

PREPARATION OF FLAME-RETARDANT BIOPOLYMER FILMS

A dissertation submitted in the partial fulfillment of
the requirement for the degree of
Bachelor of Science
in
Chemistry

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Abstract

A bio-based flame-retardant film was prepared using sodium Alginate as a base. Further, various flame retardants such as disodium hydrogen phosphate, GCN, Boric acid was added to enhance flame retardant properties of the film. Its flammability, thermal degradation were studies systemically by vertical burning (UL-94) test, thermogravimetric analysis (TGA) and Fourier transform infrared analysis (FTIR) were used to study the thermal degradation of materials, sodium alginate films inherently lack flame retardant properties. Achieving a UL-94 V-0 rating typically requires incorporating specific flame-retardant additives.

Addition of GCN derived from melamine also improved the degradation of the film due to the presence of nitrogen. When burnt nonflammable gases are produced inhibiting the contact of flame with oxygen.

Further the sodium alginate films were cross-linked with calcium, the thermal stability was improved compared to that of the film without calcium. The incorporation of calcium ions within alginate films has been shown to demonstrably reduce the emission of flammable gases during combustion.

Keywords: *Sodium Alginate , Graphitic Carbon Nitride, Thermal decomposition , Boric acid, UL- 94 flammability , Flame retardants , Melamine*

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CHAPTER 1

INTRODUCTION

1. INTRODUCTION

Biopolymers, including cellulose, lignin, chitin, chitosan, and alginates, offer a compelling combination of properties like corrosion resistance, lightweight design, and unique functionalities, making them highly sought-after for various applications in packaging, textiles, biomedical devices, and even automotive components.

One notable example of Green Polymers is alginate, a biopolymer found in brown seaweed. Due to its exceptional ability to interact with metal ions through various mechanisms, including electrostatic attractions, ionic bonding, and coordination complexes, alginate finds uses in diverse fields like food science, pharmaceuticals, biomedicine, biotechnology, and environmental remediation.

In the food industry, alginate is utilized for packaging to prevent oxidation and bacterial contamination. In pharmaceuticals, it serves as a vehicle for drug delivery. In biomedicine, alginate is used to fabricate wound dressings due to its bactericidal properties and in tissue engineering. Moreover, it finds applications in biotechnology for encapsulation agents and in environmental protection for the removal of toxic heavy metals.

The unique properties and applications of alginate make it a promising candidate for replacing traditional synthetic polymers in various sectors, contributing to a more sustainable future.

A key challenge for biopolymers like cellulose and alginate is their inherent flammability. This susceptibility to melting and burning under heat or fire significantly limits their thermal stability and overall performance in everyday applications. To address this limitation and broaden their use, researchers are actively exploring methods to enhance their flame-retardant properties through additives, fillers, or surface treatments. Flame retardants are crucial for polymeric materials as they can reduce flammability and prolong survivability when exposed to fire. While enhancing the flame retardancy of biopolymers offers significant advantages and expands their applicability, traditional flame-retardant additives often face limitations. These additives can degrade over time due to elevated temperatures and exposure to oxygen, potentially leaching harmful chemicals into the environment and raising environmental contamination concerns. Unlike conventional flame retardants, which often contain toxic agents and pose environmental risks, biopolymer-based flame retardants aim to reduce carbon footprint and emissions while minimizing water and soil contamination. Biopolymers' flame resistance can be improved through various strategies, such as embedding flame-retardant additives within the polymer matrix or chemically attaching flame-retardant moieties directly to the polymer chains. These methods improve flame retardant efficiency and durability, reducing the risk of fire hazards. Before selecting polymers for flame retardancy applications,

several parameters must be considered, including time to ignition, rate of heat release, fire propagation rate, smoke and CO₂ release, and toxicity of byproducts.

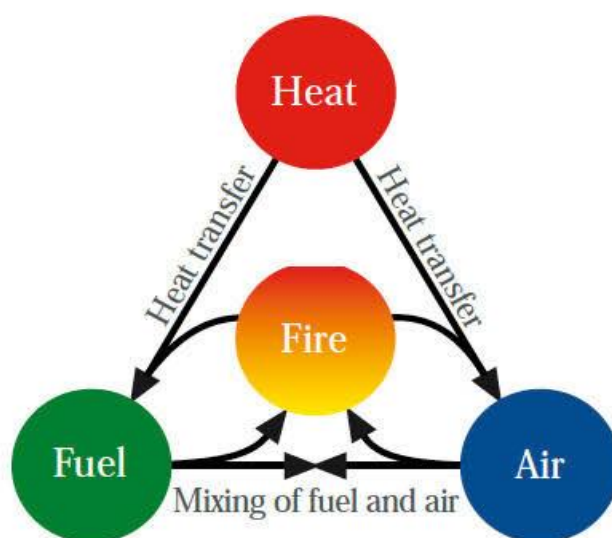


Fig 1.1 Emmon's Fire Triangle

Understanding polymer pyrolysis is essential for comprehending flame retardancy. Emmon's fire triangle [Fig.1.1], depicting the interplay of air, heat, and fuel in combustion, illustrates the life cycle of fire. In the presence of heat and oxygen, polymers decompose, producing combustible volatiles and leading to mass loss. The formation of a char layer during decomposition plays a crucial role in fire suppression. Alterations in any of these steps can prevent fire initiation or extinguish ongoing fires.

ALGINATE

Extracted from brown algae like *Laminaria hyperborea*, *Macrocystis pyrifera*, *Laminaria digitata*, and *Ascophyllum nodosum*, alginate is a water-loving (hydrophilic) polysaccharide, a complex sugar molecule built from numerous repeating units. Notably, alginate is a salt of alginic acid, featuring unbranched chains composed of two sugar building blocks, β -D-mannuronic (M) and α -L-guluronic (G) acids, linked together in a specific 1-4 pattern.

The sugar units (saccharides) within alginate chains can arrange themselves in different ways, forming blocks of mannuronic acid (M), guluronic acid (G), or alternating sequences (MG). M-blocks, composed solely of mannuronic acid, have equatorial linkages, resulting in a flat, ribbon-like conformation for the chain. In contrast, G-blocks, containing only guluronic acid, have axial linkages, leading to a more rigid structure. Interestingly, MG-blocks, where mannuronic and guluronic acid residues alternate, have different glycosidic bond positions, introducing greater flexibility to the overall alginate chain.

The physical properties of alginate depend on the ratio of uronic acids within the polysaccharide chains. Alginate rich in G-form rigid but brittle structures, while those rich in

M-form weaker but more flexible ones. The stiffness of different chain blocks follows the order MGMM < GG. The mechanical strength of alginates is determined by their chemical composition and structural block arrangement, regardless of their molecular weight.

Alginate also serves as a gel-forming agent due to its ability to form gels with multivalent cations like Ca, Ba, and Al. The gelation process relies on the presence of sufficient guluronate monomers. Water molecules are physically trapped within the alginate gel matrix due to capillary forces, although they retain the ability to migrate, rendering alginate gel a solid material.

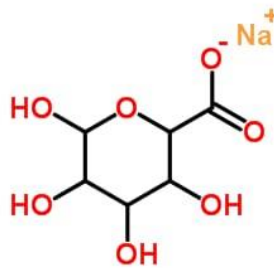


Fig 1.2 Sodium Alginate Structure

Sodium Alginate, is the sodium salt of the alginic acid (alginate), it is a polyelectrolyte and has been used in a wide range of industrial fields. It is known that NaAlg has a unique property of cross-linking and can form an ionotropic physical gel by cooperative binding with divalent cations in an aqueous media. This description is known as the "egg box" model that is generally invoked to explain how the divalent metal ions bind to the cavities formed between polymer chains. These cavities provide suitable sites for coordination of metal ions. The capacity to form this kind of interaction depends essentially on the inorganic ion and alginate ratio. The affinity of alginates for alkaline-earth and metals increases in the order Mg << Co, Ni, Mn, Zn < Ca²⁺ < Sr²⁺ < Ba²⁺ < Cd²⁺ < Cu²⁺ < Pb²⁺. The great similarity of high selectivity between ions of alkaline earth metals indicates the following characteristics. The binding mode is not only by nonspecific electrostatic binding. But is also by some chelation with G-blocks of polymer chains that contribute to the selectivity. Divalent cations such as Ca²⁺, Ba²⁺, and Sr²⁺ as well as trivalent cations Fe and Al preferentially and very closely bind to the G-blocks in the alginate as result of an ionic interaction and intramolecular bonding between these cations and the carboxylic acid groups on the polymer backbone.

Depending on the concentration of counter ions, the gels are either thermo-reversible (low concentration) or not (high concentration).

A Versatile Film-Former

One of alginate's valuable functionalities is its ability to form films. When a thin layer of alginate gel or solution dries, it transforms into a continuous film or coating. These alginate films find use in various applications where reducing water loss is crucial. This effect can be

achieved through alginate's inherent water-holding capacity or by the general protective barrier formed by the alginate polymer coating. Beyond film formation, alginates are widely employed as stabilizers and thickening agents, often fulfilling both roles simultaneously.

Alginates, being biopolymers, exhibit a range of advantageous properties in various industries. Their ability to swell, maintain stability, exhibit non-toxicity and low cytotoxicity, undergo biodegradation, possess immunological properties, and allow high permeability to diffusive mass transfer makes them versatile materials. Moreover, they can be easily molded into different forms such as beads, blocks, films, fibers, and membranes under mild conditions.

These properties stem from three key characteristics:

1. Alginates can increase the viscosity of aqueous solutions when dissolved, which is advantageous in various applications.
2. They have the ability to form gels, enhancing their utility in specific contexts.
3. Alginates can form films, fibers, and membranes, particularly sodium/calcium alginate variants, and exhibit excellent water retention capabilities.

These intrinsic hydrogel properties make alginates valuable for diverse applications.

Sodium alginate (NaAlg) is the most commonly used type, but other variations like calcium, ammonium, and potassium salts, as well as propylene glycol alginate (PGA) and esters of alginic acid, are also commercially available for specific applications.

2. REVIEW OF LITERATURE

Various researchers synthesized flame retardant biopolymer film using different flame retardants. [Yun Liu et.al 2016] This study investigated the fire resistance, thermal degradation behaviour, and decomposition mechanism of a bio-based barium alginate film. The film was created using a combination of casting and a simple ionic exchange process. Researchers employed a comprehensive approach, utilizing techniques like Limiting Oxygen Index (LOI), UL-94 vertical burning test, microscale combustion calorimetry (MCC), thermogravimetric analysis (TGA) coupled with Fourier Transform Infrared (FTIR) analysis, and finally, pyrolysis-gas chromatography–mass spectrometry (Py-GC–MS). This combined analysis revealed a significant improvement in the film's flammability resistance compared to sodium alginate film (24.5% LOI). The barium alginate film achieved a much higher LOI value of 52.0%.

Crucially, the MCC test revealed a significantly lower peak heat release rate (PHRR) for the barium alginate film compared to the sodium alginate film. This finding suggests that incorporating barium ions into the alginate film effectively minimizes the release of flammable gases during combustion. This conclusion is further supported by the analysis using Py-GC-MS and TG-FTIR, barium alginate produced significantly fewer flammable products during the entire thermal degradation process than sodium alginate. Between sodium and barium

alginate films, there were notable differences in their pyrolysis behaviours, thermal degradation, and flame-retardant qualities.

Xiubin Hou et.al (2018) investigated the development of a novel flame-retardant film using a solution casting method. The film, composed of agar, sodium alginate, and boric acid (AG/SA/BA), was created with varying concentrations of BA. Analysis confirmed the formation of C-O-B bonds between the film matrix and BA. The addition of BA significantly improved the limiting oxygen index (LOI) of the film. This enhancement is likely due to the interaction between the BA and the film matrix, possibly facilitated by the presence of excess BA within the molecular structure. Furthermore, films containing BA concentrations exceeding 5 weight percent exhibited improved thermal stability compared to films without BA. When added at the proper concentration, BA improved thermal stability and flame retardancy overall. It was looked into how the concentration of BA affected the films' thermal and flame stability. Between the molecules of BA and the polysaccharide, a new chemical bond was created. The LOI values of the film gradually increased as the concentration of BA increased, indicating that the polysaccharide material's flame retardancy was enhanced by the addition of BA. When compared to films without BA, the thermal stability of crosslinking films was improved at concentrations of BA above 5 weight percent.

Sandhya Babel et.al (2021) explored the incorporation of aluminium (BPI-COOAl) and copper (BPI-COOCu) ions into an amino acid-based bio-polyimide (BPI) salt to create flame retardant films while maintaining high optical transparency. Microscale combustion calorimetry analysis revealed that the total heat released (THR) and peak heat release rate (PHRR) for BPI-COOAl were significantly lower (18.9 kJ/g and 4.5 W/g, respectively) compared to BPI-COOCu and previously reported materials. This translates to superior flame retardancy for BPI-COOAl, further confirmed by its V-0 rating in the Underwriters Laboratories vertical burning test (UL-94). These bio-polyimide salt films achieve a remarkable balance between key material properties: transparency, thermo-mechanical stability, and flame retardancy. The starting material, BPI-COOH, possesses carboxylic acid side-chain groups. These groups were neutralized with KOH to generate the potassium salt, BPI-COOK. Subsequent ion exchange reactions, found to be exothermic, replaced K⁺ ions with the targeted multivalent metal ions Al³⁺ and Cu²⁺, resulting in the formation of BPI-COOAl and BPI-COOCu salt films, respectively. Both BPI-COOCu and BPI-COOAl demonstrated excellent flame-retardant properties, exceeding the performance of previously reported polymer films based on the THR and PHRR values. Notably, both films achieved a V-0 rating in the UL-94V test.

Siqun Wang et.al (2021) described a straightforward two-step method for preparing bamboo-based phosphorylated cellulose nanofibrils (B-PCNFs) using phosphorylation and mechanical grinding. The resulting B-PCNF films, fabricated via solvent casting, exhibit remarkable mechanical properties. These films boast a high Young's modulus of 2.5 GPa, impressive toughness reaching 41.8 MJ/m³, excellent tensile strength of 115.9 MPa, and outstanding elongation at break of 53.1%. These superior mechanical attributes are likely due to the formation of dense and uniform polymer networks strengthened by enhanced intermolecular interactions. This unique combination of exceptional mechanical performance and inherent

flame resistance, stemming from the phosphorylated cellulose content, makes B-PCNF films a promising candidate for real-world applications such as flame-retardant packaging materials. In conclusion, this work demonstrates a simple solvent casting method for producing a range of B-PCNF films with outstanding properties.

Based on the above considerations, we have used different flame retardants in different composition to increase flame retardant properties of our film.

3. Research Gap

The research gap that we've found is that very limited work has been reported on flame retardant biopolymer films. Only few studies are available to study the effect of various flame retardants on the flammability of the bio-polymers addressed. Therefore, we've added various flame retardants such as disodium hydrogen phosphate, graphitic carbon nitride in different composition to increase the flame retardancy of our synthesized biopolymer film.

CHAPTER 2

EXPERIMENTAL DETAILS

1. MATERIALS

Sodium Alginate, Disodium hydrogen phosphate, U450-4, GCN, Calcium Chloride, Boric Acid, Glycerol, all synthesis were carried out using distilled water.

2. PREPARATION OF FLAME-RETARDANT BIOPOLYMER FILMS

To synthesize sodium alginate film, 1 g of sodium alginate was first dissolved in 100 ml of distilled water. This solution was then stirred using a magnetic stirrer for two hours at room temperature. Then the solution was casted in petri dish for drying at RT. It took 5-6 days to be dried completely.

This is the basic process which we have used further we have tried different composition and chemical to increase flame retardancy of our biopolymer film.

Various FRs were used in the film such as Disodium hydrogen phosphate, boric acid, graphitic carbon nitride (GCN) derived from urea (U450) and GCN derived from melamine.

Various FRs used in the film

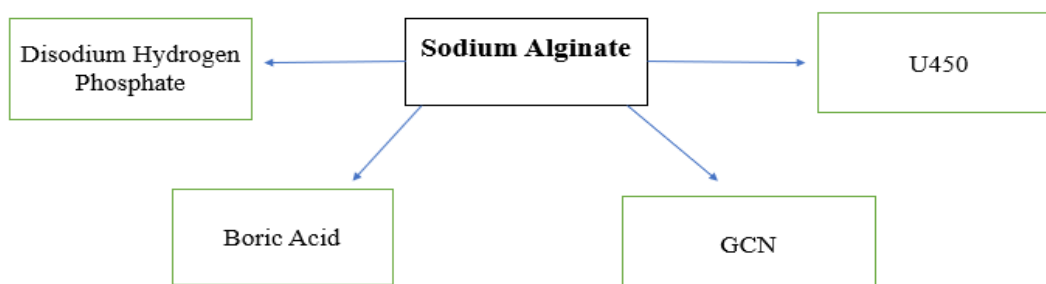


Fig 2.1 Various FR used in the film

Table:1 Different Composition used to enhance Flame Retardancy

	FR1	FR2	FR3	FR4	FR6	FR7	FR8	FR9	FR10	FR11	FR12	FR12 Ca	FR13	FR13 Ca	FR14
DI water	100ml	100ml	100ml	100ml	100ml	100ml	100ml	100ml	100ml	100ml	100ml	100ml	100ml	100ml	100ml
		25ml		25ml	25ml	25ml	25ml	25ml	25ml	25ml	25ml		25ml		25ml
Na Alg.	1g	1g	1g	1g	1g	1g	1g	1g	1g	1g	1g		1g		
Na ₂ HPO ₄		0.1g		0.1g	0.15g				0.2g						
U ₄₅₀₋₄						0.025g	0.025g	0.05g							
H ₃ BO ₃										0.1g					0.15g+gly.
GCN											0.1g		0.15g		
CaCl ₂												0.5g		0.5g	

- **FR 1-** Pure Na-Alg. Film was prepared.
- **FR 2-** 0.1g disodium hydrogen phosphate was dissolved in 25ml DW (distilled water) and poured in the Na-Alg solution then stirred on magnetic stirrer at RT then casted on petri dish for drying and film was prepared.
- **FR 3-** preparation is same as FR 1 but the heating was done at 70°C on magnetic stirrer before casting the solution in petri dish.
- **FR 4-** preparation is same as FR 2 but the heating was done at 70°C on magnetic stirrer before casting the solution in petri dish.
- **FR 6 -** 0.15g disodium hydrogen phosphate was dissolved in 25ml DW and poured in the Na-Alg solution then stirred on magnetic stirrer at RT then casted on petri dish for drying and film was prepared.
- **FR 7-** 0.025g GCN (Urea) was dissolved in 25ml DW using magnetic and mechanical stirring and added in the Na-Alg solution then stirred on magnetic stirrer at RT then casted on petri dish for drying and film was prepared.
- **FR 8-** 0.025g GCN (Urea) was dissolved in 25ml DW using probe sonicator and added in the Na-Alg solution then stirred on magnetic stirrer at RT then casted on petri dish for drying and film was prepared.
- **FR 9-** 0.05g GCN(Urea) was used further the procedure is same as FR 8.
- **FR 10-** 0.2g disodium hydrogen phosphate was dissolved in 25ml DW and poured in the Na-Alg solution then stirred on magnetic stirrer at RT then casted on petri dish for drying and film was prepared.
- **FR 11-** 0.1g boric acid(H₃BO₃) was dissolved in 25ml DW and poured in the Na-Alg solution then stirred on magnetic stirrer at RT then casted on petri dish for drying.
- **FR 12 -** 0.1g GCN (melamine) was dissolved in 25ml DW and poured in the Na-Alg solution then stirred on magnetic stirrer at RT then casted on petri dish for drying.
- **FR 12 Ca-** FR12 was dipped in CaCl₂ solution (0.5 g CaCl₂ in 100 ml DW) for 1 hr.

Then washed by DW and dried.

- **FR 13** -0.15g GCN (melamine) was dissolved in 25ml DW and added in the Na-Alg solution then stirred on magnetic stirrer at RT then casted on petri dish for drying.
- **FR 13 Ca**- FR13 was dipped in CaCl₂ solution (0.5 g CaCl₂ in 100 ml DW) for 1 hr.

Then washed by DW and dried.

3. Characterization

a. FTIR used to analyse the chemical structure of synthesized by measuring the absorption of infrared radiation , identifying functional group like – OH , -OPO, -NH, -CO etc.

b. TGA used to determine the composition, thermal stability, and decomposition kinetics of bio-based film.

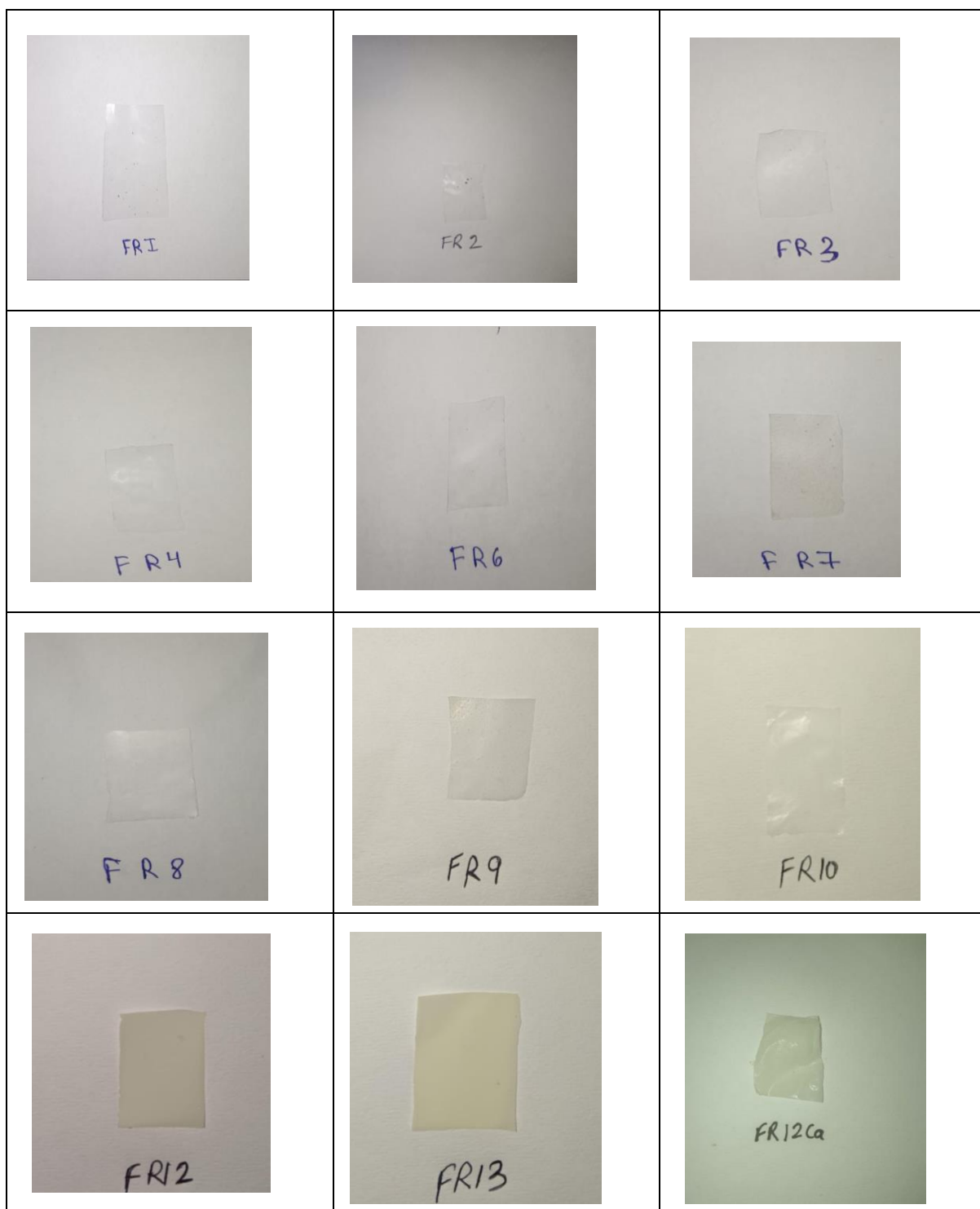


Fig 2.2 Synthesized FRs

CHAPTER 3

Results And Discussion

1. Fourier –Transform Infrared Spectroscopy Analysis

This technique relies on the characteristic absorption of infrared radiation by functional groups in molecules during vibrational motion. By analysing this absorption pattern, we can identify the chemical makeup of a sample. FTIR spectrometers function by passing infrared light through the sample and measuring the transmitted light. The resulting spectrum reveals which wavelengths of infrared radiation were absorbed by the sample.



Fig 3.1 FTIR Spectroscopy

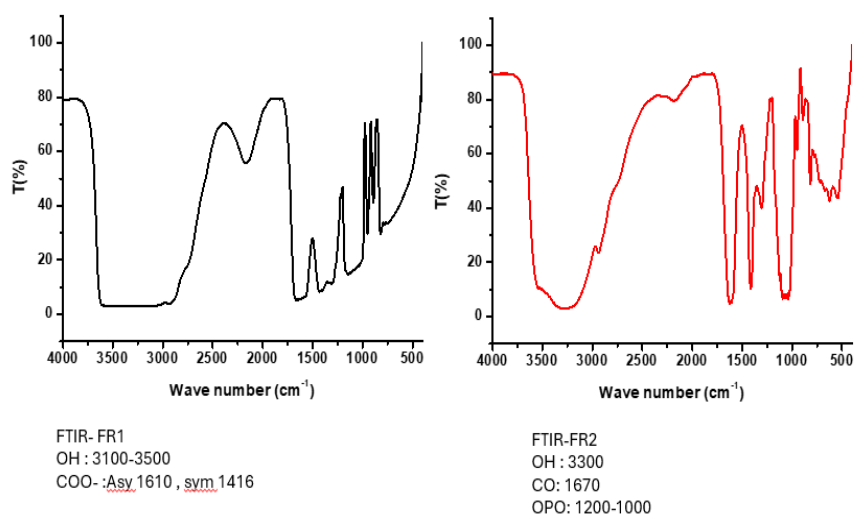


Fig 3.2 FTIR graph for FR 1 and FR2

In FR1 OH broad peak is around $3100-3500\text{cm}^{-1}$, COO^- peak of asymmetric stretch is around 1610cm^{-1} and symmetric stretch around 1416cm^{-1} In FR2 OH peak is around 3300cm^{-1} ·CO peak is at 1610cm^{-1} \and OPO around $1000-1200\text{cm}^{-1}$

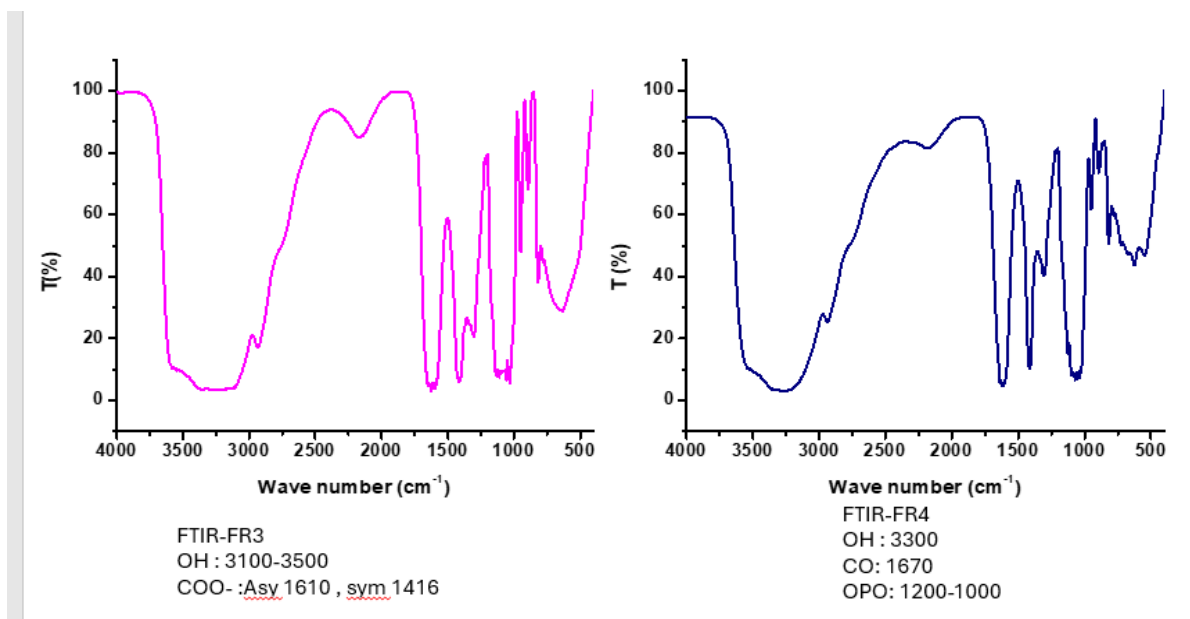


Fig 3.3 FTIR graph of FR3 and FR 4

In FR3 OH broad peak is around $3100-3500\text{cm}^{-1}$, COO^- peak of asymmetric stretch is around 1610cm^{-1} and symmetric stretch around 1416cm^{-1} . In FR4 OH peak is around 3300cm^{-1} , CO peak is at 1610cm^{-1} and OPO around $1000-1200\text{cm}^{-1}$.

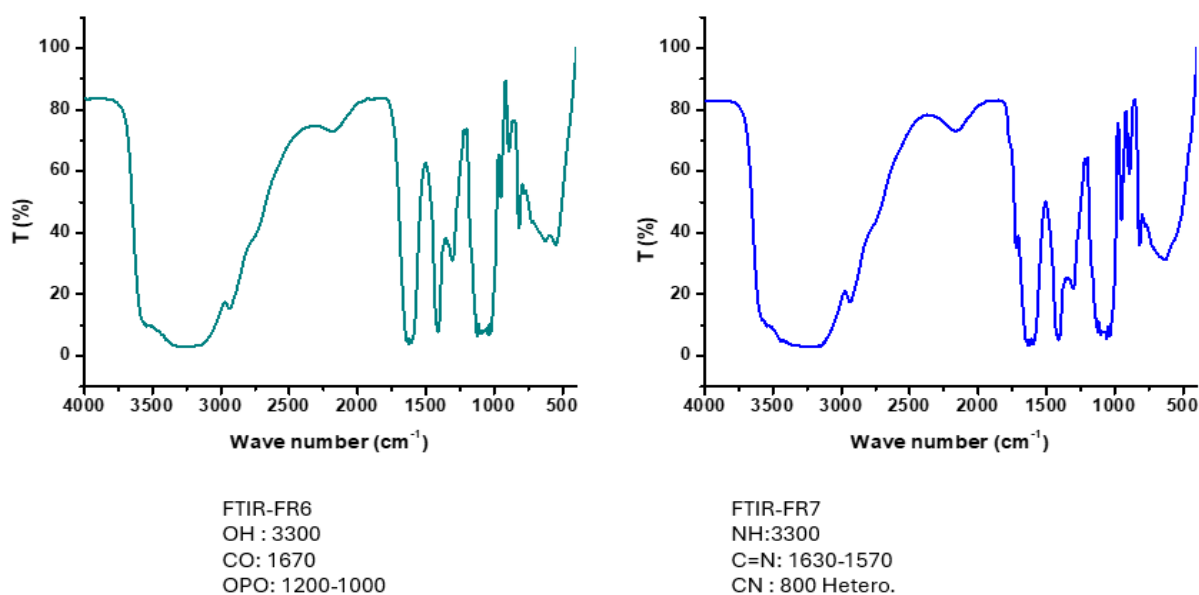


Fig 3.4 FTIR Graph for FR 6 and FR 7

In FR6 OH peak is around 3300cm^{-1} , CO peak is at 1610cm^{-1} and OPO around $1000-1200\text{cm}^{-1}$. In FR7 NH peak is around 3300cm^{-1} , C=N is at $1630-1570\text{cm}^{-1}$ and CN is at 800cm^{-1} .

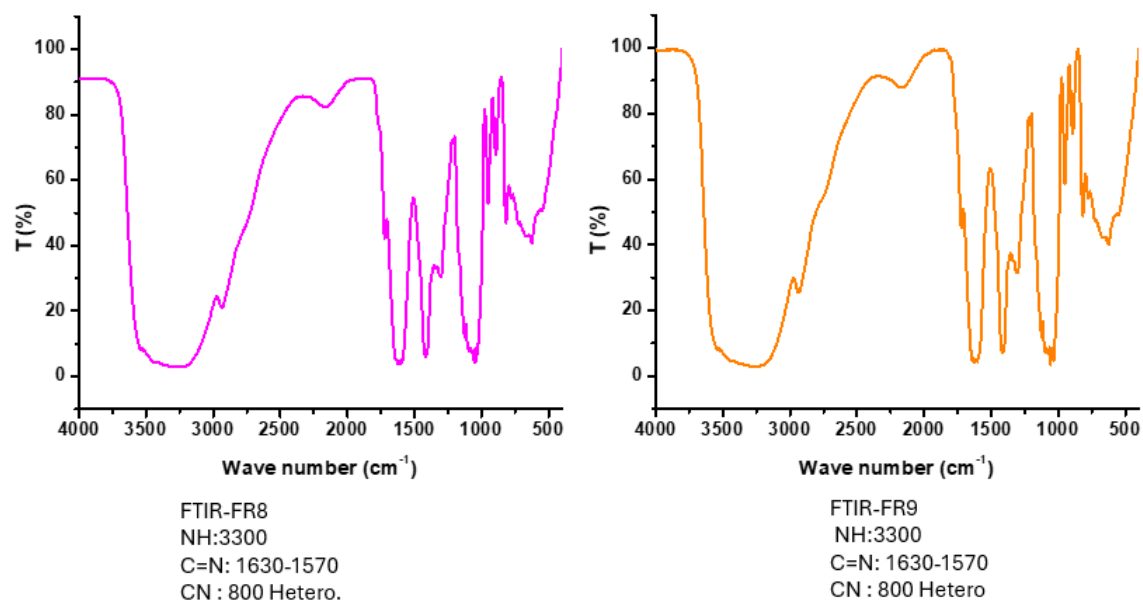


Fig 3.5 FTIR graph FR 8 and FR 9

In FR8 and FR9 NH peak is around 3300cm^{-1} , C=N is at $1630\text{-}1570\text{ cm}^{-1}$ and CN is at 800 cm^{-1} .

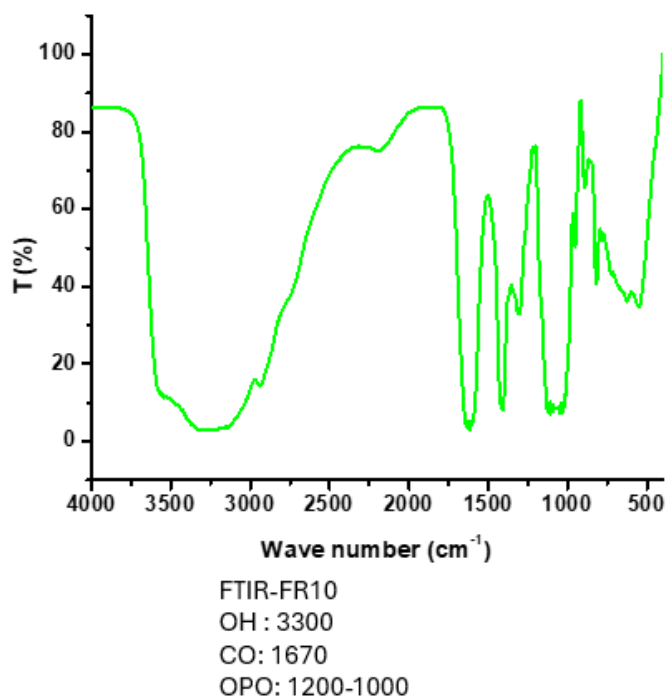


Fig 3.6 FTIR graph FR 10

In FR10 OH peak is around 3300cm^{-1} , CO peak is at 1610 cm^{-1} and OPO around $1000\text{-}1200\text{cm}^{-1}$

2. TGA (Thermogravimetric Analysis)

Thermogravimetric analysis (TGA) is a technique where the mass of a polymer is measured as function of temperature or time while the sample is subjected to a temperature program, and controlled atmosphere. It is used to evaluate thermal stability of a material.

Analyses Chemical Reactions: This technique measures changes in temperature and weight during decomposition reactions. This allows researchers to determine the quantitative composition of the material.

Material Characterization: It's valuable for analysing the composition and formulation of materials with multiple components or blended substances.

Moisture and Solvent Detection: Additionally, this method can be used to identify the water content, or any residual solvents present in a material.



Fig 3.7 Thermogravimetric Analyzer

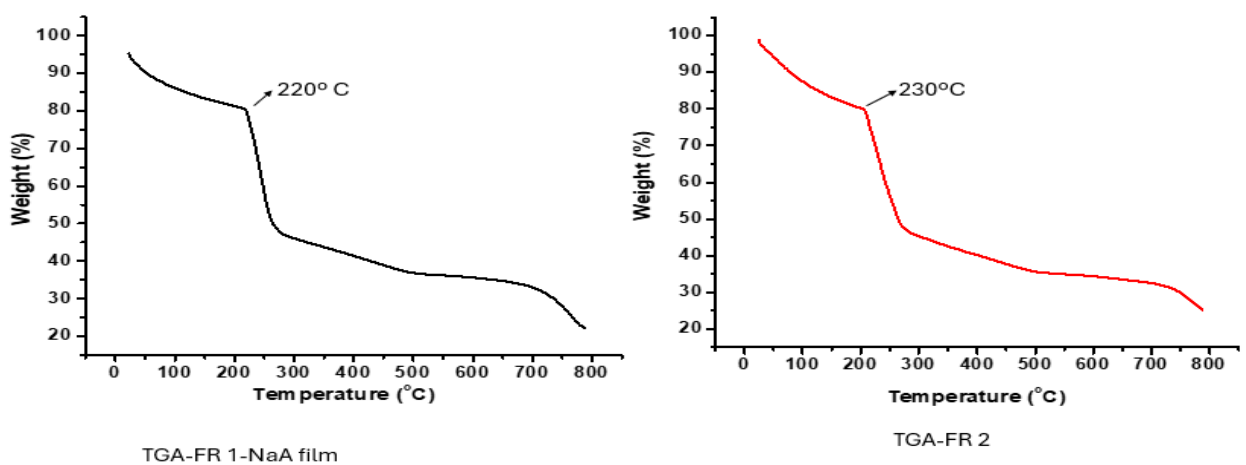
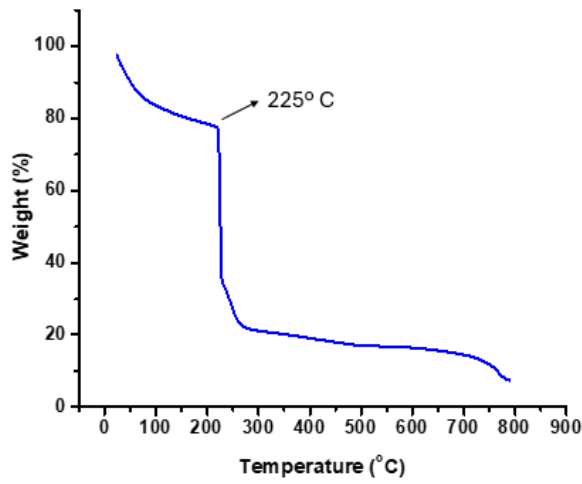
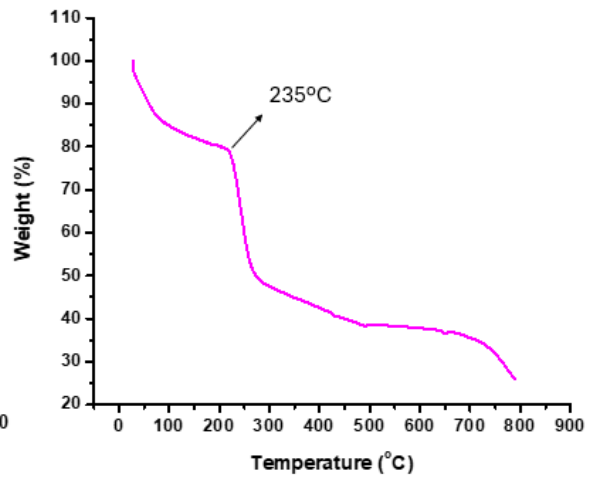


Fig 3.7 TGA for FR1 and FR 2

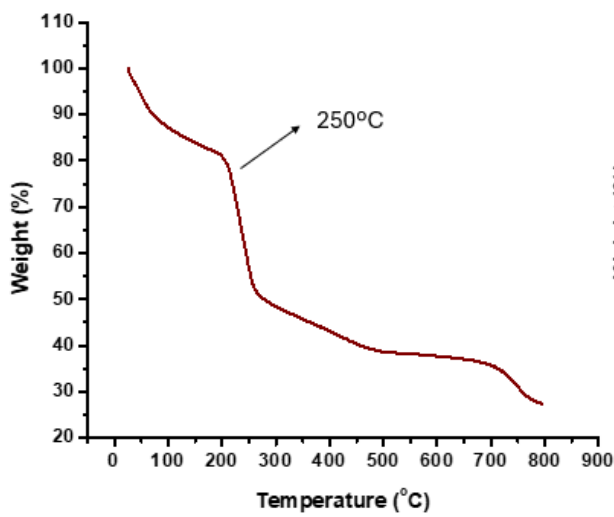


TGA-FR 3

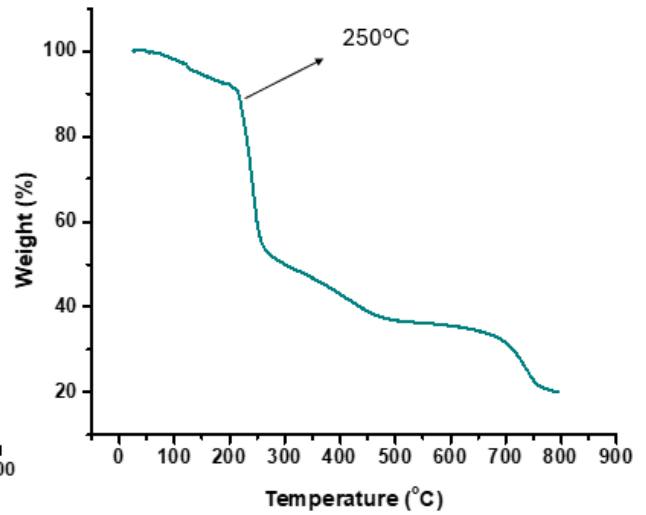


TGA-FR 4

Fig 3.8 TGA for FR 3 and FR 4

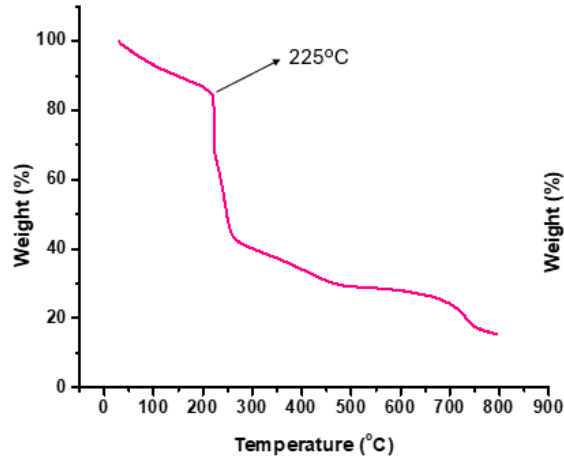


TGA-FR 6

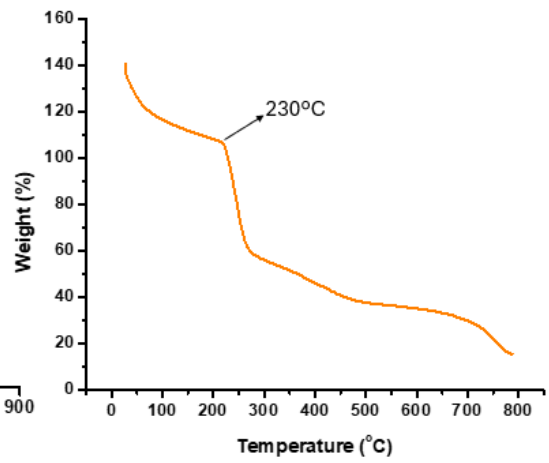


TGA-FR 7

Fig 3.9 TGA for FR 6 and FR 7

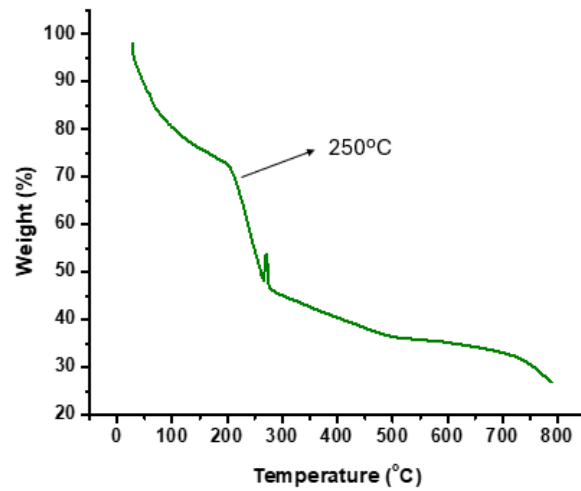


TGA-FR 8



TGA-FR 9

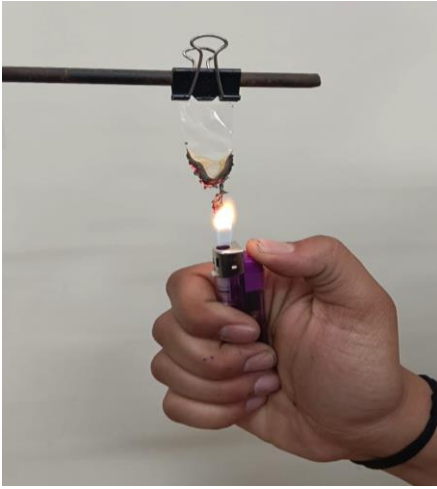
Fig 3.10 TGA for FR 8 and FR 9



TGA-FR 10

Fig 3.11 TGA for FR 10

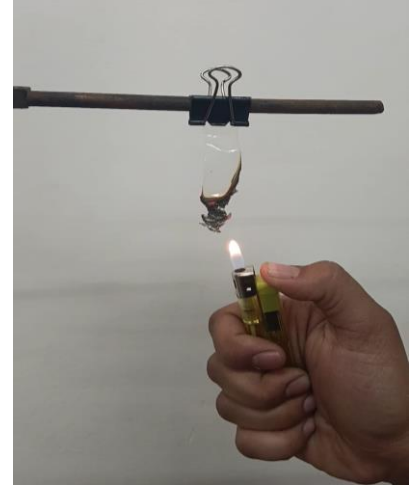
3. UL-94 Flammability Test



FR1



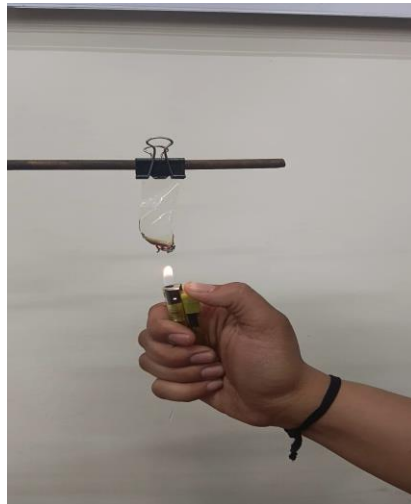
FR2



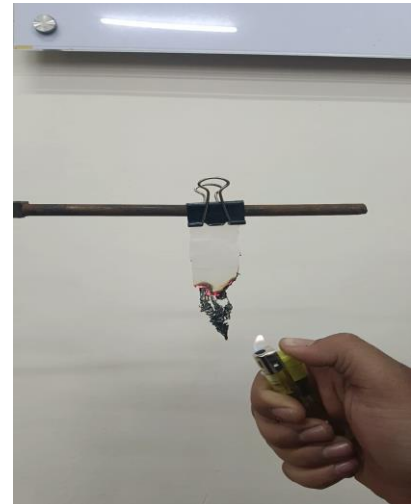
FR3



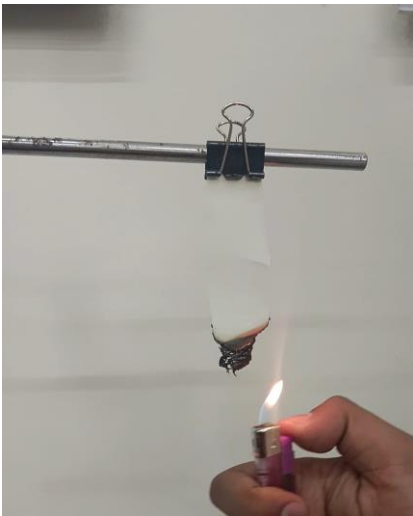
FR4



FR6



FR7



FR10



FR12

Fig 3.12 Flammability test UL-94

The material will be rated:

V-0: if the burning stops before 10 sec, no dripping

V-1: if the burning stops before 30 sec, no dripping

V-2: if the burning stops before 30 sec, dripping

Table:2 UL- 94 Test readings

Sample	FRs	Charring Time	Sample	FRs	Charring Time
FR 1	Na Alg. (1g)	30 sec	FR 10	Na Alg.(1g)+Na ₂ HPO ₄ (0.2g)	2 min 10 sec
FR 2	Na Alg.(1g)+Na ₂ HPO ₄ (0.1g)	44 sec	FR 12	Na Alg.(1g) +GCN melamine(0.1g)	2 min 15 sec
FR 3	Na Alg.(1g) + heat	1 min 40sec	FR 12 Ca	CaCl ₂ (0.5g)	4 min
FR 6	Na Alg.(1g)+ Na ₂ HPO ₄ (0.15g)	47sec	FR 13	Na Alg.(1g) +GCN melamine(0.15g)	2 min 40 sec
FR 7	Na Alg.(1g) +.GCN urea(0.025g)	1min 20 sec	FR 13 Ca	CaCl ₂ (0.5g)	4 min 20 sec
FR 9	Na Alg.(1g) + GCN urea(0.05g)	1 min 15 sec			

CHAPTER 4

Conclusion And Future Prospective

Based on our results, we have concluded that the char was formed while burning the films and in all cases after adding FRs the charring time of the film increases.

Melamine-derived flame retardants (FRs) proved particularly effective in fire tests. Their effectiveness stems from the nitrogen content, which releases **non-flammable gases** during combustion. These gases **dilute the concentration of flammable species** and **limit oxygen availability**, hindering the overall burning process.

When calcium (Ca) ions replace sodium (Na) ions within the alginate structure, the film becomes **more tightly packed** due to the smaller size of the calcium ion. This **denser arrangement** contributes to a **noticeable reduction in flammability**.

Flame retardant films represent a promising technology for future applications, aligning well with the **growing emphasis on environmentally friendly practices** being adopted by governments worldwide.

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