Potassium Fertilizer
O_2	:	Oxygen
PA	:	Polyamide or Nylon
PBAT	:	Polybutylene Adipate Co Terephthalate
PBS	:	Polybutylene Succinate
PCL	:	Polycaprolactone
PE	:	Polyethylene

Abbreviation		Meaning
PEG	:	Poly Ethylene Glycol
PET	:	Polyethylene Terephthalate, Polyester
pH	:	The Negative Logarithm of the Concentration of H^+ Ions
PHB	:	Poly Hydroxyl Butyrate
PHBV	:	Poly Hydroxyl Butyrate-Co-Valerate
PLA	:	Poly Lactic Acid
PLA-*g*-MTPS	:	Paleated Starch Grafted Poly Lactic Acid Co Polymer
PLAP	:	A biodegradable Oligomeric Polyester based on Lactic Acid, Adipic acid, and 1,2-propanediol
pMDI	:	Polymeric MDI
PP	:	Polypropylene
PS	:	Polystyrene
PVA	:	Poly Vinyl Alcohol
PVC	:	Polyvinyl Chloride
PVOH	:	Poly Vinyl Alcohol
R.H.	:	Relative Humidity
ROM	:	Ricinoleic Oxazoline Maleate
RS	:	Rice Starch
SAS	:	Starch-Alginate-Stearic acid
SEM	:	Scanning Electron Microscopy
SPC	:	Soy Protein Concentrate
SPI	:	Soy Protein Isolate
St-*g*-PLA	:	PLA Grafted Starch Copolymer
TA	:	Triacetin
T_g	:	Glass Transmission Temperature
TGA	:	Thermo Gravimetric Analysis
TOA	:	Tung Oil Anhydride
TPS	:	Thermoplastic Starch
TS	:	Thermoplastic Starch
UHMW-HDPE	:	Ultra-High Molecular Weight Polyethylene

Abbreviation	Meaning
UTM	Universal Testing Machine
UV	Ultra Violet
UVA	Ultra Violet Type A (280-320 Nano Metre)
UVB	Ultra Violet Type B (320-400 Nano Metre)
v/v	Volume by Volume
VLDPE	Very Low Density Polyethylene
w/v	Weight by Volume
wt.	Weight
WVTR	Water Vapor Transmission Rate
ZEO	Zataria multiflora Essential Oil
µ	Micron
µL	Micro Litre
^{0}C	Degree Celsius
cm	Centimetre
cm^{-1}	Centimetre Inverse
cm^3	Centimetre Cube
g	Gram
h	Hour
Kg	Kilo Gram
kV	Kilo Volt
m^2	Metre Square
mg	Milligram
min	Minute
ml	Milliliter
mm	Millimeter
MPa	Mega Pascal
MT	Metric Tons
N	Newton

CHAPTER 1

INTRODUCTION, LITERATURE SURVEY AND IDENTIFICATION OF PROBLEM AND ISSUES

1.1 Introduction

Packaging is a process of preventing chemical and physical damage of the product, increasing shelf life of packaged product, preserving the product from contamination and helps in safe transportation [1–4]. Various synthetic polymers such as polystyrene (PS), polypropylene (PP), polyvinylchloride (PVC), polyamide (PA), polyester (PET) and polyethylene (PE) are being used for packaging purposes, due to their excellent mechanical properties like tensile strength, tear strength, their barrier towards oxygen, carbon dioxide, water, aroma, including easy processability and economy [5–10]. However, these polymers pose various limitations due to their poor degradability and difficulty in recycling [11].

Packaging waste contains a significant part of postconsumer municipal solid waste, increasing the environmental concern [11–16]. Worldwide, over 140 million tons synthetic polymers are manufactured per annum, and many of these polymers are indispensable in our daily lives [4]. It is estimated that majority of commodity polymers account for 104 Million Metric tons CO_2 equivalent of Green House Gas emissions and 3.2 quadrillion of energy annually in the United States alone [17].

Due to urbanization, plastic waste generation is increasing rapidly. Plastic production of India is about 7 billion tonnes per year from which the waste generation is of 1.5 million tones every year. However only 9% of the plastic produced every year is being recycled until 2022 [18]. If we will see the global scenario, the per capita plastic waste generation is considerable, it is 100 kg in Switzerland, 98.2 kg in South Korea, 81 kg in Germany, 52 kg in Australia, 40 kg in Wales, United Kingdom and 34.1 kg in Austria [19]. Estimates indicate that per day global consumption of plastic bottles alone is about 100 million. During COVID-19 pandemic, there was additional burden of waste generated from microfibres and personal protective equipment, throughout the world [20].

Thus, the synthetic polymers pose various environmental impacts like municipal solid waste generation, load on landfill, environmental pollution, depletion of natural resources and so on [1, 11–16, 18].

Recently, to take care of the increasing ecological pollution created by` synthetic polymers, many countries/regions, Australia, Brazil, Britain, Chile, European Union (EU) member states, France, Hainan, Iceland, Korea, Macao, New Zealand, New York and Washington state including India, have implemented a ban on single use plastics [21].

The limitations of the petrochemical-based polymers and ecological problems have led an extensive research being focused towards the development of biopolymer-based packaging materials [5, 22–24].

The modern packaging materials therefore, in addition to providing the desired properties for protecting the product from adverse environmental factors, should also be biodegradable, easily recyclable and should pose minimum impact on the environment.

The desirable properties of the modern packaging materials are summarised in Figure 1.1, and the various environmental impacts posed by the packaging materials are summarised in Figure 1.2 [25]

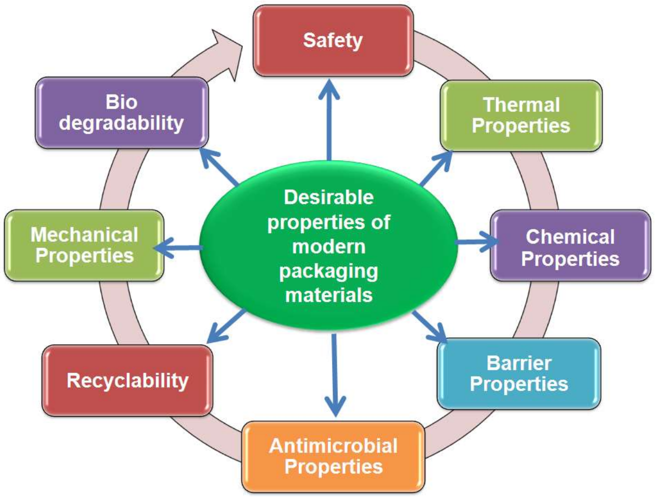

Fig. 1.1: Desirable Properties of the Modern Packaging Materials [5–8, 25]

Fig. 1.2: Environmental Impacts Posed by the Synthetic Packaging Materials [6–9]

While numerous reviews have been published on the biopolymers by various researchers [1-25]; however, this literature survey provide in-depth information about various biopolymers including their modification methods and the benefits of these modifications. The review also highlights various packaging applications developed by researchers using these biopolymers.

1.2 Biopolymers

Biopolymers are the substances, macromolecular in nature, formed by living organisms and they are also called as natural or bio-based polymers. These are the polymeric materials either occurring naturally, isolated from animals, plants, bacteria and fungi, or could be produced, from biological substances like sugars, amino acids, oils or natural fats [4, 26, 27].

It is a well-known fact that not all biopolymers are biodegradable, and all biodegradable polymers are not biopolymers. The bio-based polymers may be either biodegradable or non-biodegradable. Similarly, the biodegradable polymers may be derived from either bio-based or fossil fuel resource. Polylactic acid is an example of biodegradable bio-based polymer, and polyglycolic acid is an example of biodegradable fossil fuel-based polymer [11, 21, 28].

Biopolymers are seen as fourth generation packaging materials as a sustainable substitute for traditional synthetic polymers [29–31]. They have high potential to replace synthetic polymers [32]. Biopolymers being biodegradable, they are favorable to be exploited for packaging applications [33]. The biopolymers have received increasing attention as they provide the desired properties for various packaging applications [34, 35].

The global production of biopolymers is expected to increase from 2.11 MT in 2020 to about 2.87 MT in 2025[36]. Biopolymers isolated from various natural resources which are biodegradable and/or compostable are being explored by researchers as alternative resources to petroleum-based polymers for variety of applications [8, 37].

However, these biopolymers suffer from a few drawbacks like relatively poor mechanical properties, poor barrier properties, high water solubility, thermal instability, poor commercial processability and higher processing cost [3, 5, 33, 38–42]. Some of these properties of biopolymers can be modified by cross-linking, chemical modification, blending with synthetic polymers and by reinforcing with nano-sized compounds or fillers [31, 33, 41, 43, 44].

In the future, certain grades of biopolymers could be more cost effective owing to upcoming developments in conversion technologies [22].

1.2.1 Classification of Biopolymers

There are different types of biopolymers used in packaging field derived from various sources. These are broadly classified as natural and synthetic biopolymers. On the basis of monomers used and the biopolymer structure formed, the biopolymers are classified as polynucleotide, polypeptides and polysaccharides [1, 4, 45]. According to their source and production method, the biopolymers are divided into three groups:

Group-I: Directly extracted from biomass.
Examples: Polysaccharide, Protein, Polypeptide and Polynucleotide

Group-II: Produced using renewable bio-based monomers or mixed sources of biomass and petroleum, by classical chemical synthesis.

Examples: Poly-lactic acid, Biopolyester

Group-III: Produced by microorganism or genetically modified bacteria.
Examples: Polyhydroxy butyrate, Bacterial cellulose, Xanthene and Pullulan [26, 29, 44, 46, 47].

Based on their responsiveness to the thermal conditions, they are divided into elastomers, thermosets and thermoplastics and based on their composition, they are divided into blends, laminates and composites [26].

Figure 1.3 summarizes the broad classification of biopolymers

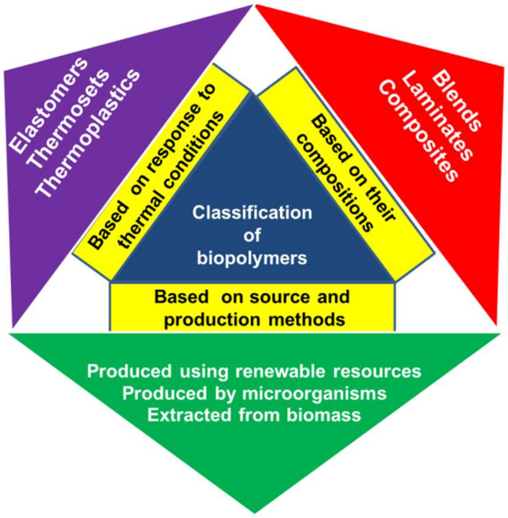

Fig.1.3: Broad Classification of Biopolymers [26, 29, 44, 46–48]

The biopolymers are sourced from different materials. The different materials from which the different biopolymers are derived are listed in the Table 1.1.

1.3 Modifications of Biopolymers for Packaging Applications

To utilise the potential of the biopolymers and also to widen their applications, the performance of biopolymers needs to be improved, and this can be done by modifying them in various ways. The modification of the biopolymers may play a crucial role in increasing their competitiveness in the market. Modification of the biopolymers can help in improving some of their properties like water resistance, oxygen and moisture barrier, mechanical strength, thermal instability and processability by using different modification techniques, to meet the specific requirements for particular application [3, 5, 40–42, 49, 22, 33–39] Plasticizing, cross-linking and compatibilisation are some of the effective methods of biopolymer modification [31, 33, 41, 43, 44, 50]

Table 1.1: Types and Origin of Different Biopolymers [4, 26, 29, 44, 51–55]

Types and Origin of Biopolymers					
Directly extracted from biomass				Synthesized from bio derived monomers	Produced directly by microorganisms
Polysaccharides	Proteins		Lipids	- Polylactic acid - Other Polyesters	- Polyhydroxyalkanoates - Poly-β-hydroxybutyrate - Poly (3-hydroxybutyrate-co-3-hydroxyvalerate - Bacterial cellulose - Xanthene - Pullulan
	Animal proteins	Plant proteins			
- Starch (potato, rice, corn, wheat etc.) and its derivatives - Cellulose (cotton, wood etc.), and its derivatives - Gums, - Alginates, - Pectin - Chitin - Chitosan	- Casein - Collagen - Fibrinogen - Gelatin - Whey	- Soya proteins - Pumpkin proteins - Wheat gluten - Zein	- Beeswax - Carnauba wax - Oils - Free fatty acids		

1.3.1 Plasticisers and Cross-Linking Agents for Biopolymers

Many researchers have reported the use of various plasticisers and cross-linking agents in the synthesis of the biopolymer coatings and films. Primarily the plasticiser improves the flexibility, moisture resistance and processability of the polymers by occupying the spaces between the polymer chains and by reducing secondary forces among them [56–58].

For instance, plasticisers helps in reducing chipping and cracking of the films during its handling and storage [57]. Plasticisation reduces both the processing and glass transition temperature of the material and improves the melt processing of the heat sensitive polymers [22].

The effects of plasticisers on the physical, chemical and functional properties of polymeric films have been reported by many researchers. Glycerol is one of the most widely used plasticisers by many researchers. Tong et al reported the glycerol addition to reduce the tensile strength and water barrier properties along with an increase in the elongation at break and water solubility [59]. While studying the effect of various plasticisers and cross-linkers on extruded films, a decrease in ultimate tensile strength on the addition of glycerol plasticiser to the sugar beet pulp was reported by Rouilly et al.

However, their research revealed that the addition of glycerol improved the processability of the film [50]. Liang et al in their study reported an increase in oxygen permeability and water vapour permeability of the film but decrease in the light transmission with an increase in the plasticiser content [60]. Similar observations are reported by many other researchers [8, 15, 18, 22].

Crosslinking is mostly used for modifying desired properties of the biopolymers [31]. As reported, chemical cross-linking is a promising way of reducing the water absorptiveness of the biopolymer films [50]. Apart from grafting, blending and composite forming, it is one of the important techniques, used for polymer modification. Cross-linking is useful for biopolymer materials derived from proteins or polysaccharides. It also improves the heat and light resistance and dimensional stability [43].

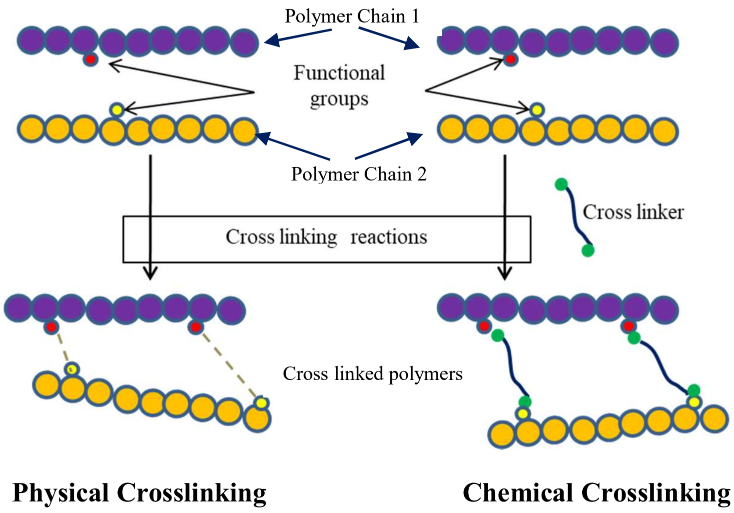

Fig. 1.4: Schematic Representation of Physical and Chemical Cross Linking Process [62]

Cross-linking bonds two polymer chains together by forming covalent or non-covalent linkages [61]. The two types of cross-linking are physical cross-linking and chemical cross-linking. The physical cross-linking process involves the non-covalent bond formation by ionic or hydrogen bonding. Chemical cross-linking involves the formation of covalent bonds between the two different polymer chains by different methods such as irradiation, vulcanization and chemical reactions [42]. Figure 1.4 depicts the physical and chemical cross-linking [62].

Chemical cross-linkers are used to alter the properties of the polymer films. Reddy et al. have reported citric acid cross-linked starch which improved the tensile strength of the film [58]. The crosslinked polymers provide a lower water vapour permeability and improved mechanical strength properties [43] The commonly used crosslinkers are glutaraldehyde, epichlorohydrin, ethylene glycol and diglycidyl ether [63].

A plasticiser based on an oligomeric polyesters, namely, lactic acid, 1,2-propanediol (PLAP) and adipic acid, studied by Jacqueline L et al. showed improved melt processability and reduced thermomechanical degradation of poly hydroxylbutyrate-co-valerate (PHBV). The addition of PLAP also decreased the glass transition and melting temperature modulus and increased the impact resistance of PHBV [64].

Plasticisers and cross-linking agents reported in the literature and respective biopolymer materials are summarised in Table 1.2.

Table 1.2: Plasticizers, Cross Linkers reported to modify Biopolymer Materials.

Biopolymer material	Plasticizer	Cross-linker	Properties of biopolymer after addition of Plasticizer/Cross-linker	Ref.
Sodium alginate and Pectin	Glycerol	Calcium chloride dehydrate	Increased plasticizer content increases volumetric swelling, flexibility, moisture content and solubility of the film in water but decreases tensile strength.	[65]
Keratin form chicken feathers	Glycerol	-	Films with 2% glycerol exhibited highest thermal and mechanical properties.	[66]
Pigskin gelatin	Glycerol	-	The effect of the plasticizer is not much on re-crystallization in the structure of the film but affected the flexibility and susceptibility to moisture.	[58]
Pullulan, Alginate, Carboxy methylcellulose	Glycerol	-	Plasticizer addition showed reduction in tensile strength, water vapor barrier, water solubility however increased in elongation at break.	[59]
Sugar-beet pulp	Glycerol, Sorbitol, Galactose, Adipic acid, fructose, urea, xylitol	Glycidyl methacrylate	Film with urea with Xylitol showed higher tensile strength than glycerol and comparable strain at break.	[50]
Corn starch	Glycerol	Citric acid	Cross-linked films showed 150% higher strength against the non cross-linked films	[67]
Bovine hide gelatin	Glycerol	Di-aldehyde carboxymethyl cellulose	Addition of cross-linker increased tensile strength and also the thermal stability however elongation at break decreased.	[68]
Pea starch and guar gum	Glycerol	-	The developed film significantly affected the transparency, viscosity, color and moisture content of the film	[69]
Cassava starch	Glycerol, yerba mate extract	-	Addition of extract improved the biodegradation of the films in compost while preserving stability in alkaline and acidic media.	[56]
Pea starch and guar gum	Glycerol, ethylene glycol, sorbitol, propylene glycol, polyethylene glycol, mannitol, glucose, sucrose, fructose, sugars galactose, xylitol and maltitol	-	Best effect of plasticization was reported with glycerol, propylene glycol, ethylene glycol, xylitol, sorbitol, mannitol, glucose, fructose, sucrose, galactose and maltitol. Increased elongation at break and reduced tensile strength, reduced young's modulus is reported	[70]

Biopolymer material	Plasticizer	Cross-linker	Properties of biopolymer after addition of Plasticizer/Cross-linker	Ref.
			with increase in plasticizers molecular weight and at increased level of relative humidity.	
Chitosan-montmorillonite	Water	-	With increase in the clay content showed flexible, transparent and crack free films	[71]
Mango seed starch, with micro particle clay	Glycerol	-	Optimum composition of clay and glycerol in mango seed starch based film is reported as 6% and 25% respectively which showed 5.567MPa tensile strength and 43.431% of elongation at break.	[72]
Jackfruit seed starch	Glycerol	-	The prepared film showed good tensile, percentage elongation and young's modulus however with moderate water vapor permeability and low opacity.	[73]
Chitosan and yellow pumpkin starch	Castor oil	-	At 40:60 composition tensile strength of 6.787±0.2274 MPa. Highest biodegradability within 5-10 days is reported in the films with ratio of 50:50.	[74]
Cellulose from oil palm empty fruit bunches, cassava starch	Glycerol	-	The study showed biodegradation of the film in plantation soil.	[75]
Cellulose derived from bagasse and chitosan	Sorbitol	-	The reported optimum tensile strength is 0.089 Kg/Cm^2. The optimum concentration of the cellulose bagasse reported for making bioplastic film was 2%.	[18]
Potato starch and guar gum	Glycerol	-	At optimum composition is of 3.7%, 0.4% and 15% that of potato starch, guar gum and glycerol respectively. Guar gum addition into potato starch showed increased crystallinity of film with high tensile strength but maintained the water vapor permeability	[76]

Biopolymer material	**Plasticizer**	**Cross-linker**	**Properties of biopolymer after addition of Plasticizer/Cross-linker**	**Ref.**
Potato starch, PLA and PVA	Glycerol	-	The samples disintegrated completely after 3 weeks. Complete biodegradation also confirmed.	[77]
Artemisia Sphaerocephala krasch gum	Glycerol, sorbitol and triethyl citrate	-	Decreased tensile strength and increased elongation at break was observed after adding plasticizer.	[60]
Corn starch, wheat starch, zein, carboxymethyl cellulose Sodium and sodium alginate	D-Sorbitol, polyethylene glycol, glycerol	Citric acid	Increased thickness, elongation at break and antioxidant capacity is reported with increased zein content but the water vapor permeability and tensile strength found decreased.	[78]
Cassava peel starch, chitosan,	Glycerol	-	Tensile strength of 96.04MPa, elongation at break of 52.27% and with 22.68% water resistance is reported	[79]
Agar, sodium alginate, & Inulin from chicory root	Glycerol	-	Films with high inulin showed high tensile and very high elongation property.	[7]
Seaweed gelidium sesquipedale, commercial grade agar	Glycerol	-	Better high humidity resistance retention of film structure in comparison with films with purified agar.	[9]
Cassava starch	Glycerol and PEG 300	Glutaraldehyde	Blends with PEG up to 0.3g showed good elongation. Blends with glycerol level above 1g showed increased WVTR. Blends having glutaraldehyde up to 0.5g showed lower water permeability	[15]
Agar, sodium alginate, stevia	Glycerol		The film showed good strength, good elasticity, high solubility and medium	[23]
Epoxidized broccoli seed oil (EBO)	-	Glutaric acid	Rubber type cross-linked materials reported low glass transition temperature (T_g) in the range of -5 to +5^{0}C	[24]
Methyl cellulose, chilean maqui (Aristotelia chilensis) berry fruit extract	Polyethylene glycol	Glutaraldehyde	Cross-linker decreased the water vapor permeability, water solubility, swelling and of film. With increase in the concentration of glutaraldehyde decrease in release of the antioxidant substances is reported	[31]
Guar gum, chitosan, polyvinyl alcohol, mint and grapefruit peel extracts	-	Tetra ethoxy silane	Increased tensile strength of 40.03MPa and elongation at break of 104.8% was observed. Films with maximum cross-linker (100µL) showed higher swelling and stability and optical properties.	[80]

Biopolymer material	**Plasticizer**	**Cross-linker**	**Properties of biopolymer after addition of Plasticizer/Cross-linker**	**Ref.**
Glandless cottonseed floor	Glycerol	Formaldehyde, glyoxal Glutaraldehyde	The resultant film was thermally stable, resistant to water absorption and readily biodegradable while showed fraction f heterogeneity in structure.	[81]
Pea starch, xanthan gum	Glycerol	-	Reduced tensile strength, puncture force and strain at break and crystallinity of the film was observed at increased concentration of glycerol. However, the increase in the elongation at break was observed	[82]
Durian seed starch, chitosan	Sorbitol	-	Optimization of mechanical properties of durian seed starch film observed at 70^{O}C heating temp.	[83]
Pea starch, bees wax	Glycerol	-	Addition of bees wax decreased water vapor permeation; tensile strength and increased O_2 permeation and elongation. At 40% concentration of bees wax showed dramatic higher thermal and physical properties of film.	[84]
Rice protein, potato protein, wheat gluten isolates	Glycerol	-	Film based on potato-protein showed complex values of modules compared to low density polyethylene.	[85]
Wheat starch, potato starch, corn starch	Anhydrous Glycerol	-	Potato starch based films showed better O_2 and water vapor barrier but weak mechanical properties than wheat and corn starch films.	[86]
Starch	Glycerol	Citric acid	The highest cross-link density with good integrity observed at 75^{0}C	[87]
Barley starch	Glycerol	-	The prototypes of amylase only starch showed a 6 times higher mechanical stress at break and 2.5 times higher strain at break compared to control sample	[88]
Rice starch and carboxymethyl Chitosan (CMCh)	Glycerol	-	CMCh addition improved the thermal stability of Rs-CMCh blended films. 50%w/w CMCh in to RS matrix showed increase in the tensile strength by 35% and elongation at break by 28% in the RS-CHCh blended film	[89]
Poly- hydroxybutyrate	-	Chitosan, vinyl alcohol, ethyl Cellulose	Insolubility in water and good UV resistance	[90]

Biopolymer material	**Plasticizer**	**Cross-linker**	**Properties of biopolymer after addition of Plasticizer/Cross-linker**	**Ref.**
Poly-hydroxybutyrate / blends Polylactic acid	Lapol 108	-	No phase separation in the PLA/PHB blend was observed. Additionally, the miscibility of PLA and PHB with plasticizer was examined using a elongation at break was enhanced due to the incorporation of the plasticizer.	[91]
Poly-lactic acid, Poly-hydroxybutyrate and cellulose nano-crystal blends	-	Dicumyl peroxide	The nano-composites and blends showed improved interfacial adhesion and enhanced the mechanical strength properties and the thermal stability.	[91]
Hemicellulose	-	Glyoxal or citric acid	Hemicellulose-based films showed improved moisture resistance	[92]
Cotton seed protein seed protein	-	Glyoxal	Glyoxal cross-linking improved the puncture strength of cotton seed protein-based films	[92]
Corn starch, high amylose corn starch, sunflower oil	Sorbitol, glycerol	-	Plasticizer addition showed improvement in water vapor barrier, while maintaining the selective gas permeability. Also improved mechanical property.	[93]
Poly (hydroxyl butyrate-co-valerate	Oligomeric polyester based on lactic acid, adipic acid, and 1,2-propanediol	-	Decrease in the melting point, glass transition temperature and stiffness are reported	[64]
Corn starch/chitosan	Glycerol	-	Decrease in the Tensile strength (TS) and increase in the elongation at break observed	[94]
Starch–carboxy methylcellulose	Rosemary essential Oil	-	Tensile strength decreased and elongation at break found increased.	[94]
Chia mucilage	Glycerol	-	Decreased tensile strength and Elongation and break is reported	[95]
Chitosan	Glycerol	-	Improved chain mobility, flexibility and strength of the film is reported	[96]
Gellan gum, 2-hydroxyethyl cellulose, and lignin	Glycerin	-	High ultraviolet UV, UVB (280–320 nm) and UVA (320–400 nm) protection observed in the composite films	[97]

1.3.2 Compatibilisation of Biopolymers

Applications of biopolymers are limited due to shortcomings such as inferior mechanical strength, poor thermal stability and higher processing cost. Moreover, the handling of most of the biopolymers is difficult at industrial scale due to their hydrophilicity, relatively high molecular weight, viscosity, crystallisation behavior, brittleness and melt uncertainty. These problems can be solved by forming the polymeric blends [98, 99].

The blending technology was developed mainly for modification of glass transition temperature, for improving fracture resistance, flexibility, processability, optical characteristics, flammability, impact resistance, biodegradability and other properties [22].

However, these blends may exhibit few inferior properties as compared with the synthetic polymers due to poor compatibility between the blended components [98, 99]. These problems can be addressed by introducing a small quantity of additive known as compatibilizing agent.

The use of compatibilizing agents in polymer blends dates to the 1960s [99]. Compatibilisation is the process in which a substance called compatibiliser is introduced in a blend of immiscible polymers to impart stability by making them compatible for blending. The compatibilisation improves the adhesion between blended components by facilitating the stress transfer from one phase to another phase. They also control the size of phase domains in the immiscible blends [98, 100].

In compatibilisation, the interactions between the polymer blends can be improved either by blending biopolymer with another biopolymer or by blending a biopolymer with another synthetic polymer having different structure and by introducing a predominantly charge interactions rather than hydrogen bonding [101]. The compatibilised blends of the biopolymers in some cases have shown better mechanical and oxygen barrier properties than conventional polymers. However, still in many cases, these biopolymers fail to compete with conventional polymers [98].

The thermodynamically immiscible polymer blends can be compatibilised by either reactive or non-reactive type of compatibilisation technology. In the reactive compatibilisation method, a compatibiliser which is miscible with one polymer and reactive with the functional group of other polymers is added for effective blending. For example, maleic anhydride can be effectively used as a reactive compatibiliser for blending polylactic acid and starch in which a free radical grafting of polylactic acid with maleic anhydride at one end and reaction with the hydroxyl group of starch at another end takes place. Compatibiliser having appropriate reactive group facilitates effective compatibilisation. Compatibilisers having different reactive groups are being used for compatibilisation of biopolymers. Schematic representations of the reactions of some of the reactive groups used in compatibilisation are shown in the Figure 1.5 [22, 98].

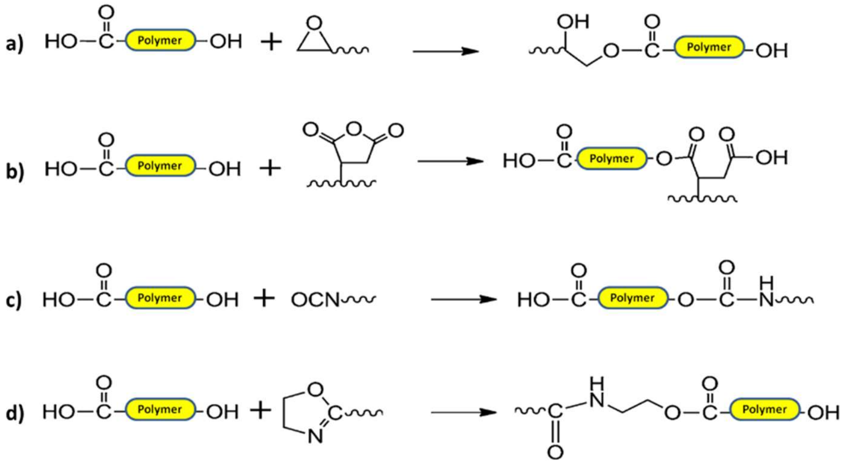

Fig. 1.5: Polymer Reactions with Different Reactive Group Compatibilisers a) Epoxy, b) Anhydride, c) Isocyanate & d) Oxazoline [98]

In the nonreactive compatibilisation method normally a pre-prepared block copolymer is added to the immiscible polymer blends. The block at the one side will get attach to the polymer which is miscible with the first polymer and the other block will get attach to the other end in which the second polymer is miscible.

Depending upon the requirements, the pre-prepared block copolymer may be either block copolymer (di-block/tri-block) or graft copolymer (Figure 1.6).

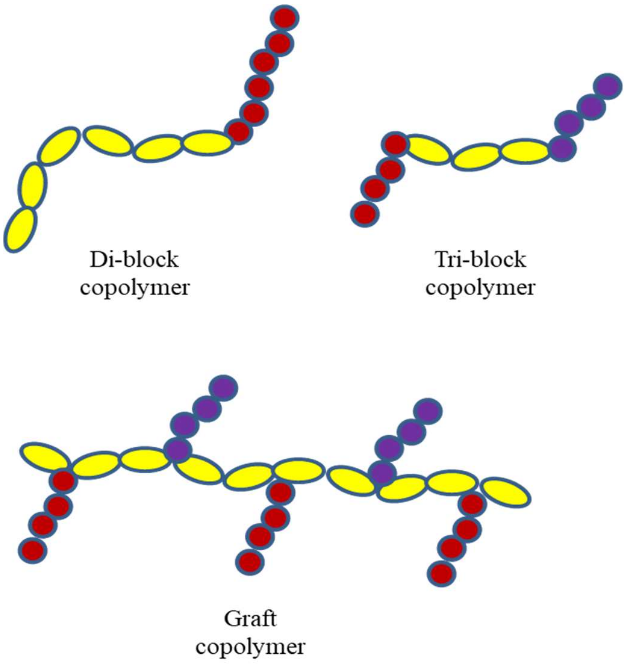

Fig. 1.6: Pre-Prepared Copolymers used in Compatibilization of Polymers [98]

The Polycaprolactone (PCL) – Polylactic acid (PLA) copolymer, Polycaprolactone (PCL)- Polyethylene glycol (PEG) copolymer and LDPE-PLA copolymer are some of the examples of the compatibilisers used in non-reactive compatibilisation technique. Both the reactive and nonreactive compatibilisation techniques are widely and effectively being used for compatibilizing various biopolymer blends [98].

The compatibilised biopolymer blends have the potential applications as a substitute for short shelf life products, including flexible and rigid packaging applications [98].

Many compatibilisers are being used for the processing of biopolymers using different processing methods. Examples of compatibilisers and processing methods used by different researchers to develop biopolymeric materials are illustrated in Table 1.3.

Table 1.3: Compatibiliser and Processing Methods Reported to Develop Bio-Polymeric Materials

Biopolymer matrix	Compatibiliser Used	Processing method	Key findings	Ref.
Starch	CO_2 colophony, EVA, glycerin, Dioctyl Phthalate	Compression molding	Packaging materials can be separated into CO_2 and H_2O after use by animalcule and H_2O and air.	[102]
Starch/ PLA	PLA grafted starch copolymer	Casting	Significant improvement observed in strain at failure for grafted St-g-PLA 25:75 blends	[103]
Starch/ PLA	PLA grafted starch copolymer	Compression molding	Increase in the tensile strength observed from 11.3MPa to 24.7Mpa and increase in the elongation observed from 1.5% to 8.7% in the 50/50 PLA/starch composite compatibilized using 10% PLA-g-st.	[104]
Starch/ PLA	PLA grafted GMA	Compression molding	Tensile strength at break increased from 18.6±3.8 MPa to 29.3±5.8MPa	[105]
Starch/ PLA	MA grafted PLA	Compression molding	MA grafted PLA blends showed much finer dispersion in the range of 1-3µm with increase in ductility.	[106]
Starch/ PLA	MA grafted TOA	Injection molding	PLA/starch blends showed improvement in the impact strength and toughness by enrichment of TOA on starch.	[107]
Starch/ PLA	HDI grafted starch	Injection molding	The improved toughness and impact strength were observed in PLA/starch blends	[108]
Starch/ PLA	Silane modified starch	Blown film	Increase in the tensile strength and elongation at break was observed.	[109]
Starch/ PLA	Starch grafted ROM	Extruded film	No impairment of the degradation values was observed.	[110]
Starch/ PLA	Maleinized Linseed oil	Injection molding	Increase in ductile property and elongation at break was observed.	[111]
Starch/ PLA	Epoxidized soybean oil	Injection molding	PLA/MGST/ESO (80/10/10) blend showed increase in elongation at break from 5% to 140%.	[112]
Starch/ PLA	Polyethylene glycol	Injection molding	Increase in the impact strength of ternary blend was observed by addition of PEG.	[113]
Starch/ PLA	Dioctyl maleate	Compression molding	Significant increase in the tensile strength was observed but not much change in the elongation at break was observed.	[114]
Thermoplastic starch/ PLA	GMA grafted poly (ethylene octane)	Compression molding	Impact strength and elongation and break were increased in ternary blends.	[115]
Thermoplastic starch (TPS)/ PLA	Maleated starch grafted PLA copolymer	Compression molding	Remarkable increase in the mechanical properties of the blends observed in PLA-g-MTPS with low pH of peroxide	[116]

Biopolymer matrix	**Compatibiliser Used**	**Processing method**	**Key findings**	**Ref.**
Starch/ PBS	PBS- grafted starch copolymer	Compression molding	PBS grafting resulted in drastic change in crystallization.	[117]
Starch/ PBS	MA grafted PCL	Injection molding	Significant increase in the strength was observed by addition of compatibilizer in small amount.	[118]
Starch/ PCL	PCL grafted starch Copolymer	Casting	Compatibilized PCL/starch improved the tensile strength and rate of biodegradation.	[119]
Starch/ PCL	MA grafted PCL	Injection molding	Increase in the water resistance of PCL-g-MAH/starch was observed	[120]
starch/ PBAT	Styrene-maleic anhydride-GMA ter-polymer	Blown film	Increase in the tensile strength and elongation at break was observed in the blends of PBAT/TPS	[121]
Starch/ PBAT	MA grafted PBAT	Extrusion foam	Improved resilience from 84% to 95% was observed in addition to increase in hydrophobicity.	[122]
Soy protein/ PCL	Methylene diphenyl di-isocyanate	Compression molding	Decrease in the T_g of Soy protein isolate was observed with increase in the PCL contents having 2% MDI	[123]
Soy protein isolate/ poly (lactic acid)	Triacetin (SPI/PLA–TA)	Injection molding	The blends showed good release properties as compared to pure NPK fertilizer were observed	[124]
Soy protein concentrate/ PLA	Poly(2-ethyl-2-oxazoline) and polymeric MDI	Injection molding	6% higher tensile strength was observed with 1 part pMDI	[125]
Soy protein concentrate/ PBAT	MA grafted PBAT	Injection molding	In the percolated SPC structure yield stress, tensile strength and elastic modulus was increased but the yield strain and strain at break was reduced.	[126]

Abbreviations: CO_2, carbon dioxide; DOP, dioctyl phthalate; EVA, ethylene-vinyl acetate; GMA, glycidyl methacrylate; HDI, hexa-methylene di-isocyanate; MA, maleic anhydride; PBAT, polybutylene adipate-co-terephthalate; PBS, polybutylene succinate; PCL, polyε-caprolactone; PLA, poly-lactic acid; ROM, ricinoleic oxazoline maleate; TOA, tung oil anhydride.

1.4 Packaging Applications of Different Biopolymers

Packaging protects and preserves the product from its manufacturing point till its consumption by preventing the chemical and physical damage of the product. It also maintains the unique freshness of the product without altering the inherent characteristics of the product and thus becomes important in today's commerce and trade [2, 127, 128].

The contemporary packaging, in addition to protecting the products from its external environmental factors and extending the shelf life by maintaining the quality of the product, should also minimise their impact on the environment [25].

Packaging being an important section in food processing industry, the researchers are getting attracted towards the biopolymeric films for food packaging applications as an answer to the disposal problems posed by conventional polymer packaging [101].

The biopolymers are increasingly used in food and consumer goods packaging, which are categorised as environmental friendly packaging materials [12, 29, 45, 53, 129, 130]. The major markets where the biopolymers can emerge are food, nonfood, personal and healthcare products and other consumer goods packaging [13].

Variety of agricultural commodities and food waste can be utilised for developing biopolymer-based coatings and films. These include starch, proteins, lipids, gums, chitin and cellulose derivatives [131]. Various biopolymers derived from proteins, polysaccharides, lipids and its derivatives are being widely used for various applications in packaging of food products [29, 132].

Polysaccharide-based polymer films provide suitable optical properties and moderate mechanical properties at low relative humidity. Polysaccharide-based films are being preferred in some applications due to their good film-forming property, colloidal nature and moderate moisture and oxygen permeability. The polysaccharide-based natural biopolymers are also preferred for edible coatings and film as a shelf life extender. Blends of proteins and polysaccharides-based biopolymer films generally express good mechanical properties and better gas barriers. However, they are poor moisture barriers because of their hydrophilicity. The edible films of polysaccharide, protein and lipid blends can be used as oxygen and/or moisture barriers which can maintain the food quality.

The composite packaging films based on polysaccharide-lipid matrix in the emulsion or laminated forms provide combined properties of both polysaccharide and lipid, that is, structural integrity with oxygen barrier and also the moisture barrier [132–136]. Silver nanoparticles can be reinforced in polysaccharide and protein-based matrices for developing active packaging for food [10]. Various chitosan-synthetic polymer blends can be used for food packaging due to their film forming ability, low toxicity and bacteriostatic action [137].

Biopolymers are increasingly used in the field of food and consumer goods packaging [12]. The biopolymers are used in different forms, namely, as coatings for many food products where it can be directly applied on the food and as films in the form of bags, envelops, transparencies, containers, lids and so on [29]. Potentially, the biopolymeric packaging materials are available in the form of disposable packaging materials, consumer goods like plates, cups, containers and boxes, for day-to-day use and personal care disposable products like napkins, diapers and sanitary pads, coatings, lamination materials and bags used for agricultural mulching [138]. They are also being used as carriers for many functional ingredients like antioxidants [29], antimicrobial agents [29], antifungal agents [132], flavours [139], colourants [139] and other nutrients [140], for improving the functionality of the targeted packaging material. The biopolymer-based films can be used as selective barriers for moisture, gas and migration of the solute [139].

Many biopolymers have shown improved mechanical strength and barrier to oxygen, aroma and flavours by use of additives. In addition, they offer better biodegradability and environmental friendliness [132, 141]. The biopolymers reduce the disposability problems posted by conventional polymers and thus can replace synthetic polymers in many applications [142].

Today, owing to their renewability and eco-friendliness in terms of biodegradability, biopolymers and their composites have received remarkable attention and cover a considerable global market in packaging, agricultural and medical field. However, it is still in the premature stage [26]. The packaging material in the future will be based on renewable resources [143].

Based on the literature, it was observed that the various biopolymers developed by researchers are being used for many applications. Table 1.4 gives the tensile strength and water vapour permeability values and elongation at break for some of the biopolymers [36, 144]

Table 1.4: Tensile Strength and Water Vapour Transmission Rate (WVTR) Values and Elongation at Break for Some of the Biopolymers

Biopolymer	Tensile Strength (MPa)	WVTR ($g/m^2/24hrs$), at (38 °C), 90% R.H.	Elongation at break (%)
Starch	4.8–8.5	7.8–9	35–100
Cellulose/Bacterial Cellulose	13–59	4.6–9	4–10
Chitosan	38–77	0.5–1.3	17–76
Polylactic Acid	44	27–50	30.7
Gelatin	17	290	20
PHB	25	1.16	5
PHBV	40	10	2.3
Myofibrillar	5.41	251	2.5
Protein isolate/gelatin blend	13.98	64	3.3
Protein isolate	0.6	28	11.6
Myofibrillar/gelatin blend	6.5	384	2.7
Myofibrillar/glycerol/tannic acid	3.9	94	15
Myofibrillar protein/Sorbitol	12.5	66	3.0

It was also observed that a wide category of biopolymers have been developed by many researchers in various forms like coatings, films and containers, for various applications in packaging [144]. Various biopolymer films and coatings are being used as better alternatives to their synthetic counterparts.

Further, addition of natural active agents like essential oils to the biopolymers has shown improvements in their mechanical, barrier, thermal and other functional properties like antimicrobial and antioxidant properties of these composite films and coatings [54, 145]. Various marine biopolymers like alginate, gelatin and chitosan are being effectively used to improve the quality as well as shelf life of the packaged products [146]. Table 1.5 represents such biopolymer films and coatings and their respective applications in packaging.

Table 1.5: Packaging Applications of Biopolymer Films and Coatings

Biopolymer matrix	**Probable application in packaging**	**Comments/Major findings**	**Ref.**
Casein, whey protein concentrate	Cheddar cheese	Casein film showed superior tensile and barrier properties than whey protein concentrate films	[127]
Corn zein	Fresh broccoli	Showed gas barrier suitable for modified atmosphere packaging for 6-day shelf life	[147]
Corn and wheat protein	Fresh foods	The films had low tear strength, low tensile strength and low gas permeability but relatively higher water vapor permeability.	[148]
Chitosan, cellulose, and polycaprolactone	MAP for sweet corn, head lettuce, whole broccoli, cut broccoli, blueberries and tomatoes	The gas permeability coefficients of the laminate linearly increased with increase in temperature.	[149]
Poly-lactic acid	Green peppers	During storage period No remarkable changes in the hardness, color, microbial levels, ascorbic acid concentration was observed.	[150]
Poly-lactide	Blueberries	At different storage temperatures, the containers showed prolonged shelf life	[151]
Banana flour and chitosan	Asparagus, baby corn, and Chinese cabbage	Protection against the microbial activity was observed in Chinese cabbage baby corn and asparagus.	[152]
Methylcellulose, polycaprolactone, and alginate	Broccoli	Significant reduction of in E. coil and L monocytogenes at short term storage of 4 days was observed.	[153]
Starch based	Tomatoes	The redness of the tomatoes increased but the flavor and firmness of the tomatoes decreased during storage.	[154]
Chitosan and Na-caseinate	Carrot slices, cheese and salami	The bactericidal properties of the blend of CH/SC found increased.	[155]
Chitosan, methylcellulose, and vanillin	Fresh cut pineapple and cantaloupe	The moisture content level and maintained the intensity of yellow color of pineapple. However, the ascorbic acid content was reduced.	[156]
Wheat gluten, bees wax, stearic and palmitic acids	Strawberries	Retention of firmness, reduced the weight loss was reported for bi-layer coating of wheat gluten and lipids.	[157]

Biopolymer matrix	**Probable application in packaging**	**Comments/Major findings**	**Ref.**
Alginate/nano-crystalline cellulose	Food products	37% increase in the tensile strength of alginate films by just 5% loading with nanocrystalline cellulose. The thermal stability was also increased.	[158]
Alginate/starch	Precooked ground beef patties	Films treated with tocopherol ($P<0.05\%$) inhibited lipid oxidation more effectively than non tocopherol based films. SAS films ($P<0.05\%$) found better in controlling moisture loss than lipid oxidation.	[133]
Agar/nano-crystalline cellulose/savory essential oil	Fresh cut pineapple	Coating formulation containing lemongrass 0.5% (w/v) significantly ($P<0.05$) lowered the firmness of fresh and sensory scores of fresh cut pineapples.	[158]
K-carrageenan/ montmorillonite/zataria multiflora biomass essential oil	Antimicrobial packaging for food	Tensile strength and elongation at break of Kappa-carrageenan film significantly improved by addition of nano-clay and ZEO	[159]
PLA/PEG/chitosan	Food products	Addition of chitin nano-fibrils reinforcement filler up to 12% by weight did not alter the properties of the material.	[160]
PLA/cellulose	Packaging	It was evident that the compatibilization improves tensile strength and charpy impact of polymeric matrix and fibers.	[161]
PVA/chitosan	Food packaging	Change in fiber morphology and decrease in the diameter was observed.	[162]
Wheat gluten and methylcellulose	Fresh kashar cheese	Reduced spore count in the cheese was observed in the Methyl cellulose film containing 5-20mg Natamycin per 10g. Wheat gluten film eliminated Aspergillus niger on the surface of cheese.	[163]
Potato starch and Chitosan with niacin and citric acid	Raw chevron chunks	The composite films of starch-chitosan with cinnamaldehyde impregnation extended the shelf life and inhibited the color, and also controlled the oxidative and microbial deterioration.	[164]
Tapioca starch with natamycin	Port salut cheese	The addition natamycin controlled the growth of microorganisms on the cheese surface during their storage.	[165]
Chitosan, maleic anhydride grafted LDPE	Tilapia fish fillets	Storage quality indices in Chitosan incorporated composite films showed good antibacterial properties and extended shelf life.	[128]

Biopolymer matrix	**Probable application in packaging**	**Comments/Major findings**	**Ref.**
Corn starch, LLDPE with citric acid	Grounded beef	Addition of high concentration of starch reduced the ultimate tensile strength, elongation at break and modulus of elasticity in the blends. Also increase in the solubility and the degree of swelling was observed with increase in the starch content.	[166]
Gelatin alone or in combination with chitosan with oregano rosemary essential oil	Sardine	The combination of edible films and high-pressure processing showed prevention of oxidation and inhabitation of microbial growth.	[167]
Chitosan with lemon essential oil	Strawberry	Addition of lemon essential oil improved the antifungal activity of Chitosan film during cold storage of strawberry inoculated with botrytis cinerea.	[168]
Alginate with lemongrass essential oil	Apple	Significant browning of fresh cut fuji apple was observed on fruits with high Leo coating concentrations (0.5 or 1% v/v)	[169]
Poly-hydroxy alkanoates	Garbage bags, shopping bags, food packaging, diaper packaging	Compostable films with easy processing, good UV and water resistance.	[90, 91]
Corn starch, chickpeas, lentils, etc.	Edible film for foods wrapping	Good film formation observed with higher content of protein and starch.	[170]
Corn, potato, wheat and rice Starch	Wrapper after some Modifications	Good barrier for O_2 and CO_2, water insoluble, Clear and tasteless film but poor mechanical strength.	[170]
Carboxymethyl cellulose, cellulose acetate, methyl cellulose, ethyl cellulose, hydroxypropyl, hydroxyethyl cellulose, cellophane,	Packaging of meat products, confectionary, and cheese.	Good mechanical strength but Poor moisture resistant.	[170]
Chitosan–gelatin	Beef steak	After 5 days storage the lipid oxidation found lowest in the beef steaks and also the color stability found improved. reduced weight loss observed during the refrigerated display	[146]
Myofibrillar protein–catechin–Kardon extract	Blue fin tuna slices	Longest shelf-life of 8 days observed with inhibited lipid oxidation and lowest psychrophilic bacteria growth.	[146]
Chitosan–apricot kernel essential oil	Bread	Improved moisture barrier and water vapor barrier. Inhibition of fungal growth and better mechanical properties	[146]

Biopolymer matrix	**Probable application in packaging**	**Comments/Major findings**	**Ref.**
Pectin from apple pomace and citrus peels	Food Packaging	Edible film with adaptable chemical and physical properties and biocompatibility and biodegradability.	[55]
Whey from Milk, yogurt and cheese	Food Packaging	Excellent O_2 and aroma barrier with oil resistance	[55]
PLA/poly butylene adipate-co-terephthalate (PBAT)	Passion fruit wrapping	Improved preservation of edible, sensory and flavor quality during storage for 21 days at $20^{O}C$	[171]
PLA films containing oregano essential oil	Iceberg salad	Better antimicrobial activity of edible oils against mold and yeast for 7 days at $4^{O}C$	[171]
PLA/PHB with fennel oil	Film wrapping of Oysters	Shelf life prolongation of 2-3 days in comparison to EVOH films (storage of 16 days at $4^{O}C$)	[171]
Carboxymethyl cellulose with Thai rice grass extract	Green tea	Shelf life increased from 32 days to 37 days in CMC and from 32 days to 44 days in HDPE at $10\,^{O}C$, $30\,^{O}C$, and $70^{O}C$ for 25 days storage.	[171]
CMC/gelatin	Cherry tomatoes and grapes	Weight loss reduced from 26.2% to 20.5%, browning index reduced from 164 to 75 by addition of tannic acid.	[171]
PHB/PCL/organo-clay nano-composites with niacin	Meat Packaging	Inhibited effect of Lactobacillus plantarum with shelf life extension.	[47]
Polylactic acid	Loose-fill packaging, compost bags, food packaging	Good compostability and probable applications in food packaging	[172]
Alginate	Fruits and Vegetables	Shelf life with improved quality of fruits and vegetables	[32]
Ceiba pentandra bark fibers and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)	packaging of fresh strawberries	Enhanced tensile strength, % crystallinity, and biodegradability of the composite compared to virgin PHBV.	[173]
Chitosan, Micro/nano clay	Food packaging	Good moisture barrier properties	[96]
Carrageenan/locust bean gum/organically modified nano clay	Shelf life extension of food	Films with 16wt% C30B composition in k-car/LBG exhibited good mechanical properties and enhanced antibacterial activity and water barrier.	[174]
Agar/nano clay	Biodegradable food packaging	Increase in tensile strength was observed with increase in clay content up to 10% and decreased with more clay content.	[175]

Biopolymer matrix	**Probable application in packaging**	**Comments/Major findings**	**Ref.**
Alginate/lemongrass essential oil	Shelf life extension of fresh cut melon	Edible coatings of malic acid were effective in extending shelf life of fresh cut melon.	[176]
Chitosan and whey protein coating	Un-ripened creamy ricotta cheese	The Chitosan/whey films showed 35% lower O_2 transmission rate and 21% Co_2 transmission rate but 3 times more water vapor transmission rate than Chitosan films.	[177]
Alginate/CaCl2	Rainbow trout fillet	The edible coating along with antimicrobial agent decreased the bacterial, yeast, and mold growth.	[178]
Alginate	Fresh cut Apple	Shelf life of coated apples was prolonged three times. Edible Coating maintained the firmness, but increased fermentative metabolites (acetaldehyde and ethanol) production.	[179]
Galactomannan with niacin	Ricotta cheese	Decrease in the O_2 permeability from 1.84 to 1.35 x 10^{-32} $Cm^3.(pa.s.m)^{-1}$; Co_2 permeability from 1.96 to 6.31 x 10^{-32} $Cm^3.(pa.s.m)^{-1}$ but increase in the opacity from 3.68 to 4.59%, elongation at break from 50.93 to 68.16%.	[179]
CMC+ Chitosan	Broccoli	Use of edible coating of Chitosan and carboxymethyl cellulose on broccoli the microbial load dropped by 1.5 and 0.9 logarithmic units respectively.	[180]
Gelatin, $CaCl_2$, and carboxymethyl cellulose	Low fat pork sausages slices	The gelatin coated low fat sausages showed less moisture loss by 32.6% but did not inhibit the growth of L. monocytogens or total plate counts.	[181]
Alginate with acrylic acid and citric acid	Fresh cut mango	The alginate with anti-browning agent preserved the original color or fresh cut mangoes and also showed increase in antioxidant potential.	[182]
Modified maize starch with oregano essential oil	Fresh pork osmotically dehydrated in Sugar beet molasses solutions	Sugar beet molasses improved stability during refrigerated storage and increased shelf life of pork meat.	[183, 184]
Chitosan	Chicken breast fillets	In the air-packed samples, decrease in color parameter L* with time was observed. A* and b* values were not affected much by Chitosan or MAP.	[185]
Carboxymethyl cellulose and polyvinyl alcohol with clove essential oil	Ground chicken meat	Increase in the PVOH concentration showed higher puncture resistance and tensile strength. Exhibited lower viable counts and 12 days shelf life.	[101]

Biopolymer matrix	**Probable application in packaging**	**Comments/Major findings**	**Ref.**
Methylcellulose with Pimpinella affinis essential oil	Fresh Silver carp fillets	Methylcellulose coating with 1.5% pimpinella affinis oil gives good antioxidant activity.	[186]
Sodium alginate with potassium sorbate	Fiordilatte cheese	The combined effect of active coating with Modified atmosphere packaging enhanced the shelf life of fiordilatte cheese up to 10 days.	[187]
Sodium alginate with silver nano-particles	Fiordilatte cheese with and without brine	The active coating helped in gas solubilization damage and also increased shelf life by 157%.	[188]
Chitosan with Cinnamomum essential oil	Cucumber	The fruits coated with Cinnamomum zeylanicum essential oil were firmer while maintaining the color and water content. It also showed the lower microbial count ($P<0.05\%$) during storage period.	[189]
Starch with montmorillonite	Cashew nuts	At the lower concentration (5-10g/100g) of montmorillonite showed increase in the tensile strength and elastic modulus. However, the higher concentration adversely affected these properties.	[190]
Whey Protein concentrate with lacto-peroxidace system	Rainbow trout fillets	The shelf life extension reported from 12 days to 16 days in presence of lacto-peroxidase system.	[191]
Chitosan/polyvinyl alcohol with titanium nanoparticles	Soft white cheese	The composite showed good mechanical properties and antibacterial activity against gram positive bacteria and fungi. Mold count, coliform, mold and yeast decreased with increased storage time and then disappeared at the end.	[192]
Gellan gum with Ca^{2+}	Mango bar	The gellan gum edible coatings improved sensory characteristics and stability during storage.	[193]
Polyhydroxy alkanoates	Coating on boxes, paper, paperboards	Good degradability and flexibility for coating applications	[90]
Gum arabic, gum karaya, gum ghatti, mesquite, etc.	Edible coatings, strawberries, tomatoes, and pecan nuts.	Good physical, chemical and biological properties. Can be potentially used for edible film formation,	[170]
Chitosan with Silver, Zinc oxide, Montmorillonite	Food packaging	Moisture barrier (zinc oxide), antimicrobial activity (silver) and mechanical strength (montmorillonite).	[96]

Based on Table 1.5 above, the packaging applications of the biopolymer films and coatings are summarised in Figure 1.7 and Figure 1.8 respectively.

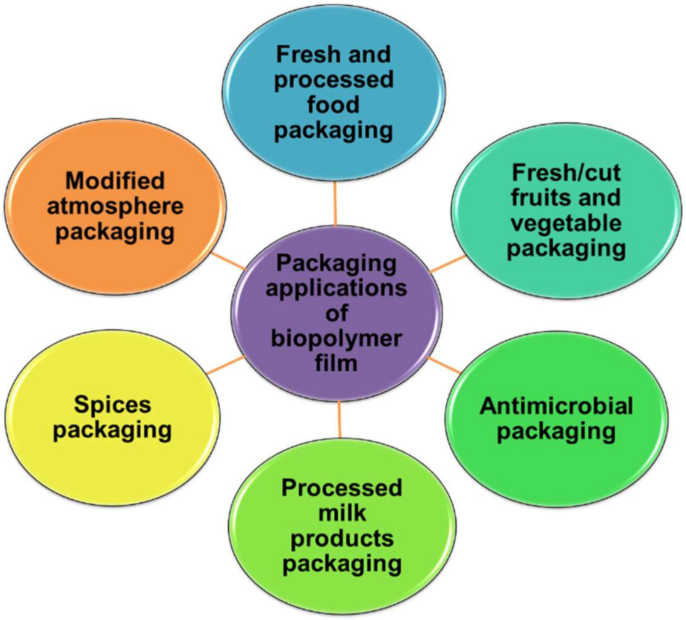

Fig. 1.7: Packaging Applications of the Biopolymer Films

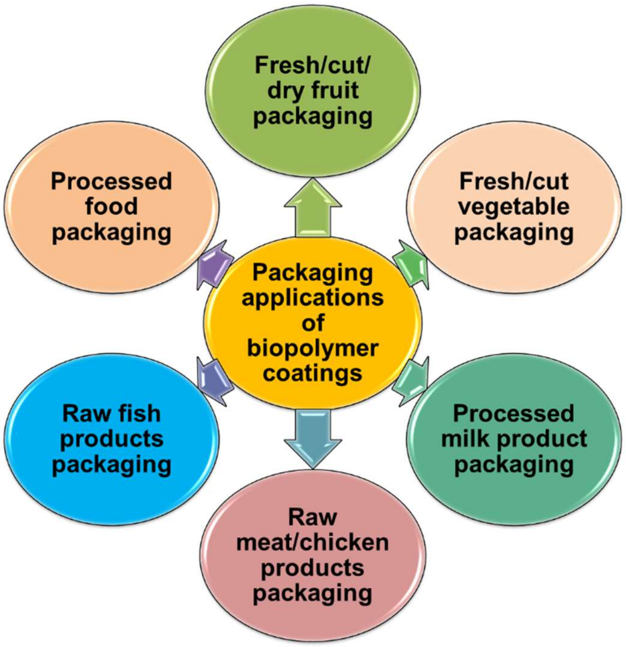

Fig. 1.8: Packaging Applications of the Biopolymer Coatings

1.5 International Standards Available For Testing and Certification of Biopolymers

As discussed above, the biopolymers have increasing demand and applications in the future. However, biopolymers could be equally problematic in the future, and thus, these polymers, therefore, require to be assessed for their biodegradability using harmonised assessments [194].

Additionally, many biopolymers have been derived from different bio-based materials. However, today, many conventional polymers like PET, PVC and polyamides are also being derived from bio-based sources. Thus, the terms biodegradable and bio-based are being used interchangeably leading to confusion. Therefore, to clear the confusion, the polymers can be tested and certified.

Certification of the biodegradable polymers is possible as per the procedure laid down in different internationally accepted standards ASTM D6400, ASTM D5338, ISO 17088, ISO 14855, AS 4736, EN 14995, EN 13432 and so on in which the compostability of the polymer is measured under specific conditions.

Similarly, for the certification of bio-based polymers which are biodegradable or non-biodegradable, EN 16640, ISO 16620-4, ASTM 6866-18 and EN 16785-1 can be referred which is based on measuring the bio-based content using ^{14}C measurements [28, 195].

Similarly, DIN 54900 is for testing the compostability of plastics and JIS K 6953 is for determination of the ultimate biodegradability and disintegration of plastic materials [196, 197]. A comprehensive list of the standards published by the important standardisation bodies on biopolymers is listed in Table 1.6.

Table 1.6: Standards Published by Important Standardization Bodies on Biopolymers

Reference standard	Scope of the standard	Ref.
ISO 17088	Specifications for compostable plastics	[34]
ASTM 6866	Determination of bio-based mass using radiocarbon analysis	[34]
EN 14995	Determination of compostability	[34]
ISO16620-4	Determination of bio-based mass by radiocarbon/elemental analysis.	[28]
EN 16640	Determination of the bio-based carbon content by radiocarbon method	[28]
EN16785-1	Determination of bio-based content using elemental analysis/radiocarbon analysis	[28]
ISO 14855; Part 1 & 2	Determination of biodegradability/disintegration under controlled composting conditions by analyzing evolved CO_2	[28, 195]
ISO 16929	Determination of the degree of disintegration under defined composting conditions	[195]
ISO 20200	Determination of the degree of disintegration under simulated composting conditions	[195]
ASTM D5338	Determination of biodegradation under controlled composting conditions	[195]
ASTM D6400	Standard specification of compostable plastics materials	[195]
EN 13432	Requirements for packaging recoverable through composting / biodegradation	[195]
ASTM D5511-18	Determination of biodegradation under high-solids anaerobic-digestion conditions	[198]
ASTM D5338- 15	Determination of biodegradation under controlled composting conditions, Incorporating thermophilic temperatures	[198]
ASTM D5988-18	Determination of biodegradation in soil	[198]
ASTM D5526-18	Determination of biodegradation under accelerated landfill conditions	[198]
AS 4736	Suitability of biodegradable plastics for composting and other microbial treatment	[199]
DIN 54900	Testing of the compostability of plastics	[196]
JIS K 6953	Determination of ultimate biodegradability and disintegration of plastics under controlled composting conditions	[197]

1.5.1 Life Cycle Analysis (LCA)

The LCA is a cradle-to-grave approach developed for quantifying the total environmental impacts of the entire value chain of alternative product or systems during its life cycle. ISO Standards ISO 14000, 14040, 14041, 14042 and 14043 provide guideline for using life cycle assessment. The methodology can be applied to study the performance of bio-based products in their manufacturing, use, disposal or recovery and may involve the following four stages [200–202]:

- **Stage-I** (Goal and scope setting): In this stage, the goal and scope of the study can be defined.
- **Stage-II** (Inventory analysis): In this stage, the environmental inputs like raw materials, water and energy and outputs like products and by products. It also releases pollutants to land, water and air associated with the product during its entire life cycle can be identified and quantified.
- **Stage-III** (Impact assessment): In this stage, the inputs and outputs from stage II are described with respect to their environmental impacts like resource depletion, ozone depletion, global warming, toxicity and degradation of ecosystem.
- **Stage-IV** (Interpretation): In this stage, the results of the study are interpreted for stated goals and scope of the study.

In the various LCA studies conducted, the bio-based polymers generally performed better compared with the petroleum-based polymers in various aspects. However, a comprehensive life cycle assessment is very essential to support this statement [200, 202, 203].

1.6 Conclusion and Social Impact

The growing concern about the environmental issues such as resource depletion, recycling and biodegradation has led to the development of novel environmentally friendly packaging materials. Biopolymers based packaging materials have emerged as a promising alternative to traditional plastics particularly in food and packaging industry. The literature survey, reveals a wide variety of biopolymer-based materials that have been successfully developed and used for packaging applications. These packaging materials are continuously being modified using different conversion technologies to enhance their properties and performance. The modifications in synthesis include the addition of plasticisers, cross-linkers, compatibilisers, synthetic polymers and other additives to meet the desired end-user applications and degradability. Owing to their renewability and eco-friendliness in terms of biodegradability, biopolymers have acquired significant interest in formulating products that provide value in today's global market.

The current trends in biopolymers have opened a new direction and have made it possible to produce biopolymer-based packaging on a commercial scale. However, the development of biopolymers and their composites is still in the premature stage, still further research in the field of developing newer biopolymers and modifying the properties of already developed one to further meet the required mechanical strength, barrier properties, including easy commercial production, suitable conversion technology and post-use issues if any.

Therefore, it is important to develop the biopolymers with competing performances with those of conventional polymers to meet the requirements of packaging industry. Great efforts therefore are being made to modify the biopolymers so that they can be used for various packaging applications on commercial scale. It is opined that with the continuous ongoing research in the development of the newer categories of biopolymers and with the developments in the manufacturing and conversion technologies, the future will definitely witness the growth in the acceptability of biopolymers in the field of packaging, and packaging materials of the next generation will be derived from renewable resources.

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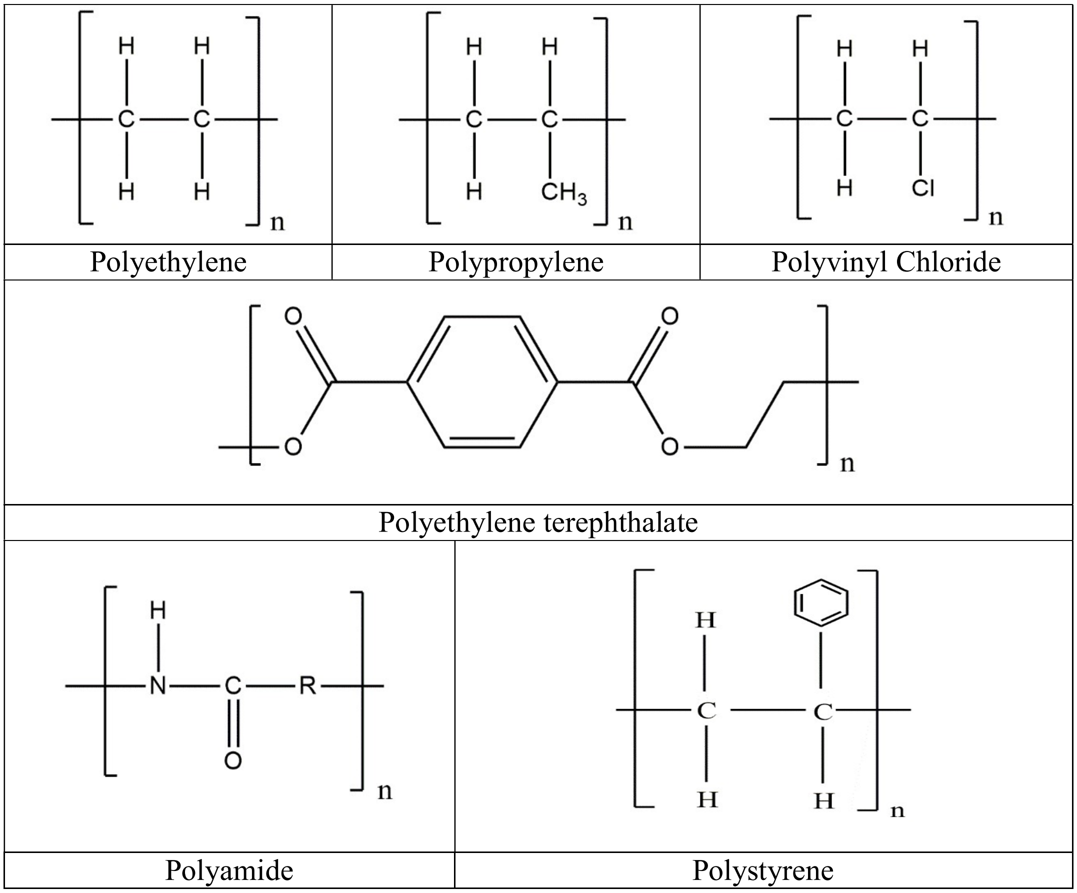
CHAPTER 2

FABRICATION AND CHARACTERIZATION OF CARBOXYMETHYL GUAR GUM BASED FILMS

2.1 Introduction

Packaging serves a pivotal role in safeguarding and extending the shelf life of products until they reach the end consumer. Conventional packaging relies heavily on synthetic polymers derived from petroleum, such as polyethylene (PE), polypropylene (PP), polyester (PET), polyamide (PA), polyvinylchloride (PVC), and polystyrene (PS) [1–3]. Structures of these widely used synthetic polymers in packaging are given in Figure 2.1 [4, 5].



Polyethylene

Polypropylene

Polyvinyl Chloride

Polyethylene terephthalate

Polyamide

Polystyrene

Fig. 2.1: Structures of widely used Synthetic Polymers in Packaging

These polymers are used in various forms and are preferred for their cost-effectiveness and beneficial properties such as good mechanical strength and effective barrier characteristics against aroma, gases, and water. Despite these benefits, the disposal and recycling of petroleum-based polymers pose significant challenges. The global annual generation of approximately 1.3 billion tons of plastic waste worsens environmental issues, underscoring the need for sustainable alternatives in packaging solutions [1, 6].

In recent years, due to the comeback of the environmental challenges posed by conventional packaging, research has shifted towards exploring the application of biopolymers for packaging purposes.

Various biopolymers due to desired properties provided by them are seen as a sustainable option for replacement of synthetic polymers for various packaging applications. The global trend of biopolymer production is expected to increase from 2.11 MT from 2020 to 2.87 MT in 2025 [3]. Biopolymers are sourced from natural materials and possess excellent biodegradability, making them more environmentally friendly [1, 6]. Biopolymers, also referred to as generation-IV packaging materials, are utilized in various forms, serving as coatings directly applied to products, as well as in the fabrication of films for items like bags, envelopes, containers, and lids. They present a promising alternative to petroleum-based synthetic polymers [6–9].

Researchers are exploring a diverse range of biopolymers derived from natural resources, including polysaccharides, proteins, and lipids, as well as those synthesized from bio-derived monomers like polylactic acid, and also those synthesized by microorganisms, such as polyhydroxyalkanoates [8].

While these biopolymers exhibit excellent film-forming characteristics, their inherent brittleness and high water absorption capacity necessitate modification through the addition of plasticizers and cross-linkers for easier handling and commercial processing. Incorporating plasticizers like glycerol enhances film flexibility by reducing intermolecular forces, and the introduction of cross-linkers, like citric acid, improves the tensile strength of the films. This research marks a significant step towards sustainable packaging alternatives, addressing the ecological impact of traditional petroleum-based polymers [8–14].

The biopolymer-based films and coatings represent a significant stride towards sustainable packaging solutions, employing materials such as alginate, chitosan, cellulose, guar gum, and starches. Notably, in our exploration of biopolymer-based materials for packaging applications, it has been observed that carboxymethyl guar gum (CMG) has yet to be used for the synthesis of biopolymer-based packaging materials. This underscores the potential novelty and unexplored possibilities in incorporating CMG into the realm of eco-friendly packaging solutions [1, 6, 10–33]

Figure 2.2 shows the structure of carboxymethyl guar gum. It is a water-soluble biopolymer, derived through the reaction of guar gum with monochloroacetic acid in the presence of sodium hydroxide (NaOH) [34–36]. This versatile derivative finds applications across various industries, like oil recovery, paints, minerals, personal care, textiles, and food [37]. It is revealed that, due to presence of carboxyl and hydroxyl groups in the CMG backbone, it can be easily cross-linked, grafted, or blended with other polymers, leading to effective film formation [38]. This excellent film-forming property of CMG opens up various applications, particularly in areas like packaging.

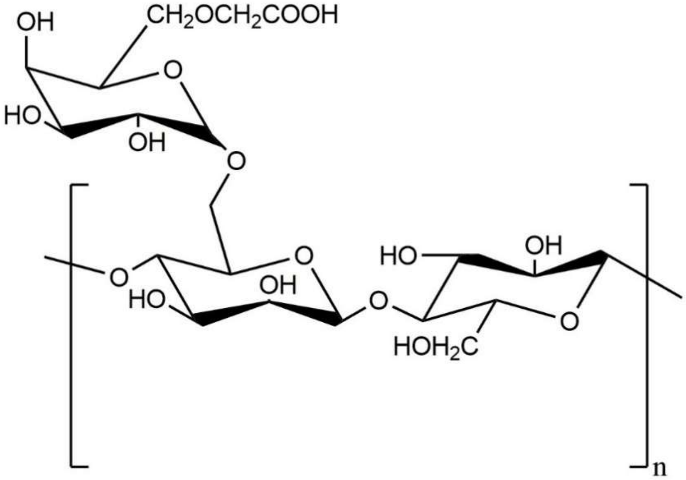


Fig. 2.2: Structure of Carboxymethyl Guar Gum

The current study proposes the development of various carboxymethyl guar gum-based films via solvent casting technique, for packaging applications. The varying amounts of glycerol (plasticizer) and glutaraldehyde (cross-linker) were employed in the fabrication of films, and the films were characterized thoroughly using Themogravimetic Analysis (TGA), Scanning Electron Microscopy (SEM), Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR), and differential scanning calorimetry (DSC) techniques.

2.2 Materials and methods

For fabrication of novel CMG based films, carboxymethyl guar gum (CMG) 0.68 degree of substitution Maruti hydrocollides, Ahmedabad, India, glycerol (Gly), Merck Life Sciences Private Ltd., India, and gluteraldehyde (Glu) solution, Central Drug House Pvt. Ltd, India, all used as obtained. Double distilled water was utilized for solution preparations and washing purposes.

2.3 Fabrication of CMG-Based Film

The series of a total 64 variants of CMG-based films as shown in Table 2.1 were fabricated by employing the different concentrations of glycerol (0 ml, 0.1 ml, 0.25 ml, 0.5 ml, 1 ml, 1.25 ml, 1.5 ml, and 2 ml) as a plasticizer and glutaraldehyde (0 ml, 0.1 ml, 0.25 ml, 0.5 ml, 1 ml, 1.25 ml, 1.5 ml, and 2 ml) as a cross-linker, via solvent casting technique at two reaction temperatures (70 °C and 75 °C).

The fixed amount (1g) of CMG was dispersed in 100 ml of distilled water at room temperature. Then, the desired volume of glycerol was added to the dispersion under stirring and heating at 70 °C on magnetic stirrer. It was then followed by the addition of glutaraldehyde to the above mixture under continuous stirring and heating. After 45 min, the resultant mixtures were immediately cast in an acrylic tray with dimensions (200 mm×150 mm×5 mm) and allowed to air dry at 25 °C for 24 h and then transferred to a hot air circulating oven maintained at 60±5 °C for another 24 h. The dried films were then peeled off and stored at 25 °C. Figure 2.3 shows the schematic representation of the fabrication of the CMG-based films. The same procedure was repeated for casting the films at temperature of 75 °C.

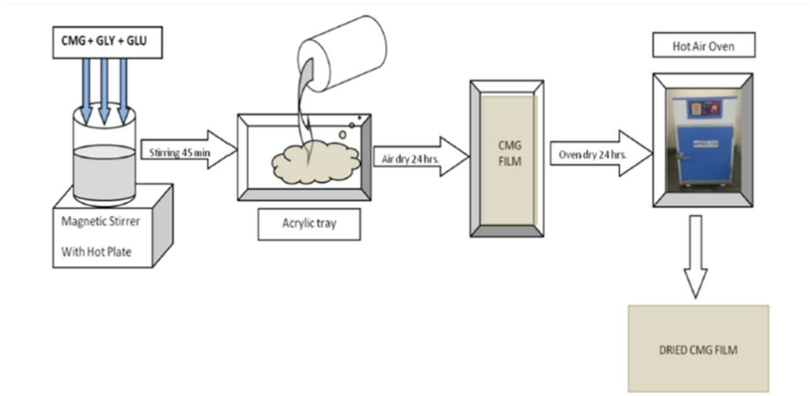


Fig. 2.3: Schematic Representation of Fabrication of CMG-Based Films

The various 64 formulations of CMG-based films were synthesized using the different quantities of glycerol and glutaraldehyde, as outlined in Table 2.1.

Table 2.1: Different Concentrations of Glycerol as a Plasticizer and Glutaraldehyde as a Cross-Linker used for Fabrication of CMG based Films

Code No.	CMG (g)	Glycerol (Gly) (ml)	Glutaraldehyde (Glu) (ml)							
			1	2	3	4	5	6	7	8
A	1.0	0.0	0.00	0.10	0.25	0.50	1.00	1.25	1.50	2.00
B	1.0	0.10	0.00	0.10	0.25	0.50	1.00	1.25	1.50	2.00
C	1.0	0.25	0.00	0.10	0.25	0.50	1.00	1.25	1.50	2.00
D	1.0	0.50	0.00	0.10	0.25	0.50	1.00	1.25	1.50	2.00
E	1.0	1.00	0.00	0.10	0.25	0.50	1.00	1.25	1.50	2.00
F	1.0	1.25	0.00	0.10	0.25	0.50	1.00	1.25	1.50	2.00
G	1.0	1.50	0.00	0.10	0.25	0.50	1.00	1.25	1.50	2.00
H	1.0	2.00	0.00	0.10	0.25	0.50	1.00	1.25	1.50	2.00

The glutaraldehyde interacts with the hydroxyl groups present in both CMG and glycerol, leading to the formation of acetyl bonds. This interaction leads to the successful development of a cross-linked CMG/Glu/Gly polymeric network. The probable mechanism underlying this process is depicted in Figure 2.4 [39].

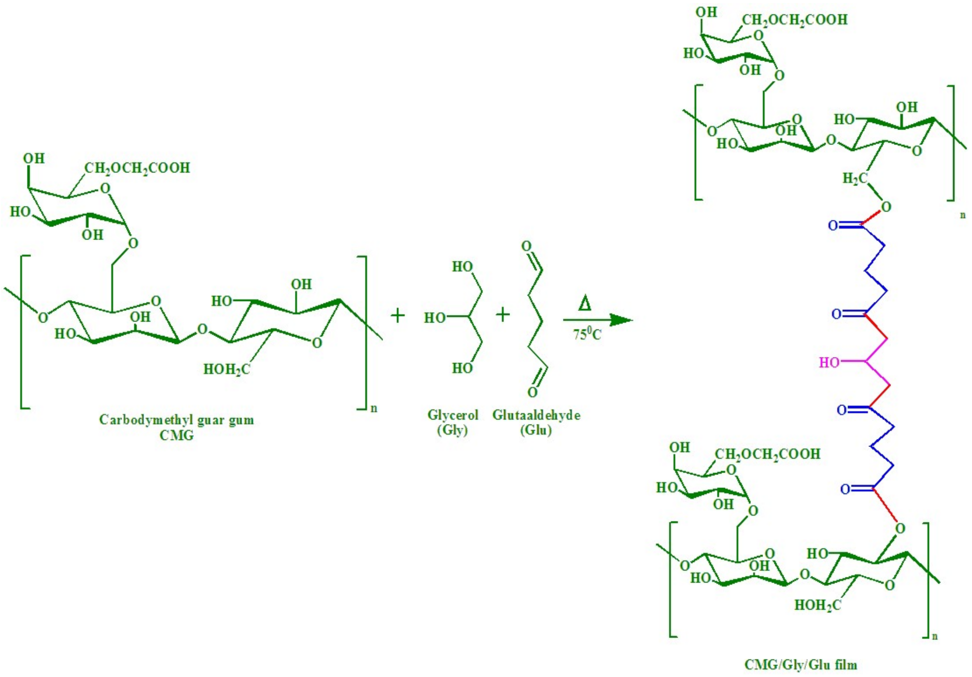


Fig. 2.4: Probable Reaction Mechanism for CMG/Glu/Gly Films

2.4 Characterization of CMG Based Films

To know about behavior of the fabricated CMG/Glu/Gly films, the optimized CMG films were then characterized using differential scanning calorimetry (DSC), thermo gravimetric analysis (TGA) and Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Scanning Electron Microscopy (SEM).

2.4.1 Differential Scanning Calorimetry (DSC)

The thermal behavior of the cross-linked CMG films fabricated at two different temperatures of 70 °C and 75 °C and CMG powder were analyzed using a Perkin Elmer (Model no.: DSC 8000) shown in Figure 2.5.

The samples (2–3 mg) were heated at a rate of 10 °C/min, at a temperature range from 0 to 200 °C.

Fig. 2.5: Differential Scanning Calorimeter (DSC 8000, Perkin Elmer) used for Characterization of CMG Based Films

2.4.2 Thermo Gravimetric Analysis (TGA)

TGA was done utilizing the Perkin Elmer instrument (Model No: TGA 4000), shown in the Figure 2.6. The sample (2–3 mg) was heated from a temperature range of 25 to 600 °C under a nitrogen atmosphere in a sample holder.

The flow rate was maintained at 50 ml/min, and the heating rate was set at 10 °C/ min. The weight change of the sample was recorded as a function of temperature.

Fig. 2.6: Thermogravimetric Analyzer (Perkin Elmer 4000) used for Characterization of CMG Based Films

2.4.3 Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR)

The FTIR spectrum of the films was recorded using a Shimadzu Corp. ATR-FTIR instrument (Model: IR Afnity-1S), shown in the Figure 2.7.

The spectra were recorded in the frequency range from 4000 to 400 cm^{-1}, at the spectral resolution of 5 cm^{-1}

Fig. 2.7: Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy used for Characterization of CMG based Films

2.4.4 Scanning Electron Microscopy (SEM)

SEM analysis was carried out using a Hitachi (model: S-3400N) as shown in the Figure 2.8 at an accelerating voltage of 5 kV, by smearing with gold coating and to examine the surface morphology of the fabricated CMG films under low vacuum pressure.

Fig. 2.8: Scanning Electron Microscopy used for Characterization of CMG Films

2.5 Results and Discussions

Results of the characterization of CMG based films done by DSC, TGA, ATR-FTIR and SEM are discussed below:

2.5.1 Differential Scanning Calorimetry (DSC)

The DSC analysis was carried out for the CMG film (Sample A-1), and CMG/Glu/Gly film (Sample E-5) fabricated at 70 °C, and 75 °C, as shown in Figure 2.9.

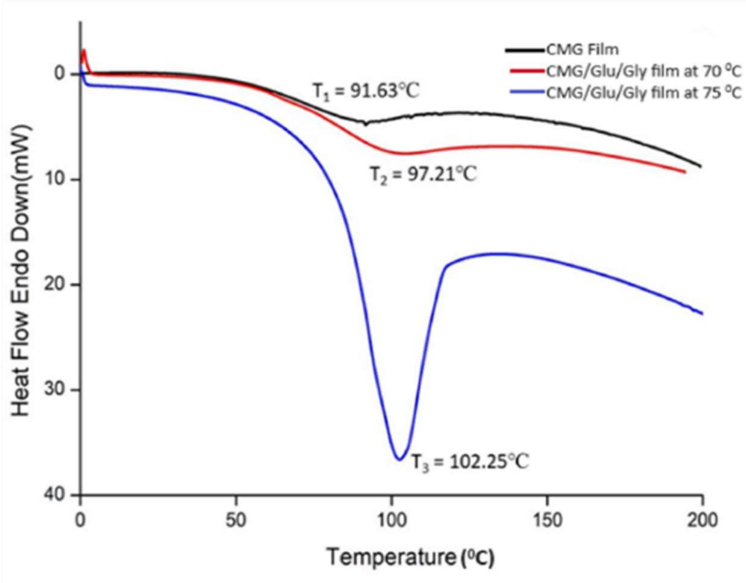


Fig. 2.9: DSC for CMG Film and CMG/Glu/Gly Films Fabricated at 70°C and 75°C

A broad peak at 91.63 °C and 97.21 °C is observed in CMG film and CMG/ Glu/Gly film fabricated at 70 °C, respectively, while a sharper peak at 102.25 °C is noticed in CMG/Glu/Gly film fabricated at 75 °C.

This sharp peak at 102.25 °C indicates an endothermic reaction associated with the melting of the film at a higher temperature. The difference in the peaks revealed the improved cross-linking at the higher reaction temperature of 75 °C compared to the reaction temperature of 70 °C [14].

2.5.2 Thermogravimetric analysis (TGA)

TGA thermograms of CMG/Glu/Gly films (Sample E-5) fabricated at two different temperatures (70 °C and 75 °C) are shown in Figure 2.10.

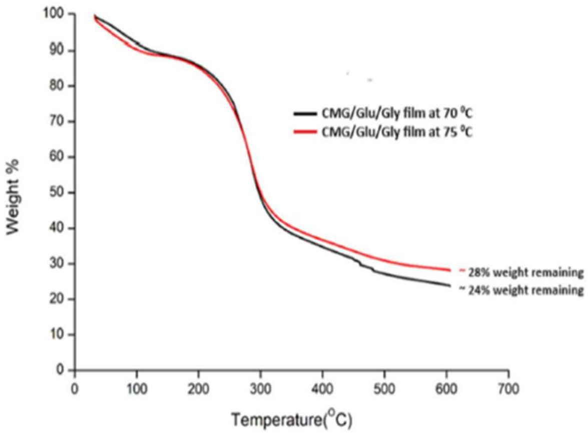


Fig. 2.10: TGA Plot for Optimized CMG/Glu/Gly Films Fabricated at Reaction Temperatures of 70 °C and 75 °C

The thermograms of both CMG-based films show three-stage weight loss. Initially, the same weight loss of 26% due to water evaporation from 30 to 245 °C was observed in CMG films prepared at 70 °C and 75 °C [14].

Secondly, again, the same weight loss of 40% from 245 to 325 °C, due to the degradation of polymer backbone (-COOH and -OH group of CMG), was found in the films synthesized at reaction temperatures 70 °C and 75 °C.

The weight loss of 20% and 16% from 325 to 600 °C signifies the breakage of the cross-linking present in the films fabricated at 70 °C and 75 °C, respectively [40–43].

Moreover, it was observed that up to the second stage, both films exhibited similar weight loss. However, beyond this temperature, the film produced at 70 °C shows a higher weight loss, compared to the film fabricated at 75 °C. This suggests that the film synthesized at the higher reaction temperature of 75 °C demonstrates greater stability, likely attributed to a higher degree of cross-linking. Consequently, the films synthesized at the 75 °C reaction temperature were selected for further analysis [14].

2.5.3 Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR)

The ATR-FTIR spectra of CMG (Sample A-1), CMG/Gly (Sample E-1), CMG/Glu (Sample A-5), and CMG/Glu/Gly (Sample E-5) films are shown in Figure 2.11.

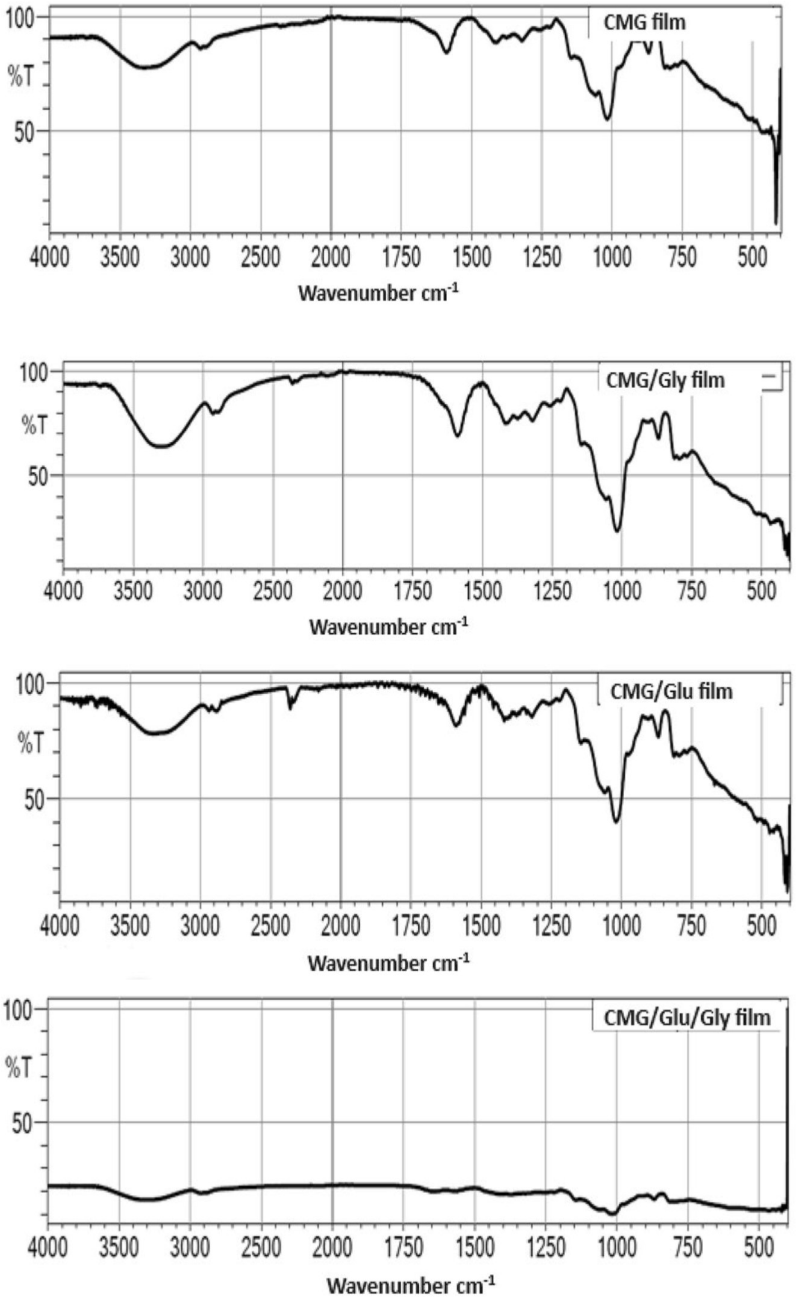


Fig. 2.11: FTIR Spectra of CMG Film, CMG/Gly Film, CMG/Glu Film and CMG/Glu/Gly Film

In the FTIR spectra of the CMG film, characteristic peaks associated with O–H stretch were observed at 3300–3400 cm^{-1}, while the peak associated with C–H stretch appears at 2800–2900 cm^{-1}.

Moreover, the C=O stretch appears at 1600–1700 cm^{-1}, and the C–H bend appears at 1300–1400 cm^{-1} [44].

In FTIR spectra of CMG/Gly film, it was observed that the addition of glycerol resulted in a notable increase in the number of alcoholic hydroxyl groups. Consequently, the intensity of the peaks within the 3300–3400 cm^{-1}, corresponding to hydroxyl groups, exhibited a significant increase in amplitude [45].

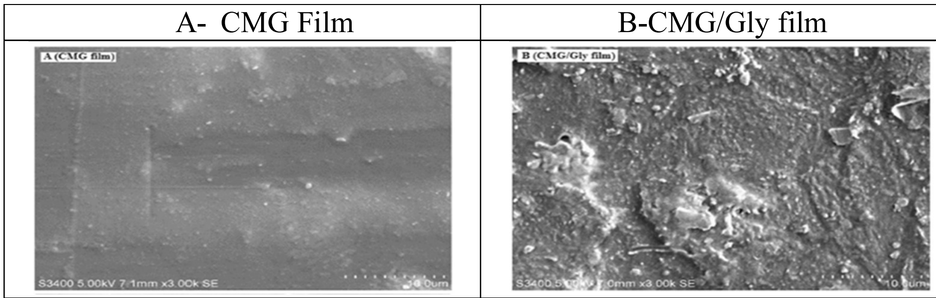
In FTIR spectra of CMG/Glu film, an increase in the intensity of the peak around 2800–2900 cm^{-1} is observed, attributed to the larger number of CH_2 groups resulting upon the introduction of cross-linker (glutaraldehyde) [46].

Moreover, in the FTIR spectra of CMG/Glu/Gly film, the disappearance of peak around 2300–2400 cm^{-1}, present in CMG/Gly film and CMG/Glu film, confirms the successful formation of a cross-linked polymeric film.

2.5.4 Scanning Electron Microscopy (SEM)

The surface morphology of the CMG (Sample A-1), CMG/Gly (Sample E-1), CMG/Glu (Sample A-5), and CMG/Glu/Gly (Sample E-5) films was analyzed by SEM. The SEM micrographs obtained for these samples are shown in the Figure 2.12.

A- CMG Film B-CMG/Gly film



C-CMG/Glu film D-CMG/Glu/Gly Film

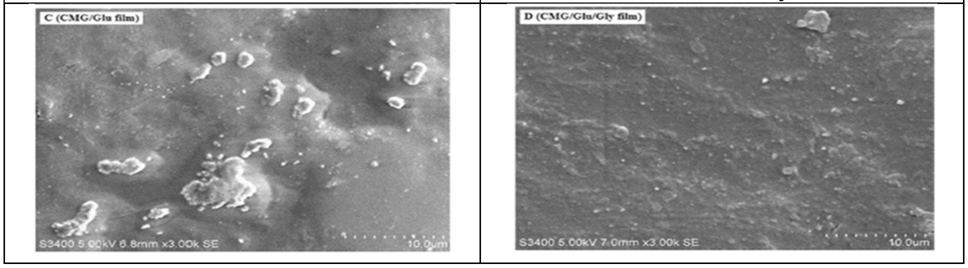


Fig. 2.12: SEM Micrographs of A- CMG Film B- CMG/Gly, C- CMG/Glu Film and D- CMG/Glu/Gly Film

In Figure 2.12 (A), the single-phase morphology was observed without any surface complexity, attributed to the solely presence of CMG.

Figure 2.12 (B) reveals the uneven surface morphology associated with the presence of cavities and air pockets resulting from the dispersion of the plasticizer within the polymer matrix.

Figure 2.12 (C) indicates a more uniform and denser surface, which signifies the successful cross-linking between CMG and the cross-linker.

Figure 2.12 (D) shows a comparatively more homogeneous surface than Figure 2.12 (C) implying the combined effect of plasticizer and cross-linker on the overall surface morphology of the films [9].

2.6 Conclusion

In this study, series of CMG-based films were successfully fabricated by utilizing glycerol as a plasticizer and glutaraldehyde as a cross-linking agent by solution casting method.

From the analysis of the DSC and TGA data of the fabricated films, it is revealed that the optimum reaction temperature for fabrication of CMG, Glu and Gly films is 75 °C. It is observed that the CMG films indicated good film forming properties at reaction temperature of 75 °C.

In the DSC characterization of the film, the sharp peak at 102.25 °C. This indicated occurrence of an endothermic reaction which is associated with the melting of the film at a higher temperature. The difference in the DSC peaks revealed the evidence of improved cross-linking at the reaction temperature of 75 °C compared to the reaction temperature of 70 °C

The TGA data reveals that the film synthesized at the 75 °C demonstrates greater stability, likely attributed to a higher degree of cross-linking. The FTIR study confirmed the successful formation of cross linked films.

The SEM micrographs also showed presence of cavities and air pockets which suggests the dispersion of the plasticiser within the polymer matrix. The cross linking was also evident from the denser and rougher surface of the cross linked CMG films.

Thus all the characterization studies of the CMG films revealed the evidence of cross linking of CMG with glutaraldehyde and glycerol.

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CHAPTER 3

EVALUATION OF CMG BASED FILMS FOR PACKAGING APPLICATIONS

3.1 Introduction

The importance of testing and evaluating the various properties of the polymers has gained a lot of interest today, due to the necessity of selective requirements of various products for their packaging with various objectives. It helps in the basic as well as in applied research to incorporate tailored properties to the packaging material and helps in generating multifunctional products with increasing acceptability for various applications. Further for the technically complex products which need to be evaluated during their development stage, its evaluation for various properties become crucial. The information on the various properties of the polymers is very much essential during designing and processing of the product to ensure the acceptability of the product for its intended use in the particular environment.

The mechanical properties of polymeric films are crucial for determining their load-bearing capacity and facilitating the development of various applications. Determination of the thermal properties of any polymeric film is vital in evaluating its performance and predicting its characteristics for processing for particular application. The optical properties of the polymer film are important for many applications, such as packaging, as they relate to the aesthetics of the final product. Similarly, the chemical properties of the polymeric films reveal the composition of the material used for fabricating a particular type of film. In addition to these, the barrier properties of the films correlate its chemical and physical stability for particular time period for specific end use application and for its storage and handling [1].

Thus the mechanical, thermal, optical, chemical and physical properties of the developed CMG based films were studied and results are reported.

In addition to this, a study was undertaken to explore the possibilities of using these developed CMG based films for extension of shelf life. In which the preservation of the cut potatoes was studied for the possible extension of its shelf life.

3.2 Evaluation of CMG Films

Thus for the purpose of evaluating various properties of our CMG based films, for developing its suitable applications, all the 64 variants of CMG based films fabricated as documented in chapter 2 Table 2.1, were evaluated for tensile strength, elongation at break, thickness, solubility in water, gloss, haze and transparency

3.2.1. Tensile Strength and Elongation at Break

The tensile strength test provides information about the mechanical strength of the material, crucial for packaging applications and the elongation test provides information about the extent to which films can elongate or withstand strain before reaching the breaking point. It is an essential consideration for processes such as lamination and printing of various polymeric films used in packaging.

The CMG based films were evaluated for tensile strength and elongation on a Universal Testing Machine(UTM)- (Shimadzu, Autograph AG–X 110 N) shown in the Figure 3.1, equipped with a 1-kN load cell capacity, as per the ASTM D 882–97 guidelines with minor modifications.

Fig. 3.1: Universal Testing Machine, Shimadzu, Autograph AG–X 110 N used for Tensile Strength and Percent Elongation at Break

For testing, the films were carefully cut into dimensions of 150 mm x 25 mm, and tested using UTM with a gauge length of 50 mm and a crosshead speed of 50 mm/ min. The tensile strength of CMG films was reported in MPa. The strain at the point of breakage was recorded and reported as percent (%) elongation at break (%EAB). Tests were conducted in triplicate.

3.2.2 Film Thickness

The film thickness measurement was done on the Mitutoyo Japan Micrometer (Model 547-400S) as shown in the Figure 3.2 as per the ASTM 6988 guideline. The sample size used is 50 mm×50 mm. A total of 10 readings were randomly taken on each variant of CMG films, and the average value is reported in microns (μ).

Fig. 3.2: Mitutoyo Japan Micrometer, Model 547-400S used for Thickness Test

3.2.3 Solubility in Water

The solubility of the film in water is referred to the percentage of soluble matter present in the film [2]. The films having dimensions of 50 mm × 50 mm and predetermined weight, were immersed in 50 ml of double distilled water at room temperature for 24 h. as shown in the Figure 3.3 below.

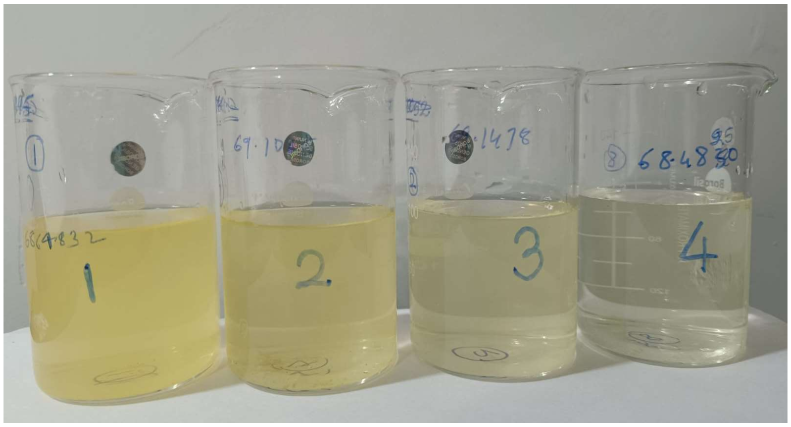

Fig. 3.3: Setup for Determination of Solubility of CMG Films in Water

Later, the water was discarded, and the films were dried in a hot air oven set at 60 °C for 24 h. as shown in the Figure 3.4.

Fig. 3.4: Hot Air Circulating Oven used for Drying

The water solubility of the film was then calculated using the Eqn. 3.1. The test was conducted in triplicate and the average readings were reported.

$$\text{Water Solubility (\%)} =$$

$$\frac{\text{(Initial dry weight-Final dry weight)}}{\text{Initial dry weight}} \times 100\ldots..(3.1)$$

3.2.4 Gloss

The glossiness of polymeric films is an essential parameter for many packaging applications. It provides information about the amount of light reflected when light is incident on the film surface from various angles.

Samples of the fabricated CMG-based films were analyzed on the Gloss meter (Model BYK Gardner) as shown in the Figure 3.5, as per ASTM D 523/ASTM D2457 guidelines, at a 20° angle. A total of 10 readings were acquired for each type of sample, and the average value was reported.

Fig. 3.5 Gloss Meter Model BYK Gardner used for Gloss Measurement

3.2.5 Haze and Transparency

As optical transparency is inversely proportional to its crystallinity, the transparency of any polymeric film plays a crucial role in its visible light barrier properties and can be correlated to its crystalline behavior [3].

The spherical haze meter, diffusion systems (M57D) shown in the Figure 3.6 was utilized for the measurement of the haze and transmittance of the film. Each sample was tested in triplicate, and the reported values signify the average percentage. The measurement was done according to the guidelines outlined in ASTM D 1003.

Fig. 3.6: Spherical Haze Meter, Diffusion Systems (M57d) used for Haze and Transparency

3.3 Results and Discussions

The results obtained for all the 64 variants of CMG-based films which were tested for evaluating their various important properties like tensile strength, elongation at break, film thickness, water solubility, gloss, haze and transparency are discussed below. This also offered important information on the effect of plasticizers and cross-linker on the particular parameter.

3.3.1 Tensile Strength of CMG Films

The impact of plasticizers on the tensile strength of the CMG films is shown in the Figure 3.7a. The figure shows the effect of plasticizer on tensile strength as it varies with changes in the concentration of cross-linker.

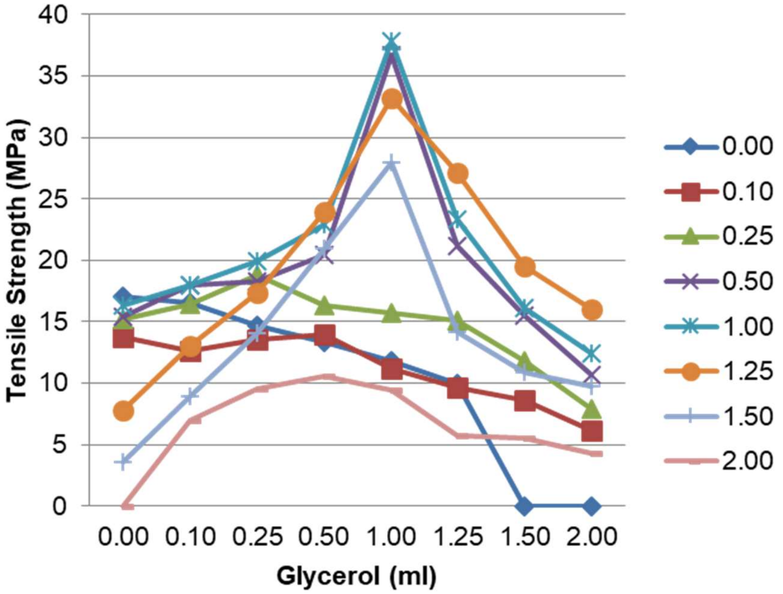

Fig. 3.7a: Effect of Plasticizer on Tensile Strength of CMG Films.

Without or with low cross-linker concentration up to 0.25 ml, with an increase in the plasticizer content, the film flexibility increases, leading to a decrease in tensile strength.

For cross-linker concentrations from 0.25ml to 1ml, with an increase in the concentration of plasticize, films tensile strength slightly increases due to presence of higher content of cross linker and also due to glycerol's participation in cross-linking.

However, beyond addition of cross linker above 1ml, with increase in the plasticizer content, the tensile strength further decreases sharply, rendering the film sticky due to excess plasticizer.

Similarly, Figure 3.7b illustrates the impact of cross-linker content on tensile strength of the CMG films.

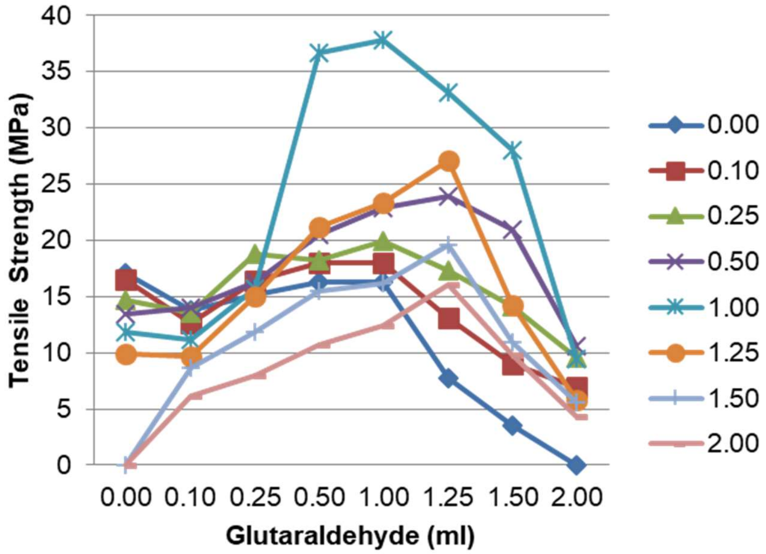

Fig. 3.7b: Effect of Cross Linker on Tensile Strength of CMG Films

At low concentrations of cross-linker (0.1–0.25 ml), tensile strength increases slowly due to insignificant cross-linking. Beyond this range, a considerable increase in the tensile strength occurs with increased cross-linking reaching a maximum at 1.25 ml of cross-linker.

Moreover, with an increase in the cross-linker content above 1.25 ml, tensile strength decreases, possibly due to excessive cross-linker hindering available cross-linking sites.

The maximum tensile strength of 37.82 MPa in Sample H-5 of CMG-based film is observed. Hence, CMG-based films can be employed for potential applications in the packaging sector [4, 5].

Overall, addition of the plasticizer increases the flexibility and addition of cross-linker increases the rigidity of the CMG films.

3.3.2 Elongation at Break

When CMG-based films were tested for their elongation at break, they demonstrated a maximum elongation of 124.20% in Sample H-2. This suggests that these films are capable of stretching significantly before breaking, indicating good flexibility and ductility. Figure 3.8a illustrates the impact of the plasticizer on the elongation at break of the CMG based films.

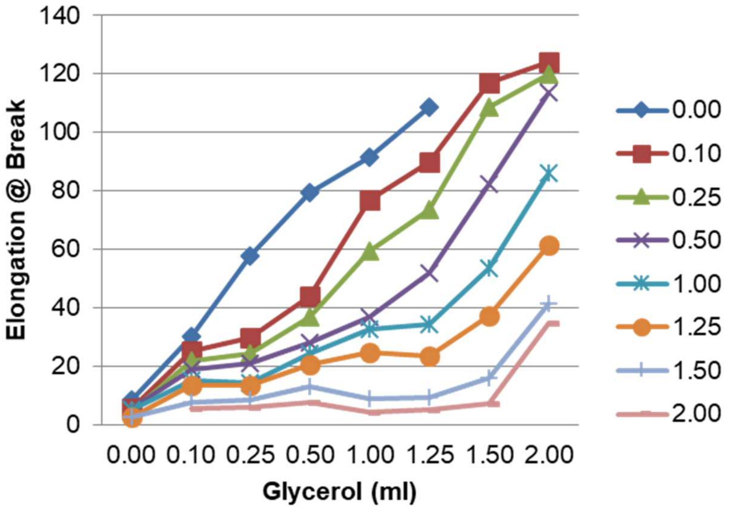

Fig. 3.8a: Effect of Plasticizer on Elongation at Break of the CMG Based Films

It is observed that with an increase in glycerol quantity, molecular mobility rises, leading to a decrease in intermolecular forces, resulting in an increase in film flexibility, consequently elongation increases. However, at lower glycerol quantities, where molecular mobility is limited, the plasticization effect is less significant [4–6].

As shown in Figure 3.8a, the addition of glycerol increases the percent elongation of the film by reducing its brittleness, which is likely due to its plasticizing effect. When glycerol is present in lower quantities, its plasticization effect is limited due to restricted molecular mobility. As the glycerol concentration increases, molecular mobility improves, resulting in increased elongation due reduced intermolecular forces and enhanced film flexibility.

Similarly, the effect of the cross-linker on the elongation at break values of the CMG based films is given in the Figure 3.8b.

As shown in Figure 3.8b an increase in the number of cross-links led to decrease in the elongation at break. This is attributed to cross-linking effect, which makes the film stiffer and reduces their flexibility as the number of cross-links increases [4–6].

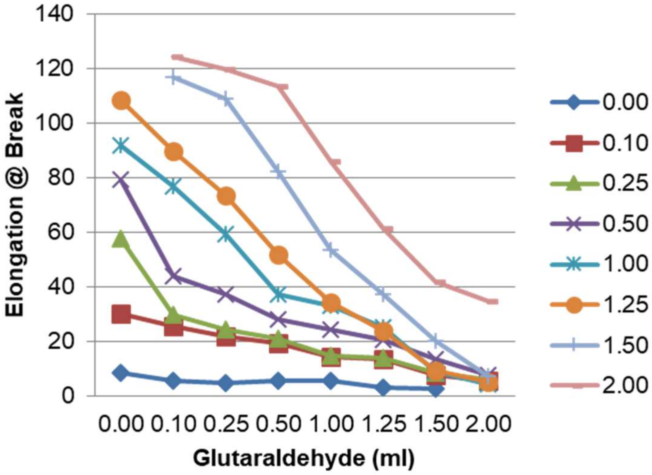

Fig. 3.8b: Effect of Cross Linker on Elongation at Break of CMG Based Films

3.3.3 Film Thickness

The maximum thickness of the film observed was 55.30 µ. The effect of the plasticizer on the average thickness of all the variants of CMG-based films is shown in Figure 3.9a.

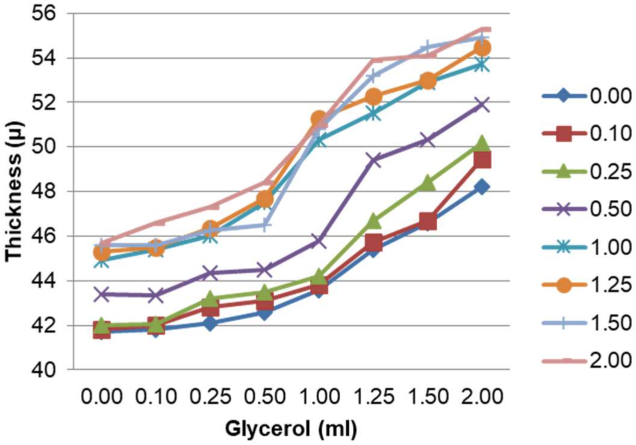

Fig. 3.9a: Effect of Plasticizer on Average Thickness of CMG-based Films

The effect of the cross linker on the average thickness of all the variants of CMG-based films is shown in Figure 3.9b below.

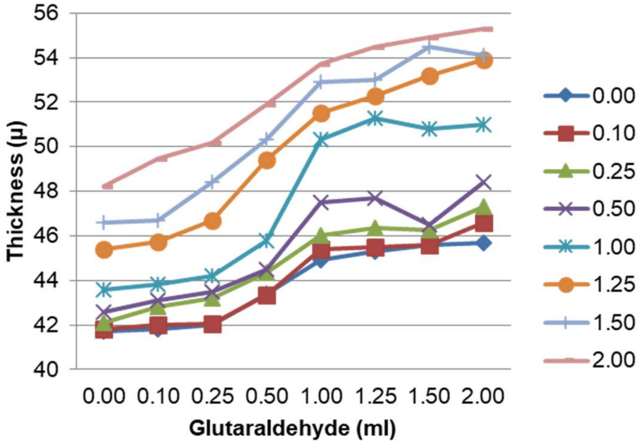

Fig. 3.9b: Effect of Cross Linker on Average Thickness of CMG Films

The thickness of the film increases with the addition of both plasticizer and cross-linkers. This is likely due to the rearrangement of intermolecular bonds, resulting in a more expanded structure caused by the plasticizer and a denser structure caused by the increased cross-linking [7–10].

3.3.4 Water Solubility

The minimum observed solubility of the fabricated CMG film was 60.42% in Sample A-8. The solubility of the synthesized CMG-based films as outlined in Table 1.1 in Chapter 1, is calculated using Eqn. 3.1, as illustrated in Figure 3.10a.

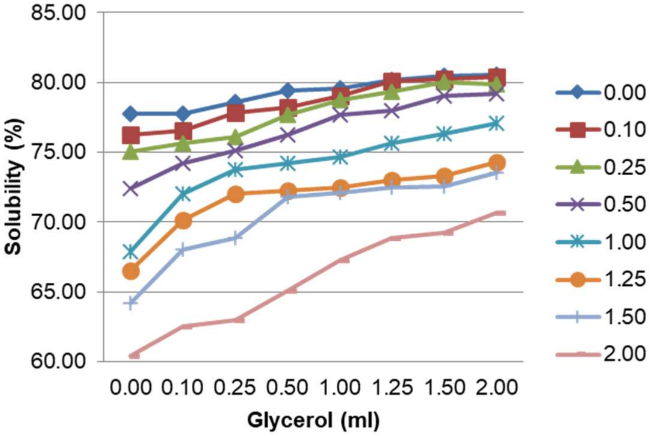

Fig. 3.10a: Effect of Plasticizer on Water Solubility of Synthesized CMG Films

The film's solubility increases with an increase in the plasticizer quantities due to the enhanced flexibility of the film and also due to glycerol separating from the hydrogen bonding site of CMG and dissolving in water [11].

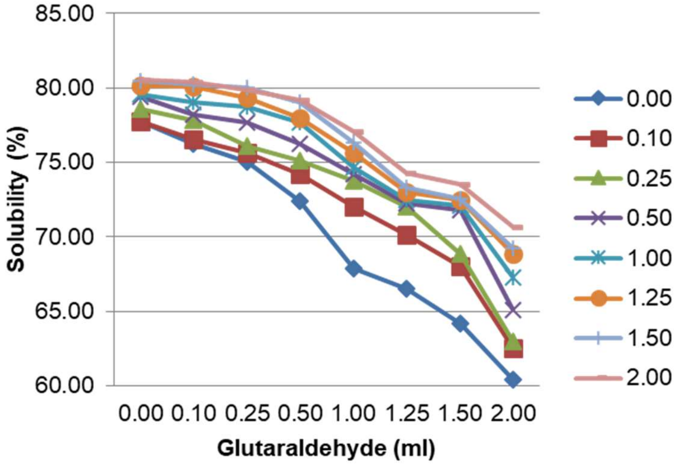

Fig. 3.10b: Effect of Cross Linker on Water Solubility of Synthesized CMG based Films

Moreover, it is evident that the solubility decreases with an increase in the quantity of the cross-linker. This is attributed to higher cross-linking, which reduces hydrogen bonding in the film matrix, resulting in slower dissolution [5].

The water solubility of CMG-based films suggests potential applications in edible packaging and water-soluble packaging materials.

3.3.5 Gloss

The CMG-based film displayed a maximum gloss of 25.52% in Sample G-5. The gloss values of the fabricated CMG-based films at a 20° angle are depicted below.

The effect of plasticizer on the gloss of the CMG based films is shown in Figure 3.11a and the effect of cross linker on the glossiness of the fabricated CMG based films is given in Figure 3.11b

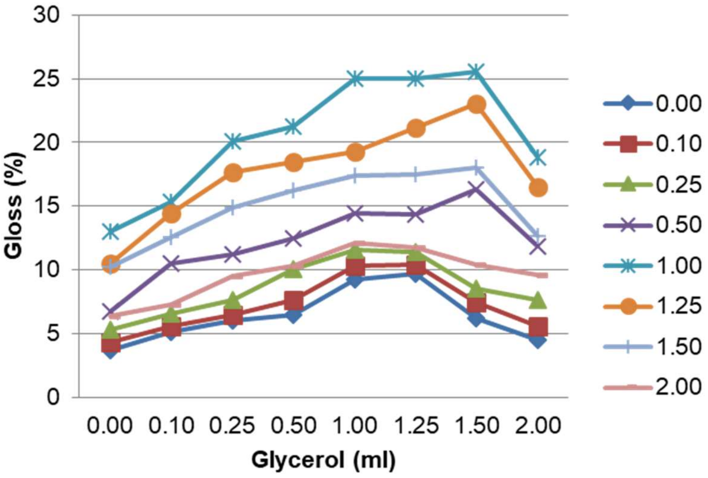

Fig. 3.11a: Effect of Plasticizer on Gloss of CMG based Films

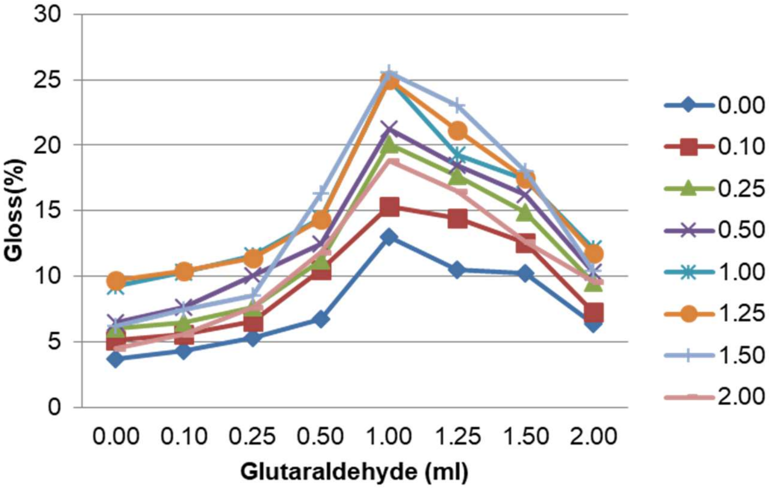

Fig. 3.11b: Effect of Cross Linker on Gloss of CMG based Films

It is observed that, notably, at lower quantities of concentration of plasticizer and cross-linker, the glossiness tends to increase, owing to the increased smoother surface of the film due to plasticization effect and low cross-linking.

However, with the addition of high quantities of plasticizer and cross linker, a reduction in glossiness occurs. This decrease may be attributed to the formation of rougher surfaces due to an increase in cross-linking [12].

3.3.6 Haze

The haze of the fabricated CMG-based films is presented below. The film exhibited a maximum haze of 41.93% in Sample H-8. The effect of the plasticizer on the haziness of the CMG based films is shown in the Figure 3.12a and effect of cross linker on haziness of CMG films is given in the Figure 3.12b.

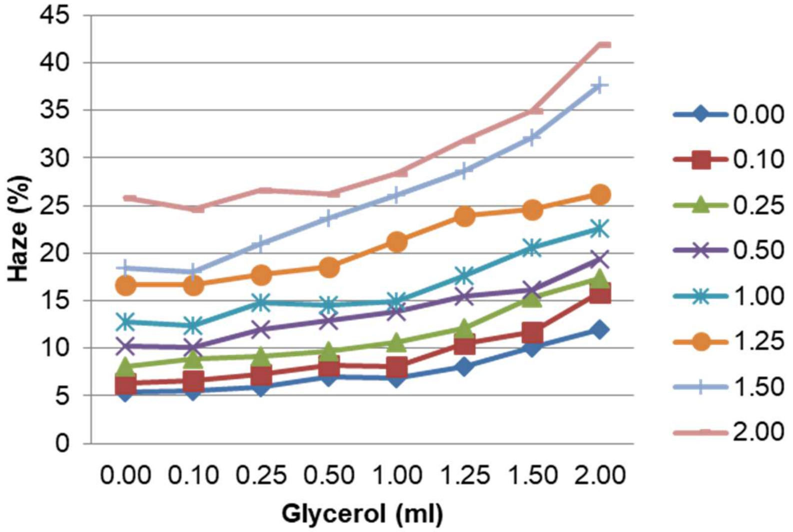

Fig. 3.12a: Effect of Plasticizer on Haze of CMG based Films

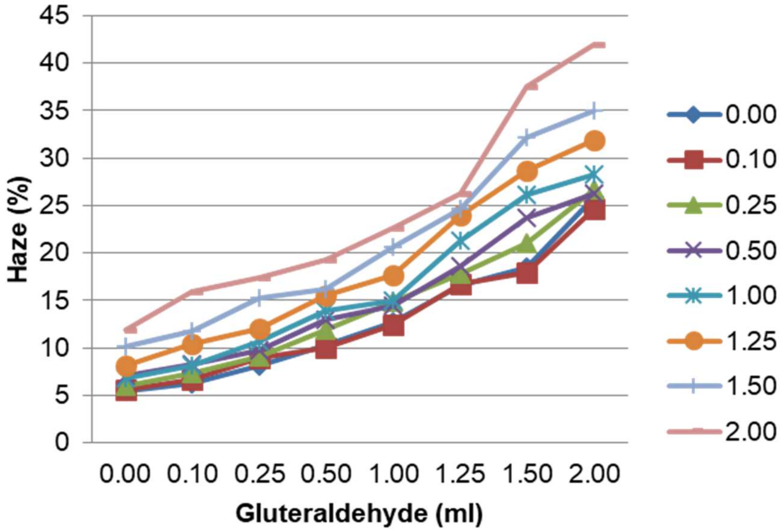

Fig. 3.12b: Effect of Cross linker on Haze of CMG based Films

It is noteworthy that the haziness of the film increases with a rise in both the plasticizer and cross-linker content. This is due to the increase of diffusion of incident light caused by increased bulkiness at higher plasticizers and cross-linking of the film due to polymeric chain compaction to a higher cross-linking [13].

3.3.7 Transparency

The transparency of the CMG- based films, is given below. The findings indicate that CMG films exhibited excellent optical transparency, with the maximum transparency observed at 88.53% in Sample A-1.

The effect of plasticizer on the transparency of the synthesized CMG-based films is presented in Figure 3.13a and effect of cross linker on transparency of the CMG based films is given in Figure 3.13b.

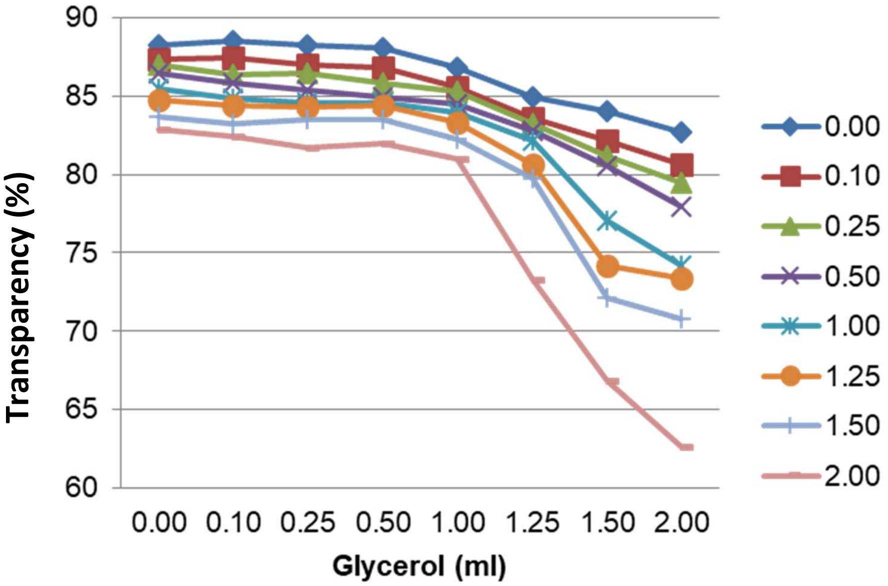

Fig. 3.13a: Effect of Plasticizer on Transparency of Synthesized CMG based Films

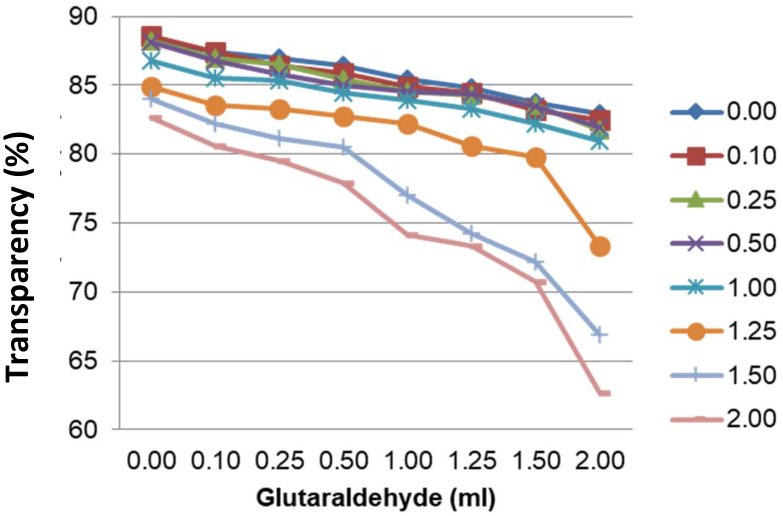

Fig. 3.13b: Effect of Cross Linker on Transparency of Synthesized CMG based Films

It is observed that as glutaraldehyde (cross linker) content in the film increases, the cross-linking increases, leading to a noticeable decrease in the transparency of the film [13].

Additionally, the transparency of the film is decreased with increase in the quantity of plasticizer. This can be attributed to the decrease in transmittance caused due to change in the refractive index by the increased polymeric chain compaction [13].

3.4 The Potato Wrapping Study

Owing to the good mechanical and optical properties evident from the evaluation of the fabricated CMG based films it is predictable that these films can be effectively used in packaging in various forms.

Thus with a view to explore the possible applications of the fabricated CMG based films a small study was undertaken to study the preservation of the cut potatoes for possible extension of their shelf life.

For this, the potato was cut into two halves and one part was wrapped with the CMG film (Sample A-1) and other part was kept as it is without wrapping as shown in the Figure 3.14 below.

a) Without CMG film b) With CMG film

Fig. 3.14: View of Potato Pieces under Study for Shelf Life Extension

Both the pieces of the potatoes, as shown in the Figure 3.14 were exposed to ambient temperature of 29^0C and observed visually for any change in color, loss of moisture and microbial growth. Following Figure 3.15 shows the photographs taken at every 24 h.

Fig. 3.15: Photographs taken during Potato Wrapping Study

It is observed that the potato wrapped in a CMG based film was fresh without any visible color change and microbial growth up to 96 h. (4 days). However, the piece of the potato which was left open without wrapping was darken on the 3rd day. In addition, moisture loss was observed with considerable visual shrinkage in the size of unwrapped potato piece.

Thus based on the above study, the CMG based films can become a promising candidate for preservation of cut fruits, vegetables and for extension of the shelf life of these products.

3.5 Conclusion

The CMG based films were evaluated for mechanical, optical, and solubility tests. The maximum values observed for tensile strength, percent elongation, gloss at a 20° angle, haze, and transparency were 37.82 MPa (Sample H-2), 124.20% (Sample H-2), 25.52% (Sample G-5), 41.93% (Sample H-8), and 88.53% (Sample A-1), respectively. All these properties revealed the possibility of CMG films for packaging applications.

The solubility test results indicated a minimum water solubility of 60.42% of these CMG films which highlights the potential applications of CMG-based films in areas such as edible coatings and water-soluble packaging.

The maximum tensile strength value of 37.82 MPa suggests that, with further refinements, CMG-based films can compete with certain biopolymer-based films and even some commercially used synthetic polyethylene films.

In addition, the potato wrapping study revealed that the CMG based films can be used for the preservation of cut fruits and vegetables and can extend their shelf life.

This study also points the CMG-based biopolymer materials as promising candidate for coatings in the packaging industry

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CHAPTER 4

FABRICATION AND TESTING OF CMG-LDPE BLENDS

4.1 Introduction

Global production of plastics today is more than 335 million tons [1]. Due to the extensive use of these synthetic polymers, there is a rise in post-consumer waste accumulation as these are disposed of indiscriminately.

In recent year due to various environmental issues like increased greenhouse gas emission, depletion of crude oil, increasing disposal load posed by synthetic packaging materials due to their poor degradability in soil and water, and changing environmental regulations, the demand for environment-friendly packaging materials derived from renewable resources is increasing.

The biopolymers are biocompatible and biodegradable and even edible in some cases. However, as reported by many researchers, some of their properties like lower tensile strength, percent elongation, water resistance and thermal stability etc., restrict their applications in packaging.

Therefore, researchers have tried various methods like blending, coating, lamination etc., for improving their performance as packaging materials. Among these methods, blending biopolymers with various synthetic polymers is a well-established technique that has been increasingly used since the 1970s. This approach is effective in overcoming the limitations of individual biopolymer and improving their desired properties for specific application. Additionally, blending biopolymers with synthetic polymers can help replace some single-use synthetic polymers that have poor degradability [1–8].

The blending of the biopolymers with synthetic polymers also helps in increasing the biodegradability of synthetic polymers as on addition of biopolymer helps in the decomposition of the synthetic polymer due to the microorganisms. The microorganisms particularly fungi grow on the surface of the biopolymer to consume the nutrients available in the biopolymer. This results in the formation of a pores matrix and further decreases the mechanical strength of the substrate and leads to degradation [9].

To date, numerous research papers have been published on the blending of biopolymers with synthetic polymers due to their diversity. Various biopolymers including proteins, polysaccharides, lipids, and their combinations, etc., are increasingly being used due to their desirable properties such as film-forming ability and barrier properties, which are the essential characteristics for any packaging material [2, 3, 8, 10]. However, to the best of our knowledge, there are no existing reports on blends of carboxymethyl guar gum (CMG) with low density polyethylene (LDPE) are available.

This study aimed to develop blends of CMG and LDPE in various proportion and evaluate their properties for potential applications in packaging and biodegradability.

In this study, blends of CMG and LDPE were made using injection molding and further characterized using Differential scanning calorimetry (DSC), Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) spectroscopy**,** Thermo gravimetric analysis (TGA), and Scanning Electron Microscopy (SEM).

With a view to understand its applications as sustainable packaging material, the blends were also tested for tensile strength, tensile modulus, elongation at break, moisture content, water absorption and solubility in water.

4.1.1 Carboxymethyl Guar Gum

Guar gum is a natural nontoxic, biodegradable polymer; a galactomannan with a galactose to mannose ratio of about 6:1 and is obtained from guar (Cyamopsis tetragonoloba) or Indian cluster beans. It is widely used due to its low cost, in food, pharmaceutical, cosmetic and biomedical industries as an emulsifier and bio-adhesive agent. The carboxymethyl guar gum is derived from guar gum by its reaction with monochloroacetic acid followed by the addition of aqueous NaOH in an aqueous organic solvent. The structure of carboxymethyl guar gum is as shown in Chapter 2, Figure 2.2 [10–12].

CMG, due to its stability, aqueous solubility and good chemical reactivity due to the presence of carboxyl and hydroxyl groups in its backbone, has created a lot of interest in the minds of the researchers. It can be blended, cross-linked, or grafted with other polymers of interest. It is a very good functional material used for multipurpose applications viz. agriculture, textile printing, tissue engineering, petroleum and oil, waste water treatment, drug delivery, and as an antibacterial agent [13].

4.1.2 Polyethylene

Polyethylene (PE) is a semi-crystalline and cheapest synthetic polymer of ethylene having tailorable properties. Among the polymers, PE has the simplest basic structure with a softening point in the range of 80-130 ^{0}C and a density lesser than water. It has good processability, excellent electrical insulation over a varied range of frequencies, good chemical resistance, good flexibility and toughness. Some of its grades also pose good transparency.

It is used for diversified applications in packaging and other industries and thus has the highest consumption among the polymers in the packaging sector. It is also know by another name, ‘polythene’ which was promoted by its first manufacturer, Imperial Chemical Industries (ICI). It is manufactured by addition polymerization having formula $(-CH_2-CH_2-)_n$ where ‘n’ is the degree of polymerization. The structure of polyethylene is given in Figure 4.1 [7, 14, 15].

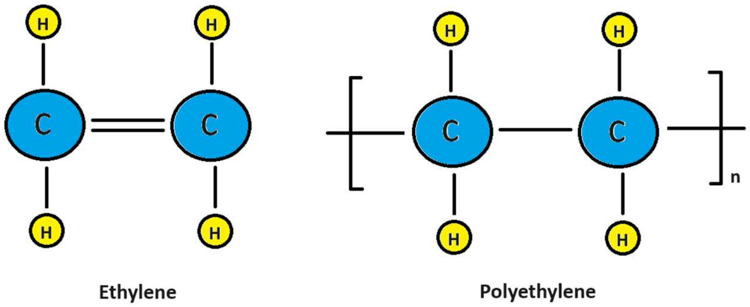


Fig. 4.1: Structure of Ethylene and Polyethylene

The various types of polyethylene based on its density and degree of branching in the main chain include very-low-density-poly-ethylene (VLDPE), linear-low-density-poly-ethylene (LLDPE), low-density-poly-ethylene (LDPE), medium-density-poly-ethylene (MDPE), high-density-poly-ethylene (HDPE) and ultra-high-molecular-weight-poly-ethylene (UHMW-HDPE).

Among these, mainly low-density polyethylene (LDPE), has good flexibility and toughness, and is widely used for packaging and industrial applications [14, 16, 17].

4.2 Materials and Methods

4.2.1 Materials

For blending purpose, the low-density polyethylene grade: 16MA400 was purchased from an authorized dealer of Reliance Industries, from Gujarat. carboxymethyl guar gum was purchased from M/s. Maruti Udyog, Ahmedabad, India. Glycerol (Merck Life Sciences Private Ltd, India) was purchased from open market.

4.2.2 CMG-LDPE Blend Preparation and Molding

The CMG powder and polyethylene granules were first dried in a hot air oven for 8 hours at the temperature of 80°C to remove the moisture. The CMG powder was mixed with polyethylene in the proportion as shown in Table 4.1, by using glycerol (1%) as a wetting agent and then extruded in a wire form of approximately 2mm x 2mm cross section.

Table 4.1: Ratio of CMG with Polyethylene used for Blending

Polymer	**CMG-LDPE Ratios Used**				
	1	**2**	**3**	**4**	**5**
CMG (%)	10	20	30	40	50
LDPE (%)	90	80	70	60	50

The blends of CMG and LDPE were prepared using a twin-screw melt extrusion process, with a screw speed of 45 rpm at a temperature profile of 140°C to 180°C from barrel to die.

It is important to highlight here that the blends with CMG 10%, 20%, and 30% were extruded easily. However, the blends with 40% and 50% CMG could not be extruded. In the case of 40% and 50% CMG blending processes, higher internal shear between LDPE and CMG as well as between the barrel and screw, led to material degradation and lumps formation. This was likely due to the increased stickiness of the material which hindered processing.

After extrusion, the blends of 10%, 20% and 30% CMG in the wire form were cooled in water, cut into small pieces of approximately 2mm length, and then dried for 8 hours in a hot air circulating oven at a temperature of 80°C.

The material was stored in an air-tight container and used for its characterization and testing. This extruded material was used for its characterization and evaluation of melt flow index, moisture content, water absorption and water solubility. Figure 4.2 shows the photographs of the extruded blends of Control, 10%, 20% and 30% CMG-LDPE samples.

Control Sample CMG (0%)


Sample A CMG (10%)	**Sample B CMG (20%)**	**Sample C CMG (30%)**
		

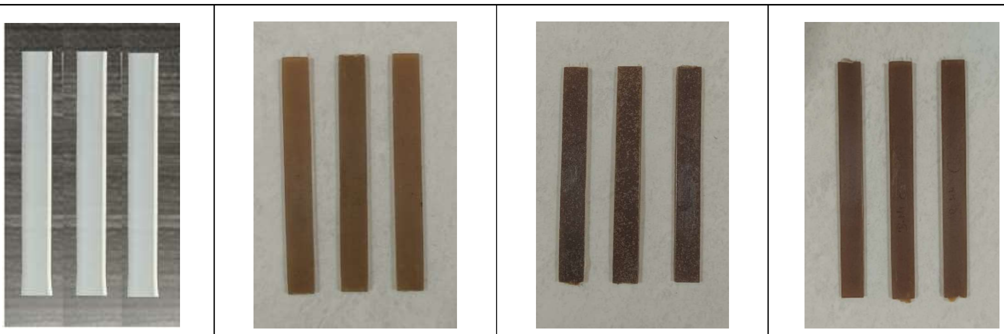
Fig. 4.2: Photographs of the Control and Extruded Blends used for Characterization and Evaluation

For conducting tensile strength, elongation at break and izod impact test the extruded material was further molded for making specimens as per ASTM D-638, and ASTM D-256 respectively, in a injection molding machine (Specific Engineering and Automates, Model ZV 2020, ALPHA) at Central Institute of Petrochemicals Engineering & Technology (CIPET) Murthal, Haryana.

The specimens were stored at air-tight container and used for testing. Figure 4.3a shows the photographs of these specimens used for tensile strength, elongation at break and Figure 4.3b shows the photographs of the specimen made for Izod impact test.

0% CMG	**10% CMG**	**20% CMG**	**30% CMG**

Fig. 4.3a: Molded Samples used for Tensile Strength and Elongation at Break.



0% CMG	**`10% CMG**	**20% CMG**	**30% CMG**

Fig. 4.3b: Molded Samples used for Izod Impact Test.

4.3. Characterization and Testing of CMG-LDPE Blends

Further the 10%, 20% and 30% CMG-LDPE blends were characterized using Differential Scanning Calorimetry (DSC), Thermo Gravimetric Analysis (TGA), Scanning Electron Microscopy (SEM) and Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR), as follows.

4.3.1 Differential Scanning Calorimetry (DSC)

The CMG-LDPE Blends were analyzed for their thermal behavior using a Perkin Elmer (Model No: DSC 8000). The samples (2-3 mg) were heated at a rate of 10°C/min., at a temperature range from 0°C to 200°C.

4.3.2 Thermo Gravimetric Analysis (TGA)

Thermogravimetric analysis was done using the Perkin Elmer instrument (Model No: TGA 4000). The sample (2-3 mg) was heated from a temperature range of 25°C to 600^{o}C under a nitrogen atmosphere in a sample holder. The flow rate was maintained at 50 ml/min and the heating rate was set at 10^{o}C/min. The weight change of the sample was recorded as a function of temperature.

4.3.3 Scanning Electron Microscopy (SEM)

SEM analysis of the CMG-LDPE blends was done using a Hitachi (Model: S-3400N) at an accelerating voltage of 5 kV, by smearing with gold coating and to examine the surface morphology of the blends having different compositions of CMG under low vacuum pressure.

4.3.4 Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR)

The FTIR spectrums of the CMG-LDPE blends were analyzed using a Shimadzu Corp. ATR-FTIR instrument (Model: IR Affinity-1S). The spectra were recorded in the frequency range from 4000-400 cm^{-1}, at the spectral resolution of 5 cm^{-1}.

4.4 Evaluation of Mechanical, Chemical and Rheological Properties of CMG-LDPE Blends

The specimens of the 10%, 20% and 30% CMG-LDPE blends were evaluated for their various properties like tensile strength (TS), elongation at break (EAB), tensile modulus, Izod impact test, melt flow index, moisture content, water absorption and water solubility,

4.4.1 Tensile Strength and Elongation at Break

The samples of the CMG-LDPE blends were tested for tensile strength (TS) and elongation at break (% EAB) on a Universal Testing Machine (UTM) (Shimadzu, Autograph AG-X 110 N) with a 1kN load cell, using ASTM D 638 guidelines with some modifications. The gauge length was 50 mm and the crosshead speed was 50 mm/minute. The results were reported in MPa. The strain at the break was reported as % EAB.

4.4.2 Izod Impact Test

The Izod impact test was performed on Izod impact tester Model No. GEC-P40419, Make: Global Engineering Corporation, India as per ASTM D 256-04. The notched sample was held between the grips of the equipment and allowed to break using a pendulum-type hammer. The energy absorbed was used to calculate impact strength.

4.4.3 Melt Flow Index

The Melt Flow Index tester, Model: EM-M01 Eqvimech Pvt. Ltd., Mumbai, India was used to study the rheological behavior of the CMG-LDPE blends having a capillary of diameter 2mm and length 8mm as per procedure B given in ASTM D 1238-04. The material in the granular form was loaded in the barrel maintained at 120ºC temperature. A weight of 2.16 kg was applied to the plunger to force the sample through the die. The extruded material was collected at intervals of 10 minutes, weighed and reported as MFI values in g/10 minutes [18].

4.4.4 Moisture Content

The moisture content of the CMG-LDPE blends was determined by using the gravimetric method. The samples of CMG-LDPE blends with different compositions of predetermined weight were dried at 105^{0}C in a hot air oven for 24h. Later the final dry weight of the samples was recorded. The moisture content of the CMG-LDPE blends was calculated using Eqn. 4.1. The samples were tested in triplicate and average values were reported.

Moisture content (%)=

$$\frac{(\text{Initial dry weight-Final dry weight})}{\text{Initial dry weight}} \times 100\ldots\ldots(4.1)$$

4.4.5 Water Absorption

The water absorption capacity of the CMG-LDPE blends was measured gravimetrically. The dried samples with a cross section area of about 10mm x 5mm x 0.5mm were tested according to the method given in ASTM D 570-98.

The dried samples with predetermined weight were soaked in 100 ml distilled water in a 250 ml beaker. The samples were taken out at the end of 24 hours. The excess water adsorbed on the surface was removed using a blotting paper and then each sample was weighed. The water absorption per unit time was calculated by using Eqn. 4.2.

$$\text{Water absorbancy (\%)} = \frac{(\text{Weight after soaking} - \text{Weight before soaking})}{\text{Weight before soaking}} \times 100\ldots..(4.2)$$

4.4.6 Water Solubility

The water solubility of the material is the percentage of soluble matter present in the sample [19]. The samples of known weight of CMG-LDPE blends were added to 50 ml distilled water and kept at room temperature for 24 h as shown in Figure 4.4.

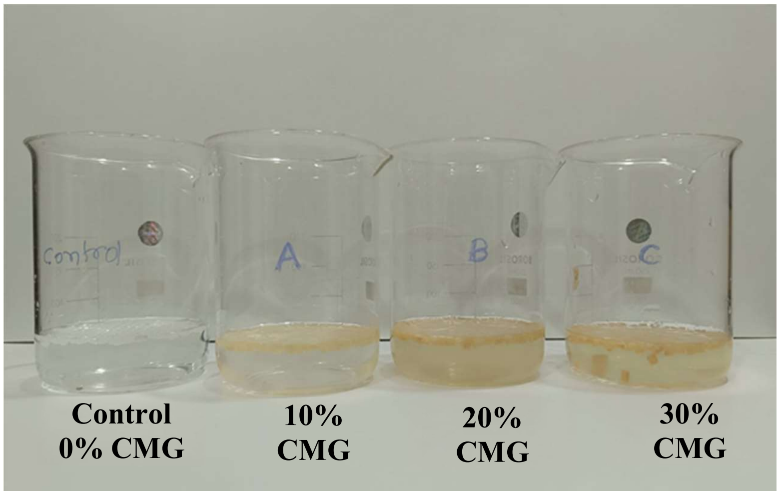


Fig. 4.4: Water Solubility Test for CMG-LDPE Blends

Further, the water was discarded, and the samples were dried in a hot air oven which was set at 60^0C for 24 h. The water solubility of the CMG-LDPE blends was calculated using Eqn. 4.3.

$$\text{Water Solubility } (\%) = \frac{(\text{Initial dry weight} - \text{Final dry weight})}{\text{Initial dry weight}} \times 100 \ldots..(4.3)$$

4.5 Results and Discussions

The detailed observations on the characterization and evaluation of CMG-LDPE blends are discussed below.

4.5.1 Differential Scanning Calorimetry

Figure 4.5 shows the DSC thermograms of the CMG-LDPE blends. The thermograms indicate that increasing percentage of CMG in the blend does not introduce any new there is no additional exothermic or endothermic peaks. This suggests that the addition of CMG does not significantly alter the thermal behavior of the blend. However, the enthalpy of LDPE melting decreases further with an increase in the CMG percentage from 10% to 30%.

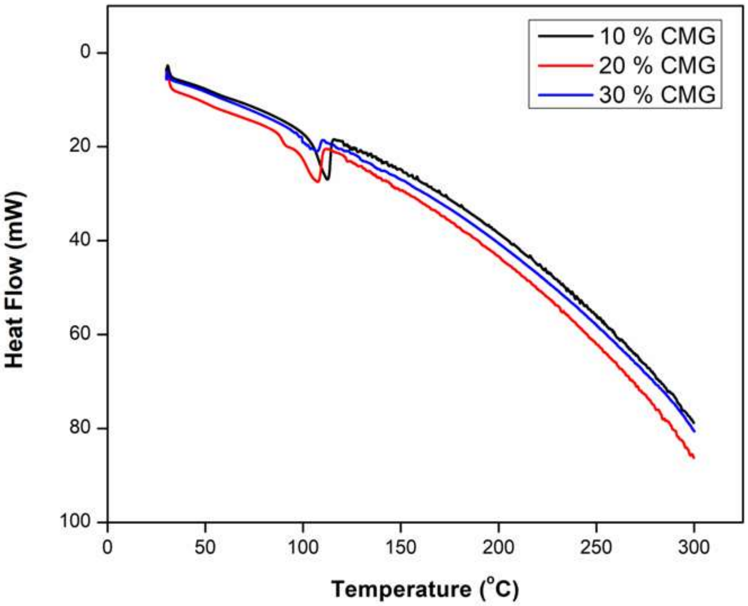


Fig. 4.5: DSC Thermograms of the CMG-LDPE Blends

All three curves show only one single characteristic peak corresponding to LDPE. However, the peak area increases with an increase in the percentage of CMG from 10% to 30%. It can also be noted that the Melting temperature (Tm) of LDPE decreases from 112.48°C to 107.18°C with the increasing CMG concentration from 10% to 30%. This decrease in the melting point may be due increased percentage of CMG in the matrix of LDPE which allows more surface area and improves the heat transfer to the LDPE molecules. The Similar observations have been reported by Rogovina SZ et al [9].

4.5.2 Thermogravimetric Analysis

Figure 4.6 shows TGA thermograms of the 10%, 20% and 30% CMG-LDPE blends. It is observed that with an increase in the CMG concentration in the blend, the weight loss decreases from 10% to 30% CMG-LDPE blends.

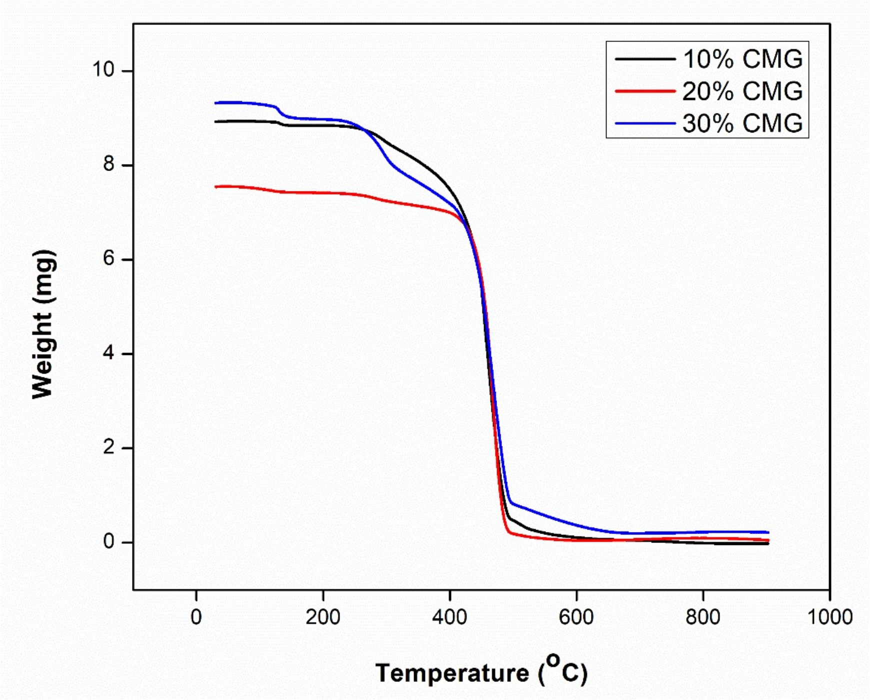


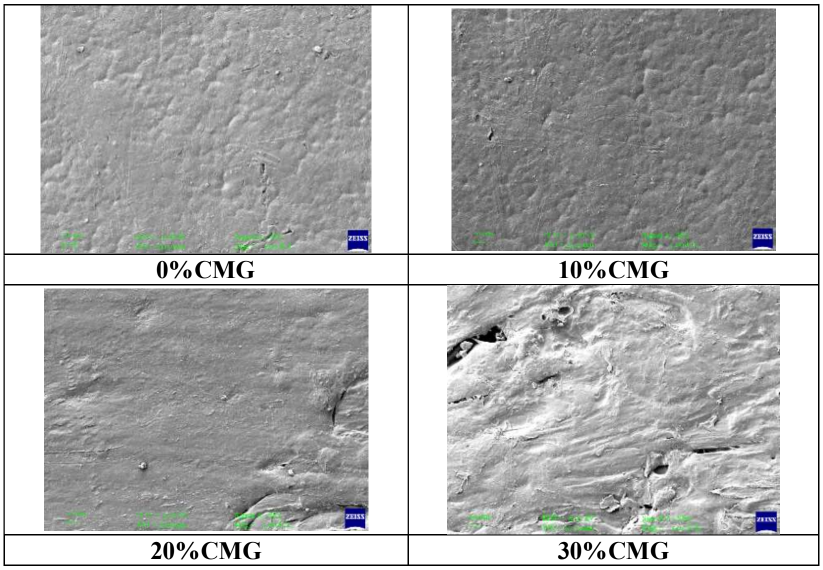
Fig. 4.6: TGA of CMG-LDPE Blends

The thermograms of CMG-LDPE blends showed a multi-stage weight loss. The thermal degradation of CMG/PE blends with 10%, 20%, and 30% CMG follows four stages of decomposition as shown in Fig. 4.6. The first stage occurs from 30 to 190 °C in case of 10%, 20%, and 30% respectively which indicates the vaporization of water and lower molecular weight component. The second stage occurs from 190-290 °C indicates the loss of functional groups such as carboxymethyl and hydroxyl groups of the polymeric backbone in the case of 10%, 20%, and 30% respectively. In the third step, degradation ranges from 290 to 450 °C may attributed to the loss of cross-linking present in CMG/PE blends with 10%, 20%, and 30%, respectively. Lastly, the weight loss from 450 to 630 °C was observed due to the complete degradation of CMG/PE blends with 10%, 20%, and 30%, respectively. In comparison with the degradation temperature of pure LDPE which is in the range of 399 to 494 °C, as reported by Cornelia Vasile et al, MA Yusof et al, and [20, 21], the degradation temperature of CMG-PE blends is much higher. This suggests the improved processing stability of the CMG-PE blends.

Therefore, it may conclude, that with an increase in the CMG concentration in the blend, the weight loss decreases from 10% to 30% CMG-PE blends. However, the initial weight loss increased from 10% to 30% CMG-PE blends. At the initial stage, the 30% CMG blend had the highest weight loss. This highest weight loss in the 30% CMG blend could be initially due to the highest moisture content in the 30% CMG blend sample. Similarly, the lowest initial weight loss may be attributed to the lowest moisture content of the 10% CMG blends. Further, in the next stage, all 10%, 20%, and 30% blends showed a similar weight loss trend. This could be attributed to the degradation of the polymer backbone

4.5.3 Scanning Electron Microscopy

Figure 4.7 shows the SEM micrographs of the CMG-LDPE blends. The analysis shows that as the percentage of CMG in the blends increases from 10% to 30%, the surface irregularities also increases.



0%CMG **10%CMG**

20%CMG **30%CMG**

Fig. 4.7: SEM Micrographs of CMG-LDPE Blends

The increase in surface roughness with an increase in CMG in the blend is likely due to the dispersion of the CMG within the LDPE matrix. This dispersion can create irregularities and imperfections on the surface of the material [22].

4.5.4 Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy

Figure 4.8 shows the FTIR spectra of the CMG-LDPE blends to observe the effect of varying CMG amounts in the CMG-LDPE blend.

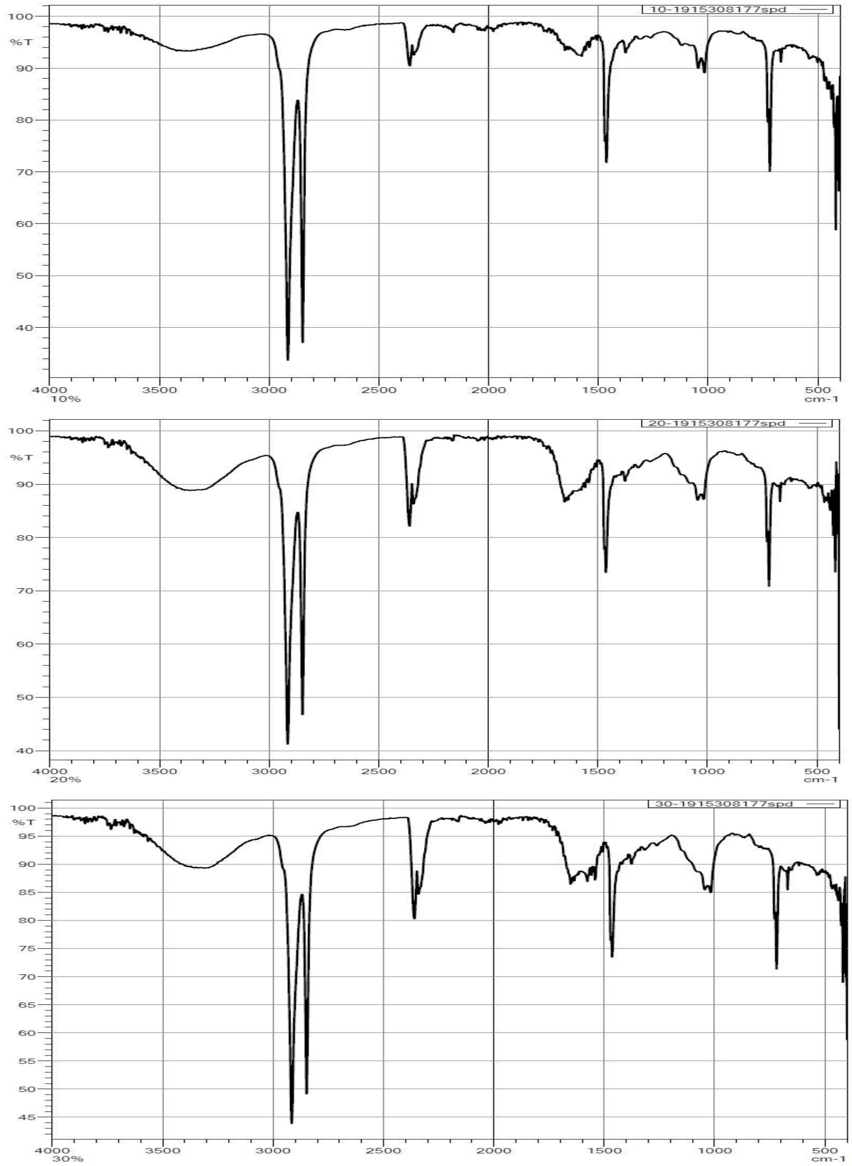


Fig. 4.8: FTIR Spectra of a) 10%, b) 20% and c) 30% CMG-LDPE Blends

In Figure 4.8, on comparing spectra a, b, and c, the peaks of OH bands are observed at around 3300-3400 cm^{-1}, the peak intensity increases as the CMG content increases, the number of hydroxyl (OH) groups increases from 10% to 30%, leading to changes in the chemical composition or interactions between the components of the blends.

The peak around 1400-1450 cm^{-1} is attributed to the carboxylic group present in the blends, and the intensity of the peak increases as the CMG content increases this may be attributed to the higher concentration of carboxylate groups in the blend. This indicates a stronger presence of the CMG component and its associated functional groups.

Almost similar spectra were observed in all blends. A small shift in peak position was observed in spectra, which may be attributed to the changes in the molecular environment or interactions between the components.

The band around 2850-2950 cm^{-1} is attributed to CH stretching, while the peak at 1429-1450 cm^{-1} denotes a COO^- symmetric stretch, the peak at 1600-1615 cm^{-1} corresponds to COO^- asymmetric stretch, and the 1020-1030 cm^{-1} denotes C-O-C peak in all spectra.

4.5.5 Tensile Strength and Elongation at Break

Figure 4.9 shows the trend of tensile strength of the CMG-LDPE blends. It is observed that the tensile strength decreases on increasing the CMG percentage from 10% to 30% in the blend. The decrease in the tensile strength may be attributed to the dispersion of CMG molecules in the matrix of polyethylene on blending and lower interfacial adhesion of CMG with polyethylene matrix. The brittleness of CMG-LDPE blends may also be the reason behind the decrease in tensile strength. The similar trend has been reported by Rogovina SZ et al and Irwanto D et al [9, 23].

The analysis shows that adding 10% CMG results in a significant decrease in tensile strength from 10.00MPa to 7.85MPa. However further increases in CMG content to 20% and 30% lead to only minimal decreases in the tensile strength, from 7.85MPa to 7.57 MPa and from 7.57 MPa to 7.39 MPa respectively.

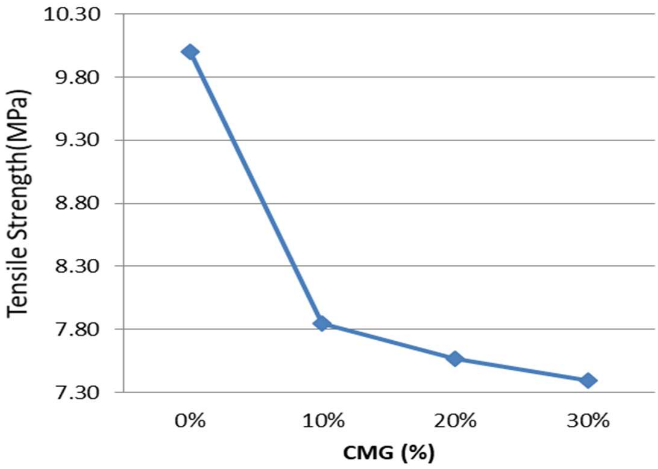


Fig. 4.9 Tensile Strength of CMG-LDPE Blends

Figure 4.10 illustrates the trend in elongation at break for the CMG-LDPE blends. The results indicate that as the percentage of CMG in the blend increases the elongation at break steadily decreases. This suggests that CMG-LDPE blends with up to 30% CMG can still be processed effectively.

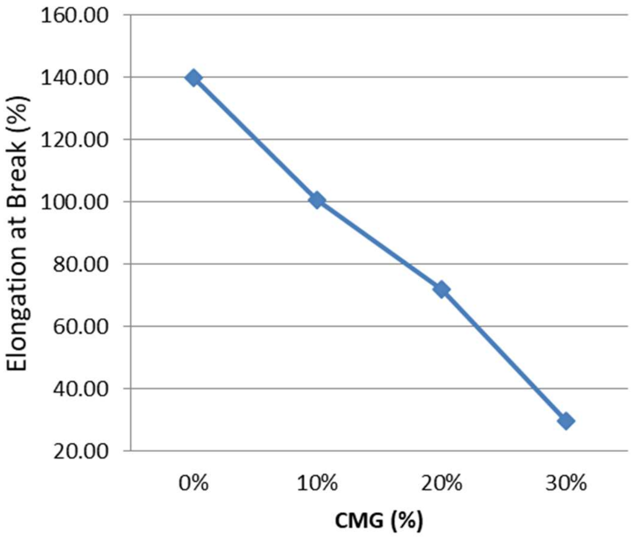


Fig. 4.10: Elongation at Break of CMG-LDPE Blends

This steady decrease in the elongation at break may be attributed to the lower inter-facial adhesion between the polysaccharide molecules with LDPE matrix [9, 23].

Further these tensile strength and elongation trends opens up the multiple windows for applications of the CMG-LDPE blends for packaging. As the tensile strength of the 10%, 20% and 30% CNG-LDPE blends is very close and comparable with various other biopolymers like starch-based films (4.8MPa to 5MPa) [24], and also with some of the synthetic polymers like polyethylene-based films (10MPa) [14], flexible CMG-LDPE blends can be used for films and comparatively rigid CMG-LDPE blends can be used for making containers for packaging of various products.

4.5.6 Izod Impact Test

Figure 4.11 provides information on the Izod impact strength of the fabricated CMG-LDPE Blends. The graph shows that the Izod impact strength decreases as the percentage of CMG in the CMG-LDPE blend increase. The decrease in the Izod impact strength is attributed to the incorporation of increasing amounts of CMG in the CMG-LDPE blends. This addition weakens the specimen matrix and reduces its toughness. (In case of 0% CMG blends as there was no break in the specimen it could not be shown in the graph)

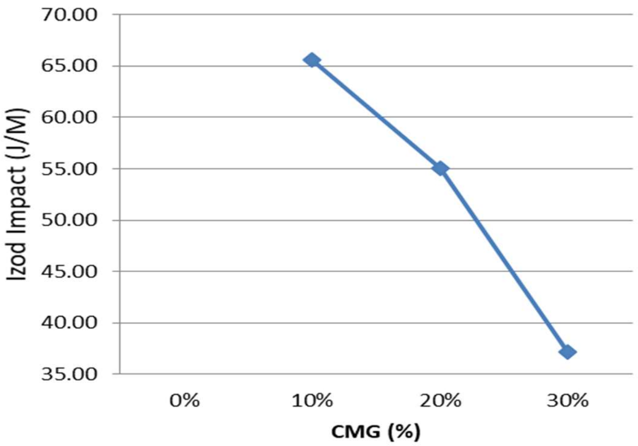


Figure 4.11: Izod Impact Strength of CMG-LDPE Blends

4.5.7 Melt Flow Index

Figure 4.12 shows the melt flow rate (MFI) of the fabricated CMG-LDPE blends at 120^0C at 2.1 kg load. It is seen that the MFI decreases with an increase in the percentage of CMG in the CMG-LDPE blend.

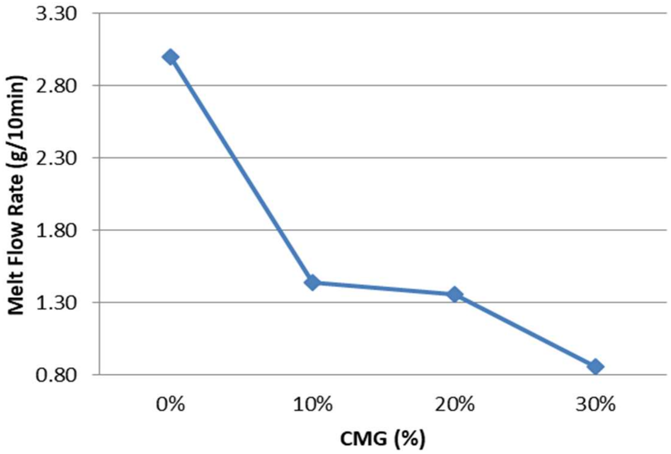


Fig. 4.12: Melt Flow Rate (Index) of CMG-LDPE Blends

The addition of CMG increases the viscosity of the CMG-LDPE blends upon melting. This reduce flowability results in a lower melt flow index (MFI).

The MFI test revealed that the internal shear between the CMG-LDPE blend material and the capillary wall of the equipment increases as the CMG content exceeds 30%. This increased shear led to the material sticking to the inner walls of capillary, which likely contributed to the decrease in MFI of the CMG-LDPE-blends on increasing the percentage of CMG in the blends. Similar observations have been reported in previous studies by Irwanto D et al [23].

4.5.8 Moisture Content

Figure 4.13 represents the moisture-holding capacity of the CMG-LDPE blends.

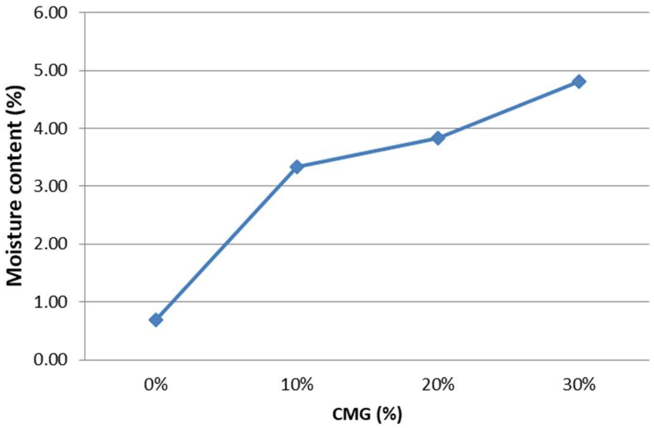


Fig. 4.13: Moisture Content of CMG-LDPE Blends

The graph illustrates that the moisture content of the CMG-LDPE blends increases with increase in the CMG percentage in the CMG-LDPE blends.

The increase in moisture content is attributed to the inherent moisture absorption property of CMG. As the percentage of CMG increases, so does the hydrophilicity of the material. This increase hydrophilicity allows for better moisture absorption from the atmosphere, leading to an increase in overall moisture content.

It's pertinent to mention that the maximum moisture content observed in the 30% CMG-LDPE blends was only 4.8%. This relatively low moisture content can be easily removed through drying before processing, suggesting that CMG-LDPE blends are suitable for commercial applications.

4.5.9 Water Absorption

Figure 4.14 shows the trend in water absorption for CMG-LDPE blends. The data indicates that as the percentage of CMG in the blend increases, the water absorption also increases.

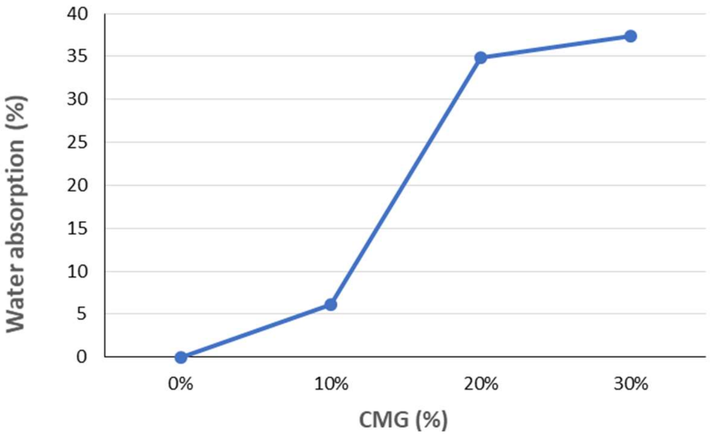


Fig. 4.14: Water Absorption of CMG-LDPE Blends

The increase in the water absorption is again due to the hygroscopic nature of the CMG. As the quantity of CMG increase in the blend higher amount of water is absorbed and thus the moisture absorption increases.

4.5.10 Water Solubility

Figure 4.15 shows the water solubility of the CMG-LDPE blends. It is observed that the water solubility of the CMG-LDPE blends increases with increase in the CMG percentage in the blends.

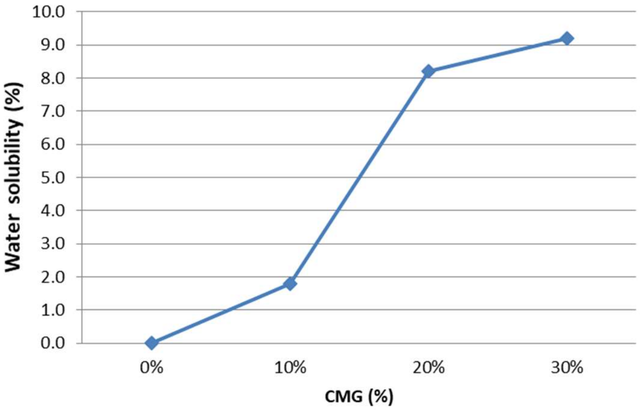


Fig. 4.15 Water Solubility of CMG-LDPE Blends

This increase in water solubility is likely due to the hydrophilic nature of CMG. As the percentage of CMG increases, the water solubility also increases. This suggests that CMG-LDPE blends have potential applications as water soluble polymers.

4.6 Conclusion

The successful fabrication of CMG-LDPE blends with 10%, 20% and 30% CMG suggests that these blends are processable on moulding machines. This indicates their potential commercial viability as packaging materials.

The DSC thermograms of the injection molded blends of CMG and LDPE suggested that the addition of CMG does not significantly alter the thermal behavior of the blend, thus shows possible commercial processing. The TGA thermograms suggests that the higher the percentage of CMG in the blend, the lower the total weight loss, attributed to the increased thermal stability of the blends with a higher CMG content. The SEM micrographs shows the irregularities and roughness on the surface of the blends which increases with an increase in CMG percentage in the blend. This confirms the dispersion of CMG within the LDPE matrix

The tensile strength of the 10%, 20% and 30% CMG-LDPE (7.85- 7.39 MPa) is comparable to that of various biopolymers like starch based films (4.85-5 MPa) and even some synthetic polymers like polyethylene based films(10 MPa). This suggests that CMG-LDPE blends have the potential to be used in applications that require similar mechanical properties.

Due to lower inter-facial adhesion between the CMG molecules with LDPE, the elongation at break steadily decreases as the percentage of CMG in the blend increases. This suggest its potential applications as flexible and rigid packaging materials by varying the percentage of CMG.

With further research, flexible CMG-LDPE blends can be used for flexible film, while comparatively rigid CMG-LDPE blends can be used for making thermoformed containers for packaging various products. Additionally, rigid CMG-LDPE composites sheets can be fabricated through compression molding for specific packaging purposes.

From the results of MFI test suggest that the CMG-LDPE blends with up to 30% CMG content can be easily processed commercially. However blends with higher CMG content i.e. 40% and 50% possess difficulty in processing due to increased internal shear and stickiness of the material.

The synthesized CMG-LDPE blends were found to be water-soluble, indicating its competitiveness with other available water-soluble biopolymers. This also suggests its probable use as water-soluble polymers in specific packaging applications.

The study revealed that on blending with LDPE, the water resistance of the CMG increases further in comparison with the water resistance of the films discussed in the chapter 3, which indicates probability of its wider applications in future.

The CMG-LDPE blends exhibit promising mechanical properties water solubility, making them potential candidates for diverse packaging applications.

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CHAPTER 5

SOIL-DEGRADATION STUDIES ON CMG-LDPE BLENDS

5.1 Introduction

With increasing concern about the disposal issues due to excessive consumption of various synthetic polymers used for packaging, the need for natural, biodegradable packaging material has been highlighted in recent years. Thus to reduce the burden of various packaging materials on the waste disposal system, the biodegradation of packaging material has gained importance. As the packaging materials made from synthetic polymers are not practically degradable, converting these synthetic polymers to biodegradable materials by mixing synthetic polymers with natural polymers will significantly help to reduce environmental burden. [1-7].

The CMG-LDPE blends were successfully extruded and molded (as discussed in chapter 4), demonstrating their potential for use as packaging materials. However, to assess their suitability for biodegradability packaging application, it is essential to evaluate biodegradability. The weight loss method using soil burial tests is a widely used approach for assessing the biodegradability of biopolymers [7–9].

Hence the soil degradation of the injection molded specimens of CMG-LDPE blends was investigated by soil burial test using weight loss method for 84 days. The weight loss in each specimen was monitored gravimetrically as a function of degradation time. The changes in chemical structure post soil-burial test were evaluated using ATR-FTIR analysis. The morphological changes were analyzed using electron microscopy (SEM) [10]. After the soil burial test, the specimens were analyzed for changes in color, weight loss, tensile strength, and elongation at break to confirming their biodegradability.

5.2 Soil Degradability of CMG-LDPE Blends

The soil degradation studies of the injection molded specimens made from CMG-LDPE blends with 10%, 20% and 30% of CMG were conducted using the soil burial method for a period of 84 days. For comparison a controlled sample of 0% CMG (100% LDPE) was also tested using the same method for 84 days.

The injection-molded specimens of each variant, measuring 25mm x 13mm x 3.2mm, were buried 5-6 cm deep in the plantation soil. The soil moisture was maintained periodically through out of 84-day study. Each specimen was retrieved at the end of every 7 days, washed thoroughly with distilled water to remove soil and other matter, and then dried in a hot air oven. The soil degradation of the CMG-LDPE blends was calculated based on the percentage weight loss.

The dried biodegraded specimens were further characterization using FTIR and SEM, and tested for change in color, tensile strength and elongation at break.

5.3. Characterization of CMG-LDPE Blends after Soil Burial Test of 84 days

After completion of soil degradation test on the CMG-LDPE blends were characterized using FTIR, and SEM.

5.3.1 Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy

The FTIR spectra of the CMG-LDPE blends after the 84-days soil burial test were analyzed using a Shimadzu Corp. ATR-FTIR instrument (Model: IR Affinity-1S). The spectra were recorded in the frequency range from 4000-400 cm^{-1}, at the spectral resolution of 5 cm^{-1}.

5.3.2 Scanning Electron Microscopy (SEM)

SEM analysis of the CMG-LDPE blends after the 84-day soil burial test was done using a Hitachi (Model: S-3400N) at an accelerating voltage of 5kV, by smearing with gold coating and to examine the surface morphology of the blends having different compositions of CMG under low vacuum pressure.

5.4 Testing of CMG-LDPE Blends after 84 Days Soil Burial Test

The specimens after completing the 84-day soil burial test were evaluated for color change, weight loss, tensile strength and elongation at break.

5.4.1 Change in Color

The change in color of all the CMG-LDPE blends after soil burial test was observed visually for any significant color change.

5.4.2 Soil Degradability by Weight Loss Method

As mentioned earlier, at the end of every 7 days, each specimen of CMG-LDPE blends was taken out from the soil and was washed properly with distilled water to remove the adhered soil and other matter from it. Then each specimen was dried in a hot air circulating oven to get a constant weight for three subsequent readings. The degradation of CMG-LDPE blends was calculated from the percentage weight loss, based on the dry weight of the specimens by taking the weight of each specimen before and after the test by using Eqn. 5.1.

Weight loss (%)=

$$\frac{(\text{Initial dry weight-Final dry weight})}{\text{Initial dry weight}} \times 100\ldots\ldots(5.1)$$

5.4.3 Tensile Strength and Elongation at Break

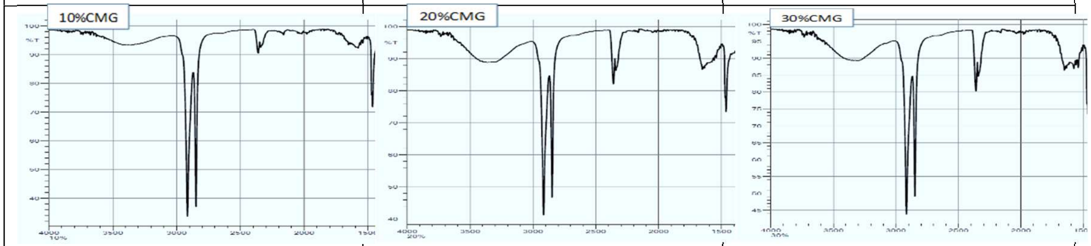
The samples of the CMG-LDPE blends were tested for tensile strength (TS) and elongation at break (% EAB) on a Universal Testing Machine (UTM) (Shimadzu, Autograph AG-X 110 N) with a 1kN load cell, using ASTM D 638 as a guideline with some modifications. The gauge length was 50 mm and a crosshead speed was 50 mm/minute. The results of tensile strength were reported in MPa and the strain at the break was reported as % EAB.

5.5 Results and Discussions

5.5.1 Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy

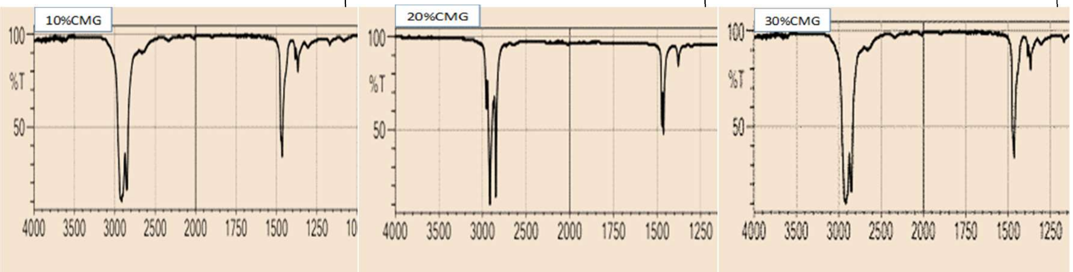
From the ATR-FTIR peaks of 10%, 20% and 30% CMG-LDPE blends shown in the Figure 5.1, it is observed that the intensity of OH peaks associated with CMG at 3300-3400 cm^{-1} vanished completely after 84 days which may be due to the degradation of CMG from the blends due to its water solubility or by bacterial action. The peak associated with the C=O bond at 1600-1700 cm^{-1} in CMG also showed a change in amplitude. This suggests a change in the chemical environment of the C=O group during the soil burial test [11, 12]. This observation along with other changes observed in the soil burial test, confirms the biodegradation of the 10%, 20% and 30% CMG-LDPE blends. The FTIR results indicate that CMG-LDPE blends are degradable in soil, suggesting their potential as alternatives to other similar biopolymers like starch in future applications. With further research, these blends could be developed into effective and sustainable packaging materials.

Before Soil Degradability test



10% CMG | 20% CMG | 30% CMG

After Soil Degradability test



10% CMG | 20% CMG | 30% CMG

Fig. 5.1: ATR-FTIR of CMG-LDPE Blends before and after Soil Degradability Test.

5.5.2 SEM Analysis

The SEM micrographs of the control sample and 10%, 20%, 30% CMG blends before and after the soil degradability test are shown in the Figure 5.2

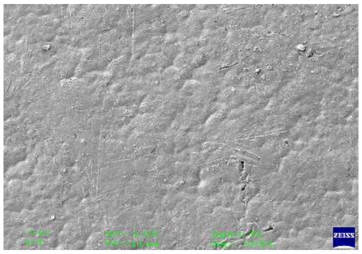
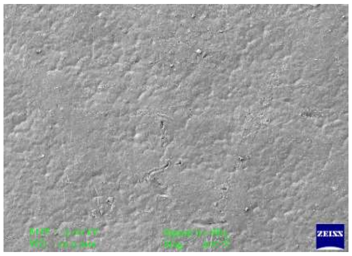
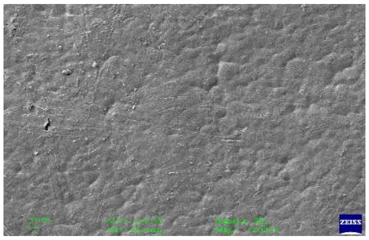
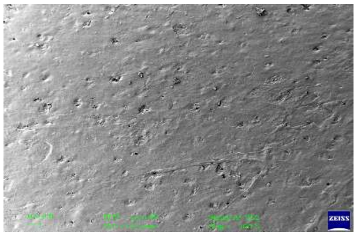
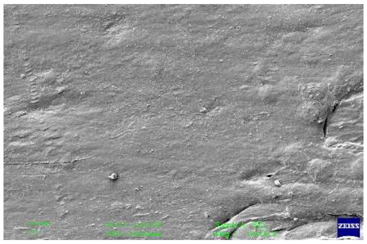
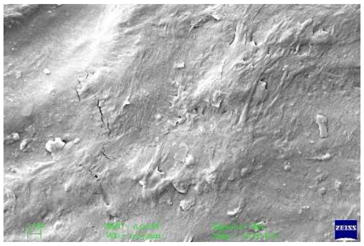
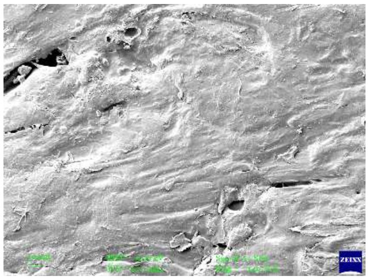
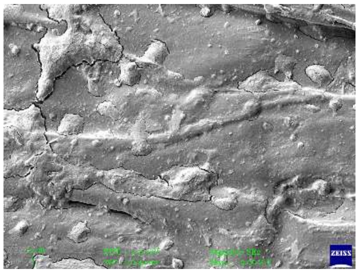
Sample	Before Soil Degradability test	After Soil Degradability test of 84 days
0% CMG		
10% CMG		
20% CMG		
30% CMG		

Fig. 5.2: SEM Micrographs of Control, 10%, 20%, 30% CMG Blends Before and After Soil Degradability Test

The SEM analysis shows that in the case of CMG blend with 0% CMG there is no change in the surface quality after soil degradability test compared to the original samples. This suggests that the 0% CMG blend (100% LDPE) maintained its surface integrity during the soil burial process.

Further the SEM analysis of 10%, 20%, and 30% CMG in the CMG-LDPE blend the surface shows

a) 10% CMG: Slight pitting of the surface but no cracking.

b) 20% CMG: More unevenness and fine cracks on the surface.

c) 30% CMG: Increased surface unevenness and roughness, with considerable surface cracking.

These results suggests that as the percentage of CMG in the blend increases, the surface degradation becomes more pronounced. This could be attributed to the increased biodegradability of the CMG component, which may lead to the breakdown of the polymer structure and the formation of surface defects.

5.5.3 Change in Color

The visual observations were taken for change in the color of all the samples tested for 84 days for soil burial test. Following Figure 5.3 shows the photographs of the specimens before and after completion of the soil burial test.

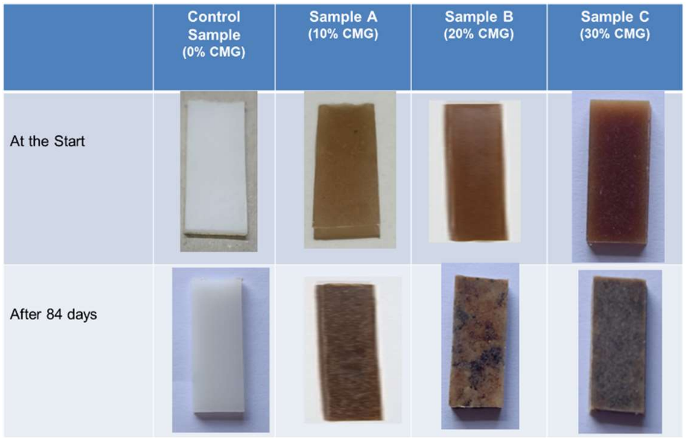


Fig. 5.3: Photographs of Specimens before and After Soil Burial Test

All the samples after 84 days of soil burial test were washed thoroughly with distilled water and dried in a hot air oven at 60^0C for 24 hrs. Further these samples were observed visually for color change.

The visual observations for the CMG-LDPE blends after the soil burial test are as follows:

a) 0% CMG: Neither colour change nor change in surface smoothness was observed.

b) 10% CMG: Very few blackish spots were observed, indicating minimal microbial growth. The surface smoothness remained largely unchanged.

c) 20% CMG: The sample turned slightly blackish, indicating increased microbial growth compared to the 10% CMG blend. The surface became slightly rougher.

d) 30% CMG: Considerable blackish spots were observed, indicating significant microbial growth. The surface became noticeably rougher.

These observations suggest that as the percentage of CMG in the blends increases, the susceptibility to microbial growth and surface degradation also increases.

An increase in the black spots on the specimens of 10%, 20% and 30% CMG blends, may be due to development of microbial growth caused by the morphological alterations indicating degradation of the blends in the soil burial test.

The visual observations revealed that in the case of 20% and 30% CMG blends, the blackish spots were visible on more than 90% area of the sample. This observation aligns with the findings from the FTIR and SEM analysis of these samples. Similar observations have been reported by Sharma K et al and Rogovina SZ et al [11, 13].

The increase in the intensity of the blackish spots on the CMG blends from 10% to 30% shows that the degradability of the blend increases with increase in the percentage of CMG in the CMG-LDPE blends.

5.5.4 Weight Loss after Soil Degradability Test

Figure 5.4 shows the weight loss of the CMG-LDPE blends over the 84-day soil burial test.

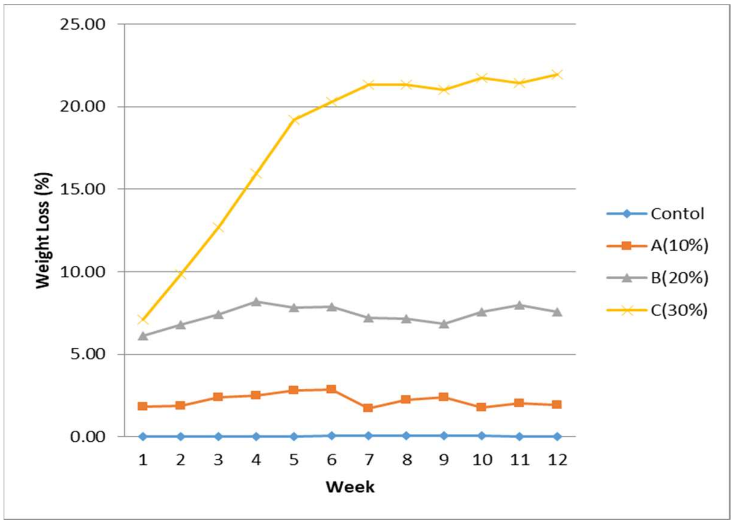


Fig. 5.4: Weight Loss Trend for Control, 10%, 20%, and 30% CMG Blends

From the graph in the Figure 5.4, it is observed that initially the rate of weight loss is rapid, however further it was slower. This trend could be associated with the dissociation and loss of CMG from the blends due to its water soluble nature. The 21.954% soil degradability observed at the end of 84 days, in case of 30% CMG-blends.

The weight loss observed in the soil burial test can be correlated to the degradation behavior of the CMG-LDPE blends. Which has indicated that the weight loss of the samples of CMG-LDPE blends which increase with increase in the percentage of CMG in the CMG-LDPE blends from 10% to 30% CMG. Thus the CMG-LDPE blends are promising as a sustainable packaging material.

5.5.5 Tensile Strength after Soil Degradability Test

Figure 5.5 shows the tensile strength of control, 10%, 20% and 30% CMG-LDPE blends before and after soil burial test. It is seen that after the soil degradation test of 84 days, tensile strength decreases with an increase in the CMG percentage in the CMG-LDPE blend.

The decrease in the tensile strength of CMG blends is due to the separation of CMG molecules from the blends due to its solubility in water, generating weakened matrix, and causing brittleness of the specimen.

There is no change in the tensile strength of control sample. However, decrease of tensile strength observed after soil burial test in all 10%, 20% and 30% CMG-LDPE blends.

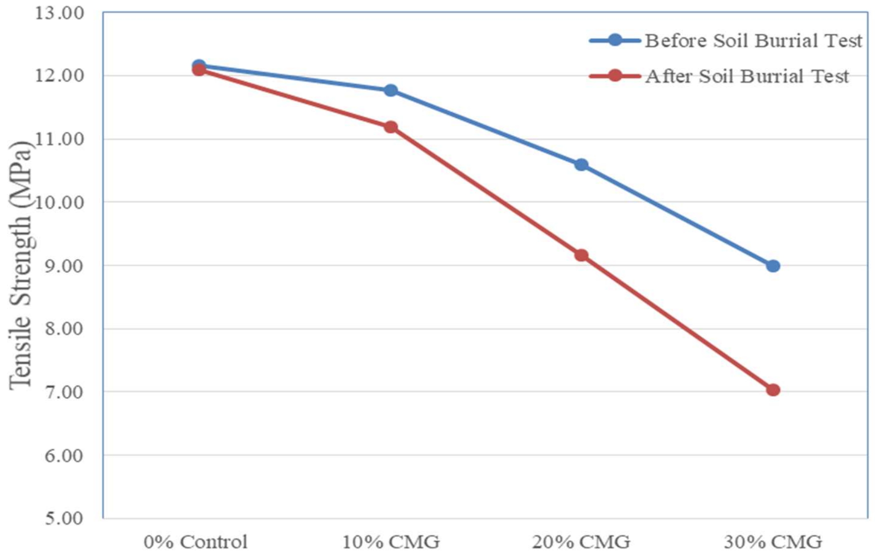


Fig. 5.5: Tensile strength of controlled, 10%, 20% and 30% CMG-LDPE blends.

5.6 Conclusion

The soil degradability of the CMG-LDPE blends was studied for 84 days. All the 10%, 20%, and 30% CMG-LDPE blends under study were found soil-degradable. This is supported by the FTIR and SEM analysis. FTIR analysis shows that the OH peaks disappeared after 84 days and the SEM micrographs showed surface erosion and cracking in the specimens.

The color of the CMG blends was found blackish due to microbial growth due to the presence of CMG in the matrix. The observation of increasing blackish spots with higher CMG content suggests that the CMG component is more susceptible to microbial degradation, leading to the formation of these dark spots.

The weight loss percentage of the CMG-LDPE blends increases with an increase in the percentage of CMG in the blend. This suggests that the biodegradability of the blends improves with higher CMG content. The observed soil degradability of

1.938%, 7.578% and 21.954% for 10% 20% 30% CMG blends respectively, demonstrates their potential as sustainable packaging materials.

The tensile strength and elongation at break of the CMG-LDPE blends were found to decrease with increasing CMG content after the 84-day soil burial test. This decrease in mechanical properties is indicative of biodegradation.

Overall, the observations suggests that CMG-LDPE blends are environmentally friendly and have competitive advantage over synthetic polymers. Their biodegradability, coupled with their reasonable mechanical properties, makes them promising candidate for sustainable packaging applications.

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CHAPTER 6

CONCLUSION, FUTURE SCOPE AND SOCIAL IMPACT

The main objective of this research was to fabricate and analyze the biopolymeric materials for packaging applications. It is important to highlight that the biopolymer-based films and coatings represent a significant stride towards sustainable packaging solutions by employing materials such as alginate, chitosan, cellulose, guar gum, and starches.

The literature survey in chapter 1, highlighted that carboxymethyl guar gum (CMG) has yet to be explored for packaging material applications. This suggests the potential novelty and untapped possibilities of incorporating CMG into eco-friendly packaging solutions. As a result, this research work was divided into the following areas:

1. Fabrication and characterization of Carboxymethyl guar gum (CMG) based material using suitable plasticizers and crosslinkers for packaging applications.
2. Optimization of the process parameters for fabricated biopolymer material
3. Assessing commercial-scale production and evaluation of properties by blending with synthetic polymers.
4. Testing of the fabricated films and blends for packaging applications.

The research findings indicate that CMG based biopolymer and their blends with LDPE are promising biopolymeric materials for packaging applications. This conclusion is based on the following studies conducted in this research.

6.1 CMG Based Films

- Series of CMG-based films were successfully fabricated by utilizing glycerol as a plasticizer and glutaraldehyde as a cross-linking agent by solution casting method.
- The reaction temperature was optimized at 75 ^{o}C by using DSC and TGA. CMG films indicated good film-forming properties at 75 ^{o}C temp.

- SEM and FTIR studies indicated evidence of cross-linking of CMG with glutaraldehyde and glycerol
- CMG-based films were evaluated for tensile strength, elongation at break, thickness, gloss, haze, transparency, and water solubility.

The maximum values observed were:

- Tensile strength: 37.82 MPa,
- Elongation at break : 124.20%
- Gloss 25.52%
- Haze 41.93%
- Transparency 88.53%.

These values suggest that the CMG based films exhibit good mechanical properties, flexibility, and optical clarity, making them suitable for various packaging applications.

- Solubility test results indicated a minimum water solubility of 60.42% which indicates the potential applications of CMG-based films in areas such as edible coatings and water-soluble packaging. The water solubility of the CMG-based films decreases with the increase in the concentration of cross linker (Glutaraldehyde)
- The potato wrapping study indicated the applications of CMG-based films for cut fruits and vegetable packaging
- All the above properties of the fabricated CMG-based films indicate the possibility of their packaging applications.

6.2 CMG-LDPE Blends

- The CMG-LDPE blends were successfully fabricated with 10%, 20% and 30% CMG. This suggests that these blends are processable on commercial molding machines, indicating their potential for large-scale production and commercial applications.

- The CMG-LDPE blends with more than 40% and 50% CMG could not be successfully fabricated due to increased internal shear between LDPE and CMG as well as between barrel and screw. The high shear let to material degradation and lump formation due to the increased stickiness of the material making processing difficult.
- The water resistance of CMG-LDPE blends was found to be higher than that of CMG-based films. This increased water resistance that CMG-LDPE blends have potential applications in packaging where water resistance is a crucial requirement.
- With further research the flexile CMG-LDPE blends can be used as flexible packaging and rigid blends can be used for thermoformed containers.

6.3 Soil Degradability of CMG-LDPE Blends

- The soil degradability of the CMG-LDPE blends was studied for 84 days by using the weight loss method. All the 10%, 20%, and 30% CMG-LDPE blends were found to be biodegradable. This conclusion is supported by the FTIR and SEM analysis. The FTIR spectra showed decreased in the intensity of OH peaks after 84 days while the SEM micrographs revealed surface erosion and cracking in the specimens.
- The soil degradability of the CMG-LDPE blends increases with an increase in the percentage of CMG in the blend. This is evident from the observed soil degradability values of 1.938%, 7.578% and 21.954% for 10%, 20% and 30% CMG blends respectively.
- The tensile strength and elongation at break of the CMG-LDPE blends decreased with an increase in the percentage of CMG after 84-day soil burial test. This decrease in mechanical properties is a positive indication of the blend’s biodegradability.
- The blackish spots observed on the CMG-LDPE blends after 84 days of soil burial are likely due to microbial degradation of CMG component within the LDPE matrix. The intensity of these blackish spots increased with an increase in

the percentage of CMG from 10% to 30% in the blends, suggesting a greater degree of microbial activity and degradation.

- Overall, the observations suggests that CMG-LDPE blends have potential for packaging applications. These blends demonstrate environmental friendliness and offer competitive advantages compared to synthetic polymers.

6.4 Future Scope of Work

- The present research work indicates that CMG and its cross-linked derivatives, as well as their blends with synthetic polymers, have potential applications in packaging. This suggest that these material offer promising alternatives for sustainable and eco-friendly packaging solutions.
- The fabricated CMG-based films, which are transparent, fairly durable, and soil degradable, have potential applications in packaging for food and related products. This suggest that CMG-based packaging materials could be used for coatings, films, and containers in various food packaging applications.
- By modifying the plasticizers and cross-linkers used in CMG-based materials, it is possible to develop a new and improved categories of packaging materials. This approach can help to tailor the properties of CMG-based materials to meet specific packaging requirements.
- Further research on CMG could lead to its use as a soil-degradable additive in packaging materials. Additionally, CMG could potentially serve as a shelf life extender for packaging of cut fruits and vegetables.
- While CMG-LDPE blends have shown potential as packaging materials, further research is needed to explore their applications in rigid packaging.

6.5 Social Impact

Potential Societal Impact of CMG-Based Packaging Materials

The research presented in this thesis on CMG-based packaging materials has the potential to make a significant positive impact on society in several ways:

1. **Waste Reduction**
   - **Soil degradability:** The soil-degradable nature of CMG-based packaging materials can help reduce waste disposal problems globally.
   - **Reduced reliance on synthetic polymers:** By replacing synthetic polymers with biodegradable CMG-based materials, the burden on solid waste disposal can be significantly decreased
2. **Advancements in Food Packaging:**
   - **Edible and Water-Soluble Packaging:** CMG-based packaging materials can be developed for use in the food industry, offering alternatives to traditional synthetic packaging materials. This could lead to more sustainable and environmentally friendly food packaging solutions.
3. **Competitive Advantage:**
   - **Sustainability:** CMG-based packaging materials can compete with existing packaging materials on the basis of their sustainability. This could encourage the adoption of more eco-friendly packaging solutions.
4. **Increased Consumer Awareness:**
   - **Sustainable Biopolymers:** The development of CMG-based packaging materials can help raise consumer awareness about sustainable biopolymers and their advantages over synthetic polymers.
5. **Environmental Benefits:**
   - **Reduced Environmental Burden:** By reducing reliance on synthetic polymers, CMG-based packaging materials can help decrease the environmental burden associated with plastic waste.
   - **Resource Conservation:** The use of biodegradable materials can contribute to resource conservation and reduce the consumption of non-renewable resources

LIST OF PUBLICATIONS

Journal Articles

1. Subodh K. Juikar, and Sudhir G. Warkar*, 2023, Biopolymers for packaging applications: An overview, *Packaging Technology and Science-An International Journal, Wiley Online Library, Volume 36 (4), pages 229-251 (April 2023). https://doi.org/10.1002/pts.2707.*

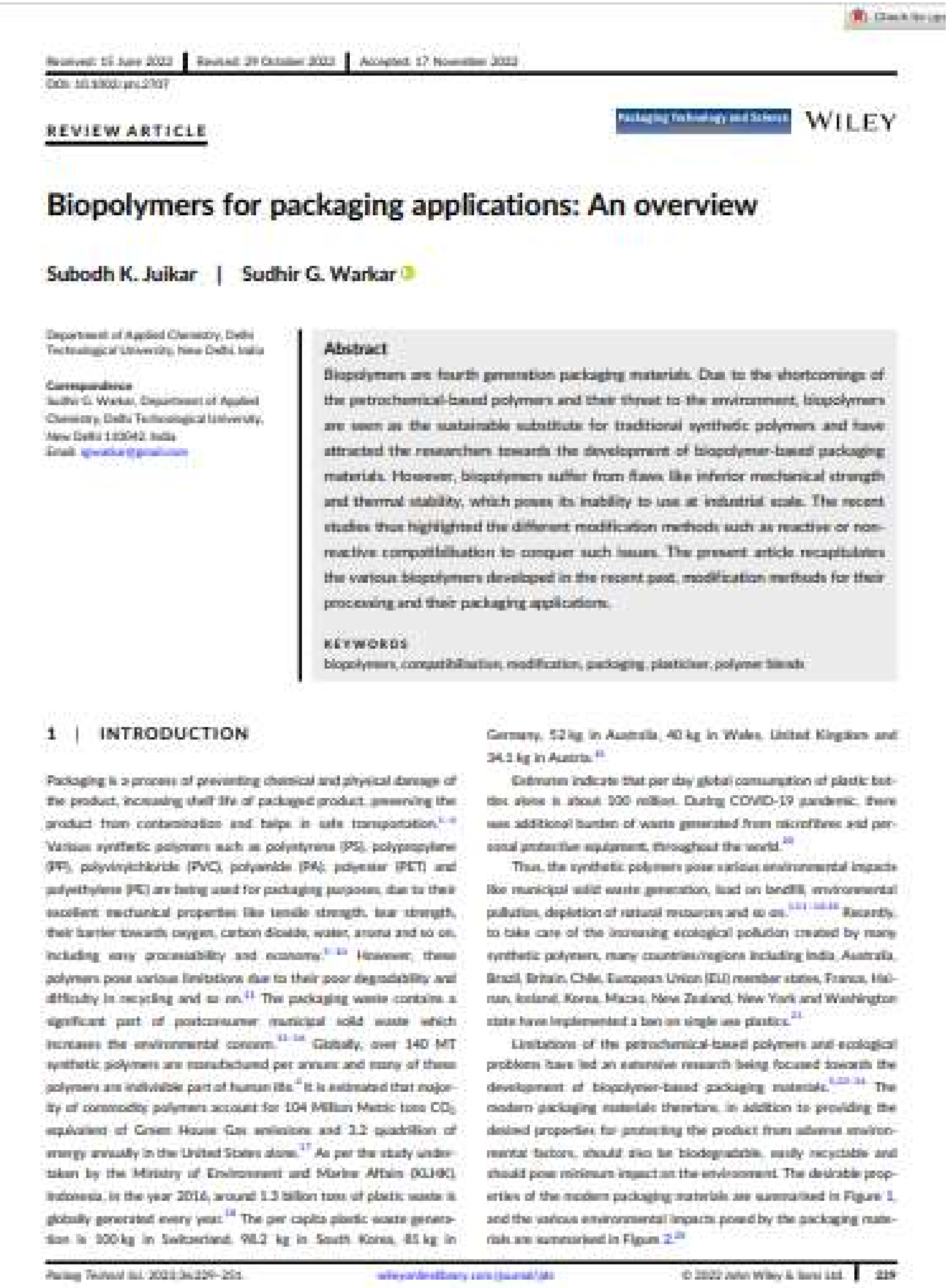
2. Subodh K. Juikar and Sudhir G. Warkar*, Fabrication and assessment of carboxymethyl guar gum-based sustainable films for packaging application, *Colloid and Polymer Science, Volume 302, pages 1137-1148 (April 2024).*

   https://doi.org/10.1007/s00396-024-05257-8

Conference Presentations:

1. “Biopolymers” at Research Conclave during International “Asian Packaging Congress” on “Packaging 3-S; Safe, Secure, Sustainable; 17th and 18th March 2023, New Delhi.

2. ‘Biopolymers for Packaging Applications” at International Hybrid Conference on Nano-Structured Materials and Polymers; 12th – 14th May 2023, held at M. G. University, Kerala.



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REVIEW ARTICLE

Packaging Technology and Science WILEY

Biopolymers for packaging applications: An overview

Subodh K. Juikar | **Sudhir G. Warkar**

Department of Applied Chemistry, Delhi Technological University, New Delhi, India

Correspondence
Sudhir G. Warkar, Department of Applied Chemistry, Delhi Technological University, New Delhi 110042, India
Email: sgwarkar@gmail.com

Abstract

Biopolymers are fourth generation packaging materials. Due to the shortcomings of the petrochemical-based polymers and their threat to the environment, biopolymers are seen as the sustainable substitute for traditional synthetic polymers and have attracted the researchers towards the development of biopolymer-based packaging materials. However, biopolymers suffer from flaws like inferior mechanical strength and thermal stability, which poses its inability to use at industrial scale. The recent studies thus highlighted the different modification methods such as reactive or non-reactive compatibilisation to conquer such issues. The present article recapitulates the various biopolymers developed in the recent past, modification methods for their processing and their packaging applications.

KEYWORDS
biopolymers, compatibilisation, modification, packaging, plasticiser, polymer blends

1 | INTRODUCTION

Packaging is a process of preventing chemical and physical damage of the product, increasing shelf life of packaged product, preserving the product from contamination and helps in safe transportation.[1–4] Various synthetic polymers such as polystyrene (PS), polypropylene (PP), polyvinylchloride (PVC), polyamide (PA), polyester (PET) and polyethylene (PE) are being used for packaging purposes, due to their excellent mechanical properties like tensile strength, tear strength, their barrier towards oxygen, carbon dioxide, water, aroma and so on, including easy processability and economy.[5–10] However, these polymers pose various limitations due to their poor degradability and difficulty in recycling and so on.[11] The packaging waste contains a significant part of postconsumer municipal solid waste which increases the environmental concern.[12–16] Globally, over 140 MT synthetic polymers are manufactured per annum and many of these polymers are indivisible part of human life.[4] It is estimated that majority of commodity polymers account for 104 Million Metric tons CO_2 equivalent of Green House Gas emissions and 3.2 quadrillion of energy annually in the United States alone.[17] As per the study undertaken by the Ministry of Environment and Marine Affairs (KLHK), Indonesia, in the year 2016, around 1.3 billion tons of plastic waste is globally generated every year.[18] The per capita plastic waste generation is 100 kg in Switzerland, 98.2 kg in South Korea, 85 kg in Germany, 52 kg in Australia, 40 kg in Wales, United Kingdom and 34.1 kg in Austria.[19]

Estimates indicate that per day global consumption of plastic bottles alone is about 100 million. During COVID-19 pandemic, there was additional burden of waste generated from microfibres and personal protective equipment, throughout the world.[20]

Thus, the synthetic polymers pose various environmental impacts like municipal solid waste generation, load on landfill, environmental pollution, depletion of natural resources and so on.[1,11–14,16] Recently, to take care of the increasing ecological pollution created by many synthetic polymers, many countries/regions including India, Australia, Brazil, Britain, Chile, European Union (EU) member states, France, Hainan, Iceland, Korea, Macau, New Zealand, New York and Washington state have implemented a ban on single use plastics.[21]

Limitations of the petrochemical-based polymers and ecological problems have led an extensive research being focused towards the development of biopolymer-based packaging materials.[5,22–24] The modern packaging materials therefore, in addition to providing the desired properties for protecting the product from adverse environmental factors, should also be biodegradable, easily recyclable and should pose minimum impact on the environment. The desirable properties of the modern packaging materials are summarised in Figure 1, and the various environmental impacts posed by the packaging materials are summarised in Figure 2.[25]

Packag Technol Sci. 2023;36:229–251. wileyonlinelibrary.com/journal/pts

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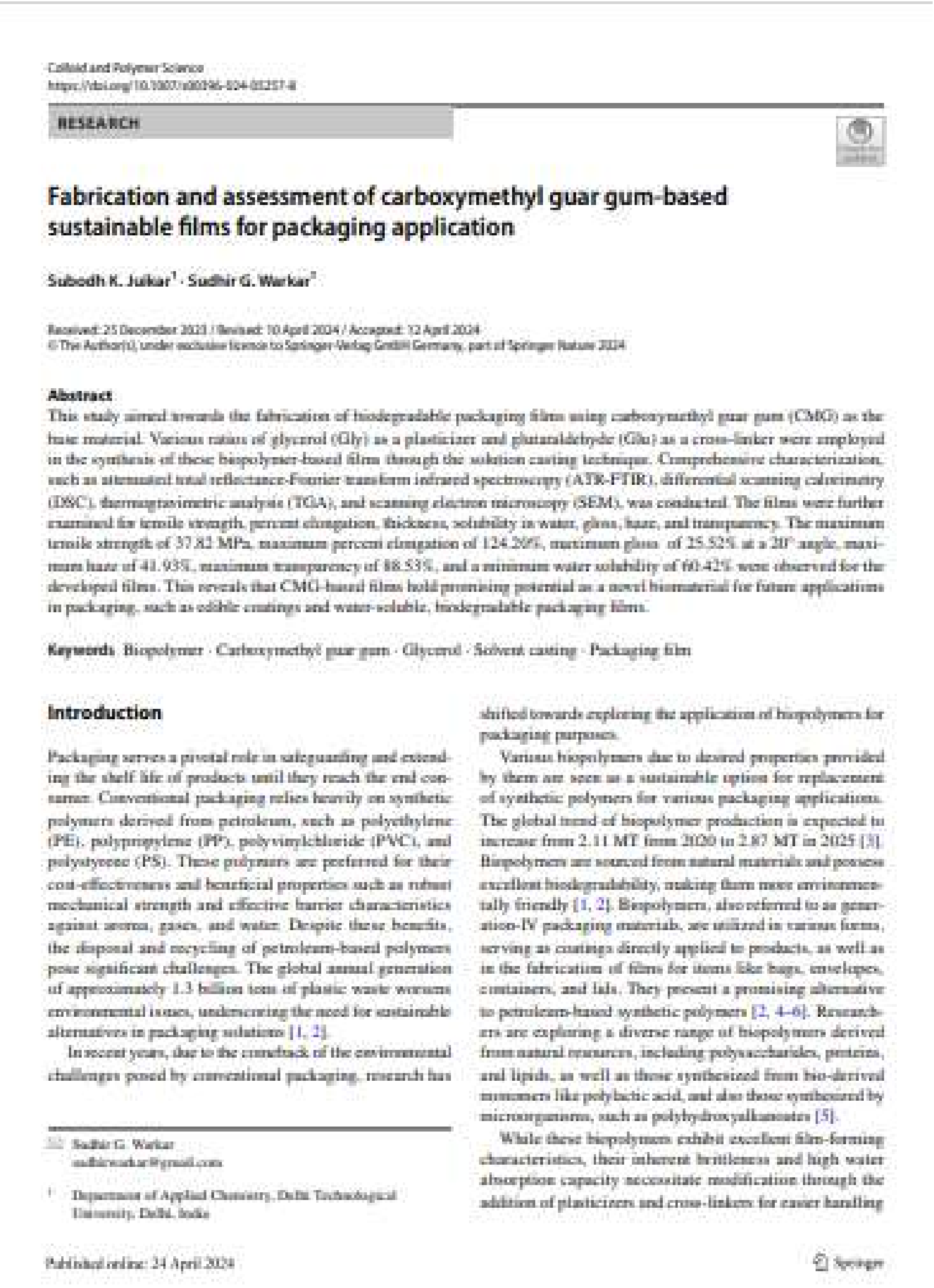

Colloid and Polymer Science
https://doi.org/10.1007/s00396-024-05257-8

RESEARCH

Fabrication and assessment of carboxymethyl guar gum-based sustainable films for packaging application

Subodh K. Julkar[1] · **Sudhir G. Warkar**[2]

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Abstract
This study aimed towards the fabrication of biodegradable packaging films using carboxymethyl guar gum (CMG) as the base material. Various ratios of glycerol (Gly) as a plasticizer and glutaraldehyde (Glu) as a cross-linker were employed in the synthesis of these biopolymer-based films through the solution casting technique. Comprehensive characterization, such as attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM), was conducted. The films were further examined for tensile strength, percent elongation, thickness, solubility in water, gloss, haze, and transparency. The maximum tensile strength of 37.82 MPa, maximum percent elongation of 124.20%, maximum gloss of 25.52% at a 20° angle, maximum haze of 41.93%, maximum transparency of 88.53%, and a minimum water solubility of 60.42% were observed for the developed films. This reveals that CMG-based films hold promising potential as a novel biomaterial for future applications in packaging, such as edible coatings and water-soluble, biodegradable packaging films.

Keywords Biopolymer · Carboxymethyl guar gum · Glycerol · Solvent casting · Packaging film

Introduction

Packaging serves a pivotal role in safeguarding and extending the shelf life of products until they reach the end consumer. Conventional packaging relies heavily on synthetic polymers derived from petroleum, such as polyethylene (PE), polypropylene (PP), polyvinylchloride (PVC), and polystyrene (PS). These polymers are preferred for their cost-effectiveness and beneficial properties such as robust mechanical strength and effective barrier characteristics against aroma, gases, and water. Despite these benefits, the disposal and recycling of petroleum-based polymers pose significant challenges. The global annual generation of approximately 1.3 billion tons of plastic waste worsens environmental issues, underscoring the need for sustainable alternatives in packaging solutions [1, 2].

In recent years, due to the comeback of the environmental challenges posed by conventional packaging, research has shifted towards exploring the application of biopolymers for packaging purposes.

Various biopolymers due to desired properties provided by them are seen as a sustainable option for replacement of synthetic polymers for various packaging applications. The global trend of biopolymer production is expected to increase from 2.11 MT from 2020 to 2.87 MT in 2025 [3]. Biopolymers are sourced from natural materials and possess excellent biodegradability, making them more environmentally friendly [1, 2]. Biopolymers, also referred to as generation-IV packaging materials, are utilized in various forms, serving as coatings directly applied to products, as well as in the fabrication of films for items like bags, envelopes, containers, and lids. They present a promising alternative to petroleum-based synthetic polymers [2, 4–6]. Researchers are exploring a diverse range of biopolymers derived from natural resources, including polysaccharides, proteins, and lipids, as well as those synthesized from bio-derived monomers like polylactic acid, and also those synthesized by microorganisms, such as polyhydroxyalkanoates [5].

While these biopolymers exhibit excellent film-forming characteristics, their inherent brittleness and high water absorption capacity necessitate modification through the addition of plasticizers and cross-linkers for easier handling

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✉ Sudhir G. Warkar
sudhirwarkar@gmail.com

[1] Department of Applied Chemistry, Delhi Technological University, Delhi, India

DELHI TECHNOLOGICASL UNIVERSITY
(Formerly Delhi College of Engineering)
Shahbad Daulatpur, Main Bawana Road, Delhi-42

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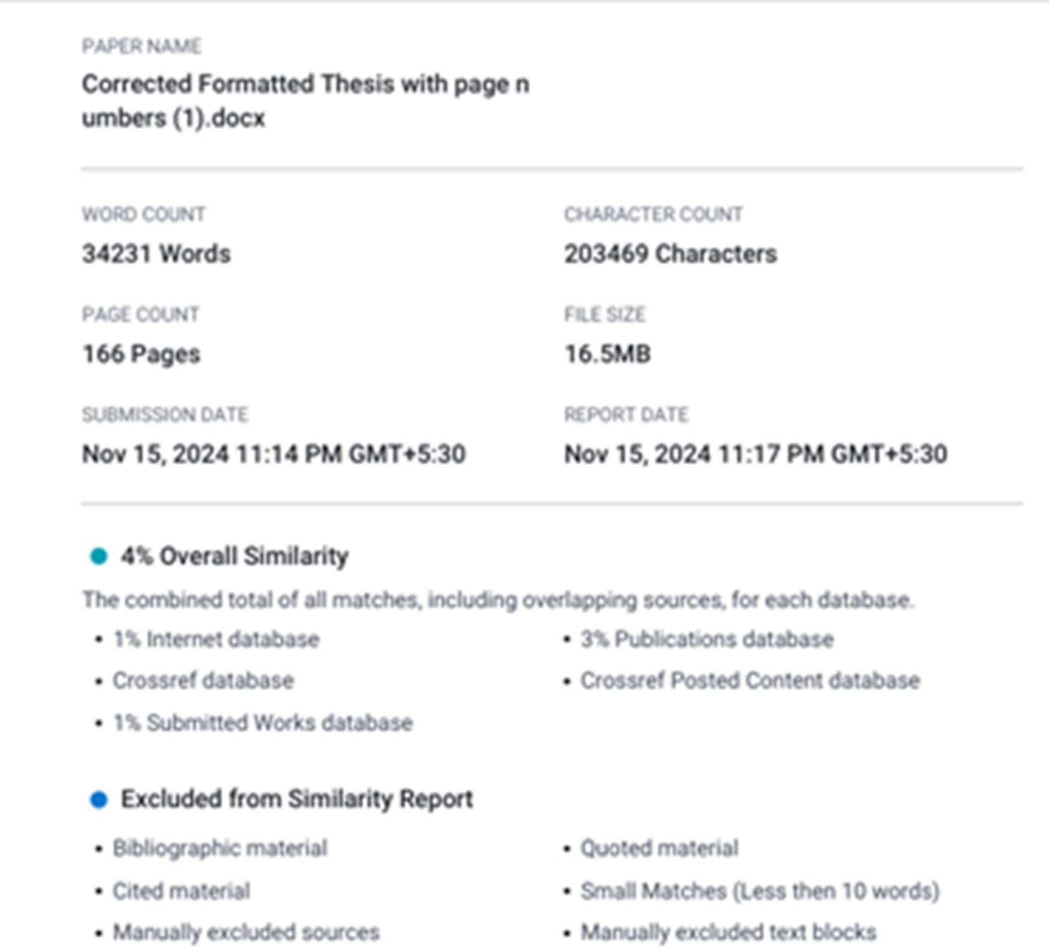

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CURRICULUM VITAE

Name	SUBODH KAMALAKAR JUIKAR
Date of Birth	01.06.1969
Male/Female	MALE
Marital Status	MARRIED
Fathers Name	KAMALAKAR RAMACHANDRA JUIKAR
Nationality	INIDAN
Address for correspondence	138/807, SARITA VIDYA MAHAL, NEHRU NAGAR, KURLA EAST, MUMBAI : 400 024
Mobile Number if any	09910204704
Email	subodh.k.juikar@gmail.com
Orchid ID	0009-0009-8736-9866
Research Gate	*https://www.researchgate.net/profile/Subodh-Juikar*
Google Scholar	*https://scholar.google.com/citations?view_op=new_profile&hl=en*

Education	***Branch / specialization***	***Year of passing***	***Name of the Institution***	***University/Board***
Ph. D	Chemistry	*2024*	Delhi Technological University	Delhi Technological University
M.Sc.	Chemistry	2010	Madurai Kamraj University	Madurai Kamraj University
M.B.A.	Operation Research	2001	K J Somaiya College Mumbai	Indira Gandhi National Open University
Advance Diploma in Computer Applications	Computer Applications	2004	Karrox Mumbai	Indira Gandhi National Open University
Intensive Training Course in Packaging	Packaging Technology	1998	Indian Institute of Packaging, Mumbai	Indian Institute of Packaging
OMCP Group –1 Supervisory Trade	Engg. Drawing, Instrumentation, Chemical Analysis, Workshop, Etc.	1990	Advance Training Institute Mumbai (ATI)	Directorate General of Training, Ministry of Skill Development and Entrepreneurship, Govt. Of India,
B. Sc.	Chemistry With Drug & Dyes	1989	NG Acharya & DK Marathe College Mumbai	Mumbai University

Other Qualification:			
Training Course On Dangerous Goods Transport By Air	Recurring Course July 2022	GPs Institute Of Dangerous Goods	IATA Accredited Training School
Training Course On Dangerous Goods Transport By Air	Basic Course August 2018	GPs Institute Of Dangerous Goods	IATA Accredited Training School
Awareness and Internal Audit on " Quality Management System"	May 2016	Indian Institute of Packaging, Delhi	Bureau of Indian Standards (BIS)
Laboratory Quality Management System & Internal Audit	February 2015	Indian Institute of Packaging, Delhi	NABL
Estimation of Uncertainty Measurement	September 2014	Indian Institute of Packaging, Delhi	Govt. Of India, STQC DEIT, MoCIT
HINDI – Pragya Examination	2002 87% (Stood First)	Indian Institute of Packaging, Mumbai	Ministry of Home Affairs, Dept. of languages,

Work Experience: Total years of Experience till date: 35 YEARS +				
Name/Address of employer	***Last/current Post held***	***Period from***	***Period to***	***Duration***
Indian Institute of Packaging, Mumbai	Deputy Director	May 1995	Till Date	29 Years & 6 Months
Mazda Dye-Chem Limited, Navi- Mumbai.	Production/ Shift Supervisor	April 1994	May 1995	13 Months
U. S. Vitamin (India) ltd., Mumbai.	Trainee Operative Technician	March 1992	February 1994	One Year & 11 Months
Engineering & Allied Services, Mumbai.	Supervisor Cum Office In-charge	May 1990	March 1992	One Year & 10 Months
RCF, Mumbai	Trainee supervisor	April 1989	May 1989	One Month

Member of Bureau of Indian Standards (BIS) Technical Committees on:

1. **SSD-01:** Transport Services Sectional Committee
2. **CHD-15**:Paper and Its Products Sectional Committee
3. **CHD-16:** Paper based packaging materials Sectional Committee

Travel/study Abroad*:* Düsseldorf, Germany - April 2005 (Interpack-2005)

Languages known: *English, Hindi and Marathi*

Place:

Date: ***Subodh K Juikar***