STUDIES ON CARBOXYLIC ACID CROSSLINKED POLYVINYL ALCOHOL AND THEIR APPLICATIONS

A Thesis Submitted

for the Degree of

DOCTOR OF PHILOSOPHY

by

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Dedicated to my Loving Parents

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CANDIDATES DECLARATION

I **Leela Gautam** hereby certify that the work which is being presented in the thesis entitled **"Studies on Carboxylic Acid Crosslinked Polyvinyl Alcohol and their Applications"** 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 19 July 2019 to 15 April 2025 under the supervision of **Prof. Sudhir G. Warkar**, Professor, Department of Applied Chemistry, DTU and co-supervision of **Dr. Manish Jain**, Assistant Professor, Department of Applied Chemistry, DTU.

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

Place: Delhi

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

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CERTIFICATE BY THE SUPERVISOR(s)

Certified that **Leela Gautam (2K19/PHDAC/03)** has carried out her search work presented in this thesis entitled **"Studies on carboxylic acid crosslinked polyvinyl alcohol and their applications"** for the award of **Doctor of Philosophy** from Department of Applied Chemistry, Delhi Technological University, Delhi, under our supervision. The thesis embodies the results of original work, and studies are carried out by the student herself, and the contents of the thesis do not form the basis for the award of any other degree to the candidate or to anybody else from this or any other University/Institution.

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ABSTRACT

Chemical crosslinking is a widely used method to alter the properties of polymers like polyvinyl alcohol (PVA). The physicochemical properties of PVA are greatly affected by the type of crosslinking agent used. This thesis work gives detailed insights into the effect of molecular structures of various carboxylic acids employed as crosslinking agents on the physicochemical properties of PVA. The carboxylic acids crosslinked PVA films were synthesized using the solution casting method. Various carboxylic acids were compared for PVA crosslinking and effects of varying the number of carbon atoms (odd-even), number of carboxyl groups and taking account of single and double bonds in carboxylic acids. The prepared films were characterized by techniques such as ATR-FTIR, XRD, SEM, AFM, DSC, TGA, Rheology, Tensile strength, Gel content, Percent swelling, and Sessile drop contact angle.

PVA films crosslinked with dicarboxylic acids containing an even number of carbon atoms displayed translucency, roughness, and an irregular matrix. In contrast, films crosslinked with dicarboxylic acids incorporating an odd number of carbon atoms were transparent, homogenous, and densely packed. Furthermore, films crosslinked with acids containing an even carbon atom exhibited relatively lower crystallinity, and lower melting temperature (T_m). They displayed an unexpected irregular trend in swelling as crosslinker concentration increased compared to films containing dicarboxylic acids with an odd number of carbon atoms, exhibiting a consistent swelling with increasing crosslinker concentration. These results are attributed to the difference in the solubility and crystal structures of the odd-even series of dicarboxylic acids.

On proceeding further, based on the degree of crosslinking and thermal properties, unsaturated carboxylic acid was found to be more effective compared to saturated acid. This was evident in the comparison between succinic acid (single bond) and maleic acid (double bond), where the crosslinking degree of the maleic acid crosslinked film was determined to be 6.47 times higher than that of the PVA-SA film. Also, malic acid crosslinked film displayed lower crystallinity and a higher contact angle (80.60) in contrast to succinic acid (76.0) crosslinked film and uncrossed PVA (30.4) film.

When compared amongst di, tri and tetra carboxylic acid crosslinked PVA film, the degree of crosslinking, tetra acid demonstrated superior crosslinking performance and resulting in the highest mechanical strength and thermal stability. The highest strength was observed in the tetra acid crosslinked film, which exhibited a 127% increase over neat PVA. Regarding thermal stability, the decomposition temperature followed the order of tetraacid > triacid > diacid.

Lastly, the synthesized crosslinked films were used to assess their efficacy in the adsorptive dye removal process using a cationic dye, namely crystal violet as a model dye. The results showed that the adsorption capacity of the films increases with an increase in the number of carboxylic groups of crosslinkers and surface roughness. A high dye removal efficiency (>90%) and adsorption capacity (38.53 mg/L) were observed for 30 wt% of tetracarboxylic acid crosslinked film for the dye concentration of 20 ppm with a contact time of 105 min at room temperature.

Overall, the thesis emphasizes the critical importance of considering the molecular structure of carboxylic acids during the crosslinker selection process. These considerations play a crucial role in tailoring PVA films to achieve specific properties for diverse applications.

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LIST OF SYMBOLS AND ABBREVIATIONS

AFM	Atomic force microscopy
ATR-FTIR	Attenuated total reflectance-Fourier transform infrared
BTCA	Butane tetracarboxylic acid
CV	Crystal violet
M_C	number average molecular mass
CA	Citric acid
Cm	Centimeter
COO^-	Carboxylate
DSC	Differential scanning calorimetry
G	Gram
GA	Glutaric acid
MA	Malonic acid
MAL	Maleic acid
mL	Millilitre
M_n	Average Molecular weight
MW	Molecular weight
Nm	Nanometer
OA	Oxalic acid
OH	Hydroxyl
PVA	Polyvinyl alcohol
SA	Succinic acid
SEM	Scanning Electron Microscopy
TGA	Thermal gravimetric analysis
DTGA	Differential thermogravimetric analysis
WCA	Water contact angle
XRD	X-ray Diffraction

Chapter 1

Introduction and Literature Review

1.1 Introduction

1.1.1 Polyvinyl alcohol

Polyvinyl alcohol (PVA) is a synthetic, linear, semi-crystalline polymer composed of a carbon chain as a backbone and a hydroxyl group as a functional group. It is obtained by the hydrolysis of polyvinyl acetate and its physical properties are affected by its degree of hydrolysis i.e. complete or partial. Therefore, PVA is available commercially in two grades: fully hydrolyzed and partially hydrolyzed. It is also available in different molecular weights, mainly due to the variation in the length of the polymeric chain [1, 2]. PVA exhibits many important features like it is readily available, low cost, biodegradable, biocompatible, non-toxic, water soluble, has excellent film-forming ability, is thermo-stable, and has good chemical resistance and adhesive. All these features make it a very valuable material in a wide range of applications.[3-7] However, the presence of hydroxyl groups enhances water adsorption capacity. It makes PVA water-soluble, which in turn leads to a reduction in its mechanical and thermal properties, hence limiting its applicability. Water adsorption or water solubility can be controlled by partial crosslinking of the polymer chains [2] [4].

1.1.2 Crosslinking

Crosslinking can be defined as the formation of chemical bonds between different polymer chains. It is an established and simple method to obtain new materials with improved qualities. At the micro level, crosslinking restricts the mobility of polymeric chains and thus may affect crystal structure, crystal size distribution and degree of crystallinity [5]. In general, crosslinking reduces the degree of crystallinity and increases the amorphous region. In PVA, crosslinking occurs through the hydroxyl groups. Therefore, partial crosslinking of PVA reduces the density of hydroxyl groups available for hydrogen bonding with water and reduces the water absorption capacity of the polymer. Additionally, the reduction of chain movability with crosslinking also restricts the swelling phenomenon of polymer and controls the free volume available for water molecules inside the polymeric matrix [6]. As crosslinking makes chemical bonds between different molecules, it improves the mechanical properties and thermal stability of PVA [7].

1.1.3 Methods of crosslinking

PVA can be crosslinked using two different approaches either by physical methods or by chemical methods. Physical crosslinking comprises techniques like freeze-thawing and gamma irradiation whereas chemical crosslinking is carried out by chemical reagents which can react with the hydroxyl groups of PVA to bond the two different polymeric chains [3, 5, 8]. Physical methods of crosslinking of PVA are less popular due to high cost, difficulties in controlling the degree of crosslinking and also due to the damage to polymer chains [3]. On the other hand, chemical modification of hydroxyl groups of PVA through crosslinking agents is simpler, cost-effective, and can be easily controlled. It opens new fields of applications and therefore, it is an admirable material for many researchers.

1.1.4 Crosslinking agents

Many organic and inorganic agents were reported as crosslinking agents with PVA such as dialdehydes [9-13], acid anhydrides [14-16], diisocyanates [17-20], transglutaminase [21, 22], polyurethane [23, 24], genipin [25,26], boric acid [27,28], epichlorohydrin [29, 30], mono /di/polycarboxylic acids [31-33], alkoxysilane [34,35], dimethyl carbonate [36,37], epoxy compounds [38], polyphenol [39], carboxymethyl-chitosan [40], acrylic acid [41], etc. have been used as crosslinkers. However, among them, several agents have some drawbacks, such as cytotoxicity an unpleasant odor, reduced biodegradability of PVA, or negative impacts on the different properties of PVA [42]. Therefore, these crosslinker limits the utility of PVA. Carboxylic acids are one of the cross-linking agents for PVA, which has received the great attention of the scientific community since last decade. Carboxylic acids are easily available, odorless, environment-friendly, inexpensive, non-toxic, biodegradable, non-accumulative, and therefore considered ideal “green crosslinking agents”. [43]. The reaction for the formation of crosslinked PVA by crosslinking reaction between PVA and carboxylic acid is shown in Fig.1.1.

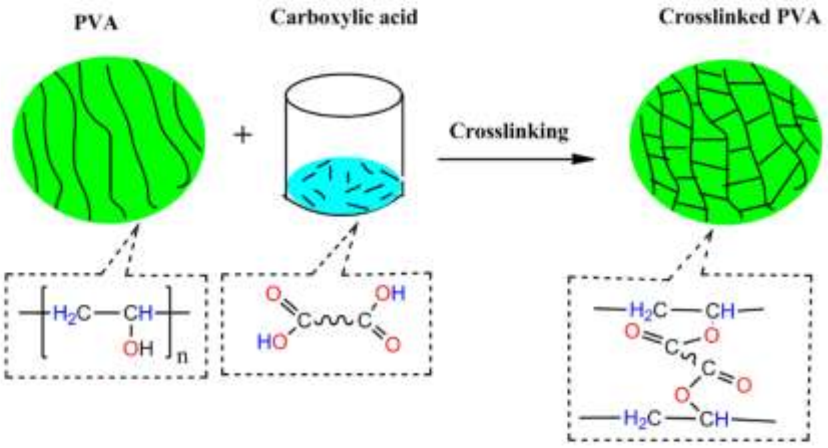


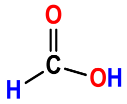
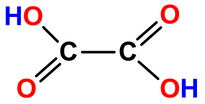
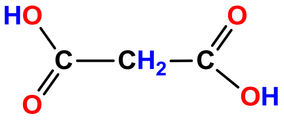
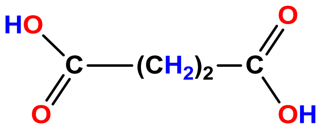
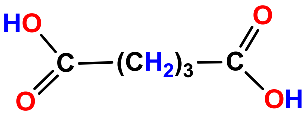
Fig. 1.1: *Method of preparation of carboxylic acid crosslinked PVA*

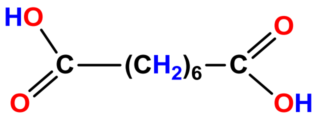
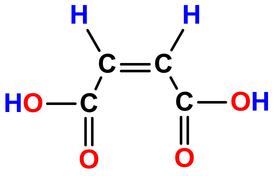
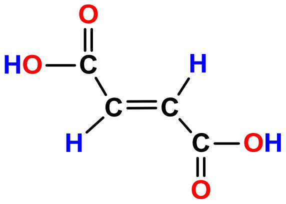
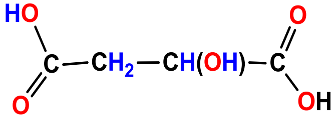
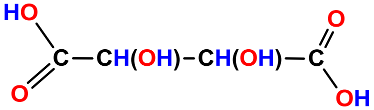
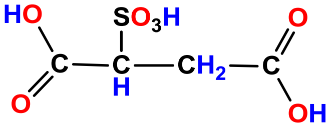
1.2 Literature survey

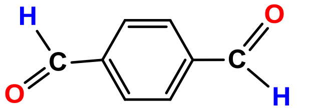
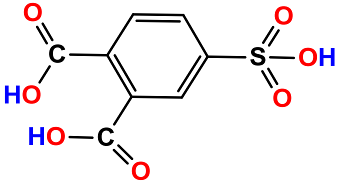
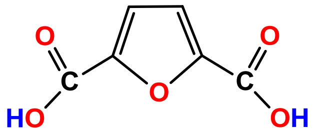
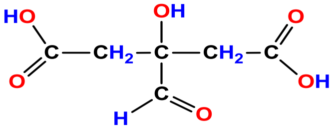
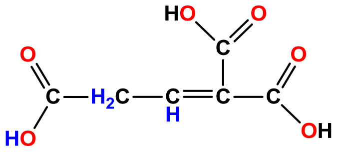
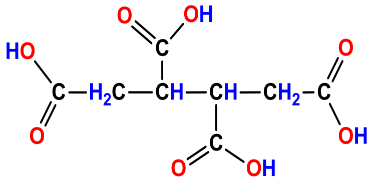
1.2.1 Various carboxylic acids used as crosslinking agent

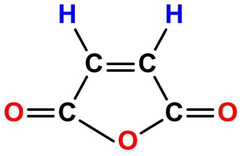
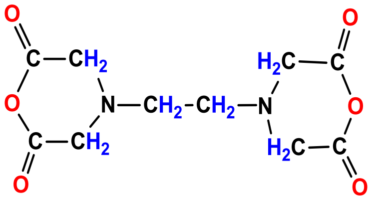
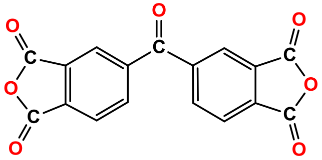
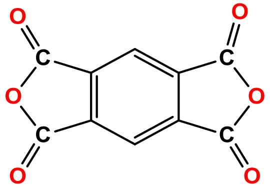
Different carboxylic acids reported as crosslinking agents for PVA are tabulated in the Table. 1.1 Often, PVA has been crosslinked by carboxylic acids of different types like mono, di, tri and polycarboxylic acids and also by its derivatives as acid anhydrides and acid chlorides. Formic acid [31] has been used as mono-carboxylic acid whereas a large number of dicarboxylic acids such as oxalic acid [64], malonic acid [65], succinic acid [50], glutaric acid [55], adipic acid [66], malic acid [67], fumaric acid [5], maleic acid [68], tartaric acid [69], suberic acid [6], terephthalic acid [6], 4-sulphopthalic acid [70], sulfosuccinate acid [61, 71], Furandicarboxylic acid [72] have been used as crosslinkers. Being a non-toxic and inexpensive chemical, citric acid[53, 56, 73] is the most favorable tri-carboxylic acid crosslinking agent, though, in this series, acotinic acid [48] has also been used by some researchers. Among poly-carboxylic acids, butane-1,2,3,4-tetracarboxylic acid[54, 74] has been reported by many researchers. Among acid anhydrides, maleic anhydride [75], ethylenediaminetetraacetic dianhydride [76], 3,3,4,4-benzophenone tetracarboxylic dianhydride [44], 4,4-oxydiphthalic anhydride [44], and pyromellitic carboxylic acid dianhydride [44] have been reported as crosslinking agents.

Table 1.1: The structure of different carboxylic acids and their derivatives used as a crosslinker with PVA

Name of the carboxylic acids	Nature of the carboxylic acids	Structure of the carboxylic acids	Applications	References
Formic acid	Mono carboxylic acid		Separation process	[31]
Oxalic acid	Dicarboxylic acid (Aliphatic)		Food packaging/Solid Polymer Electrolyte	[62, 77]
Malonic acid	Dicarboxylic acid (Aliphatic)		Iodine release systems/lithium-ion battery membrane/biomaterial	[78-80]
Succinic acid	Dicarboxylic acid (Aliphatic)		wound dressing /food packaging/fuel cell/ drug delivery	[77, 81-83]
Glutaric acid	Dicarboxylic acid (Aliphatic)		Food packaging/Desalination	[55, 84]
Adipic acid	Dicarboxylic acid (Aliphatic)		PVA-supported catalytic membranes/Optical and electrochemical sensors /solid polymer electrode	[63, 32]

Suberic acid	Dicarboxylic acid (Aliphatic)		sensors /solid polymer electrode	[6]
Maleic acid	Dicarboxylic acid (unsaturated)		Reverse osmosis/ Wound dressing /Metal uptake in aqueous systems	[81, 85, 86]
Fumaric acid	Dicarboxylic acid (unsaturated)		Pervaporation/Drug delivery	[82, 87]
Malic acid	Dicarboxylic acid (aliphatic with additional hydroxyl group)		RO/Pevaporation/waste water treatment/ drug delivery/food packaging	[81, 88-90]
Tartaric acid	Dicarboxylic acid (aliphatic with additional two hydroxyl groups)		food packaging/pervaporation/ Tissue engineering	[91, 92]
Sulfosuccnic acid	Dicarboxylic acid (aliphatic with additional sulfo group)		solid polymer electrode /Pervaporation /wastewater treatment	[93-95]

Terephthalic acid	Di-carboxylic acid (Aromatic)		Development of polysulfone (PS) membranes	[48]
4-sulfophthalic acid	Di-carboxylic acid (Aromatic)		Pervaporation/fuel cell	[70, 96]
Furandicarboxylic acid	Di-carboxylic acid (Aromatic)		Separation processes	[72]
Citric acid	Tri-Carboxylic acid (aliphatic)		Drug delivery/desalination/food packaging/fuel cell /tissue engineering/hemodialysis/wound dressing	[73, 96-101]
Acotinic acid	Tri-Carboxylic acid (unsaturated)		Development of polysulfone (PS) membranes	[48]
1,2,3,4-butanetetracarboxylicacid	Tetra-Carboxylic acid (aliphatic)		Wound dressings/Wastewater treatment/Tissue engineering/ food packaging	[43, 54, 102, 103]

Maleic anhydride	Acid Anhydride		Reverse osmosis/ Separation processes/ drug delivery.	[57, 72, 104]
Ethylenediaminetetraacetic dianhydride	Acid Anhydride		pervaporation	[44]
3,3,4,4-benzophenone tetracarboxylic dianhydride (BTDA	Acid Anhydride (aromatic)		pervaporation	[44]
Pyromellitic carboxylic acid dianhydride (PMDA)	Acid Anhydride (aromatic)		pervaporation	[44]

1.2.2 Methods of preparation of carboxylic acid crosslinked PVA films

As per the literature, Carboxylic acid crosslinked PVA films are synthesized in three steps (Fig.1.2). The first one is the mixing of PVA and carboxylic acid and making a homogeneous solution with water. The second is to cast the film or prepare fibers. The third step includes further promoting the crosslinking by curing the crosslinked polymeric film via direct heating or microwave irradiation. [48, 107].

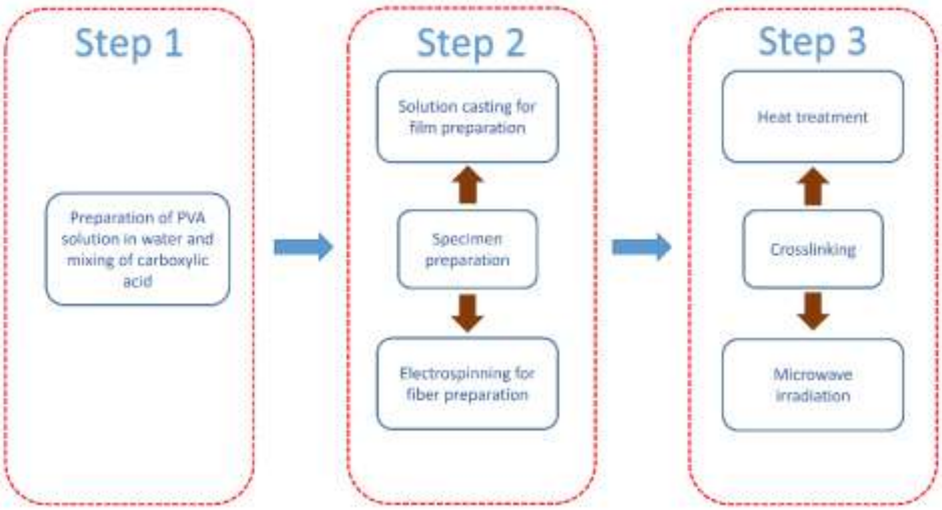


Fig. 1.2: *Method of preparation of carboxylic acid crosslinked PVA*

Fibers of crosslinked PVA can be produced by Electrospinning. In this process, the polymeric solution is exposed to a high electrical field. Polymeric solution is forced towards the oppositely charged plate using electrical potential. During this process solution formed a fiber structure with a diameter in the range of nanometers. [108]. This process is used to create nets or sheets of nanofibers, which are used as membranes for separation processes, tissue engineering, and wound dressing. [109]. Electrospinning has been used to create the carboxylic acid crosslinked PVA in different studies [53, 54].

Solution casting is widely used to manufacture polymeric films, sheets, and membranes. This process is especially suitable for crosslinked polymers. In this method, the polymeric solution is cast into the film on a flat surface using a smooth blade (doctor blade). Then the solvent is removed by evaporation or phase inversion method. [110]. This process is especially reported for carboxylic acids crosslinked PVA films for food packaging applications. [77, 91].

The casted film/fibers need to be further processed to complete the esterification reaction to achieve the required degree of crosslinking, which can be achieved by direct thermal treatment or by microwave irradiation**.**

Heat treatment method is a simple method in which the prepared film of PVA crosslinked with carboxylic acid as crosslinker is thermally treated at a high temperature in an air oven at a fixed temperature for a definite period [87, 111]. Such heat treatment facilitates the esterification reaction between PVA and carboxylic acid to produce a crosslinked network and affects the crystalline structure of crosslinked PVA film or membrane [33, 58].

The microwave irradiation method is another way besides the conventional heating method, which has been used as a source of heating for PVA cross-linking. It reduces the duration of crosslinking reactions and shows a higher yield than thermal treatment [47, 107]. On comparison of PVA cross-linked by dicarboxylic acid with microwave irradiation and conventional heat treatment, it was observed that the former technique yielded better properties as compared to the heat treatment method [47]. In a similar work [92], Cellulose–PVA composite films crosslinked with tartaric acid were compared with the direct heating method. In this study, it was found that composites prepared using Microwave and conventional heating show similar properties but microwave takes only 14 minutes compared to 2 hours in case of direct heating.

1.2.3 Mechanism of crosslinking with carboxylic acids

Various carboxylic acids, like dicarboxylic and polycarboxylic acids and their derivatives are used as good crosslinkers as they possess two or more reactive sites which help in the formation of strong, stable and high density crosslinked networks [44]. These acids have two or more reactive carboxylic functional groups present in their structure, which react with hydroxyl groups of PVA through an esterification reaction and form intermolecular or intramolecular covalent bonds as shown in Fig. 1.2 [6]. Fig. 1.3 (a) shows cross-linking of PVA with various dicarboxylic acids with different carbon chain lengths such as oxalic acid (n=0), malonic acid (n=1), succinic acid (n=2), glutaric acid (n=3), and adipic acid (n=4), etc, where “n” represents the number of methylene (CH_2) groups present in carboxylic acids. Whereas Fig.1.3 (b) depicts crosslinking between a polycarboxylic acid, like citric acid (containing three carboxylic functional groups) and PVA. The reaction of Maleic acid anhydride as a cross-linker with PVA is revealed in Fig.1.3 (c).

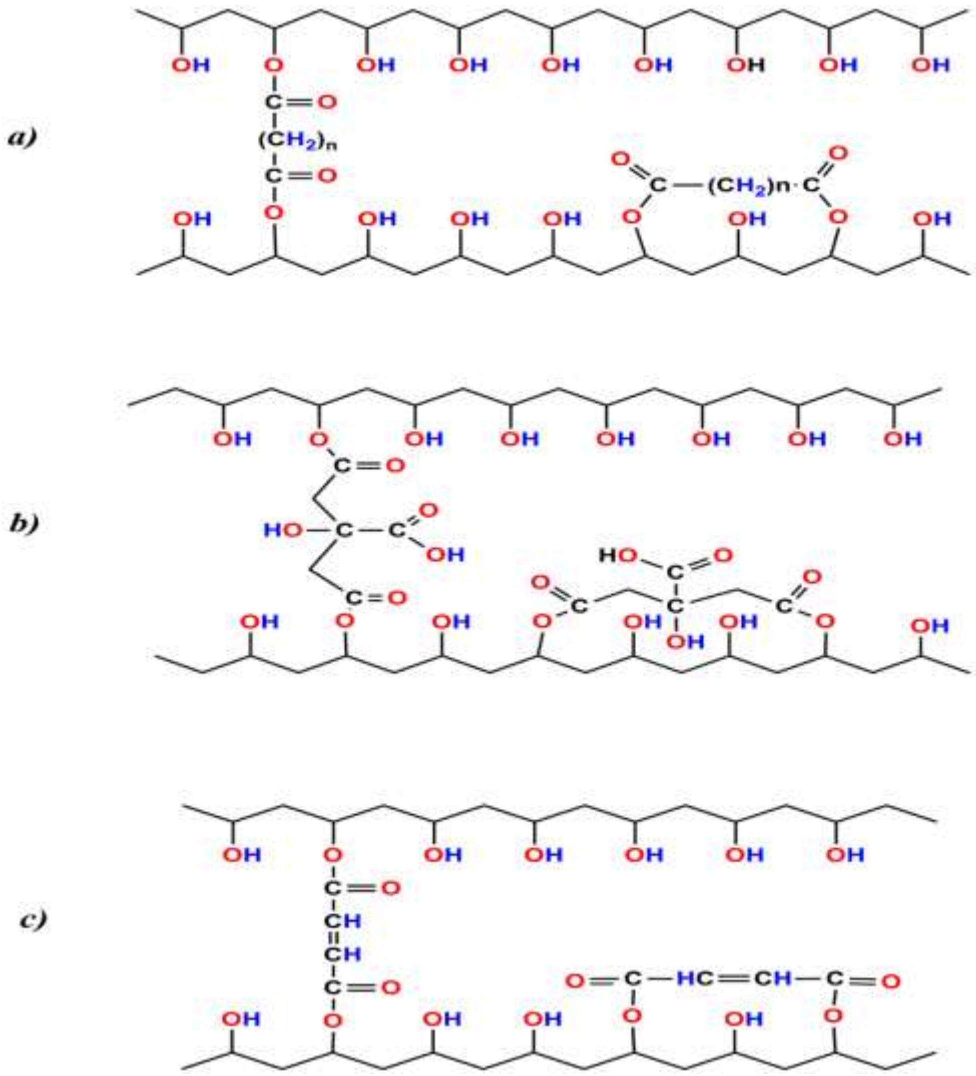


Fig. 1.3: *Intermolecular and intramolecular crosslinking reactions (via esterification) of various carboxylic acids with PVA: (a) dicarboxylic acids, (b) polycarboxylic acids, and (c) acid anhydrides*

1.2.4 Techniques to characterize carboxylic acid crosslinked PVA

The carboxylic acid crosslinked PVA has been evaluated by studying its different physicochemical properties. The swelling studies of crosslinked PVA suggest its water resistance [6] and thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) Analysis it determine its thermal behavior[45, 46].

Fourier transform infrared (FTIR)/Attenuated total reflection- Fourier transform infrared (ATR-FTIR) analysis confirms the crosslinking reaction by looking at the modifications that occur in the chemical structure [47] and the contact angle measurement can be used to measure the hydrophilic/hydrophobic characteristics [48] .Some researchers also studied morphology and topographical imaging of the membrane by scanning electron microscopy (SEM) and Atomic force microscopy (AFM), respectively [48,49]. Various researchers studied the crystalline and amorphous nature of crosslinked polymeric material by X-ray diffraction (XRD) [50] and mechanical properties by tensile strength test [5,51]. Based on the physicochemical properties of crosslinked PVA, it has been used in drug delivery [52], tissue engineering [43, 53], wound dressing [54], food packaging [45], an antibacterial membrane against the polluted air [55, 56], in the desalination of water a reverse osmosis (RO) membrane [57], pervaporation process [58,59] Filtration/ separation of metal ions [60], solid polymer electrolytes [61-63].

1.2.5 Effect of different carboxylic acids on the properties of crosslinked PVA

PVA crosslinking by carboxylic acid affects its physicochemical properties (chemical structure, hydrophilicity, and degree of swelling). Effects of the molecular structure of carboxylic acids on the properties of crosslinked PVA are summarized in Table 1.2.

Table 1.2: Effects of the molecular structure of carboxylic acids on the properties of crosslinked PVA

Variation in the structure of the Carboxylic acid	Examples of the acids	Effects	References
Length of the carbon chain	Succinic acid and adipic acid	More carbon atoms lead to more space in between the PVA chains, which in turn leads to more hence with the increase of carbon atoms, hydrophilicity increases.	[66]
Aliphatic and aromatic	Suberic acid and terephthalic acid Aconitic acid and phthalic acid	The aliphatic chain has better crosslinking as it penetrates the polymeric chain network easily and hence shows less swelling	[6, 48]
Position of the carboxylic group in the aliphatic chain (Cis and Trans)	Fumaric and maleic acid Trans aconitic acid and cis aconitic acid	The trans structure gives much more packing, the polymer chain gives better selectivity and also shows less hindrance, hence better crosslinking and less hydrophilicity	[48, 97]
Position of the carboxylic group in the aromatic chain (Ortho /meta/ para)	Phthalic acid, Isophthalic acid, Terephthalic acid	The para position is more suitable for crosslinking because of less steric hindrance and hence better crosslinking, which in turn imparts less hydrophilicity	[48]
The presence of additional groups like -OH and –SO_3H groups	Malic acid and 4-sulfophthalic acid	The sulfonic group and hydroxyl group enhance the hydrogen bond density with water molecules and then help to increase hydrophilicity	[87, 94]

The extent of modification in properties of PVA mainly depends upon the density of the carboxylic group present in the acid (mono/di/tri/tetra), additional functional groups present in the acid, and the nature of the hydrocarbon chain attached to the carboxylic group in acid (aliphatic/unsaturated/aromatic) and the processing parameters of crosslinking such as amount of crosslinker, crosslinking time and operating temperature of crosslinking reaction.[77].

Hydrophilicity is an important property of Hydrogels. Hydrogels based on PVA crosslinked with polycarboxylic acids generate nanopores that absorb large amounts of water but themselves do not dissolve into it [105]. The type of crosslinker and its concentration show a great impact on the pore size of crosslinked PVA. Hence pore size of hydrogels can be controlled by controlling the degree of crosslinking. It was observed in many research studies that a high density of crosslinking agent bonded to PVA creates a more rigid and compact structure and, therefore, less structural porosity [106]. Additionally, the hydrophilicity of the crosslinked PVA was found to be dependent on the chemical structure of the crosslinking agents. It has been reported that several hydroxyl groups present in crosslinkers affect the hydrophilicity of crosslinked PVA material, as malic acid, which contains one extra hydroxyl group, is found to be more hydrophilic than succinic acid, although both possess a similar number of carbon atoms [87]. Those carboxylic acids that show geometrical isomerism, like fumaric acid and maleic acid, both have a carbon double bond on their molecules, but fumaric acid has the trans isomerism in comparison with the cis structure of maleic acid, the steric hindrance effect of fumaric acid is lower than that of maleic acid [87]. Hence, the trans-position of the reacting group showed a better extent of crosslinking with PVA than cis and resulted in less hydrophilicity in the case of fumaric acid-PVA as compared to maleic acid-PVA (Fig.1.4). Though high content of sulfonic group present in the crosslinkers favors the transport of water molecules hence enhancing the hydrophilicity of PVA. It was also found that a crosslinking agent, 4-sulfophthalic acid (SPTA), containing a sulfonic group enhances the hydrogen bond density with water molecules. This improves the water flux in membrane-based separation applications [70, 94]. It was also reported that aliphatic carboxylic acids show more effectiveness as PVA crosslinkers than aromatic carboxylic acids because they penetrate polymeric chain networks easily

[48]. In the case of aromatic carboxylic acids, the positioning of the carboxylic group decides its effectiveness. It was found that ortho-positioning of the carboxylic groups possesses more steric hindrance as compared to meta and para [48]. Therefore, terephthalic acid containing carboxylic groups at the para position is found more suitable for PVA crosslinking than phthalic acid, which contains carboxylic groups at the ortho position as depicted in Fig. 1.5.

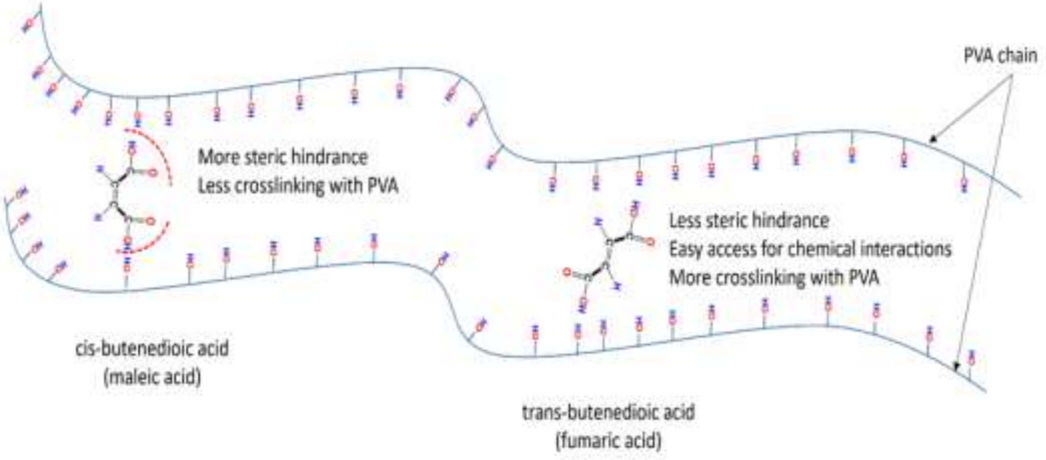


Fig. 1.4: *Effect of structure of crosslinkers on crosslinking of PVA: (a) Maleic acid (CIS), and (b) Fumaric acid (TRANS)*

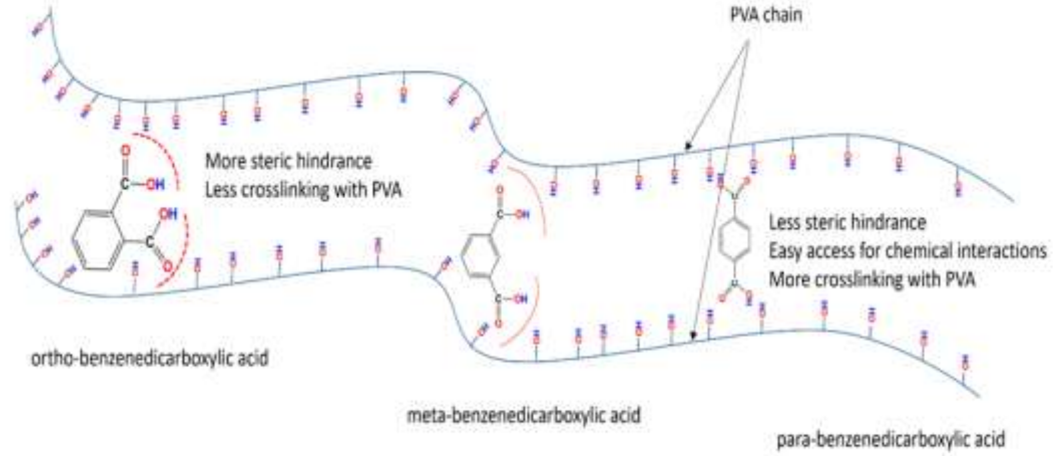


Fig. 1.5: *Effect of structure of crosslinkers on crosslinking of PVA: (a) Phthalic acid (ortho-benzene dicarboxylic acid), (b) Isophthalic acid (meta-benzene dicarboxylic acid), and (c) Terephthalic acid (para-benzene dicarboxylic acid)*

1.2.6 Applications of Carboxylic Acid Crosslinked PVA films

Being a hydrophilic and mechanically stable polymer, carboxylic acid crosslinked PVA was reported for its biomedical applications. It has also been used as a food packaging material to preserve foods from spoiling and damage. It was also identified as a versatile material to synthesize membranes for separation applications due to its thermal and chemical resistant behavior, high water flux, and anti-fouling properties. Some of the important areas of applications of carboxylic acid crosslinked PVA have been represented in Fig. 1.6

Fig. 1.6: *Applications of carboxylic acid crosslinked PVA*

1.2.6.1 Tissue Engineering

Tissue engineering is used to develop artificial/natural tissues in laboratories, and to serve this purpose, it requires a biocompatible polymer that promotes cell growth and proliferation of seeded cells. PVA is a promising biocompatible and suitable candidate for tissue engineering applications. It becomes more useful when crosslinked with carboxylic acids; the green crosslinkers. Literature revealed several studies of carboxylic acid cross-linked PVA for medical applications.

Citric acid crosslinked PVA nanofibers were synthesized for medical purposes [53]. Cross-linking was done at 150 °C and confirmed by FTIR and the crosslinked fibers were studied for their water resistance, elongation, thermal stability, and biocompatibility. It is reported that crosslinking has not only improved water resistance but also increased the thermal stability and elongation of the fibers. Cell culture studies revealed that crosslinked PVA nanofibrous mats were helpful in supporting the growth and proliferation of fibroblast cells.

Similarly, citric acid crosslinked PVA electro-spun was used for the muscle cell culture [99]. Crosslinked PVA film was found less hydrophilic and hence more cytophilic than virgin PVA film when studied for contact angle. The film was found to be nontoxic and good supporting material for the muscle cell culture.

In another study [43], PVA/chitosan electro-spun nanofibers were prepared using the electrospinning technique and crosslinked with three different multicarboxylic acids, namely succinic acid (diacid), citric acid (triacid) and1,2,3,4-butanetetracarboxylic acid (tetraacid). The swelling properties of the nanofibrous material could be tuned by crosslinking with different carboxylic acids.

Similarly, citric acid crosslinked PVA films reinforced with hydroxyapatite as nanoparticles were synthesized [123]. Thermal crosslinking was done in an oven at 140° for 4 hrs. FTIR analysis confirmed that crosslinking has occurred through multiple esterification phenomena. It was also observed that the composite film has significantly less membrane swelling with water than non-crosslinked membranes and also shows thermal stability and hydrophobic nature.

1.2.6.2 Wound Dressing

PVA crosslinked with carboxylic acids generates flexible and transparent films Capable of being handled well during the treatment of wounds, provides stronger mechanical protection, and allows evaluating the process of healing step by step. Several studies have been performed on synthesizing the hydrophilic hydrogel-based wound dressing using carboxylic acid crosslinked PVA [54, 81, 120, 124].

In a theoretical work [81], the drug release properties of crosslinked PVA hydrogels were evaluated for 20 different carboxylic acids using a molecular dynamics approach. For in vivo examination, succinic, aspartic, maleic, and malic acids crosslinked PVA were found as the best hydrogels for wound healing applications. The experimental study revealed that the films were identified as useful in accelerating the healing rate of artificial wounds in rats and showed excellent biocompatibility and were suggested as a very promising dressing material for skin wound healing [89].

Likewise another study [120], the hydrogels were synthesized using citric acid crosslinked PVA with carboxymethyl cellulose (CMC) blending. In this study, copper nanoparticles (CuNPs) were also added to make the hydrogel as an antibacterial material. The chemical crosslinking via esterification was done at 70 °C for about 16 h. The prepared hydrogel nanocomposites were applied against Staphylococcus aureus and Escherichia coli and found effective.

Furthermore, A. Çay et al. [54] crosslinked Electrospun PVA nanofibres with 1,2,3,4 butane tetracarboxylic acid (BTCA) and citric acid (CA) and evaluated for wound dressing. crosslinking was done at 180 ^{o}C for 30 minutes. Results revealed that films were stable in water. The degree of swelling was found to be higher for citric acid crosslinked films than BTCA crosslinked films. However, both toxicity and cell proliferation performance properties were found to be excellent for both types of films and they could be applied as wound dressing.

Similarly, 1,2,3,4 butanetetracarboxylic acid (BTCA) was used as a crosslinker for the crosslinking of PVA nanofibers obtained by the electrospinning technique [124]. The results revealed that electrospun nanofibrous PVA-BTCA are stable in water and nontoxic in nature and believed to be a good material for wound dressings.

1.2.6.3 Drug Delivery

PVA crosslinked with carboxylic acid produces materials with good adsorption and permeation properties of water soluble compounds. Thus, crosslinked PVA can be used to control the delivery of water soluble drugs. Hence it is worth investigating and exploiting for drug delivery systems through their crosslinking with different Carboxylic acids.

PVA-based formulation for drug delivery was designed using 20 dicarboxylic acids as crosslinkers [125]. In this study, the release of prednisone (PDN) drug was investigated in a controlled environment. Succinic acid crosslinked PVA shows the best drug release properties. Developed materials also had good biocompatibility with mouse connective tissue fibroblasts and excellent mechanical properties. They can be utilized for drug release to treat dermatological diseases.

In a similar study [97], PVA and Carboxymethylcellulose (CMC) hydrogel films crosslinked with citric acid (CA) as a crosslinking agent were developed using the solution casting method. The films were evaluated for the release of gentamicin sulfate (GTM), a water soluble drug. The prepared films were hemocompatible. The CMC-PVA hydrogel films were found as a potential biomaterial for the delivery of the water soluble drug.

In another study [82], dicarboxylic acids, succinic acid, fumaric acid, and malic acid were used as crosslinkers in the PVA-OLN (amorphous olanzapine) system to improve drug loading and delivery efficiency of the film. Synthesized films showed good stability in long-term storage and reduced the risk of drug recrystallization. Similarly, A. López-Córdoba [126] investigated the fabrication of PVA electrospun mats to carry TC (Tetracycline hydrochloride, a broad-spectrum antibiotic), using a green crosslinker, citric acid (CA). To initiate the chemical crosslinking, mats were heat-treated at 150 °C or 190 °C for 3 minutes. The results reveal that the crosslinked PVA-citric acid electrospun mats have a very low value of water solubility and are thermally more stable. Drug release studies showed that crosslinked mats have a high rate of release of drugs as compared to non-crosslinked PVA and are proposed as antibiotic local delivery systems for wound healing.

PVA/citric acid(CA)/Ag nanoparticles (NPs) hydrogels were produced for pH-sensitive and antibacterial drug delivery [52].This study showed that the presence of free carboxylic acid groups on CA not only causes crosslinking but is also responsible for both pH responsiveness and antibacterial activity in PVA hydrogels.

1.2.6.4 Fuel Cell/ Solid polymer electrolyte

Being a low-cost, eco-friendly, and versatile material, PVA is a promising material to be used in fuel cells. However, PVA is a poor proton conductor because it does not have enough negatively charged ions; these limitations can be overcome by introducing the charge-conducting material and then crosslinking with carboxylic acid or its derivatives.

Proton conducting membranes based on PVA were synthesized using the solution casting method [96], where Citric acid and 4-sulfophthalic acid were used as crosslinkers. The synthesized films were characterized by TGA, degree of swelling, relative refractive index, and real part of dielectric constant by spectroscopy ellipsometry, and conductivity using electrochemical impedance spectroscopy (EIS). The conductivity values of the synthesized cationic membranes were compared with Nafion®, a commercially available membrane by EIS and found to be the same hence, crosslinked PVA cationic membranes were found to be a potential material to be used as proton exchange membranes. Similarly, PVA was crosslinked with succinic acid by the solution casting method to produce an ion-conducting polymer electrolyte [83]. Results showed an increase in the DC conductivity of PVA with increasing concentration of Succinic acid. However, after a certain concentration, the conductivity started to fall.

In a similar work, a polymeric membrane based on PVA and sulfosuccinic acid as crosslinker (SSA) was developed by a solution casting method, compared with the commercially available Nafion membrane [61]. This study showed that the PVA/ SSA ionomer is as good as Nafion at the anode catalyst layer. Though the Maximum power density of a crosslinked membrane-based cell was found only 35% that of Nafion-based cells, but shows lower costs and can be considered as a potential candidate for the large-scale production of Proton exchange membrane fuel cells.

Adipic acid crosslinked PVA membranes were developed by the solution casting technique to produce proton conducting solid polymer electrolytes [127]. The developed polymer electrolytes were studied by XRD, DSC, AC impedance, and Wanger’s DC Polarization and studies revealed that ion conductivity as well as thermal stability both increased due to the addition of adipic acid.

In the same vein, nanofibrous PVA crosslinked with sulfonated succinic acid (SSA) incorporated with graphene oxide (GO) was used to produce functionalized membranes. Crosslinking reaction of PVA with sulfosuccinic acid (SSA) was performed at 110 °C for 2 h in a convection oven. The prepared membrane showed improved thermal, and hydrothermal stability, and also, along with the presence of GO, brought more proton conductivity. [128]

1.2.6.5 Pervaporation

Pervaporation is a clean, cost effective, and energy-saving process used to separate different components from a liquid mixture were distillation processes encounter difficulties. A hydrophilic membrane prepared from crosslinked PVA is widely used to remove water impurities from organic mixtures, such as the dehydration of alcohol. In this regard, crosslinked PVA has been a matter of interest for many scientists across the world.

An asymmetric sulfosuccinic acid (SSA) crosslinked PVA membrane was prepared by casting the PVA/SSA mixture on a porous polyacrylonitrile (PAN) ultrafiltration membrane [51]. Crosslinked Membranes were found to have excellent water permeability with relatively lower swelling in comparison to non-crosslinked membranes.

In a similar study [87], a PVA based composite membrane coated on a PAN porous support membrane was synthesized via the solution casting method. Three different carboxylic acids, namely fumaric acid, maleic acid, and malic acid, were used as crosslinkers. The swelling degree, permeation flux and separation factor of the prepared membranes were observed to follow the trend of plain PVA > malic acid-PVA > maleic acid-PVA> fumaric acid-PVA. Crosslinking of PVA membrane with dicarboxylic acids at high temperatures was found to achieve a higher separation factor but lower flux.

Three different dianhydride crosslinkers, benzophenone tetracarboxylic dianhydride (BTDA), oxydiphthalic anhydrides (ODPA), and pyromellitic carboxylic acid dianhydride (PMDA), were used to produce crosslinked PVA membranes [44]. The crosslinking degree was found in order of pure PVA < PVA/BTDA-2 < PVA/ODPA-2 < PVA/PMDA-2, while the hydrophilicity and glass transition temperature were in the opposite trend. Crosslinked membranes were found to show higher fluxes but lower separation factors when compared with the pure PVA membrane. Observations also suggested that more crosslinking of PVA chains disturbs the crystalline region of PVA, resulting in a loose chain packing density and high fractional free volume in the PVA matrix, therefore a higher flux of the crosslinked PVA membranes.

Similarly, tartaric acid crosslinked PVA pervaporation membranes were developed by the solution casting method and tested for the dehydration of acetic acid separation [69]. Crosslinking was confirmed by FTIR, swelling studies, DSC, and contact angle testing. Results revealed that prepared membranes have higher water permeability and separation ability than other membranes.

A hybrid polymer-inorganic PVA/Silica particles composite membrane was prepared by using maleic acid (MA) as a crosslinker [46]. It was found that the addition of crosslinkers lowers the swelling and crystallinity of the membrane. On the other hand, the presence of silica nanoparticles in the PVA matrix enhanced the free volume and thus, the water permeability of the membrane.

1.2.6.6 Capacitive deionization

Capacitive deionization (CDI) is a desalination process where ions present in the liquid mixture in trapped inside oppositely charged conductors under an applied potential and then get desorbed on the application of a reverse potential**.** The CDI process is considered an energy-efficient process as it operates at a relatively low voltage, where no electrolysis reactions occur. Higher wetted surface area is an important parameter for increasing the efficiency of CID. Crosslinked PVA can be a good candidate for increasing the wettability of polymer-bonded carbon electrodes because of its hydrophilic nature.

A.S. Kumar et al. [84] used Glutaric acid crosslinked PVA to enhance the wettability of carbon electrodes. The prepared electrodes were found stable in boiling water and showed higher salt absorption efficiency at lower concentrations and the energy consumption during the experiments was also found to be very low. Hence, it can be successfully employed in CDI applications.

Likewise, PVA was used as a binder to fabricate the carbon electrodes using glutaric acid as a crosslinker to enhance the wettability of CDI electrodes [129].

Morphological properties of modified electrodes were ascertained by SEM. The performance of PVA/carbon composite electrodes was investigated to investigate the efficiency of the electrodes with varying salt concentrations. Results showed that developed electrodes were feasible for the desalination of brackish water. The energy consumption during experiments was also found to be low.

In another study [98]PVA based carbon electrodes were fabricated using citric acid (CA) as a crosslinking agent. The carbon electrode was dried in an oven for one hour at a temperature of 120 °C for a crosslinking reaction between PVA and CA. The performance of CDI cells using prepared electrodes for desalination of NaCl solution is also studied and results revealed that the salt-removal percentage for the desalination of NaCl was 49.15 %, which is a good desalting performance.

Similarly, PVA based cation exchange membranes were fabricated using SSA and CA as crosslinking agents [130]. The crosslinked CA/SSA/PVA composite membrane results in high desalination efficiency due to the addition of sulfonic acid groups and carboxyl groups. It was also observed that the adsorption capacity and the charge efficiency of the modified membrane can be enhanced by 18% and 28%, respectively to the CDI.

1.2.6.7 Reverse Osmosis and Waste Water Treatment

Reverse Osmosis (RO) is a membrane-based water purification process used to separate different salts and ionic impurities from the water solution. In this process, membranes are hydrophilic, and thus, PVA membranes are suitable for the RO process. Carboxylic acid crosslinking helps to make the membrane water insoluble and stable.

PVA and polyethylene glycol (PEG) based composite thin membranes were fabricated and maleic acid was selected as a crosslinker [131]. The solution casting method was used to crosslink PVA with maleic acid. The composite thin membranes were successfully employed to purify brackish and seawater using the RO process.

Similarly, A. Saraf et al. [85] studied the osmotic performance and membrane properties of PVA crosslinked membranes, taking two crosslinking agents like maleic acid and glutaraldehyde. Membranes based on PVA crosslinked with maleic acid showed significantly higher water flux in both RO and forward osmosis (FO) systems as compared to glutaraldehyde crosslinked membranes for seawater desalination. However, both membranes showed similar performance for brackish water desalination.

In a similar study [57], the virgin thin film composite (TFC) RO membrane was exposed to the mixture of PVA and maleic anhydride (as a crosslinker) to increase the water flux for the thin film composite reverse osmosis membrane (TFC-RO). The membrane that was treated with PVA-maleic anhydride was found to give high salt rejection and increased water flux as compared to the virgin TFC-RO membrane.[57]

Likewise, PVA-based nanofiltration (NF) membranes were prepared by casting a thin PVA layer on a polysulfone ultrafiltration membrane [88]. Here, malic acid was selected as a crosslinker for PVA. Prepared membranes were used to separate magnesium sulfate ($MgSO_4$) and sodium chloride (NaCl) salts from water solutions. It was found that the degree of crosslinking increases with increasing content of malic acid and it also disrupts the crystallinity of the PVA membrane, which in turn increases the salt rejection and water permeability.

Sulfosuccinic acid crosslinked PVA membranes were prepared for the removal of strontium (Sr^{2+}) from contaminated water [95]. It was found that the crosslinked membrane has all the desirable properties of including good mechanical stability and excellent Sr^{2+} selectivity.

In the same vein, a crosslinked PVA hydrogel was synthesized for the absorption of organophosphorus pesticide dimethoate from water [105]. Various dicarboxylic acids as crosslinkers and their effectiveness were analyzed. Among them, malic acid crosslinked PVA had the highest interaction energy with dimethoate.

Similarly, malic acid (MA) was used as a crosslinker to synthesize PVA-based hydrogels for the absorption of another pesticide, methamidophos (MMP) from an aqueous solution [90]. The experimental analysis of MMP removal was performed. The prepared hydrogel was able to remove 86% of MMP from aqueous solutions.

Moreover, 1,2,3,4 butanetetracarboxylic acid (BTCA) crosslinked PVA nanofibrous membranes were synthesized using electrospinning for the removal of dye from wastewater [102]. The results revealed that crosslinking improved both thermal and water stability of the nanofibrous membranes and films are capable of removing approximately more than 80% of the dye. In another work [132]PVA/PES composite membranes were synthesized using malic acid as a crosslinker. The crosslinking agent was found effective in enhancing thermal and chemical stability and exhibited good fouling resistance and flux.

1.2.6.8 Food Packaging

PVA is widely used as a food packaging material because of its biodegradability, biocompatibility, and non-toxicity. Further, its cross-linking with nontoxic crosslinkers, i.e., carboxylic acids, provides chemical and thermal stability and increases the mechanical properties of the material. The effect of crosslinked PVA on bactericidal activity as an active packaging material for food is being investigated by many researchers [77, 91, 103, 133].

Succinic acid, oxalic acid, and citric acid crosslinked PVA films were prepared and their physicochemical and biological properties were studied [77]. It was found that crosslinkers enhance physical and chemical properties and improve bactericidal activity. Among various crosslinked films, PVA crosslinked with citric acid showed higher bacterial inhibition efficiency it can alter the local pH and also affect the permeability of microbial membranes.

In the same vein [91], three different dicarboxylic acids; malic acid (MA), tartaric acid (TA), and lactic acid (LA) were used as crosslinkers to obtain crosslinked films by the solution casting method for food packaging application. Crosslinked films were found to be hydrophobic and thermally stable as compared to virgin PVA films. PVA-LA crosslinked films were found to have the highest bacterial inhibition, hence the demise of germs. The crosslinked film was found to be a potential material for food packaging.

A nanocomposite based on PVA-starch-graphene was synthesized by the solution casting method, where citric acid (CA) was used as a crosslinker [133]. Citric acid was found an effective crosslinker. The tensile strength and modulus of the prepared film were increased significantly. Films were quite stable in water.

Likewise, 1, 2, 3, and 4-butane tetracarboxylic acid (BTCA) was also used as a crosslinker to prepare a biodegradable blend film of PVA/Xylan via the solution casting method [103]. It was found that blended films showed effective biodegradation properties within 30 days of experiments.

Overall, various carboxylic acids have been used for PVA crosslinking for different applications. The physical/chemical properties of these acids affect the properties of the final product in various applications. Structure-property correlation of main carboxylic acids for different applications is summarized in Table 1.3.

Table 1.3: Performance of various carboxylic acids cross-linked PVA in different fields of applications

Field of Applications	Various carboxylic acids used as cross-linkers	Advantages/Limitations	References
Food packaging	Glutaric acid (GA)	Only a higher concentration of acid provides a stable system with long-lasting antibacterial effects. Excess GA impairs the mechanical properties of the film	[55]
	Tetracarboxylic acid (BTCA)	Water absorption values were found to be decreased with increasing the amount of BTCA due to its moisture barrier properties. The addition of BTCA also shows a positive influence on film degradation.	[103]
	Malic acid, tartaric acid and lactic acid	Lactic acid was found to be the best among them. It acts as an antimicrobial agent, reduces the local pH of the bacteria, and also alters the film permeability, leading to bacterial cell death.	[45]
	Oxalic acid, succinic acid and citric acid	Among them, citric acid was found to be the best. It enhances the film properties by establishing a balance between its hydrophobic and hydrophilic microstructure. It acts as an antimicrobial agent and decreases the internal pH of bacteria as well, which helps in the killing of microbes. Citric acid was found to be a potential cross-linker that fulfills most of the criteria to produce a film that could be used as a packaging material for food packaging, such as flexible, mechanically strong, antimicrobial, and biodegradable, with impacts on moisture permeability. Such cross-linked packaging films have the potential to replace petroleum product-based food packaging films.	[77]

Tissue engineering	Succinic acid (SA), citric acid (CA) and 1,2,3,4-butanetetracarboxylic acid (BTCA)	Nanofibrous mats containing SA, CA, and BTCA were found to be non-toxic. Succinic acid crosslinked nanofibrous mats showed the best optimum condition for cell proliferation. Among them, citric acid crosslinked PVA possesses good biocompatibility and anticoagulant properties. A scaffold with good cell adhesion and proliferation is an important criterion for tissue engineering. Tetracarboxylic acid contains more crosslinking sites than other di and tricarboxylic acids, which enhances the fiber stability. The surface charge of the scaffold and the cell membrane also plays an important role in cell adhesion.	[43, 99]
Wound dressing	Citric acid (CA)	The presence of free groups of carboxylic acid on citric acid in CA crosslinked PVA film shows better responsiveness towards pH and antimicrobial activities.	[52]
	Tetracarboxylic acid (BTCA)	BTCA increases the thermal stability of cross-linked films and an increase in the concentration of it in the cross-linked film leads to a decrease in its swelling as evidenced by artificial serum absorbency tests. It was shown that the cell proliferation performance of CA cross-linked PVA was found to be better. For wound dressing materials, a mechanically stable, sustained value of swelling index that correlates with the diffusion process of encapsulated bioactive compounds in the cross-linked polymer network are essential requirement. The nature of cross-linkers alters not only the mechanical properties but also promotes cell proliferation with good durability in an aqueous medium.	[54, 124]

Pervaporation	Tartaric acid	Permeation flux and swelling of the membrane decrease significantly with an increase in tartaric acid concentration in the cross-linked film. The high concentration of it increases the cross-linking rate, which leads to a decrease in the free volume of the membrane.	[69]
	Maleic acid (MA)	Cross-linking of PVA with MA results in the formation of a film with a rigid and compact structure, which disrupts the polymer chain packing and thus leads to a high salt rejection.	[46]
	Fumaric acid	Cross-linking of PVA with fumaric acid shrinks the membrane, which indicates that the decrease in the free volumes of the membrane results in low flux. It has a negative impact on the permeation flux of large molecules like isopropanol than with small molecules like water.	[5, 87]
	Sulfosuccnic acid (SSA)	The hydrophilicity of the membrane was found to be strongly enhanced by using SSA as a cross-linker that increases the permeation flux. In this process, sulfonic acid groups present on the membrane reversibly react with water and act as fixed facilitative transport agents. Water diffusivity of a cross-linked membrane with SSA was found, hence its high water flux rate. The chemical structure of the cross-linkers affects both the physicochemical properties and separation performance of the crosslinked PVA membranes. The swelling behavior of the membrane plays an important role in its separation performance.	[51, 70]
Drug delivery	Succinic acid, fumaric acid and malic acid .	Carboxylic acids cross-linked PVA decrease the risk of recrystallization of the encapsulated drug by altering the molecular mobility of the cross-linked	[82]

		film. Malic acid cross-linked film was found to have the strongest ability to maintain the content of amorphous drug in the cross-linked PVA film, which disintegrates rapidly in the oral cavity, and the amorphous drug dissolves and absorbs in the gastrointestinal tract easily. There should be a strong interaction force between the drug and the film that helps it in transportation to the drug target.	
Wastewater treatment	Maleic acid and citric acid	Citric acid cross-linked PVA membranes are more selective towards metal uptake as compared to the maleic acid cross-linked PVA membrane. Cross-linked PVA membranes with low concentrations of malic acid are suitable for the removal of pesticides from contaminated water. Carbonyl groups available in the pores of cross-linked membranes were the reason behind the super absorption of pesticides from water.	[86]
	Sulfosuccinic acid (SSA)	Cross-linked PVA membrane with a lower concentration of SSA exhibits greater thermal stability with excellent removal of Sr^{2+} over a wide range pH range. Both the content of the cross-linker and its chemical structures in the cross-linked PVA membrane work synergistically in the treatment of wastewater.	[95]
Polymer electrolyte	Oxalic acid and citric acid	Electric conductivity of citric acid cross-linked PVA are higher than its counterpart oxalic acid as earlier contains three carboxyl groups per molecule and later possesses only two carboxyl groups.	[62]

	4-sulpho-phthalic acid	PVA membrane crosslinked with 4-sulpho-phthalic acid was found to show good thermal stability with a low value of degree of swelling. As the sulphonic group is a better crosslinker and good for the transport of protons as well.	[96]
	Malonic and succinic acid	Both malonic acid and succinic acid contribute protons for the conduction but also enhance the amorphous region in a polymer, reducing its crystallinity. The DC conductivity of malonic acid cross-linked PVA film was found to be better than succinic acid cross-linked film. It was observed that the conductivity of PVA cross-linked films depends on the nature of cross-linkers and their chemical structures as well.	[61]

1.3 Conclusion

The present chapter outlines the introduction and comprehensive literature on crosslinking of PVA with carboxylic acids involves an esterification reaction between carboxyl groups of acids and hydroxyl groups of PVA, leading to the formation of an ester bridge-group network. Being non-toxic and environment-friendly crosslinkers, carboxylic acids are known as green crosslinkers. There are many factors, like crosslinker concentration, duration of crosslinking, and curing temperature, that play an important role in the modification of carboxylic acids crosslinked PVA samples. Crosslinking reaction with carboxylic acids induces many alterations in the properties of PVA such as reduced crystallinity, improved thermal stability and mechanical properties, reduced hydrophilicity, enhanced tensile strength and elongation properties, increased water stability, developed antibacterial activity and proton transportation, etc. These induced properties have made PVA-based membranes versatile materials to be used in various fields such as pervaporation, supporting membranes in reverse osmosis, drug delivery systems, antimicrobial food packaging, fuel cells, desalination, air filters, biodiesel synthesis, ion exchange, separation of metals, and others. The literature discussed above has been published as a review paper in the Journal of Polymer Engineering and Science. [134]

1.4 Research Gap

The above discussion suggests that the properties of the crosslinked PVA can be altered by using different types of carboxylic acids as crosslinkers. However, only a few studies have been performed to establish the structure-property correlations between acid molecular structures and desired properties in final products. Therefore, the following research gaps were found after the literature survey.

- **Influence of Molecular Structure:** Limited research exists on how the molecular structure of carboxylic acids affects the extent of PVA cross-linking.
- **Impact on Properties:** The effects of the molecular structures of carboxylic acids on the physicochemical properties of PVA were not well understood.
- **Comparative Analysis:** Detailed comparisons of how different carboxylic acids affect the properties of PVA were still lacking.

- **Challenges in Application Optimization:** The research gap makes it difficult to choose the appropriate crosslinker for specific applications, highlighting the need for further investigation.

1.5 Objectives

The following objectives have been set to address the research gaps identified in the literature:

I. To investigate the effects of the number of carbon atoms in a homologous dicarboxylic acid (both odd and even) when used as crosslinkers on PVA.

II. To analyze the effects of both saturated and unsaturated dicarboxylic acids when used as crosslinkers.

III. To explore the impact of di, tri and tetracarboxylic acids as crosslinkers on the properties of PVA.

IV. To evaluate the effectiveness of synthesized crosslinked PVA films in dye removal by analyzing their structure-property relationships.

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Chapter 2

Materials, Method & Characterization

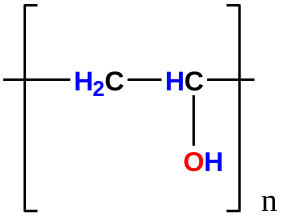
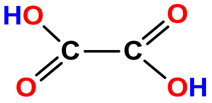
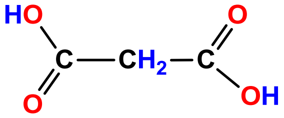
2.1 Introduction

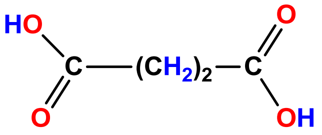
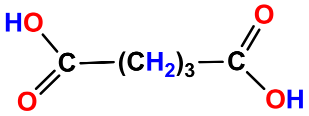
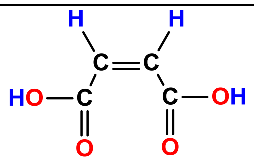
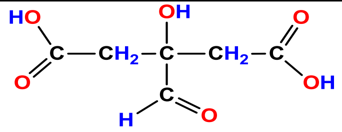
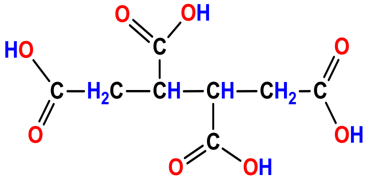
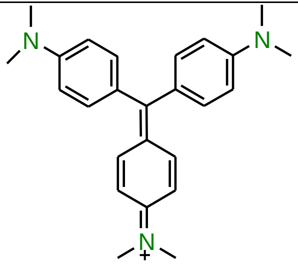
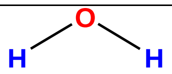
The present chapter offers a detailed overview of the preparation and evaluation of PVA films crosslinked with carboxylic acids. It covers the specifics of the reagents used, the procedure of synthesis of the crosslinked films, and the underlying mechanism behind the crosslinking. Additionally, it includes the description of characterization and testing techniques used to examine the structural, morphological, thermal, mechanical, rheological, and adsorption properties of the crosslinked films, with adsorption analysis performed using a UV spectrophotometer.

2.2 Reagents

Polyvinyl alcohol (PVA) (M.W. = 145000 g/mol, fully hydrolyzed) was procured from Sigma-Aldrich, USA. Seven distinct dicarboxylic acids: Oxalic acid (OA), Malonic acid (MA), Succinic acid (SA), Glutaric acid (GA), Maleic acid (MAL), Citric acid (CA) and 1,2,3,4-butenetetracarboxylic acid (BTCA) were obtained from Loba Chemie. A cationic dye was ordered from CDH for the adsorption process. The deionized water was used as a solvent for all experimental procedures. Table 2.1 provides the structure of all the reagents used.

Table 2.1: Chemical structure of the reagents used

S. No.	Reagent	Structure
1.	PVA	
2.	Oxalic acid	
3	Malonic acid	

4.	Succinic acid	
5.	Glutaric acid	
6.	Maleic acid	
7.	Citric acid	
8.	1,2,3,4-butenetetracarboxylic acid	
9.	Crystal violet dye	
10.	Water	

2.3 Method of preparation

The synthesis of films was achieved via the solution casting method [1]. The preparation procedure of crosslinked PVA film is illustrated in Fig. 2.1. The process can be divided into two parts: 1. solution preparation and film casting, and 2. solid-phase crosslinking during curing. PVA solution (8% w/v) was prepared by dissolving PVA in water under stirring at a temperature of 80 °C for about 1 h, ensuring a homogeneous and clear solution. 20 mL of PVA solution was taken in a round bottom flask attached to a condenser and a calculated amount of dicarboxylic acid was added to it. After the addition of the calculated amount of dicarboxylic acid, the resultant solution was kept under stirring in a water bath for 1 h at 80 °C for complete homogenization. The obtained clear solution was poured into molds of flat glass sheets for complete evaporation of water under environmental conditions to form the film. The dried films were peeled off and kept in the oven for heating to further promote crosslinking. To remove the unreacted acid, films were suspended in distilled water. During washing, water was changed several times to remove the extracted dicarboxylic acids from the films. The washed crosslinked films were left in the air at room temperature for drying and later kept in sealed plastic bags for further investigation. The same procedure was used for each dicarboxylic acid.

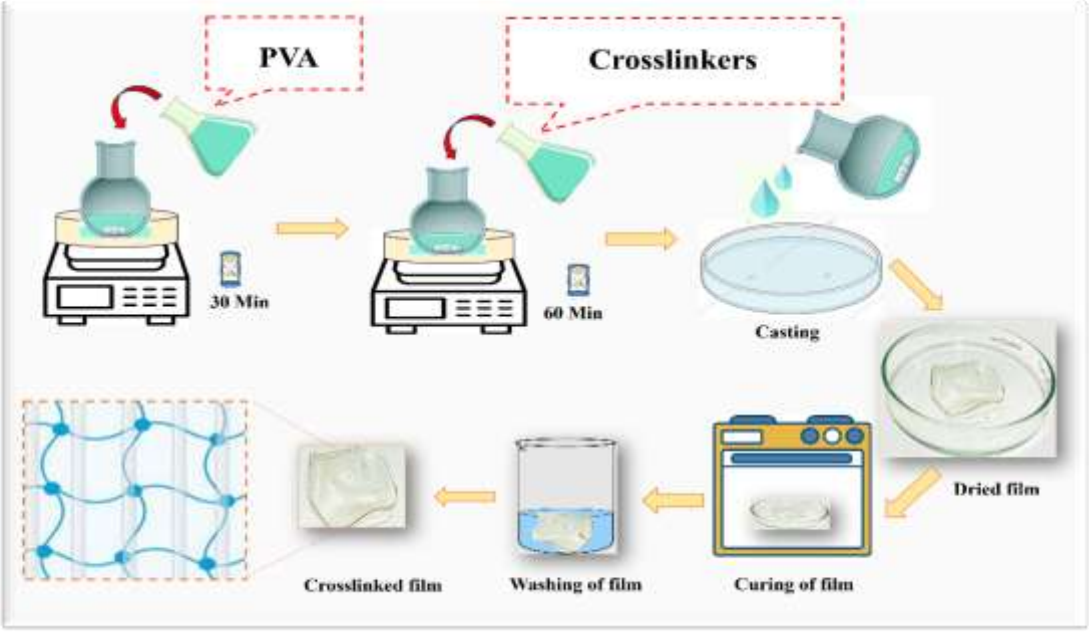


Fig. 2.1: *Schematic diagram of the preparation of crosslinked PVA film*

2.4 Mechanism

The fabrication of crosslinked PVA films involved a catalyst-free esterification reaction. The mechanism is achieved through simple drying and curing processes. The reaction mechanism in Fig.2.2 illustrates the interaction of dicarboxylic acids with PVA through esterification. During the drying and curing stages, the carboxyl group of dicarboxylic acids is likely to react with the hydroxyl group of PVA, resulting in the formation of ester bonds [2]. Additionally, the drying and curing steps play an important role in eliminating water molecules, facilitating the progression of the reversible esterification reaction in the forward direction [3]. It is worth noting that effective chemical crosslinking may occur only when the two COOH groups of a dicarboxylic acid react with two OH groups of two adjacent PVA chains to form ester bonds. If only one COOH group of a dicarboxylic acid reacts with PVA, the resulting ester bond does not contribute to chemical crosslinking. However, the unreacted COOH group can form H-bonds with PVA, enhancing the overall crosslinking of the films.

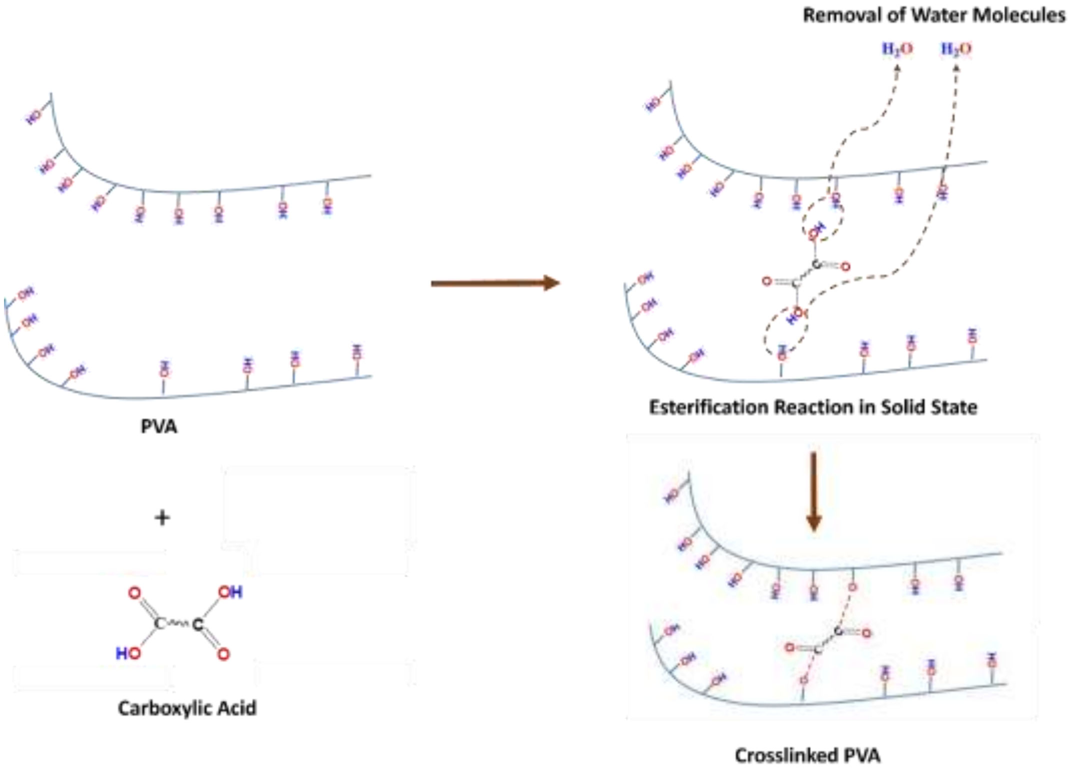


Fig. 2.2: *Esterification reaction between dicarboxylic acids and PVA*

2.5 Characterization and testing techniques

Table 2.2: List of characterization and testing techniques

S. No.	Technique	Analysis done
1.	Fourier Transform Infrared Spectroscopy (FTIR)	Chemical Structure
2.	Scanning Electron Microscopy (SEM)/ Field Emission Scanning Electron Microscopy (FESEM)	Surface morphology
3.	Atomic Force microscopy	3-D images of surface roughness
4.	X-ray Diffraction Spectroscopy (XRD)	Crystalline nature
5.	Thermal gravimetric analysis (TGA)	Thermal degradation
6.	Differential scanning calorimetry (DSC)	Thermal
7.	Rheology	Rheological
8.	Tensile strength	Mechanical
9.	Water contact angle measurement (WCA)	Hydrophilicity/hydrophobicity
10.	Swelling percentage and Crosslinking density	Water uptake capacity
11.	Gel content	Uncrosslinked portion

2.5.1 FTIR spectroscopy

To confirm the presence of characteristic functional groups, ATR-FTIR analysis was conducted using the Bruker Optics Spectrum instrument. The FTIR spectra of all the crosslinked films were recorded at a resolution of 4 cm^{-1}, and the number of scans was 48 in the range of 4000–500 cm^{-1}.

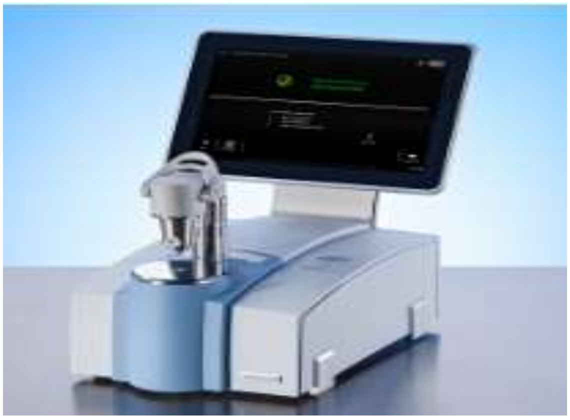


***Fig. 2.3**: Bruker Optics Spectrum instrument, like the one used in this study (Source: https://www.bruker.com)*

2.5.2 Scanning Electron Microscopy (SEM)

To observe the change in the morphology of the surface of the PVA crosslinked films, SEM images were captured using a JEOL (model number 6610LV) scanning electron microscope (SEM). The films were coated with gold-palladium and observed at a voltage of 20 and 15 kV, respectively

***Fig. 2.4:** JEOL (model number 6610LV) scanning electron microscope, like the one used in this study*

(Source:http://www.umms.sav.sk/6554-en/jeol-jsm-6610lv-scanning-electron-microscope)

2.5.3 Atomic Force Microscopy (AFM)

AFM images were recorded using the Asylum Research MFP3D-BIO atomic force microscope to observe the 3-D image and estimate the Roughness of the films.

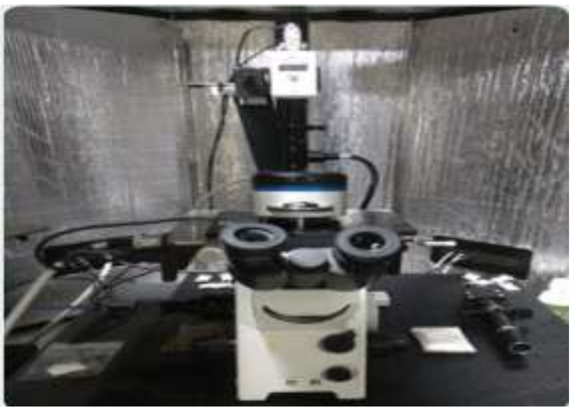


Fig. 2.5: *Asylum Research MFP3D-BIO atomic force microscope, like one used in this study*

(Source:https://crf.iitd.ac.in/All-Facilities-/Atomic-Force-Microscope)

2.5.4 X-ray diffraction (XRD) Analysis

To study the crystalline structure of the PVA crosslinked films, XRD patterns of all crosslinked films were recorded using the X'Pert PRO model, diffractometer (PANalytical, Netherlands) [λ(Cu-Kα) =1.54 A]. Scattered radiations were recorded in the range of 2θ ranging from 5 to 60. The relative percent crystallinity of the crosslinked films was determined using the following equation 2.1[4]

$$x\% = \frac{Ac}{Ac + A_A} \times 100 \tag{2.1}$$

where A_C is the crystalline area and A_A is the amorphous area.

Fig. 2.6: *X'Pert PRO model, diffractometer (PANalytical, Netherlands), like the one used in this study*

(Source: https://crf.iitd.ac.in/All-Facilities-/XRD-Sonipat.html)

2.5.5 Thermal gravimetric analysis (TGA)

To observe the thermal stability and decomposition temperature of neat PVA and crosslinked PVA samples, thermal gravimetric analysis (TGA) and DTGA were recorded using PerkinElmer TGA 4000 with an N_2 atmosphere in the range of 30–700 °C at the rate of 10 °C/min.

Fig. 2.7: *PerkinElmer TGA 4000, like the one used in this study* ***(****Source: https://www.perkinelmer.com)*

2.5.6 Differential scanning calorimetry (DSC)

DSC analysis was performed to examine the change in Glass transition temperature (T_g) and melting point of the PVA crosslinked films. The heat flow measurement was recorded using the Perkin Elmer model DSC8000 analyzer. The samples of nearly 10 mg mass of pure PVA and crosslinked PVA films were heated from 30 to 300 °C at a rate of 10 ^{0}C/min under N_2 atmosphere.

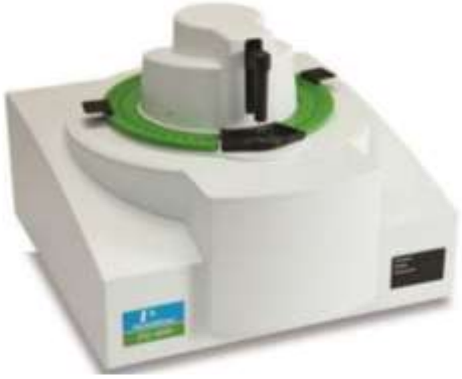


Fig. 2.8: *Perkin Elmer model DSC8000 analyzer, like the one used in this study (Source: https://www.perkinelmer.com/)*

2.5.7 Rheology

Dynamic rheological studies of neat PVA and crosslinked PVA films were conducted using an Anton Paar MCR 702 rheometer in torsional setup mode. The frequency-dependent measurements were taken at room temperature with a fixed strain ($\gamma = 0.3\%$) across a frequency range of 0.01 to 100 Hz.

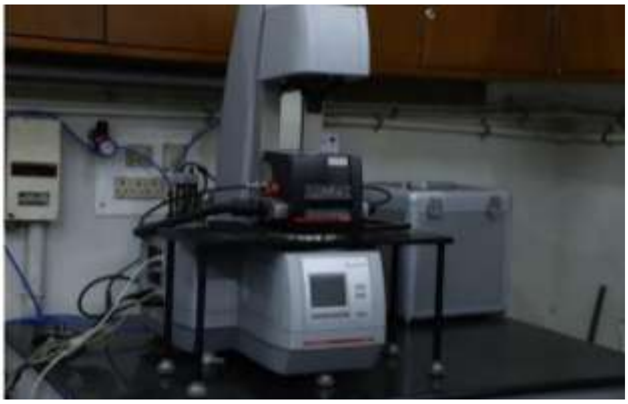


Fig. 2.9: *Anton Paar MCR 702 rheometer, like the one used in this study (Source: https://www.anton-paar.com)*

2.5.8 Tensile strength

The tensile tests of the PVA and crosslinked films were performed on Zwick Roell Z010 according to ASTM D638 and ASTM D790, respectively. Three samples were tested for each set, and the mean value was reported.

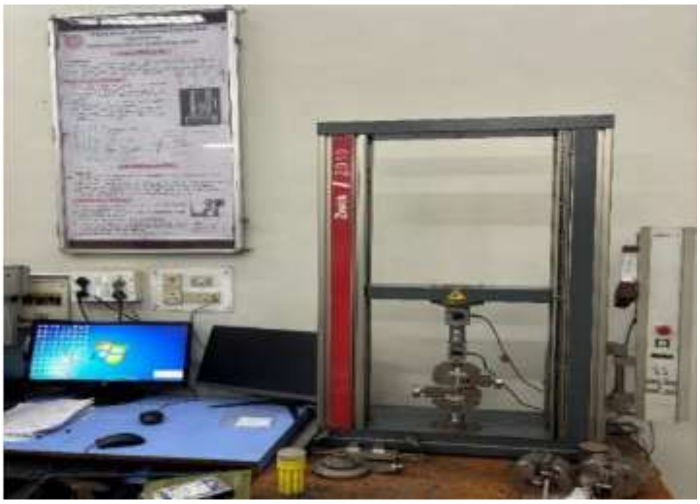


Fig. 2.10: *UTM, Zwick Roell Z010, like the one used in this study (Source: https://crf.iitd.ac.in)*

2.5.9 Water contact angle measurement (WCA)

The hydrophilicity of the PVA crosslinked films was investigated by a Kruss Advanced 1.6.2.0 sessile drop contact angle Goniometer at ambient temperature. A deionized water droplet of 2 μL was dropped by a micro syringe onto the top surface of the films. For each film, a minimum of 5 points was measured to get the average.

Fig. 2.11: *Kruss Advance 1.6.2.0 sessile drop contact angle Goniometer, like the one used in this study*

(Source: https://www.kruss-scientific.com)

2.5.10 Swelling percentage and Crosslinking density

Small sections of crosslinked PVA films, with different dicarboxylic acids, were cut into 1 cm × 1 cm pieces. They were weighed and placed in deionized water at room temperature. The swollen films were taken out after regular intervals, excess water was wiped off with filter paper, weighed and then they were put back into the water. This process continued until the films reached equilibrium swelling. The degree of swelling was calculated using equation 2.2

$$S\,\% = \frac{W_S - W_D}{W_D} \times 100 \qquad 2.2$$

where S, W_S and W_D are the degree of swelling in percent, the weight of the films in the swollen state, and the weight of the film in the dry state, respectively.

To better understand the swelling properties of the crosslinked films, parameters like the number average molecular mass between crosslinks (Mc), cross-link density (q), and mesh size (ξ) were calculated. The Flory-Rehner equation, provided below, was used to calculate Mc.

$$\frac{1}{\mathrm{Mc}} = -\frac{\frac{\mathrm{v}}{\mathrm{V}}([\ln 1-\varphi]+\varphi+\chi\varphi^{2})}{\varphi^{\frac{1}{3}}-\frac{1}{2}\varphi} \qquad 2.3$$

Here, V represents the molar volume of water ≃molar mass of water (18.1 g/mol). The Flory-Huggins polymer–water interaction parameter, denoted as χ, ≃is 0.498. The specific volume of the polymer (v) is 0.788 $\mathrm{cm^3/g}$. The polymer volume fraction in the swollen state, denoted as φ, was estimated from equilibrium swelling results using the relation given in equation number 2.4 [5].

$$\varphi = \left[1 + \frac{\mathrm{d_p}}{\mathrm{d_s}}\left(\frac{\mathrm{m_a}}{\mathrm{m_b}}\right) - \frac{\mathrm{d_p}}{\mathrm{d_s}}\right]^{-1} \qquad 2.4$$

To determine φ using Equation 2.4, the calculation involved the following parameters: the mass of the film before swelling (m_b), the mass of the film after swelling (m_a), the density of the film (d_p), and the density of the solvent (d_s). The density of the films was calculated using Equation 2.5.

$$\mathrm{d_p} = \frac{\mathrm{W}}{\mathrm{S}\times\mathrm{X}} \qquad 2.5$$

In the given context, X denotes the average thickness of the film, S represents the cross-sectional area and W corresponds to the weight of the film. The density (ρ) of the films was determined using the following equation 2.6.

$$\rho = \frac{1}{\mathrm{v.Mc}} \qquad 2.6$$

The mesh size (ξ) was calculated using the Flory characteristic ratio of the polymer C by the following equation 2.7 [6]:

$$\xi = \varphi^{\frac{-1}{3}}\left[\mathrm{C_n}\left(\frac{\mathrm{M_c}}{\mathrm{M_r}}\right)\right]^{\frac{-1}{2}}.\mathrm{l} \qquad 2.7$$

Here, Cn is the Flory ratio (with a value of 8.3), l represents the bond angle between the C−C bond (measured at 1.54 Å), M_r is the molecular weight of the repeating units of PVA, and M_C represents the number average molecular mass between crosslinks.

2.5.11 Gel content

Gel analysis was conducted to determine the uncross-linked part of the prepared PVA crosslinked films [7]. For this analysis, the dried crosslinked sample was initially weighed and then subjected to Soxhlet extraction using distilled water as the solvent at 100°C for 4 hours. Following the extraction process, the sample was dried in an oven at 80 °C until a constant weight was achieved. The gel fractions were then calculated using the following equation 2.8:

$$\text{Gel content} = \frac{W_i}{W_o} \times 100 \qquad 2.8$$

Here, W_o refers to the original weight of the crosslinked film, whereas W_i refers to the weight of the insoluble portion of the film, respectively.

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Chapter 3

Influence of number of carbon atoms of dicarboxylic (odd-even) as crosslinker on polyvinyl alcohol

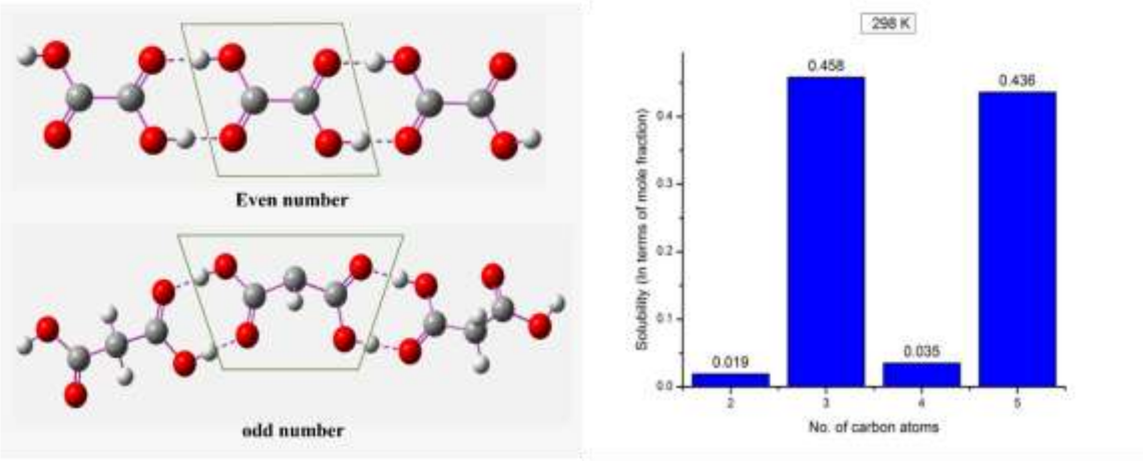
3.1 Introduction

In recent years, carboxylic acids have gained attention as potential crosslinking agents due to their easy accessibility, lack of odor, environmentally friendly nature, cost-effectiveness, non-toxicity, biodegradability, and non-accumulative properties, earning them the designation of green crosslinkers [1, 2]. Over the past decades, numerous studies have highlighted the advantages of crosslinking polyvinyl alcohol (PVA) with carboxylic acids in various applications [3–6]. A recent review comprehensively summarizes the applications and properties associated with carboxylic acid-crosslinked PVA [7].

Some of the studies have compared the effect of different carboxylic acids as a crosslinker with PVA and investigated their effects on the properties of the PVA cross-linked films [8, 9] and showed that the molecular structure of carboxylic acids also affects the extent of crosslinking with PVA and the properties of cross-linked films (details in chapter 1). It is well established in many types of research that a homologous series of dicarboxylic acids exhibits an alteration in the packing of crystal structures, affecting their physicochemical properties. This phenomenon is known as the odd-even effect [10–18]. The difference in the packing of the carboxyl group within the crystal planes of the dicarboxylic acid in their solid state was found to be responsible for this effect (Fig. 3 .1). In odd series of dicarboxylic acids, the carboxyl groups get twisted to avoid repulsion between oxygen atoms of neighboring chains. As a result, the carboxyl groups in the odd series turn out-of-plane relative to the methylene chains, causing molecular distortion, which makes loose interlayer packing. In contrast, in an even series, the carboxyl groups remain within the same plane, therefore less repulsion between oxygen atoms. This leads to no torsions in the carbon chain and results in compact packing [19–22] (Fig.3.1).

The difference in the solubility of dicarboxylic acids was reported in a trend with an odd-even effect by Zhang et al. [14, 15]. They calculated the solubility of these acids by modifying the Apelblat Equation, which correlates the solubility of different solutes with temperature. In their findings, they reported that dicarboxylic acids having an even number of carbon atoms are more soluble than acids having an odd number of carbon atoms. The melting point alternation in dicarboxylic acids was studied by Thalladi et al. [23]. Their work established that dicarboxylic acids having an even number of carbon atoms have a higher melting point than an odd number. In another study, it was reported that hardness exhibits are odd-even–even alternation, with dicarboxylic acids having an even number of carbon atoms found softer and the odd ones harder [12].

The present chapter is dedicated to investigating the effect of an odd and even number of carbon numbers present in a series of dicarboxylic acids as crosslinkers on the properties of PVA films. For this study, polyvinyl alcohol (PVA) was crosslinked with a homologous series of four different dicarboxylic acids, $HOOC(CH_2)_{n-2}COOH$ (n= 2 to 5) viz. oxalic acid (OA; C2), malonic acid (MA; C3), succinic acid (SA; C4) and glutaric acid (GA; C5) containing odd and even number of carbon atoms. The characterization and assessment of synthesized crosslinked films were done using ATR-FTIR, XRD, SEM, AFM, DSC, rheology, percent swelling and sessile drop contact angle. The odd-even effect of dicarboxylic acids was observed to significantly influence the physicochemical properties of PVA when employed as a crosslinker. These results are attributed to the difference in the solubility and crystal structures of the odd-even series of dicarboxylic acids. Results discussed in this chapter have been published in the Journal of Applied Polymer Science. [41]



(a) (b)

Fig. 3.1: *Schematic representation of layer structures of even number dicarboxylic acids; (a) Parallelogram section and odd number dicarboxylic acids; trapezium section (b) Solubility of even-odd dicarboxylic acids in water*

3.2 Experimental

The properties and molecular structures of the carboxylic acids used in this study are presented in Table 3.1. Crosslinked PVA films were prepared by the solution casting method using three different ratios of each dicarboxylic acid, ranging from 30-50% of the PVA weight (details in Chapter 2). The composition and formulation details of these films are provided in Table 3.2.

Table 3.1: Description of molecular structure and properties of the carboxylic acids

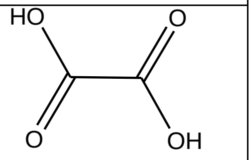
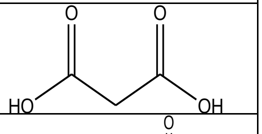
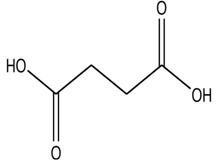
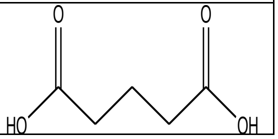
Name of Dicarboxylic acid	Nature of the dicarboxylic acid	Number of Carbon atoms	Molecular weight (g/mol)	Solubility (mole fraction)	Structure
Oxalic acid (OA)	Even	2	126.07	0.0230	
Malonic acid (MA)	odd	3	104.06	0.2176	
Succinic acid (SA)	Even	4	118.09	0.0133	
Glutaric acid (GA)	Odd	5	132.11	0.1506	

Table 3 2: Compositions and formulation of crosslinked PVA films

Designation	PVA (mL)	Oxalic acid (g)	Malonic acid (g)	Succinic acid (g)	Glutaric acid (g)	Curing Temperature (^{0}C)	Curing Time (Min.)
POA	20	0.48 0.64 0.80	-	-	-	100	90
PMA	20	-	0.48 0.64 0.80	-	-	100	90
PSA	20	-	-	0.48 0.64 0.80	-	100	90
PGA	20	-	-	-	0.48 0.64 0.80	100	90

3.3 Results and Discussion

3.3.1 Physical Appearance of Crosslinked Films

The images in Fig.3.2 depict the synthesized cross-linked PVA films, prepared at a 30% w/w concentration of dicarboxylic acid, a curing temperature of 100 °C and a curing time of 90 minutes. Notably, PVA cross-linked with dicarboxylic acids containing an even number of carbon atoms; POA and PSA exhibited an opaque appearance. In contrast, films cross-linked with di-carboxylic acids containing an odd number of carbon atoms, PMA and PGA, appeared transparent. Furthermore, POA and PSA films exhibited a slight brittleness and this brittleness was found to be increased with higher concentrations of the dicarboxylic acids. Conversely, PMA and PGA films displayed flexibility, allowing for easy folding even in their dried state, even at higher acid concentrations.

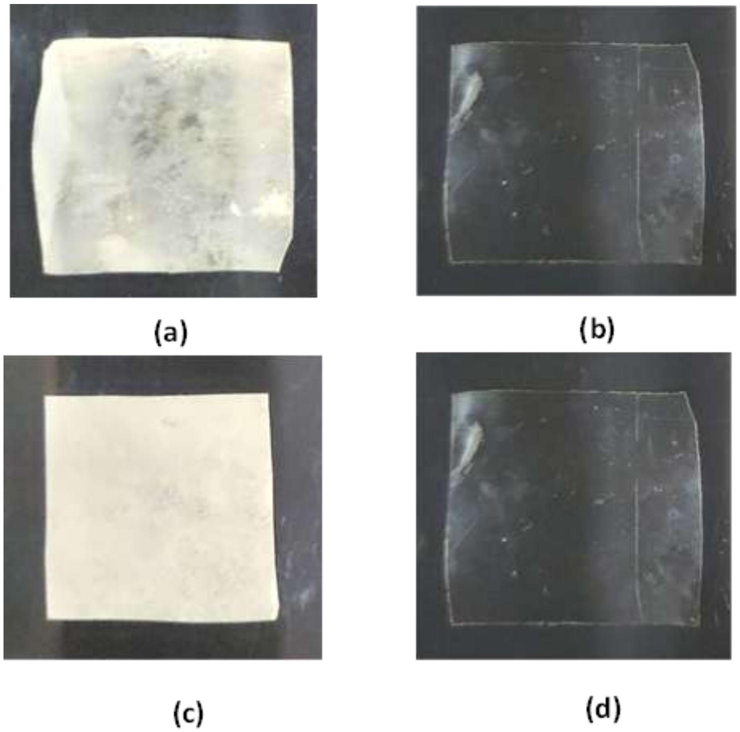


Fig. 3.2: *Photographs of dicarboxylic acids crosslinked films: (a) Oxalic acid crosslinked films; POA (b) Malonic acid crosslinked film; PMA (c) Succinic acid crosslinked film; PSA (d) Glutaric acid crosslinked film; PGA*

3.3.2 Attenuated Total Reflectance (ATR) – FTIR spectroscopy

To confirm the crosslinking, FTIR was conducted for all the films crosslinked with dicarboxylic acids of odd and even numbers of carbon atoms: PVA-oxalic acid (POA), PVA-malonic acid (PMA), PVA-succinic acid (PSA), PVA-glutaric acid (PGA). The ATR-FTIR spectra of neat PVA and crosslinked PVA films are shown in Fig.3.3. In the spectrum of PVA, the O-H group is assigned to the broad band 3257 cm^{-1} whereas the peak at 2929 cm^{-1} is due to symmetric and asymmetric vibrations of the C-H bond. The peak observed at 1417 cm^{-1} corresponds to the C-H bending of the methylene group. Peaks at 1664-1668 cm^{-1} are related to the C-O bending associated with the hydroxyl group of PVA [24]. However, in all ATR-FTIR spectra of crosslinked films; POA, PMA, PSA and PGA, a new peak emerges in the region of 1717-1735 cm^{-1}, corresponding to ester carbonyl stretching [25]. This peak is prominently highlighted in the FTIR graphs (Fig.3.3 (a-d)). The presence of this peak indicates that an esterification reaction has occurred between PVA and the dicarboxylic acids used in the process [26]. This reaction leads to the formation of ester linkages, thereby confirming effective chemical crosslinking.

In the FTIR spectra of PMA and PGA (Fig. 3.3 (b) and Fig. 3.3(d) respectively), it was observed that the intensity of the ester peak increased with higher concentrations of the acids. This trend suggests that the formation of ester bonds, and consequently the extent of crosslinking in the films, also increased as the acid concentration increased. Conversely, the FTIR spectra for POA and PSA films, depicted in Fig. 3.3(a) and 3.3(c), showed different behaviors. For POA films, the intensity of the ester peak unexpectedly decreased when the concentration increased from 30% to 50%. This indicates a reduction in the formation of ester bonds at higher concentrations. The unexpected and peculiar results observed for POA and PSA can be explained by the odd-even effect concerning solubility and differences in crystal packing, as shown in Fig.3.1. The molecular structure of dicarboxylic acids with an even number of carbons is symmetrical, leading to less strain during crystal packing. Consequently, these crystals are more thermally stable and exhibit lower dissolution rates. Dicarboxylic acids with an even number of carbons tend to self-assemble rather than mix well with PVA, especially at higher concentrations. As a result, portions of the OA and SA may remain unreacted and subsequently leach out during washing, which does not contribute to an increase in cross-linking. This particular observation is also supported by SEM and AFM analysis discussed in sections 3.3.4 and 3.3.5.

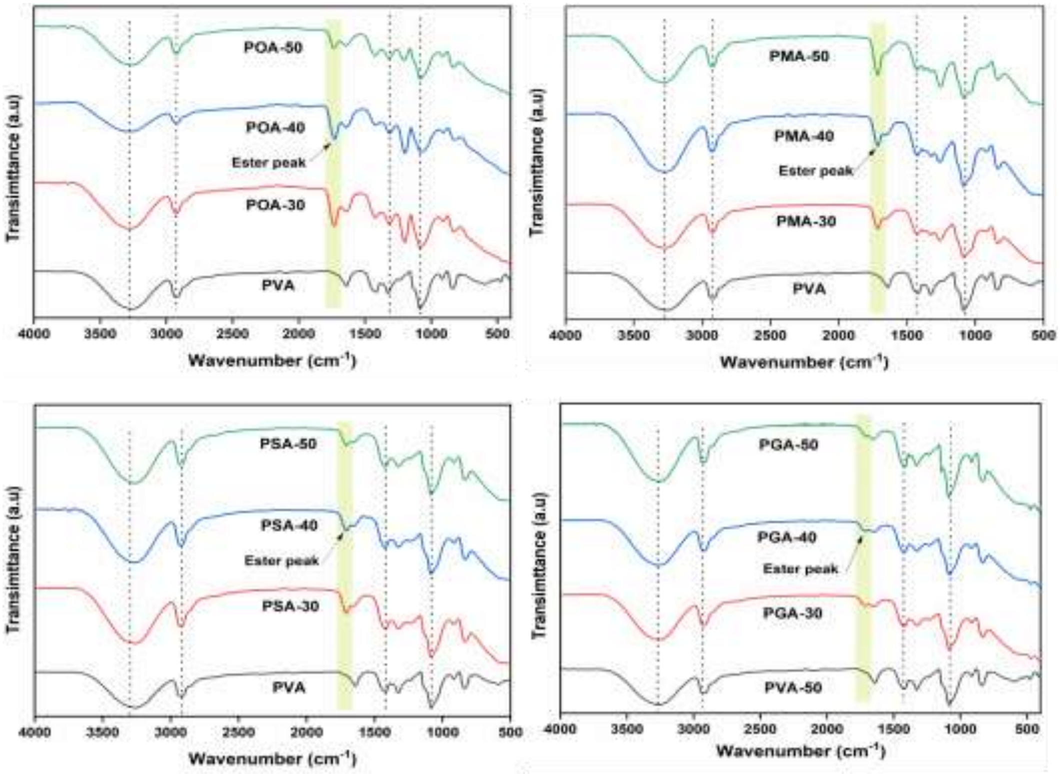


Fig. 3.3: *FTIR analysis of the carboxylic acids crosslinked PVA films; (a) Oxalic acid crosslinked films; POA (b) Malonic acid crosslinked film; PMA (c) Succinic acid crosslinked film; PSA (d) Glutaric acid crosslinked film; PGA*

3.3.3 Gel content analysis

To determine the insoluble portion of the synthesized POA, PMA, PSA, and PGA films, gel content analysis was performed and compared with pure PVA. When the crosslinked films were immersed in heated deionized water at 100°C, the PVA crystallites could be disrupted, strongly H-bonded dicarboxylic acids could be removed, and some of the uncrosslinked PVA chains extracted. Consequently, the gel content measurement reflects only the chemically bonded dicarboxylic acids with PVA. Pure PVA left no insoluble residue after the analysis, whereas the gel content of all crosslinked samples increased significantly, confirming the successful crosslinking of PVA by odd and even dicarboxylic acids.

It is important to note that effective chemical crosslinking in the films occurs only when the two carboxyl groups of a dicarboxylic acid react with two hydroxyl groups from two adjacent PVA chains to form ester bonds. If only one carboxyl group of a dicarboxylic acid reacts with PVA, the resulting ester bond does not contribute to chemical crosslinking. However, the unreacted carboxyl group can form H-bonds with PVA, enhancing the overall crosslinking of the films.

Gel content values listed in Table 3.3 show that all crosslinked films have significant gel content (>70%), which confirms the crosslinking. Variations in percent gel content values for different acids can be explained based on the structural differences between dicarboxylic acids with odd and even numbers of carbon atoms, as illustrated in Fig.3.1. Dicarboxylic acids with an even number of carbon atoms exhibit greater symmetry in their geometry, with terminal groups arranged in a zigzag pattern. This structural symmetry may facilitate efficient interaction between the functional groups of PVA and dicarboxylic acids, enhancing their involvement in the crosslinking reaction. Conversely, dicarboxylic acids with an odd number of carbon atoms have less symmetrical molecular structures, with functional groups positioned on the same side. This asymmetry may lead to reduced participation in the crosslinking reaction compared to even-numbered acids. Additionally, when comparing the odd and even series films, the values followed the trend of POA > PSA and PMA > PGA. Therefore, steric hindrance may also be taken into account to explain this observed trend.

Table 3.3: Gel content of the PVA and PVA crosslinked films

Film Sample	Gel content %
PVA	0
POA	88.5±1.5
PMA	80.71±1.2
PSA	71.15±0.8
PGA	72.67±2.5

3.3.4 Scanning Electron Microscopy (SEM)

The morphology of the 30% dicarboxylic acids cross-linked PVA was investigated using SEM images (Fig.3.4). Results demonstrate that the PVA films crosslinked with dicarboxylic acids containing an odd number of carbon atoms; PMA and PGA appear homogeneous, dense and smooth, suggesting effective dispersion of the crosslinker within the PVA matrix. Whereas films containing an even number of carbon atoms, POA and PSA, exhibit an irregular, noncontinuous matrix and a relatively irregular surface with the presence of voids. The reason for the different morphologies of crosslinked films can be explained using the differences in solubility between dicarboxylic acids containing odd and even numbers of carbon atoms, higher solubility of an odd number of carbon atoms in dicarboxylic acid; MA and GA may lead to relatively a better dissolution of MA and GA with the PVA resulting in no agglomeration or voids, showing a homogeneous surface [13, 14, 27–29]. Whereas for OA and SA, it may be assumed that due to their lower solubility, some of the acids may remain unreacted and may form an agglomerate and these agglomerates may wash off during washing and leave voids as visible in Fig. 3.4 (b) and 3.4 (d). For a more in-depth examination, SEM images of unwashed films for all four crosslinked films were also captured. Fig.3.4 (a) and 3.4 (c) illustrate the presence of unreacted acid residues in the POA and PSA films, contributing to roughness and inhomogeneity. Subsequent washing of these films results in voids. whereas in the case of PMA and PGA films, no such crystals were found and a smooth surface of the films was seen. Therefore, the solubility of the dicarboxylic acids in water and the type of morphology are correlated. Similar results were reported by Pot M et.al [18]. The above outcomes may be used to explain the physical appearance of the crosslinked films. The porous structures with rough surfaces obstruct the clear passage of light, resulting in reduced transparency. Therefore, this insight helps to understand the transparent nature of the PMA and PGA and the translucent nature of POA and PSA (Fig. 3.1). Additionally, the above discussion provides a further basis for understanding the ATR-FTIR results obtained for POA and PSA (Fig No. 3.4(a) and 3.4(c)). However, the presence of voids, as seen in the case of POA and PSA films, may affect water absorption capacity and result in higher swelling compared to PMA and PGA films. The details are discussed in Section 3.11

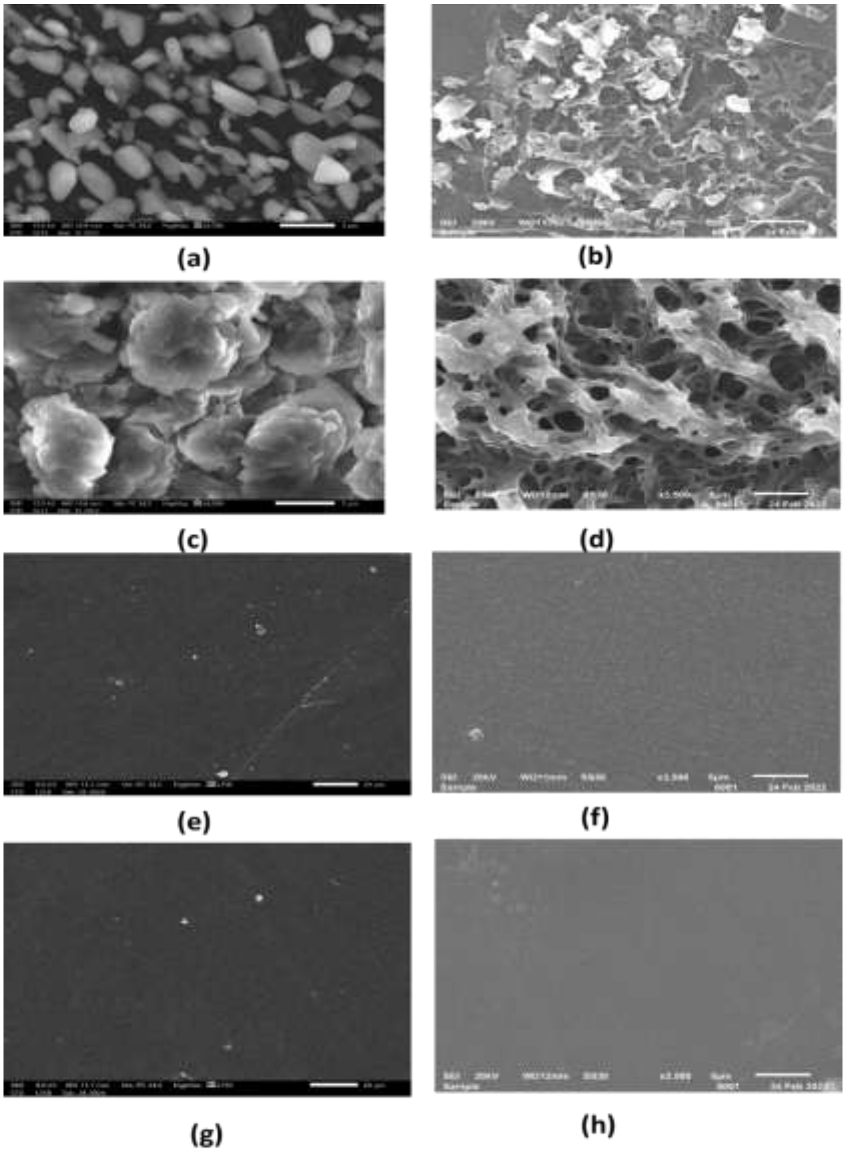


Fig. 3.4: *Surface SEM images of PVA crosslinked films before and after washing* ***(a-b)*** *POA; Oxalic acid crosslinked film* ***(c-d)*** *PSA; Succinic acid crosslinked film after washing* ***(e-f)*** *PMA; Malonic acid crosslinked film* ***(g-h)*** *PGA; Glutaric acid crosslinked film*

3.3.5 Atomic Force Microscopy (AFM)

AFM images were recorded to get the 3-D images and to estimate the roughness of both pure PVA and crosslinked films of PVA-oxalic acid (POA), PVA-malonic acid (PMA), PVA-succinic acid (PSA), PVA-glutaric acid (PGA), containing 30% concentration (Fig.

3.5(a-d)). The image of the pure PVA shows a comparatively smooth surface with low height and a low R_a (Average Surface Roughness) value. Whereas, for all crosslinked films, the roughness and height increased, and there are changes in the surface morphology confirming the chemical reaction, i.e., crosslinking has occurred [30, 31]. For all the films, a direct relationship was found between height and roughness. The order of increasing height and roughness can be arranged as PSA (750nm, 384.6nm) > POA (530nm, 236.6nm) > PGA (460nm, 199.9 nm) > PMA (300nm, 126.8nm)> PVA (210nm, 30.7nm). By comparing the order of R_a values for crosslinked films, the highest roughness was found for the PSA film, whereas the lowest was assigned to PMA. The AFM analysis revealed a consistent odd-even trend in both height and roughness, as depicted in Fig.3.6. Notably, PSA and POA films exhibited more pronounced height and Ra compared to PMA and PGA also their surfaces displayed more humps and grooves, indicating the formation of an irregular and rough structure, consistent with the observations obtained from the SEM analysis (Fig 3.4(b) and 3.4 (d)).

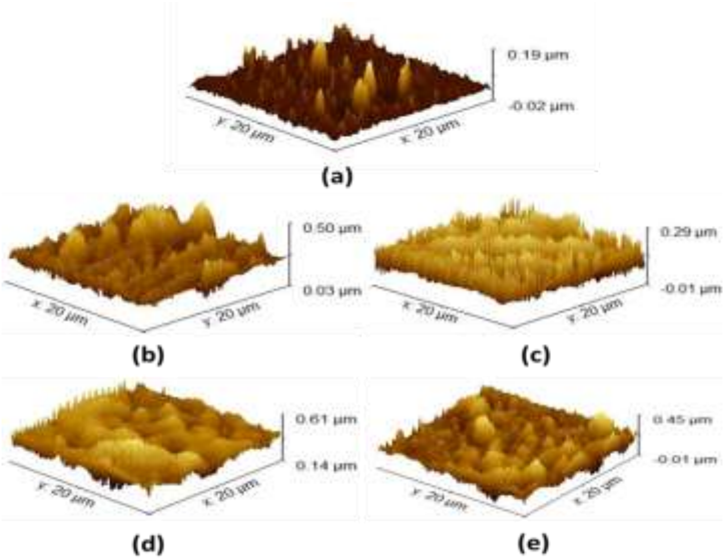


Fig. 3.5: *AFM images of PVA and PVA crosslinked films: (a) PVA, (b) Oxalic acid crosslinked film POA, (c) Malonic acid crosslinked film; PMA, (d) Succinic acid crosslinked film PSA, (e) Glutaric acid crosslinked film; PGA.*

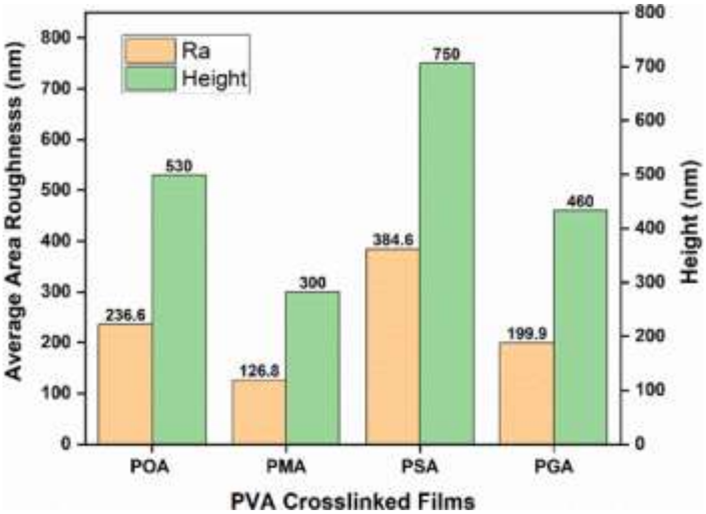


Fig. 3.6: *Variation of Ra and Roughness with PVA; crosslinked with Oxalic acid (POA), Malonic acid (PMA), Succinic acid (PSA) and Glutaric acid (PGA)*

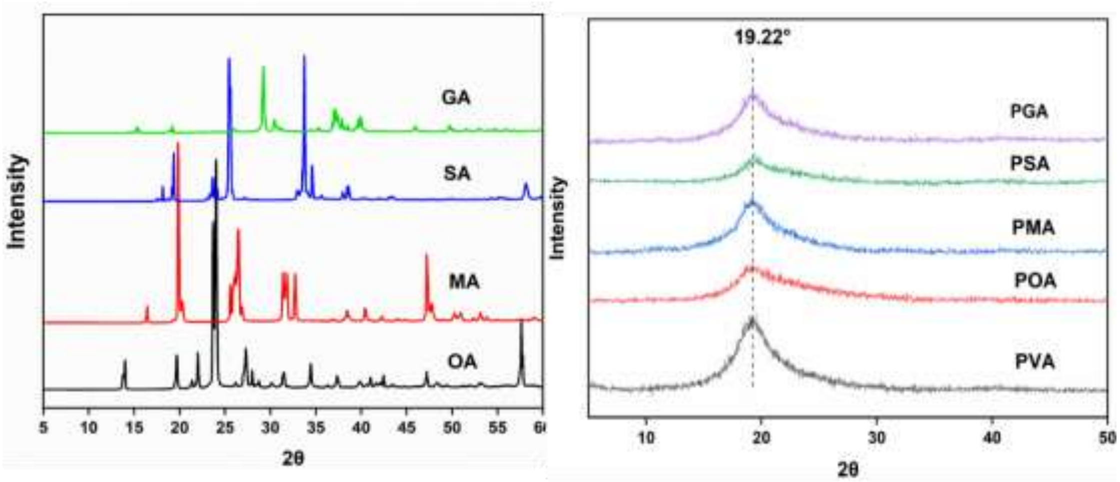
3.3.6 X-ray Diffraction Analysis (XRD)

XRD analysis of oxalic acid, malonic acid, succinic acid and glutaric acid, along with PVA and its cross-linked films, namely, POA, PMA, PSA, and PGA, was performed to investigate the effect of dicarboxylic acids containing odd and even numbers of carbon atoms as cross-linkers. The major peaks position (2θ) values of cross-linked PVA; POA, PMA, PSA and PGA are compared with pure oxalic, malonic, succinic and glutaric acids along with PVA to find out the structural changes in PVA (Fig.3.7). PVA is recognized as a semicrystalline polymer, featuring both a crystalline phase and an amorphous matrix. The predominant peak observed at 2θ = 19.22° in the XRD graph of PVA is attributed to its ordered arrangement and crystalline phase. The characteristic peak intensity of PVA at 2θ = 19.22° was found to decrease in all the cross-linked samples after cross-linking. This reduction in peak intensity suggested that the PVA matrix in all crosslinked films exhibited a lower crystallinity and strongly suggested the increment in the amorphous nature of the PVA matrix [32]. Upon comparing the XRD patterns of cross-linked PVA with those of pure PVA and dicarboxylic acids, it's notable that the peaks corresponding to the pure acids are absent in the cross-linked samples. The disappearance of peaks associated with the pure acids implies their involvement in the crosslinking reaction with PVA, leading to the creation of new molecular arrangements or structures, consistent with FTIR results.

However, comparing intensities of XRD diffractograms of POA and PSA and PMA and PGA, slightly higher intensity peaks were observed in the case of PMA and PGA (PVA crosslinked with dicarboxylic acids with an odd number of carbon atoms) as compared to POA and PSA (PVA crosslinked with dicarboxylic acids with an even number of carbon atoms). The observed phenomenon resonates with the results obtained from gel content analysis and can likely be attributed to the structural differences between dicarboxylic acids with odd and even numbers of carbon atoms, as shown in Fig.3.1. Consequently, films containing odd-numbered acids like PMA and PGA show less pronounced reductions in PVA peak intensity. The values of relative percent crystallinity and crystallite size are given in table 3.4 Also, the crystallite size was calculated using the Scherrer equation.

Table 3.4: XRD profile of the crosslinked PVA films

Samples	**PVA**	**POA**	**PMA**	**PSA**	**PGA**
Crystallite size (nm)	2.36	2.10	2.14	1.36	2.29
Crystallinity (%)	54.03	48.90	49.99	49.08	50.36



(a) (b)

Fig. 3.7: *XRD diffractograms of (a) Pure Oxalic, Malonic, Succinic and Glutaric acids (b) PVA and cross-linked PVA with Oxalic acid (POA), Malonic acid (PMA), Succinic acid (PSA) and Glutaric acids (PGA).*

3.3.7 DSC analysis

DSC analysis was done for PVA and dicarboxylic acids cross-linked PVA films; POA, PMA, PSA, and PGA, Fig. 3.8. The sharp endothermic peak in pure PVA appears at 229.59 ^{0}C, which is attributed to the melting of its crystalline phase (T_m), with the peak area representing (ΔHm) in the melting region indicating the crystallinity of the films. All the crosslinked PVA films showed lower melting temperatures and lower melting enthalpy values than pure PVA. The values are as follows; PVA (229 °C, 140.86 J/g), POA (199.16 °C, 92.71 J/g), PMA (206.91°C,110.36 J/g), PSA (219.88 °C, 126.811 J/g) and PGA (223.43°C, 130.45 J/g). Crosslinking induces disruption in the crystalline region, leading to an increase in the amorphous region and, consequently, a decrease in T_m and melting enthalpy [33, 34]. XRD results (Table 3.4) confirm that all crosslinked films have lower percent crystallinity and smaller crystals than pure PVA film, which may be responsible for the reduction in melting points and lower melting enthalpy. The maximum reduction in T_m and minimum melting enthalpy was found for the POA film, which can be directly correlated with its lowest percent crystallinity and smaller crystal size. On the other hand, the least decrease in the T_m in the case of PGA can be ascribed to higher percent crystallinity and larger sized crystals (Table 3.4) observed from the XRD studies.

Moreover, a linear increase in melting point, observed in all crosslinked films may be attributed to the increased molecular weight and structural complexity of longer dicarboxylic acids that can impart greater resistance to thermal degradation, resulting in a higher melting point. Therefore, when compared separately as odd and even, the PSA and PGA films showed higher melting temperatures than POA and PMA may be due to the presence of a longer chain of methylene (CH_2) group in SA and GA which may further lead to the formation of long-chain cross-linked structure and could increase the melting point.

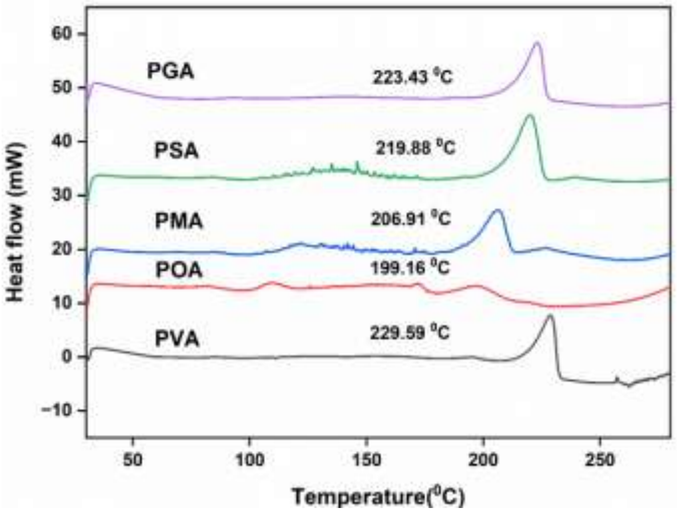


Fig. 3.8: *Differential Scanning Calorimetry (DSC) of PVA and cross-linked PVA with various di-carboxylic acids; oxalic (POA), malonic (PMA), succinic (PSA) and glutaric acids (PGA).*

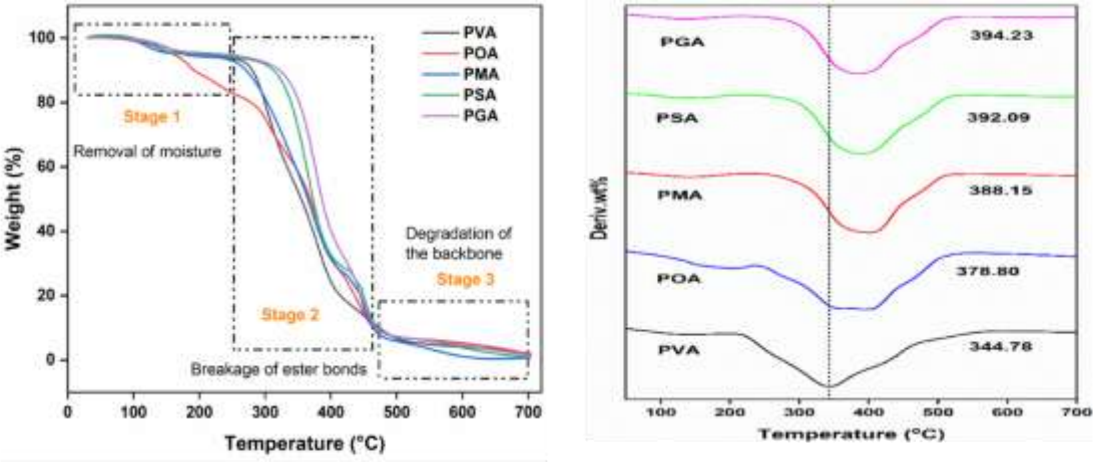
3.3.8 Thermal gravimetric analysis (TGA)

The TGA and DTG thermogram of the pure PVA and crosslinked films are shown in Fig. 3.9(a).

All TGA graphs show three-stage degradation. For PVA, initial mass loss is observed due to the moisture evaporation (30°C-200 °C, 8% loss). The main degradation starts from the second stage (263 °C-498 °C, 85.5 % loss) due to the removal of hydroxyl groups in the form of water and the formation of polyene macromolecules [35]. The third stage (502°C-689°C, 5%) is because of the overall decomposition of the backbone of PVA. For crosslinked films, the first stage that corresponds to a minimal mass loss is due to the removal of moisture, and the second stage at elevated temperatures (269°C-481°C) which may be due to the breakage of ester linkage or decarboxylation of free carboxylic acids present in the film. The third stage should result from the degradation of the backbone of crosslinked films [36].

At 350 °C, the neat PVA film retained 52.40% of its original weight, whereas the crosslinked films showed residues of 58.65%, 60.48%, 78.39%, and 80.20% for POA, PMA, PSA, and PGA films, respectively. This trend correlates with the increasing molecular weight of the added crosslinker.

In the DTG analysis (Fig. 3.9b), it was observed that all four crosslinked films exhibited higher maximum decomposition temperatures compared to the neat PVA film. The decomposition temperature for the PVA film was recorded at 344.78 °C, while the crosslinked films displayed the following trend: 378.80 °C (POA) < 388.15 °C (PMA) < 392.09 °C (PSA) < 394.23 °C (PGA). These results indicate a clear trend based on increasing molecular weight, consistent with the findings from the DSC analysis.



(a)

(b)

***Fig. 3.9**: (a) TGA and (b) DTGA of PVA and cross-linked PVA with various di-carboxylic acids; oxalic (POA), malonic (PMA), succinic (PSA) and glutaric acids (PGA).*

3.3.9 Water contact angle (WCA)

The surface hydrophilicity of pure PVA and crosslinked films was studied by the WCA measurement (Fig 3.10). All crosslinked films were found to have higher water contact angles than PVA film, indicating that the lower hydrophilicity of crosslinked films is probably due to a reduction in the number of free -OH groups after crosslinking [36, 37]. The contact angle was observed to follow the trend of PVA (42.31) > PSA (69.45) > POA (75.04) > PGA (77.19) > PMA (81.06). The obtained order showed an odd-even trend which can again be attributed to the odd-even behavior of dicarboxylic acids. The probable cause of this odd-even trend is discussed in subsequent swelling studies.

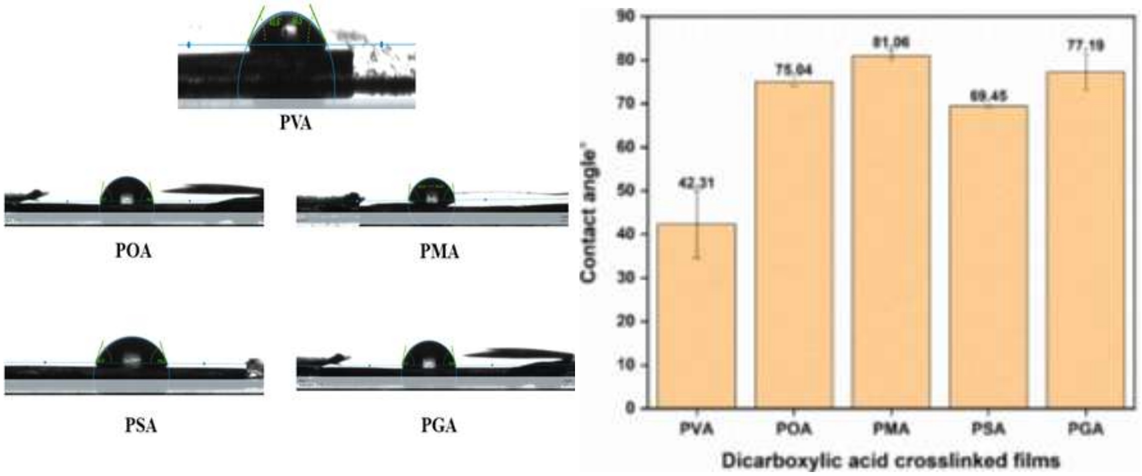


Fig. 3.10: *Variation of contact angle of PVA and PVA crosslinked films with Oxalic acid (POA), Malonic acid (PMA), Succinic acid (PSA) and Glutaric acids (PGA).*

3.3.10 Swelling studies (water uptake analysis)

The swelling behaviour of PVA is primarily influenced by the presence of hydrophilic -OH groups, attracting numerous water molecules and the inter-chain spaces among PVA chains connected by hydrogen bonding. Crosslinking serves a dual purpose; it utilizes -OH groups of PVA in esterification reactions, reducing their availability and simultaneously restricts the movement of PVA chains, limiting water access to the inter-chain spaces. The post-crosslinking space available for water is notably influenced by the structure of the dicarboxylic acids used. Therefore, the overall impact of crosslinking on water uptake is a balance between diminishing -OH groups and constraining PVA chain mobility. Swelling analyses were conducted for all three concentrations of POA, PMA, PSA, and PGA films with a graphical representation in Fig. 3.11. Remarkably, all crosslinked films exhibited water insolubility (discussed in section 4.1) and demonstrated lower hydrophilicity compared to pure PVA, confirming the occurrence of crosslinking (Fig 3.11). It was seen that PVA films crosslinked with dicarboxylic acid of an odd number of carbon atoms; PMA and PGA show the usual trend of decreasing swelling with increasing crosslinker concentration whereas unusual trends of swelling were observed with the films having dicarboxylic acid with an even number of carbon atoms; POA and PSA. Using the graphs, POA and PSA films can be arranged based on a decreasing trend in swelling in the following order 50% >40% > 30%, and 40% □50% > 30% respectively where the percentage represents the amount of dicarboxylic acid used in the crosslinked film. The above peculiar trend of swelling of POA and PSA films was found to match with the results obtained in ATR-FTIR, where POA and PSA films had less intense peaks of ester group as we move from 30 to 50 % concentration of acids but ester peak intensity of PMA and PGA films found increased with increasing concentration of acid. However, the crosslinked films can be arranged in increasing order of swelling as PMA < PGA < POA < PSA. Interestingly, the swelling of the POA and PSA films was higher than that of the PMA and PGA films, exhibiting an odd-even trend in the swelling pattern. The probable reason for the high swelling of the POA and PSA films can be associated with their surface structure, as revealed by SEM and AFM results (Fig.3.4, 3.5, and 3.6). These films contain high roughness, voids, and an irregular matrix, which may facilitate the diffusion of water molecules, leading to the observed higher swelling [30, 31, 38]. Additionally, a small amount of OA and SA could remain in the crosslinked films despite the cross-linking process, which may alter the pH of the water (observed pH after 24 hrs was 2.35 and 4.67 for POA and PSA films, respectively). This acidic environment can lead to the hydrolysis of ester bonds, creating more space for water to penetrate, thus resulting in increased swelling. The hydrolysis of ester bonds in POA is expected to occur more rapidly than in PSA due to the smaller size of the alkyl groups. When compared separately as odd and even, the swelling was increased with an increasing number of carbon atoms in the dicarboxylic acid. This may be due to the smaller size of OA resulting in a more rigid structure of the crosslinked film and anticipated to allow less amount of water in comparison to the larger size of SA as it has two extra carbon atoms and may provide more space in between the PVA chains [39]. The same reason can be given for the higher swelling of PGA films than PMA films.

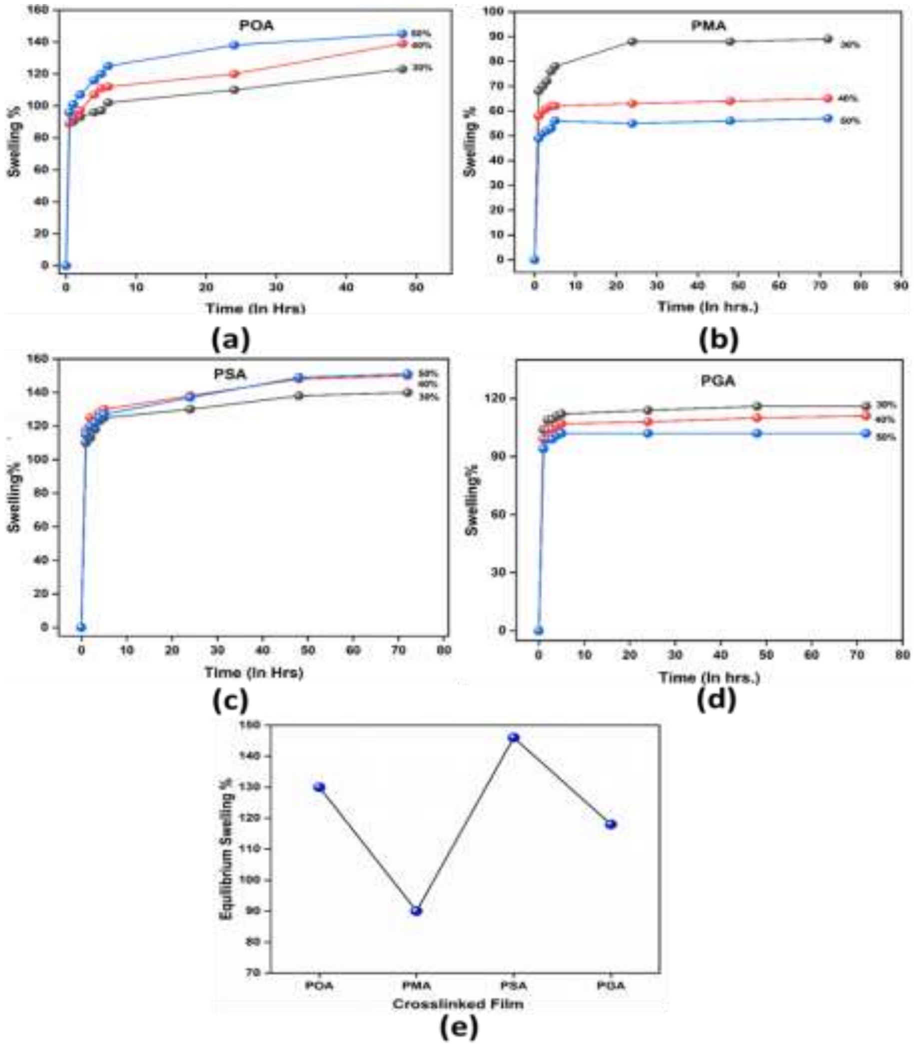


Fig. 3.11: *Swelling analysis of the carboxylic acids crosslinked PVA films; (a) Oxalic acid crosslinked films; POA (b) Malonic acid crosslinked film; PMA (c) Succinic acid crosslinked film; PSA (d) Glutaric acid crosslinked film; PGA (e) Variation of equilibrium swelling in crosslinked films*

3.3.11 Rheological studies

Rheological measurements were carried out to determine the viscoelastic behavior of the PVA and films crosslinked with OA, MA, SA, and GA. Frequency-dependent viscoelastic response of storage modulus (G′) is shown in Fig.3.12. It is well known that the storage modulus of crosslinked polymeric material depends on factors like the extent of crosslinking and crystallinity. When a crosslinker is introduced into a semicrystalline polymer, such as the PVA chain, it induces crosslinking but also affects the existing crystallinity. The obtained findings can be explained by focusing on the above two competitive factors during the crosslinking process. From the graph, it is evident that the inclusion of odd-even crosslinkers has a significant impact on the storage modulus values of all four crosslinked films, which are higher than those of neat PVA.

Interestingly, despite its maximum gel content, the POA film's storage modulus (G') is lower than the rest of the crosslinked films. This discrepancy can be attributed to the lowest crystallinity observed in the POA film, as supported by DSC and XRD findings, which show a greater reduction in crystallinity in the POA film relative to the other films. The significant reduction in crystallinity in the PVA-MAL film effectively offsets the impact of its higher crosslinking, resulting in a lower storage modulus.

The G' of all the films increased with increasing frequency and remained almost constant. However, an odd-even effect of dicarboxylic acids was observed on the G' values at higher frequencies. The G' values for POA and PSA films significantly increased, whereas those for PMA and PGA films sharply decreased. This suggests different elasticity behaviors due to variations in cross-linking as discussed in section 3.3.3.

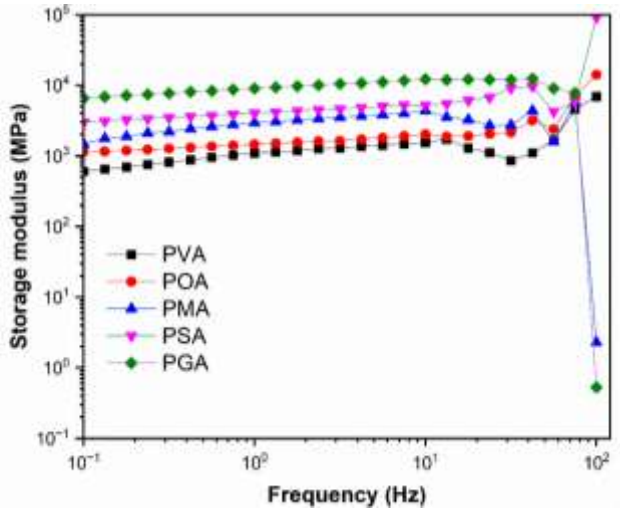


Fig. 3.12: *Storage modulus of PVA and PVA crosslinked films*

3.3.12 Tensile Properties

Fig. 3.13 displays the typical tensile stress-strain curves for neat PVA and crosslinked films, with values reported in the Table 3.5. Nearly all crosslinked films exhibited higher tensile strength than the neat PVA film, except for the POA film. These results can be understood by examining three competitive factors during the crosslinking process: variations in crosslinking degree, changes in intermolecular hydrogen bonding and the structural characteristics of the crosslinkers [33].

The introduction of carboxylic acids creates new ester bonds but also significantly reduces hydrogen bonding and disrupts crystallinity, resulting in lower rigidity and the formation of amorphous regions [40]. This can reduce tensile strength by creating a less crystalline phase with decreased inherent rigidity from hydrogen bonding. Therefore, the final properties reflect a balance among these factors. The higher tensile strength observed in most crosslinked films [24] can be attributed to the dense network structure formed by ester bonds, which strengthen intermolecular forces within the film. In contrast, the lower tensile strength and elongation observed in the POA film may be explained by its crosslinking degree (discussed in the gel content section) and significant crystallinity reduction (discussed in the XRD section).

Interestingly, films crosslinked with an even number of carboxyl groups exhibited lower tensile strength than those with an odd number, similar to the trend seen in POA. This suggests an odd-even effect in tensile strength as well.

Furthermore, crosslinking comes at the expense of hydrogen bonding, reducing rigidity, which can increase elongation in the films. This greater elongation may be linked to the flexible structure introduced by the longer carbon chains present in the crosslinkers.

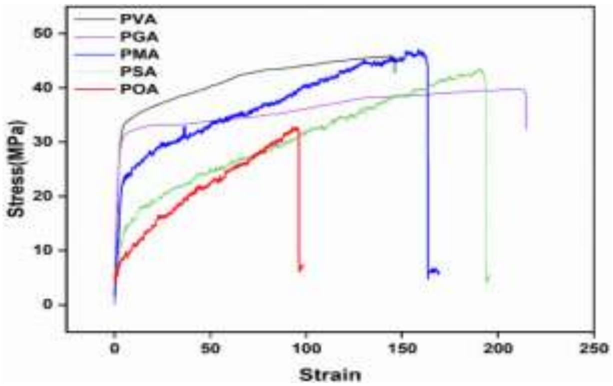


Fig. 3.13: *Typical stress-strain curve of polyvinyl alcohol (PVA) and PVA crosslinked films*

Table 3.5: Effect of crosslinking on mechanical properties of PVA crosslinked films

S.No.	Designation	Tensile strength (MPa)	Elongation (%)
1.	PVA	38.10±4.62	146.72±5.02
2.	POA	32.55±2.47	95.29±6.71
3.	PMA	46.74±3.12	160.24±4.26
4.	PSA	39.41±1.45	212.27±1.35
5.	PGA	43.45±4.21	194.91±2.82

3.4 Conclusion

Four different dicarboxylic acids of a homologous series notably; oxalic acid (C2), malonic acid (C3), succinic acid (C4) and glutaric acid (C5) containing odd and even numbers of carbon atoms were selected as crosslinkers with PVA. The physicochemical characteristics of the above PVA crosslinked films were observed to differ when dicarboxylic acids with an even number of carbon atoms were used compared to those with an odd number of carbon atoms. Films crosslinked with dicarboxylic acids consisting an even number of carbons were found to be translucent, rough and brittle, displaying an unexpected irregular trend in swelling behaviour as crosslinker concentration increased. In contrast, films crosslinked with dicarboxylic acids with an odd number of carbon atoms were transparent, having smoother surfaces and exhibiting a consistent swelling behaviour with increasing crosslinker concentration. Moreover, these films were found to have more crystallinity and showed higher melting temperature (T_m) in comparison to the films containing dicarboxylic acids with an even number of carbon atoms. However, in terms of tensile strength the PVA crosslinked with odd number acids showed higher values as compared to even number acids. These results were correlated with the difference in the solubility and crystal structures of the odd-even series of dicarboxylic acids.

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Chapter 4

Comparative evaluation of polyvinyl alcohol films crosslinked with saturation and unsaturated dicarboxylic acid

4.1 Introduction

Maleic acid (MAL) or cis-butenedionic acid consists of four carbon atoms. However, its molecular structure includes a carbon-carbon double bond (C=C), introducing rigidity in terms of group rotations around the C–C axis. This double bond restricts the rotation of the COOH groups about the C–C bond, restricting certain molecular motions [1]. In comparison, succinic acid (SA) comprises only single bonds and has free rotations around the C–C axis, resulting in a comparatively more flexible structure than maleic acid (MAL). While independent reports exist in the published literature regarding the properties of PVA crosslinked with saturated and unsaturated crosslinkers, there was an absence of a comprehensive comparative study conducted under uniform experimental conditions [2-5].

In the present chapter, crosslinked films of PVA were prepared using two dicarboxylic acids: saturated succinic acid (SA) and unsaturated maleic acid (MAL) as crosslinkers. This experimental work specifically aims to elucidate the impact of single and double bonds present in the crosslinking agents. The study involves a comparative assessment of the chemical structure, hydrophilicity, swelling degree, thermal, tensile, and morphological properties of crosslinked PVA films using various techniques such as ATR-FTIR, XRD, SEM, AFM, DSC, tensile, rheological, swelling measurements and Sessile drop contact angle analysis. The detailed findings of these investigations are presented and correlated with the structure of the dicarboxylic acids. Findings of this chapter has been published in Journal of polymer engineering and science [26].

4.2 Experimental

The properties and molecular structures of the carboxylic acids used in this study are presented in Table 4.1. Crosslinked PVA films were prepared by the solution casting method using a 30% ratio of both the dicarboxylic acids of the PVA weight (details in Chapter 2). The composition and formulation details of these films are provided in Table 4.2.

Table 4.1: Description of molecular structure and properties of the carboxylic acid

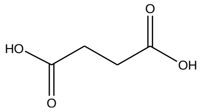
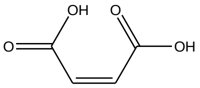
Acid Name	Nature of the acid	Carbon chain length	Molecular weight (g/mol)	Solubility (Mole fraction)	Structure
Succinic acid	Dicarboxylic (Saturated)	4	118.09	0.01337	
Maleic acid	Dicarboxylic (Unsaturated)	4	116.07	0.1109	

Table 4.2: Compositions and formulation of crosslinked PVA films

Designation	PVA (mL)	Succinic Acid (g)	Maleic Acid (g)	Curing Temperature (°C)	Curing Time (Min.)
PVA-SA	20	0.48	-	100	90
PVA-MAL	20	-	0.48	100	90

4.3 Results and Discussions

4.3.1 Physical appearance

The visual images of the synthesized crosslinked PVA films, which were cured at a temperature of 100°C for 90 minutes are displayed in Fig.4.1. Notably, PVA cross-linked with succinic acids containing a single; PVA-SA exhibited an opaque appearance. In contrast, films cross-linked with maleic acids containing double bonds; PVA-MAL appeared transparent. Furthermore, PVA-SA films exhibited a slight brittleness whereas PVA-MAL film displayed flexibility, allowing for easy folding even in their dried state.

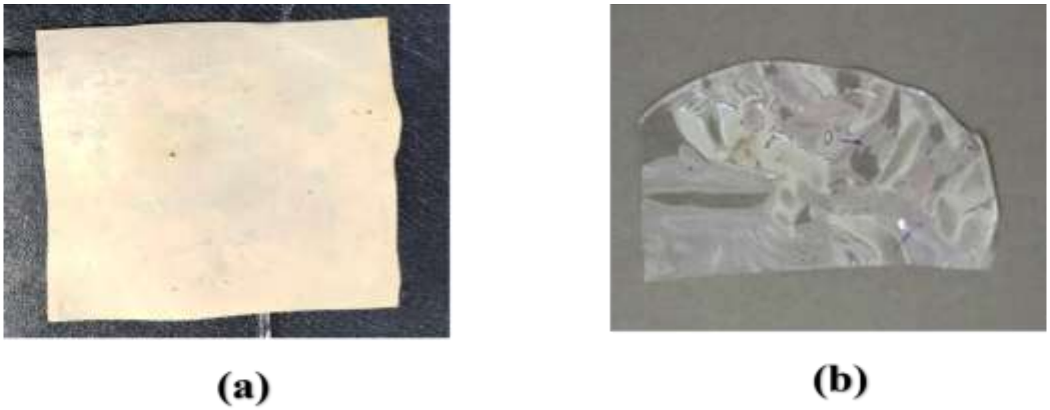

(a) (b)

Fig. 4.1: *Photographs of dicarboxylic acids crosslinked films: (a) Succinic acid crosslinked films; PVA-SA (b) Maleic acid crosslinked film; PVA-MAL*

4.3.2 Attenuated Total Reflectance (ATR) – FTIR spectroscopy

The ATR-FTIR spectra and data of neat PVA, SA, MAL, and Crosslinked PVA films are shown in Fig.4.2. From the graph, it is evident that when SA and MAL were used as crosslinkers with PVA, new peaks emerged in the FTIR spectrum at 1725 cm^{-1} for PVA-SA and 1720 cm^{-1} for PVA-MAL films. These peaks indicate that an esterification reaction has occurred between PVA and both acids. The peaks correspond to the C=O stretching frequency, confirming ester formation as a result of crosslinking. The lower wavenumber for the ester peak in PVA-MAL suggests the formation of unsaturated esters due to intermolecular or intramolecular cross-linking of the chains [6].

As the crosslinking process does not alter the existing methylene groups (1420 cm^{-1}) in the crosslinked films, the intensity of the methylene group peak remains constant. Therefore, the extent of crosslinking can be quantitatively determined using the band index method, which involves calculating the area ratio of the C=O (ester bond) peak to the CH_2 (methylene group) peak [7]. The results revealed that the ratio for the PVA-MAL film (0.63) film is higher than the PVA-SA (0.38). This observation suggests an increment in the carboxyl group content and further indicates more crosslinking in the PVA-MAL film. This could be due to the higher solubility of maleic acid than succinic acid and may be due to the cis orientation of carboxyl groups.[8]

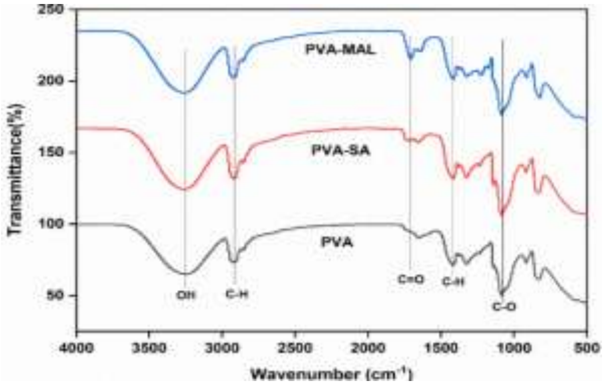


Fig. 4.2: *FTIR analysis of PVA, Succinic acid crosslinked film; PVA-SA and Maleic acid crosslinked film; PVA-MAL*

4.3.3 Gel content

Gel content analysis was performed to determine the insoluble or uncrosslinked portion of the synthesized crosslinked films i.e. PVA-SA and PVA-MAL and compared with pure PVA film. Pure PVA left no insoluble residue, while the gel content of both the crosslinked samples increased significantly, confirming effective crosslinking. As shown in Table 4.3, both the crosslinked films exhibited a substantial gel content (>80%), further validating the crosslinking.

Variations in gel content between saturated and unsaturated acids can be linked to differences in their structures, as illustrated in Table 4.1. The enhanced crosslinking ability of maleic acid compared to succinic acid is likely due to its smaller size and lower steric hindrance, allowing it to more easily integrate into the PVA chains and approach the hydroxyl groups of PVA. This enables maleic acid to participate more effectively in crosslinking. Additionally, the presence of a double bond makes it more reactive, which can lead to a higher degree of crosslinking and create a denser, more interconnected polymer network within the crosslinked film. In contrast, succinic acid is relatively larger and more sterically hindered than maleic acid, which may limit the space available for the esterification reaction, resulting in a lower degree of crosslinking. Also, the presence of a single bond may make it less reactive to participate in crosslinking.

Table 4.3: Gel content of the PVA and PVA crosslinked films

Film Sample	Gel content %
PVA	0
PVA-SA	80.1±2.5
PVA-MAL	89.71±1.1

4.3.4 Swelling analysis

The swelling behaviour of PVA is primarily influenced by the presence of available free OH groups that attract water molecules and the ease of diffusion of water molecules in the space present between the chains. Crosslinking of PVA with dicarboxylic acids, known for enhancing water resistance, involves the consumption of OH groups in esterification reactions. Additionally, crosslinking covalently binds PVA chains, reducing the available space for water molecules to come inside**.** Saturated and unsaturated dicarboxylic acids, when employed as crosslinkers, exhibit varying effects on the swelling behaviour of PVA, as depicted in Fig.4.3. The Intermolecular or intramolecular crosslinking generates numerous succinate and maleate ester groups, leading to a reduction in swelling percentage. Notably, the reduction in swelling percentage was found more pronounced in PVA-MAL compared to PVA-SA film. This may be due to the presence of double bonds present in MAL resulting in a more rigid structure of the crosslinked film and anticipated to allow less amount of water in comparison to the relatively flexible structure of SA molecule and may provide more space in between the PVA chains.

To go deeper into the analysis, the equilibrium swelling data was utilized to calculate the essential network parameters, including the average molecular weight between consecutive crosslinks (Mc), crosslinking density (ρ), and mesh size (ξ), as presented in Table 4.4. The crosslinking density is particularly crucial in understanding swelling behaviour, as a lower crosslinking density indicates greater distances between crosslinking points. Additionally, the mesh size provides insights into the available space for water molecules to permeate. As can be seen in Table 4.4, the average molecular weight between crosslinks and mesh size values was found proportional to the swelling capacity of the film. The Mc, ρ, and ξ values obtained for PVA-SA films were found to align with swelling results.

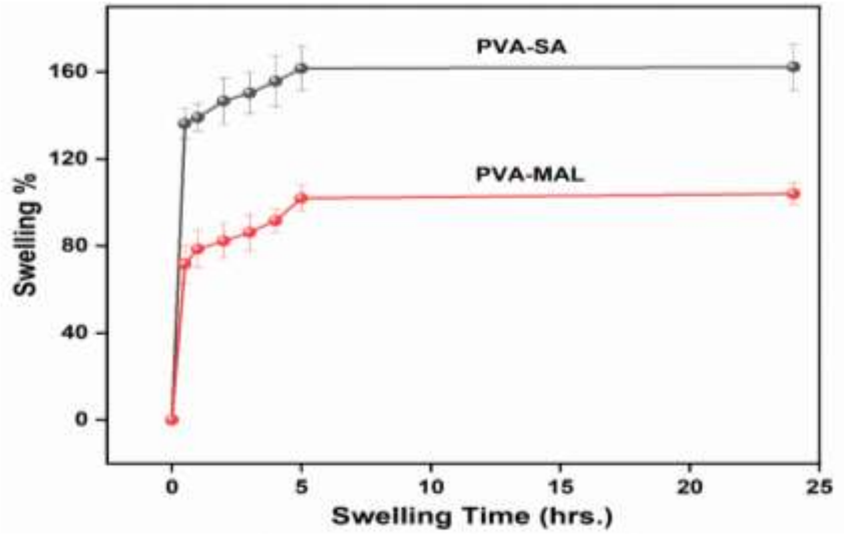


***Fig 4.3**: Swelling analysis of the dicarboxylic acids crosslinked PVA films; PVA-SA and PVA-MAL*

Table 4.4: Network parameters of the crosslinked films

Crosslinked Film	**φ**	**Mc (g/mL)**	**ρ (mol/cm^3)**	**ξ (Å)**
PVA-SA	0.30	980.39	1.29×10^{-3}	95.29
PVA-MAL	0.36	151.97	8.35×10^{-3}	16.39

4.3.5 Water Contact Angle Measurement (WCA)

The Water contact angle (WCA) is an effective method for assessing the hydrophilicity/hydrophobicity of a surface. Fig.4.4 illustrates a reduction in the WCA of crosslinked films compared to neat PVA. The corresponding images reveal water droplets spreading differently on the film surfaces. PVA enhances water adhesion due to its polar OH groups, resulting in a lower contact angle. Crosslinking with SA and MAL acids removes numerous polar OH groups from the PVA chain, leading to higher contact angles. [9]. The maximum contact angles for PVA, PVA-SA, and PVA-MAL were observed to be 30.40, 76.0, and 80.60, respectively. Through crosslinking, PVA films transition from a highly hydrophilic state to a moderately hydrophobic state.[10]. These results demonstrated that PVA-MAL has the maximum contact angle, showing more effective crosslinking than PVA-SA. The above results are in agreement with FTIR and Swelling results.

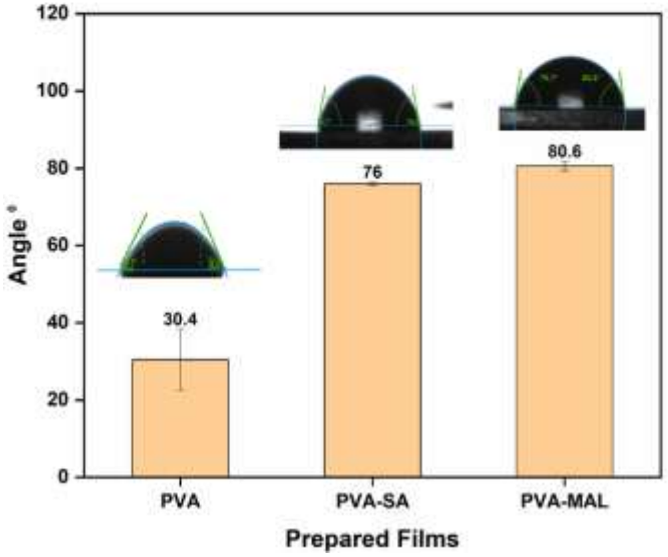


Fig. 4.4: *Variation of contact angle of PVA and PVA crosslinked films with Succinic acid (PVA-SA), Malonic acid (PVA-MAL)*

4.3.6 X-ray diffraction (XRD) Analysis

The XRD graphs of crosslinked films, namely PVA-SA and PVA-MAL were examined and compared with the XRD graph of pure PVA film Fig.4.5. PVA is recognized as a semicrystalline polymer, featuring both a crystalline phase and an amorphous matrix. The predominant peak observed at 19.28 in the XRD graph of PVA is attributed to its ordered arrangement and crystalline phase. Upon cross-linking, the characteristic peak intensity of PVA at 19.28° was noted to decrease in both PVA-SA and PVA-MAL films.

This reduction in peak intensity signifies a decrease in the crystallinity of PVA after crosslinking [11]. The decrease in crystallinity is attributed to the incorporation of large dicarboxylic acid moieties into the structure through interactions with free hydroxyl groups in PVA, resulting in the formation of ester bonds. These changes not only indicate modifications in the crystalline phase of PVA but also suggest increasing molecular disarrangement in the PVA matrix. The relative percent crystallinity of the crosslinked films was determined with respect to the 19.28 peak of PVA [12].

It was observed that the crystallinity of PVA-MAL (47 %) film is lower compared to both PVA-SA (49%) and pure PVA (56%) films. These results regarding crystallinity are in agreement with the outcomes obtained from ATR-FTIR analysis, providing further support to the findings of the study.

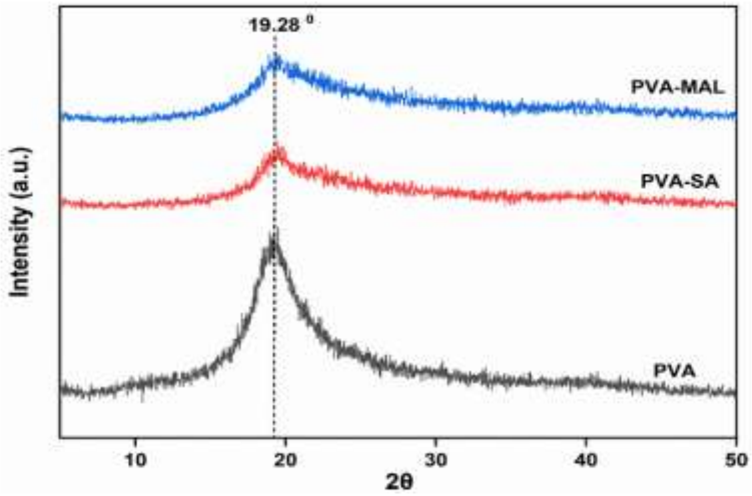


Fig 4.5: *XRD diffractograms of PVA and PVA crosslinked films with Succinic acid (PVA-SA), Maleic acid (PVA-MAL)*

4.3.7 Field Emission Scanning Electron Microscopy (FESEM)

The surface morphology films crosslinked with succinic acid and maleic acid were investigated using FESEM images. Fig. 4.6 illustrates the morphological distinctions between PVA-SA and PVA-MAL films. Notably, the PVA-MAL film displayed a dense structure and a higher level of uniformity and appeared homogenous and smooth which is somewhat similar to the dense layer morphology, suggesting effective dispersion of the crosslinker within the PVA matrix. In contrast, the surface of the PVA-SA film appeared rough and exhibited some pores. Similar results were reported by Gautam et al. [13]. This observation signifies that, when subjected to identical processing conditions, the film morphology is significantly influenced by the structure of the crosslinker. The compact structure observed in the PVA-MAL film may be attributed to the effective interlocking of polymer chains, facilitated by the presence of a double bond in MAL.

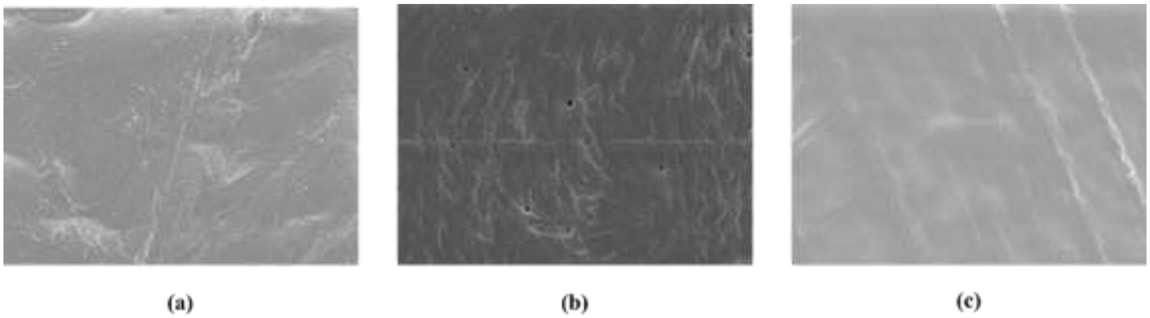
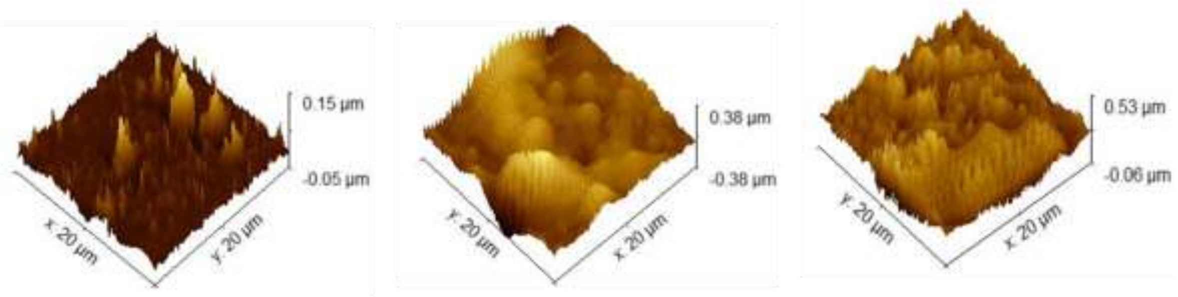


Fig. 4.6: *Surface FESEM images PVA crosslinked films: (a) PVA; (b) Succinic acid; PVA-SA (c) Maleic acid; PVA-MAL*

4.3.8 Atomic Force Microscopy (AFM)

The 3-D AFM images of PVA and its crosslinked films i.e. PVA-SA and PVA-MAL were analyzed to characterize their surface properties, including roughness and height (Fig.4.7). The obtained data reveals that the roughness parameters of crosslinked PVA films are greater than the neat PVA. film. In the case of PVA, the AFM image reveals a smooth surface with low height (200 nm) and moderate average roughness. Upon crosslinking with SA and MAL, notable changes occurred. The height increases to 760 nm and 590 nm for PVA-SA and PVA-MAL films, respectively. Additionally, there is an increase in roughness values, confirming the occurrence of a chemical reaction during the crosslinking process [14] [15]. For PVA, PVA-SA and PVA-MAL, the increased R_a (Average Surface Roughness) value follows the order of PVA (53nm) < PVA-MAL (196 nm) < PVA-SA (245 nm). Notably, PVA-SA exhibits significantly higher roughness parameters compared to PVA-MAL also the surface displays distinct humps and grooves, suggesting the formation of voids. The above result matches the findings of SEM analysis.

Also, the obtained roughness values can be further used to validate the swelling analysis. It was noted that the crosslinked films treated with MAL exhibited relatively less roughness and consequently showed less swelling. This consistency in results could be related to the fewer surface irregularities that restrict water absorption, facilitating a more controlled swelling process [14] [16].



(a) **(b)** **(c)**

Fig. 4.7: *AFM images of PVA and PVA crosslinked films: (a) PVA (b) Succinic acid crosslinked film; PVA -SA (c) Maleic acid crosslinked film; PVA-MAL*

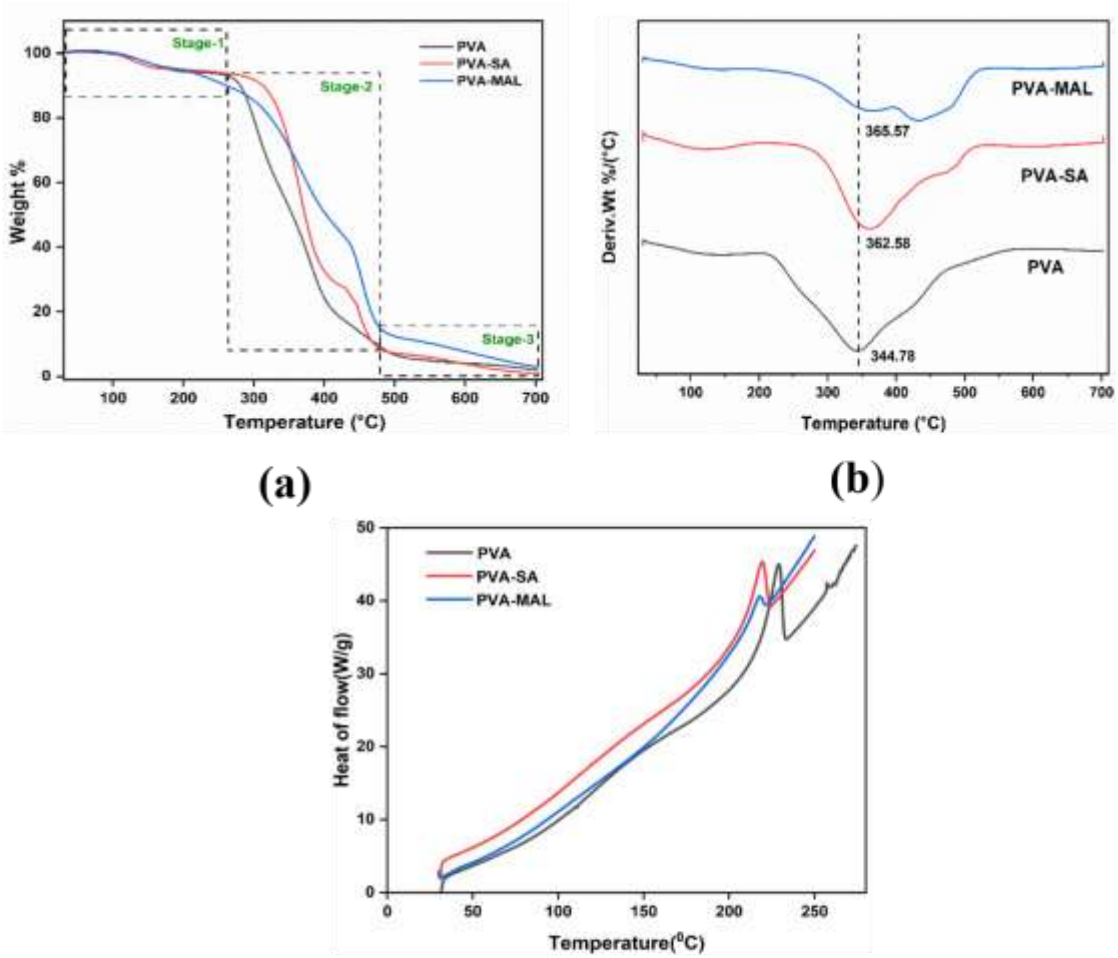
4.3.9 Thermal gravimetric analysis (TGA)

The TGA and DTG thermogram of the pure PVA and crosslinked films are shown in Fig. 4.8(a).All TGA graphs show three-stage degradation. For PVA, initial mass loss is observed due to the moisture evaporation (30-200 °C, 8% loss). The main degradation starts from the second stage (263-498 °C, 85.5 % loss) due to the removal of hydroxyl groups in the form of water and the formation of polyene macromolecules [17]. The third stage (502°C-689°C, 5%) is because of the overall decomposition of the backbone of PVA [10]. For crosslinked films, the first stage that corresponds to a minimal mass loss is due to the removal of moisture and the second stage at elevated temperatures (269°C-481°C) which may be due to the breakage of ester linkage or decarboxylation of free carboxylic acids present in the film. The third stage should be the result of the degradation of the backbone of crosslinked films [10]. Additionally, there is a difference in decomposition rates of PVA-SA and PVA-MAL films which can be attributed to the different crosslinking degrees. At 350 °C, PVA-MAL film retains 72 % of its original weight whereas PVA-SA and PVA have 71% and 52%. The PVA-MAL film also showed a slightly higher residue left at 700°C than the other two films. In the DTG analysis, Fig 4.8(b), it was observed that the PVA-MAL film exhibited a higher maximum decomposition temperature compared to PVA-SA and PVA. The decomposition temperature for PVA film was recorded at 344.78 °C, whereas for PVA-SA and PVA-MAL, the decomposition temperatures were noted at 362.58 °C and 365.57 °C, respectively. These findings indicate that the PVA-MAL films demonstrate enhanced thermal stability compared to the PVA-SA film.

4.3.10 Differential scanning calorimetry (DSC)

The DSC curves of the pure PVA and crosslinked films are shown in Fig.4.8 (c). In the DSC curves, the endothermic peak around 145°C is associated with the evaporation of bound water (T_e), representing the energy needed to vaporize water bound within the films. Another endothermic peak at approximately 229 °C corresponds to the crystalline melting (T_m) of the PVA film, with the peak area (ΔH_m) in the melting region indicating the crystallinity of the films. The addition of SA and MAL results in a reduction of the T_e value, indicative of a chemical cross-linking effect [18][19]. This implies that PVA films crosslinked with SA and MAL exhibit reduced hydrophilicity compared to pure PVA. Crosslinking induces disruption in the crystalline region, leading to an increase in the amorphous region and, consequently, a decrease in T_m [20]. Pure PVA, being semicrystalline with a more ordered structure, exhibits a higher melting temperature and a sharp endothermic curve. In contrast, PVA-MAL and PVA-SA show lower melting temperatures and broadened peaks, confirming effective crosslinking. The melting temperature (T_m) and ΔHm values of the crosslinked PVA films are lower than those of pure PVA, following the order: PVA (229 °C, 141.68 J/g) > PVA-SA (211 °C, 129.77

J/g) > PVA-MAL (209 °C, 21.811 J/g). This indicates that the addition of a crosslinker has diminished the overall crystallinity of the films [19], matching with the previously discussed XRD results. Consequently, the discussion leads to the conclusion that the PVA-MAL film exhibits the highest thermal stability among the three, consistent with the trends observed in swelling and FTIR results.



(a) **(b)**

(c)

Fig. 4.8: *(a) TGA (b) DTG (c) DSC graphs of PVA and PVA crosslinked films*

4.3.11 Tensile study

The typical tensile stress-strain curves of the PVA, PVA-SA and PVA-MAL films are shown in Fig.4.9. Neat PVA film exhibited higher tensile strength than PVA-SA and PVA-MAL films. The tensile strength values follow the order PVA -MAL (30.41±9.02 MPa) < PVA-SA (35.85±3.33 MPa) < PVA (42.77±3.145 MPa). The higher tensile strength observed in PVA can be attributed to its crystalline phase and inherent rigidity resulting from strong hydrogen bonding. The decline in tensile strength in crosslinked films may be linked to a reduction in crystallinity and rigidity caused by the introduction of SA and MAL as crosslinkers [21]. The inclusion of crosslinkers, significantly weakens hydrogen bonding and interrupts crystallinity, resulting in lower rigidity and the formation of amorphous regions which further leads to the reduction in the tensile strength [22]. The higher recorded crosslinking density in PVA-MAL films may be used to explain their lower tensile strength compared to PVA-SA films. Similar results have been reported in some of the studies [23]. Notably, despite the reduction in tensile strength, the crosslinked films exhibit greater elongation when compared to the neat PVA, with % values of 145.06±2.93, 210.07±4.53 and 151.41±1.09 for PVA, PVA-SA and PVA-MAL respectively. The increased elongation may be associated with the flexible structure of four carbons present in both crosslinkers. However, MAL, with its double bond, promotes more interlocking of chains, resulting in lower elongation for PVA-MAL compared to PVA-SA. It can be concluded that both the crosslinking density and flexibility of the crosslinker affect the mechanical properties of the crosslinked films.

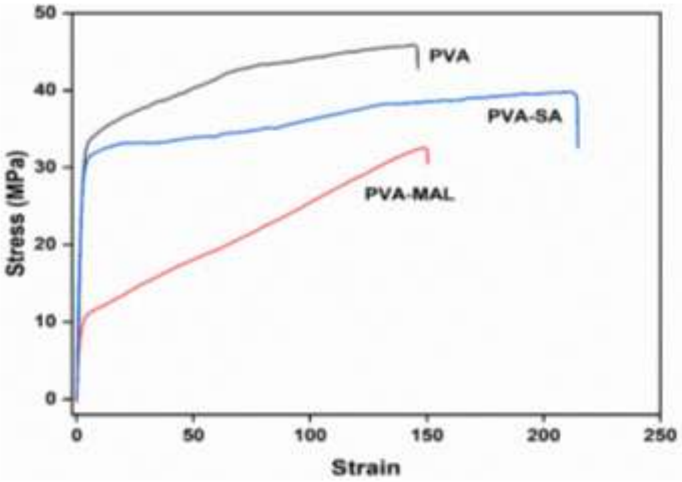


Fig. 4.9: *Typical stress-strain curve of PVA and PVA crosslinked films: Succinic acid crosslinked film; PVA-SA and Maleic acid crosslinked film; PVA-MAL*

4.3.12 Rheological studies

Rheological measurements were carried out to determine the viscoelastic behavior of the PVA, PVA-SA and PVA-MAL films. Frequency-dependent viscoelastic response of storage modulus (G′) is shown in Fig.4.10. It is well known that the storage modulus of crosslinked polymeric material depends on factors like the extent of crosslinking and crystallinity[24, 25]. When a crosslinker is introduced into a semicrystalline polymer, such as the PVA chain, it induces crosslinking and affects the existing crystallinity. The obtained findings can be explained by focusing on the above two competitive factors during the crosslinking process. From the graph, it is evident that the inclusion of a crosslinker has a significant impact on the storage modulus values of PVA-SA and PVA-MAL films, which are both higher than those of neat PVA. This confirms that effective crosslinking has occurred in both types of films.

Interestingly, the storage modulus (G') of the PVA-SA film is higher than that of the PVA-MAL film, despite the PVA-SA film having a lower crosslinking density. This discrepancy can be attributed to the higher crystallinity observed in the PVA-SA film compared to the PVA-MAL film. The DSC and XRD findings support this observation by showing a greater reduction in crystallinity in the PVA-MAL film relative to the PVA-SA film. The more significant reduction in crystallinity in the PVA-MAL film effectively offsets the impact of its higher crosslinking density, resulting in a lower storage modulus when compared to the PVA-SA film.

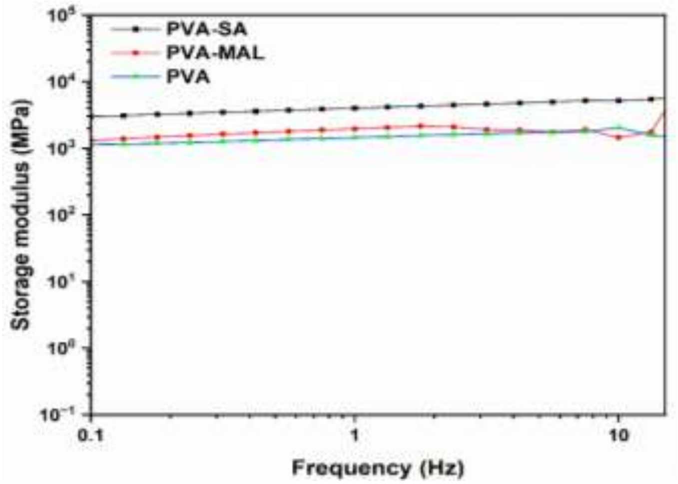


Fig. 4.10: *Storage modulus of PVA and PVA crosslinked films: Succinic acid crosslinked film; PVA-SA and Maleic acid crosslinked film; PVA-MAL*

4.4 Conclusion

The study aimed to compare the effect of saturation (single bond) of succinic acid (SA) and unsaturation (double bond) of maleic acid (MAL) as crosslinkers on the properties of PVA films. The crosslinked films were synthesized without the use of any catalyst, highlighting a catalyst-free approach. The calculated crosslinking density of the PVA-MAL film was noticed to be 6.47 times higher than that of the PVA-SA film. Consequently, PVA-MAL films exhibited minimal swelling. Morphological analysis further revealed that PVA-MAL films displayed smoother surfaces than PVA-SA films which gives an idea of better dispersion of MAL over SA as crosslinker. In thermal analysis, the PVA-MAL film demonstrated superior properties compared to the PVA-SA film. The maximum decomposition temperature recorded for maleic acid-crosslinked

PVA samples was 365.57°C, higher than succinic acid-crosslinked PVA samples (362.58°C) and neat PVA (344.78°C).

XRD results indicated that crosslinking led to a decrease in the overall crystallinity of PVA films, resulting in lower percentages of crystallinity for both crosslinked films. whereas from DSC results, it was seen that PVA-MAL film has less crystallinity % than PVA-SA film. Additionally, a more significant reduction in hydrophilicity was observed in the PVA-MAL film compared to both PVA-SA and neat PVA films. Also, crosslinked films displayed enhanced elasticity and resilience in comparison to neat PVA, with the order of elasticity being PVA-SA (210.07±4.53)> PVA-MAL (151.41±1.09) > PVA (145.06±2.93), which may be due to the difference in crosslinking density, disruption in intermolecular hydrogen bonding due to crosslinking and incorporation of flexible crosslinkers.

In summary, the collective findings emphasize that crosslinkers with double bonds can create dense networks, resulting in less swelling. Additionally, double bonds improve the thermal behaviour and surface properties of PVA more effectively than single bond containing crosslinkers. These considerations are crucial for tailoring PVA films to achieve specific properties for diverse applications of PVA films but also contribute significantly to the comprehension of green crosslinking processes.

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Chapter 5

Effect of carboxylic acids (di, tri and tetra groups) as crosslinkers on polyvinyl alcohol

5.1 Introduction

Poly (carboxylic acids) are well-recognized as a promising alternative to toxic cross-linkers for safe and effective crosslinking [1–3]. While independent reports exist on the properties of PVA films crosslinked with di, tri, and tetra acid crosslinkers [4][5][6], there is a lack of comparative studies conducted under identical experimental conditions to precisely determine the effect of the number of carboxyl groups of polycarboxylic acids on PVA film properties. This experimental work is, therefore, specifically aimed at investigating the impact of varying numbers of carboxylic acid groups on the physicochemical properties of PVA.

In this chapter, three polycarboxylic acids with varying numbers of carboxyl groups were employed to crosslink PVA; Malonic acid as a diacid (MA), Citric acid as a triacid (CA), and 1,2,3,4-butane tetracarboxylic acid as a tetraacid (BTCA). This experimental work is specifically aimed at investigating the impact of varying numbers of carboxylic acid groups on the physicochemical properties of PVA. The crosslinking abilities of these acids were compared using physical, chemical, mechanical, morphological, thermal, and swelling measurements to assess their impact on the physicochemical properties of the resulting films. Various techniques such as ATR-FTIR, XRD, SEM, AFM, TGA, DSC, tensile testing, swelling measurements, and sessile drop contact angle analysis are employed for this assessment. The detailed findings from these investigations are presented and correlated with the structural characteristics of the di, tri, and tetracarboxylic acids. Findings of this chapter have been published in the Journal of Colloid Polymer Science [23].

5.2 Experimental

The properties and molecular structures of the carboxylic acids used in this study are presented in Table 5.1. Crosslinked PVA films were prepared by the solution casting method using a 30% ratio of each dicarboxylic acid of the weight of PVA weight (details in Chapter 2). The composition and formulation details of these films are provided in Table 5.2.

Table 5.1: Description of molecular structure and properties of the carboxylic acids

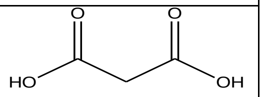
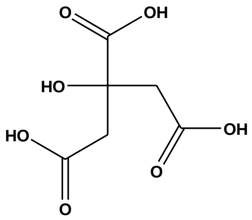
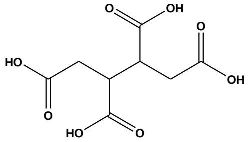
Acid Name	Nature of the acid	Carbon chain length	No. of the carboxyl group	No. of the hydroxyl group	Molecular weight (g/mol)	Structure
Malonic acid	Dicarboxylic acid	3	2	0	104.06	
Citric acid	Tricarboxylic acid	6	3	1	192.13	
1,2,3,4-butanetetra carboxylic Acid	Tetracarboxylic acid	8	4	0	234.16	

Table 5.2: Compositions and formulation of crosslinked PVA films

Designation	PVA (mL)	Malonic acid (g)	Citric acid (g)	1,2,3,4-butanetetracarboxylic acid (g)	Curing Temperature (°C)	Curing Time (Min.)
P-MA	20	0.48	-	-	140	10
P-CA	20	-	0.48	-	140	10
P-BTCA	20	-	-	0.48	140	10

5.3 Results and Discussions

5.3.1 Physical appearance

The visual images of the synthesized crosslinked PVA films, which were cured at a temperature of 140°C for 10 minutes are displayed in Fig.5.1. The crosslinked films were found to have a clear, transparent appearance across all samples, with no visible signs of phase separation. This transparency and uniformity suggest that the di, tri and tetracarboxylic acids used as crosslinkers have mixed thoroughly and homogeneously with the PVA matrix, resulting in a uniform structure throughout each crosslinked film.

Fig. 5.1: *Photographs of carboxylic acids crosslinked films: (a) Malonic acid crosslinked films; P-MA (b) Citric acid crosslinked film; P-CA (c) 1,2,3,4-tetracarboxylic acid crosslinked film; P-BTCA.*

5.3.2 Attenuated Total Reflectance (ATR) – FTIR spectroscopy

Fig.5.2 displays the ATR-FTIR spectra for both neat PVA and crosslinked PVA. In the PVA spectrum, the broadband at 3257 cm^{-1} corresponds to the hydroxyl group's stretching, and the peak at 2929 cm^{-1} is a result of symmetric and asymmetric vibrations of the C-H bond. The 1419 cm^{-1} peak represents the C-H bending of the methylene group, and the 1664-1668 cm^{-1} peaks are linked to the C-O bending associated with the hydroxyl group in PVA. In the crosslinked films, a distinct and sharp peak emerges in the 1712-1720 cm^{-1} range, indicating ester carbonyl stretching [7]. Additionally, peaks in the 1230-1260 cm^{-1} region confirm asymmetric stretching of C-O-C in ester bonds, verifying an esterification reaction between PVA and acids. This reaction results in chemical crosslinking via ester linkage and induces C=O stretching. During the crosslinking process, the existing methylene groups (1419 cm^{-1}) in the films remain unchanged, maintaining the intensity of the methylene group peak. The quantification of crosslinking can be achieved using the band index method, calculating the area ratio of the C=O (ester bond) peak to the CH_2 (methylene group) peak [8]. Results indicated a slightly higher ratio for the P-BTCA film (0.57) compared to P-CA (0.54) and P-MA (0.52) among the three films, suggesting a greater contribution of tetracarboxylic acids to in-situ crosslinking in PVA. The enhanced cross-linking ability of BTCA over CA and MA can be linked to its extra carboxylic groups, which can cross-link with multiple OH groups of PVA. Therefore, a direct association was identified between the extent of crosslinking and the number of carboxylic groups.

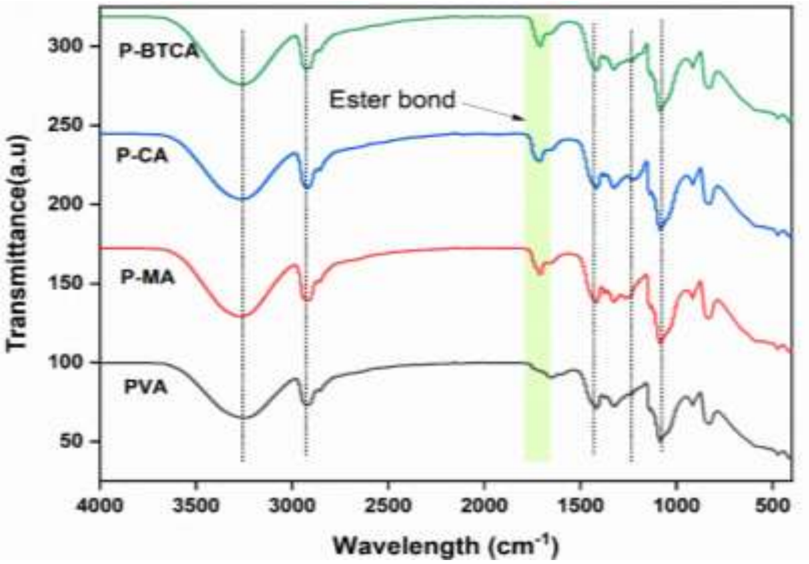


Fig. 5.2: *FTIR spectra of the PVA and PVA crosslinked films with di, tri and tetra acids*

5.3.3 Gel content

Gel content analysis was performed to determine the uncrosslinked portion of the synthesized crosslinked films i.e. P-MA, P-CA, and P-BTCA and was compared to pure PVA film. Pure PVA left no insoluble residue, while the gel content of all crosslinked samples increased significantly, confirming effective crosslinking. As shown in Table 5.3, all crosslinked films exhibit a substantial gel content (>85%), further validating the crosslinking.

Variations in gel content across different acids can be attributed to the number of carboxyl groups in their structures, as illustrated in Table 5.3. The enhanced crosslinking ability of BTCA compared to CA and MA is likely due to its additional carboxylic groups, which can form crosslinks with multiple OH groups on PVA. This suggests a direct relationship between the degree of crosslinking and the number of carboxylic groups. These results provide additional confirmation of the FTIR findings and also align with the observed trend in it.

Table 5.3: Gel content of the PVA and PVA crosslinked films.

Film Sample	Gel content %
PVA	0
P-MA	86.56 ± 0.95
P-CA	94.15 ± 2.10
P-BTCA	97.67 ± 0.60

5.3.4 Swelling analysis

The swelling behavior or hydrophilicity of PVA is primarily influenced by the abundance of free OH groups which attract water molecules and the ease with which water molecules can diffuse between the chains. The crosslinking of PVA with carboxylic acids is widely recognized for enhancing water resistance. As OH groups are consumed during crosslinking, PVA chains become covalently linked, reducing the available space for water molecules to penetrate[9]. However, the reduction in the degree of swelling varies with the type of crosslinker used. The impact of di, tri, and tetracarboxylic acids as crosslinkers on the swelling behavior of PVA is illustrated in Fig.5.3. All three crosslinked films maintained their dimensional stability and did not disintegrate in water throughout the study, confirming the effectiveness of crosslinking and the formation of numerous ester groups. The swelling behavior of the crosslinked films followed the order of P-CA > P-MA > P-BTCA with swelling percentages of 192%, 132%, and 106%, respectively.

The variation in swelling can be explained based on the structural aspects of MA, CA, and BTCA, as detailed in Table 5.1. PVA-CA exhibited the maximum swelling, despite having more crosslinking than P-MA, possibly due to the presence of one OH group in its structure, facilitating greater water attraction. Similar results were reported by Ahmet Cay et al. [10].

Furthermore, various parameters like MC, ξ, and ρ are used to further explain the swelling behavior of the films. These parameters can easily be determined from the Flory–Rehner swelling equilibrium theory [11]. On the application of this theory, it has been observed that the M_C and ξ values are found to be higher in cross-linked PVA films having low ρ as shown in Table 5.4. The crosslinking density is particularly crucial in understanding the swelling behavior, as a lower crosslinking density indicates greater distances between crosslinking points [11].

Additionally, the mesh size provides insights into the available space for water molecules to permeate. As can be seen in Table 5.4, the average molecular weight between crosslinks and mesh size values was found proportional to the swelling capacity of the film. The Mc, ρ and ξ values obtained for crosslinked films were found aligned with swelling results.

Table 5.4 : Network parameters of crosslinked PVA films

Crosslinked Film	**% Swelling**	**Φ**	**Mc (g/mL)**	**ρ (mol/cm^3)**	**ξ (Å)**
P-MA	132	0.37	509.42	2.49×10^{-3}	21.02
P-CA	192	0.34	683.06	1.85×10^{-3}	25.04
P-BTCA	106	0.42	339.44	3.47×10^{-3}	16.45

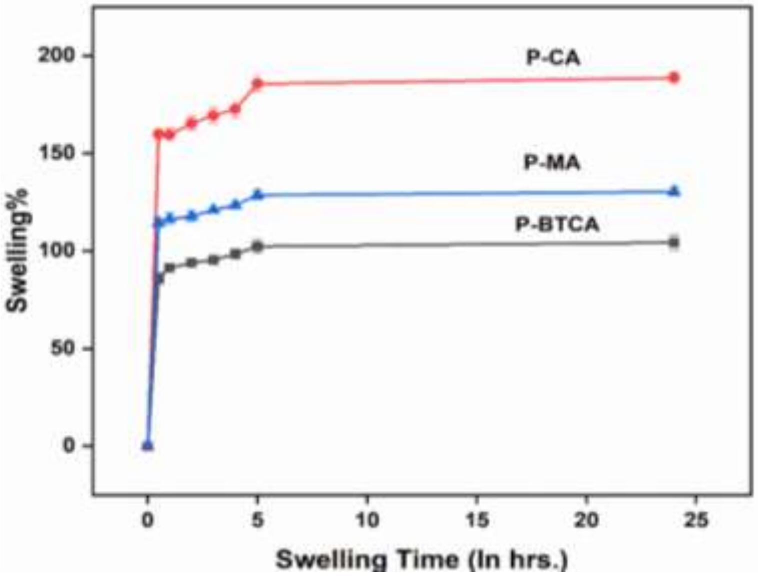


Fig. 5.3: *Swelling analysis of the crosslinked PVA films with di, tri and tetraacids*

5.3.5 Water Contact angle measurement (WCA)

Water contact angle (WCA) serves as a crucial means to estimate the hydrophilicity or hydrophobicity of a surface. As depicted in Fig.5.4, there is a significant reduction in the WCA of crosslinked films when compared to pure PVA film. This reduction is an indication of alterations in surface properties which is further elucidated by the corresponding images showing distinct behaviors of water droplets on the film surfaces. The presence of polar hydroxyl (OH) groups in PVA enhances its affinity for water, thereby leading to a lower contact angle. However, through the process of crosslinking with carboxylic acids, many of these polar OH groups are removed from the PVA chain, increasing the contact angle [12].

As shown in Fig.5.4, the contact angles of PVA, P-MA, P-CA, and P-BTCA films were 43.6, 82.3, 81.6, and 104.9, respectively, emphasizing a significant transition in surface properties upon crosslinking. This transition signifies a shift from a highly hydrophilic state to a moderately hydrophobic state [22]. Notably, P-BTCA exhibits the highest contact angle among the films, indicating more effective crosslinking compared to the others. These findings are consistent with ATR-FTIR spectroscopy and swelling studies.

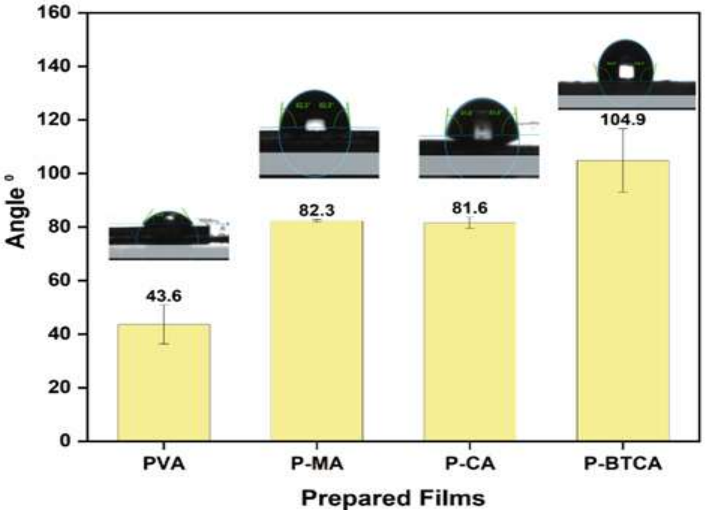


Fig. 5.4: *Variation of contact angle of PVA and crosslinked films with di, tri & tetraacid.*

5.3.6 X-ray diffraction (XRD) Analysis

The XRD graphs of crosslinked films, namely P-MA, P-CA, and P-BTCA, were analyzed and compared with the XRD graph of pure PVA film shown in Fig.5.5. PVA is acknowledged as a semicrystalline polymer, characterized by both a crystalline phase and an amorphous matrix. The primary peak observed at around 2θ of 19.17 ° in the XRD graph of PVA is attributed to its orderly arrangement and crystalline phase, resulting from hydrogen bonding among the OH groups [13]. Post crosslinking, the intensity of PVA's characteristic peak at 19.17° was noted to diminish and broaden in all crosslinked films. This reduction in peak intensity indicates a decrease in PVA's crystallinity after crosslinking due to the consumption of OH groups in PVA [14]. The decline in crystallinity is associated with the integration of large carboxylic acid moieties into the structure through interactions with free hydroxyl groups in PVA, leading to the formation of ester bonds. These alterations not only suggest changes in PVA's crystalline phase but also imply increasing molecular disorganization within the PVA matrix. The relative percent crystallinity of the crosslinked films was determined relative to the 19.17° peak of PVA The calculated relative percent crystallinity exhibited a trend of increasing crystallinity in the order of PVA (57.04%) >P-MA (53.60%) >P-

CA (51.20%)>P-BTCA (50.03%), likely influenced by variations in the number of carboxylic acids. Importantly, these results on crystallinity are consistent with those obtained from ATR-FTIR analysis, reinforcing the conclusions of the study.

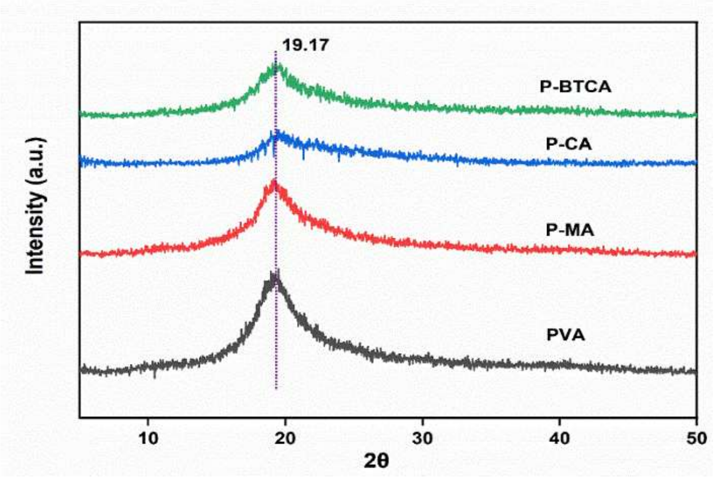


Fig. 5.5: *XRD diffractograms of PVA and crosslinked films with di, tri and tetra acid.*

5.3.7 Surface analysis using SEM and AFM

The surface morphology of PVA and PVA films prepared with MA, CA, and BTCA as crosslinkers were investigated using SEM images. Fig.5.6 illustrates that the surface of the PVA film appears homogeneous and smooth, whereas the crosslinked films exhibit a relatively rough surface, possibly due to the incorporation of carboxylic acids. However, SEM images of all the films displayed no breaks and pores, suggesting effective dispersion of the crosslinker within the PVA matrix. These results align perfectly with the findings from the gel content analysis, further validating the variation in crosslinking efficiency resulting from differences in the structure of the crosslinkers.

Fig.5.7 illustrates AFM topography images, revealing distinct surface morphologies for each film. The pure PVA film exhibited a mean roughness of 9.30 nm and a root mean square (RMS) of 16.31 nm. In contrast, films crosslinked with MA, CA, and BTCA displayed mean roughness values of 49.14 nm, 126.30 nm, and 30.53 nm, with RMS values of 63.0 nm, 170.6 nm, and 45.88 nm, respectively. These observations align well with SEM images, further proving the observed roughness differences. Additionally, these roughness values provide valuable insights into swelling studies. A consistent trend was observed, where a reduction in roughness followed the order of P-BTCA < P-MA < P-CA, correlating with a similar trend observed in the decrease in swelling. This relationship suggests that smoother surfaces exhibit more controlled swelling behavior due to reduced surface irregularities, which limits water absorption [16].

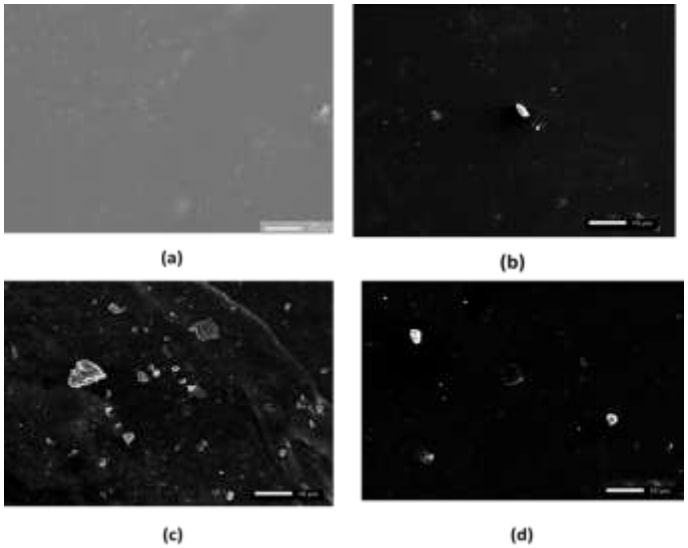


Fig. 5.6: *SEM images of (a) PVA (b) Diacid crosslinked film; P-MA (c) Triacid crosslinked film; P-CA (d) Tetraacid crosslinked film; P-BTCA*

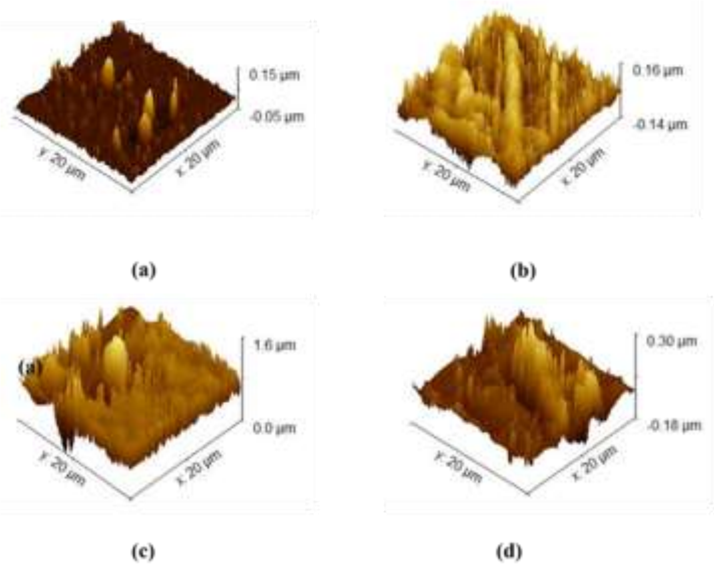


Fig. 5.7: *AFM images of (a) PVA, (b) Diacid crosslinked film; P-MA (c) Triacid crosslinked film; P-CA (d) Tetraacid crosslinked film; P-BTCA*

5.3.8 Thermal gravimetric analysis (TGA)

The TGA and DTG thermograms of the pure PVA and PVA-crosslinked films are shown in Fig. 5.8 (a) and 5.8(c). All TGA graphs show three-stage degradation. For PVA, initial mass loss is observed due to the water evaporation (80-220 °C, 8% loss), both bound water and adsorbed on the surface of the film. The second stage (265-498 °C, 85.5 % loss) shows the main degradation and the largest weight loss due to the removal of hydroxyl groups and the formation of polyene macromolecules [17]. The third stage (500°C-690°C, 5%) is because of the overall decomposition of the backbone of PVA [18]. For PVA crosslinked films, the first stage (85-210 °C) corresponds to a minimal mass loss due to the removal of moisture, and the second stage at elevated temperatures (260°C-475°C) which may be due to the breakage of ester linkage or decarboxylation of free carboxylic acids present in the film. The third stage should result from the degradation of the backbone of crosslinked films [18]. Additionally, there is a difference in decomposition rates of crosslinked films than PVA films which can be attributed to the different crosslinking degrees. At 350 °C, PVA film retains only 52.05 % of its original weight, whereas P-MA, P-CA and P-BTCA retain 57.65%, 71.48% and 76.03%, respectively. Among all three crosslinked films, the P-BTCA film showed a slightly higher residue left at 700°C than the other two crosslinked films.

In the DTG analysis shown in Fig.5.8(c), a noticeable shift in decomposition temperature was observed in all crosslinked films, indicating the formation of an ester network between the PVA chains, thereby imparting thermal stability to the crosslinked networks. Particularly, the P-BTCA films exhibited the highest decomposition temperature, with two decomposition peaks observed. The initial peak, above 350°C, indicates the shift in decomposition temperature of PVA accompanied by its cyclization, while the subsequent peak at 450°C can be attributed to the complete degradation of cyclized PVA [15]. The order. These results indicate that the crosslinked films display improved thermal stability compared to pure PVA

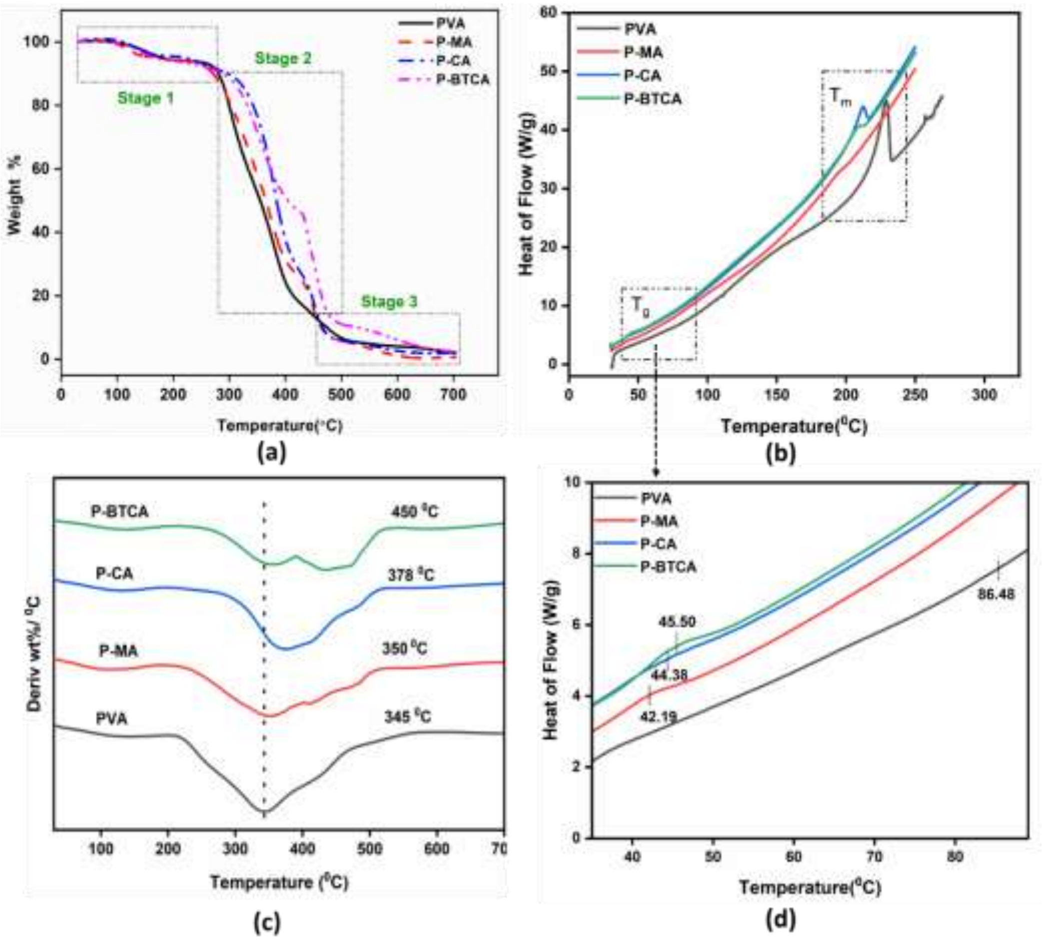


Fig. 5.8 *(a) TGA (c) DTG (b,d) DSC graphs of PVA and PVA crosslinked films with di, tri and tetra acids.*

5.3.9 Differential scanning calorimetry (DSC)

The DSC curves of both pure PVA and PVA films crosslinked with MA, CA, and BTCA are depicted in Fig. 5.8 (b) and 5.8(d). In the DSC curve of pure PVA, the glass transition temperature (T_g) was observed at 86.48°C. The T_g values of all crosslinked PVA films were found to be lower than that of pure PVA film, following the order: pure PVA (86.48°C) > P-BTCA (45.50°C) > P-CA (44.38°C) > PVA-MA (42.19°C). To elucidate the aforementioned findings, several factors must be taken into account that can influence the T_g values of crosslinked polymers, such as the inherent rigidity of existing polymer chains, the density of crosslinking and the chemical structure of the crosslinking agent [19]. The presence of hydroxyl groups in PVA contributes to the polymer's stiffness through hydrogen bonding. Introducing a crosslinking agent reduces the number of hydroxyl groups and weakens hydrogen bonding interactions, resulting in decreased stiffness. Conversely, crosslinking enhances rigidity, and the characteristics of the newly introduced moieties can impact T_g differently, depending on their structure. In the current study, three distinct crosslinking agents were employed, each with varying numbers of crosslinking sites. As a result, the bonds formed between PVA and BTCA may be more rigid due to the higher number of carboxyl groups and maximum crosslinking density. Conversely, MA and CA offer fewer carboxyl groups than BTCA, potentially resulting in a comparatively less rigid structure. In our case, the observed trend of T_g decreasing despite higher crosslinking density may be attributed to the compensatory effect of the weakening of intermolecular hydrogen bonding, chemical network formation hence lower rigidity. Furthermore, the inclusion of acids may also contribute to some plasticizing effects [5]. Similar results were reported by Sheng Xu et al. [20]

Pure PVA, is known for its semi-crystalline nature and demonstrates a higher melting temperature, with a sharp endothermic peak around 228°C corresponding to crystalline melting (T_m). The peak area (ΔH_m) in the melting region serves as an indicator of the film's crystallinity. The introduction of crosslinkers results in lower melting temperatures and broader peaks, indicating effective crosslinking. This crosslinking disrupts the crystalline region, increasing the amorphous region and subsequently reducing T_m. The melting temperature (T_m) and ΔHm values of the PVA and crosslinked PVA films follow the order: PVA (228.59°C, 139.72 J/g) > P-CA (212°C, 29.81 J/g) > P-BTCA (208.73°C, 13.78 J/g) > P-MA (195.84°C, 5.57 J/g). This suggests that the addition of a crosslinker has reduced the overall crystallinity of the films, consistent with the XRD results discussed earlier. However, P-MA exhibits the lowest Tm and ΔHm values among the films, which could be attributed to structural changes in some parts of its polymer structure during crosslinking.

5.3.10 Tensile Study

The typical tensile stress (σ)–strain (ε) curves of PVA, P-MA, P-CA, and P-BTCA films presented in Fig. 5.9 highlight the significant changes in tensile properties resulting from the crosslinking process using di, tri, and tetracarboxylic acids. For neat PVA, the recorded tensile stress (σ) and strain (ε) values are 39.62±3.14 MPa and 148.06±2.79 MPa, respectively. The summarized results in Table 5.5 reveal that all crosslinked films exhibited slightly higher tensile strength than pure PVA and displayed greater elongation.

The above results can be better understood by applying the same arguments as discussed in thermal analysis, focusing on three competitive factors during the crosslinking process: variations in crosslinking density, alterations in intermolecular hydrogen bonding, and the structural characteristics of the crosslinkers. The higher tensile strength observed in crosslinked films can be attributed to the dense network structure formed by chemical ester bonds, which strengthen intermolecular forces within the film [21][22]. Analysis of FTIR results and the Mc value reveals that BTCA creates more crosslinks compared to MA and CA, thereby contributing to the maximum tensile strength of P-BTCA films (127% more than neat PVA).

However, this increase in crosslinking comes at the cost of substituting hydrogen bonding, which decreases rigidity, which in turn can impart more elongation in the films. Additionally, an inverse relationship was found between elongation and the number of carboxylic groups present in crosslinkers. Films containing crosslinkers with fewer carboxyl groups, such as MA and CA, afford greater flexibility to the overall structure of PVA, consequently exhibiting 122% and 102% more elongation compared to P-BTCA. These findings are supported by DSC and TGA analysis, highlighting the significant impact of both the crosslinking process and the structure of the crosslinker on the mechanical properties of the films.

Table 5.5: Effect of crosslinking on mechanical properties of PVA–crosslinked films

S.No.	Designation	Tensile strength (MPa)	Elongation (%)
1.	PVA	39.62±3.14	148.06±2.79
2.	P-MA	44.75±4.74	183.28±7.26
3.	P-CA	43.62±4.09	154.24±5.93
4.	P-BTCA	50.41±1.45	150.72±1.44

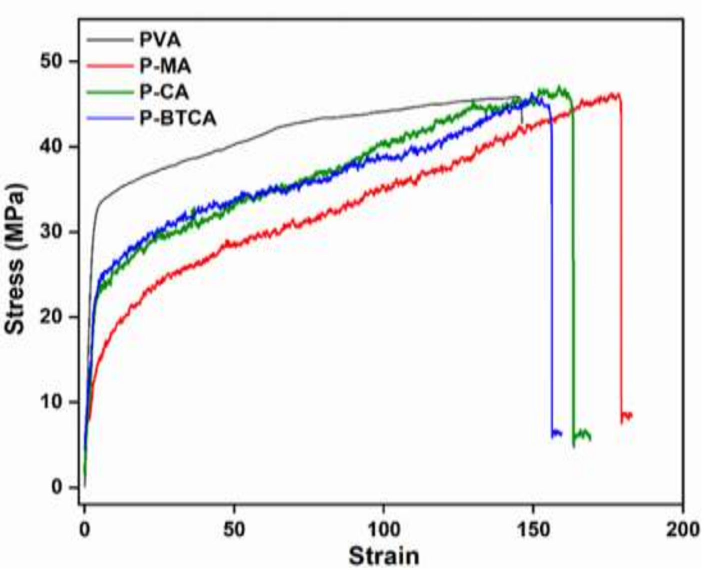


Fig. 5.9: *Typical stress-strain curve of PVA and PVA crosslinked films with di, tri, and tetraacids*

5.3.11 Rheological study

Rheological measurements were conducted to assess the viscoelastic behavior of PVA, P-MA, P-CA, and P-BTCA films. Fig.5.10 shows the frequency-dependent storage modulus (G′), revealing that adding a crosslinker notably increases the storage modulus of all three crosslinked films compared to neat PVA, indicating successful crosslinking.

Interestingly, the storage modulus (G′) of the P-BTCA film was found to be higher than that of the P-MA and P-CA films, suggesting the highest crosslinking density in PVA with tetraacid. This can be explained by the greater number of carboxyl groups present in the tetraacid, as the storage modulus tends to increase with increasing carboxyl groups of crosslinkers. These results are consistent with the FTIR and XRD findings.

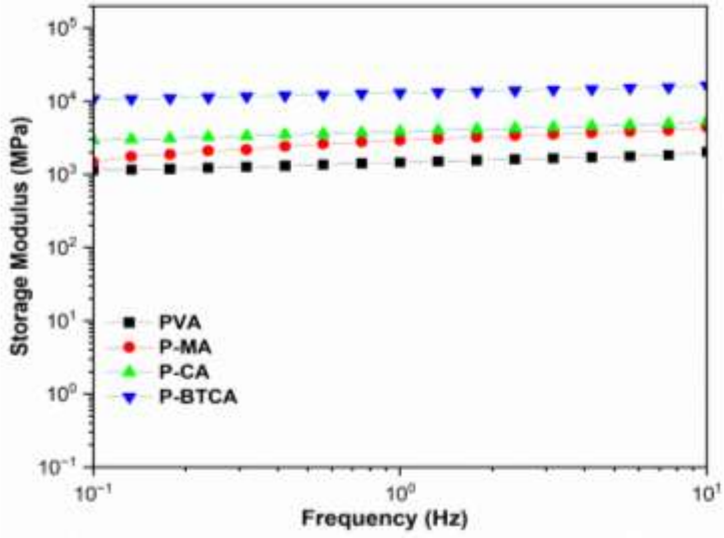


Fig. 5.10: Storage modulus of PVA and PVA crosslinked films with di, tri and tetra acids

5.4 Conclusion

The study aimed to compare the effect of variation of carboxyl groups of polycarboxylic acids i.e. MA (diacid), CA (triacid), and BTCA (tetra acid) as crosslinkers on the properties of PVA films. The calculated crosslinking density of the tetra acid crosslinked film was found to be the highest among all crosslinked films and, consequently, exhibited the least swelling. In thermal analysis, the tetra acid crosslinked film demonstrated superior properties compared to the di and triacid crosslinked films. From DTG graphs, the order of decomposition temperature for crosslinked was found in order of P-BTCA (450 °C)>P-CA (378 °C)>P-MA (350°C). XRD results indicated that crosslinking led to a decrease in the overall crystallinity of PVA films, resulting in lower percentages of crystallinity for all crosslinked films. Additionally, a more significant reduction in hydrophilicity was observed in the tetra acid crosslinked film compared to both di and triacid crosslinked PVA films. Also, all crosslinked films displayed enhanced elasticity and tensile in comparison to neat PVA, with the order of elasticity being P-MA >P-CA >P-BTCA probably because of the difference in crosslinking sites available in crosslinkers.

In summary, the collective findings emphasize the critical importance of considering the molecular structure of carboxylic acids during the crosslinker selection process. These considerations play a crucial role in tailoring PVA films to achieve specific properties for diverse applications. This study not only provides valuable insights into the influence of different crosslinkers on the physicochemical properties of PVA films but also contributes significantly to the comprehension of green crosslinking processes.

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Chapter 6

Application of synthesized crosslinked polyvinyl alcohol films for the adsorptive removal of crystal violet dye

6.1 Introduction

Dye contaminated wastewater has become a significant global environmental concern, leading to the depletion of freshwater resources and posing serious health risks, including carcinogenic, mutagenic, and allergic effects [1][2]. Various industries, such as textiles, pharmaceuticals, paper production, and tanneries, discharge large amounts of dyes into water systems [3, 4]. Without proper treatment, these pollutants contaminate water sources, threatening both ecosystems and human health [5].

To address this issue, several dye removal technologies are available, like chemical, biological, and physical methods [6–8]. Physical methods include adsorption, ion exchange and filtration processes. These methods are quite popular in industrial practices because of their high efficacy and comparatively low operational costs [9–12]. Among these, adsorption stands out because of its simplicity, high efficiency, sustainability and cost-effectiveness [13,14]. However, its success is highly dependent on the choice of adsorbent, as it should be easily accessible, economical, porous and capable of being recycled, while also possessing numerous active sites for effective dye removal.

Despite extensive research on carboxylic acid crosslinked PVA for various applications, their use in dye adsorption remains relatively unexplored [15]. Studies have demonstrated the potential of citric acid crosslinked PVA for methylene blue removal [16] and 1,2,3,4-butanetetracarboxylic acid crosslinked PVA for the adsorptive removal of reactive red 141 dye from wastewater [17].

In this work, PVA films crosslinked with various carboxylic acids were selected for the removal of the cationic dye via adsorption. The study also aimed to explore the established structure-property relationship influenced by the molecular structure of the carboxylic acids used. For instance, an increased number of carboxylic groups may create more negatively charged sites, which enhances electrostatic interactions with positively charged dye molecules. Additionally, morphological changes resulting from these carboxylic acids can significantly impact adsorption capacity.

To explore this, PVA films crosslinked with four carboxylic acids namely, oxalic acid (OA) and malonic acid (MA) as dicarboxylic acid, citric acid (CA) as a tricarboxylic acid, and 1,2,3,4-butanetetracarboxylic acid (BTCA) as a tetracarboxylic acid, were used for the adsorption process. Crystal violet (CV) dye was selected as a model cationic dye for the experiments. Their dye adsorption capacity was evaluated using a UV spectrophotometer.

The PVA-BTCA film, which showed the highest efficiency in CV dye removal, was further investigated in detail through batch experiments to determine the impact of BTCA content, contact time, adsorbent dose, dye concentration, pH of dye solution, and the adsorption cycle count on its efficiency. Findings of this chapter have been submitted to the Journal of ChemistrySelect for publication.

6.2 Experimental: Adsorption Studies

Batch studies were conducted to assess the effectiveness of synthesized crosslinked films on adsorptive removal of CV dye at room temperature. To investigate the impact of di, tri, and tetra-carboxylic groups on dye removal capacity, 0.15 g of each film was placed in 100 mL of a 20 ppm CV dye solution. The experiments were conducted in a shaker at 150 rpm/min for 120 minutes until equilibrium was reached. The CV dye concentrations before and after adsorption were recorded using a UV spectrophotometer at 580 nm. After determining the most effective crosslinked film based on maximum dye removal efficiency, further optimization was done by taking the variations in the amount of crosslinker (10-50%), adsorbent dose (0.05–0.2 g/100 mL), dye concentration (20 –100 mg/L), reaction time (15–120 min), and pH (2–9).

To quantify the results, mathematical formulations were employed to determine the removal efficiency (%) and the quantity of dye adsorbed. The equations used are as follows:

$$R\% = \frac{C_0 - C_e}{C_0} \tag{6.1}$$

$$q_e = \frac{C_0 - C_e}{W} \times V \tag{6.2}$$

$$q_t = \frac{C_0 - C_t}{W} \times V \tag{6.3}$$

Where V denotes the volume of adsorbate solution in Liters, C_0 $C_e$and C_t represent dye concentration at the initial stage, at equilibrium, and at time t and W represents the weight of adsorbent (mg).

6.3 Results and Discussions

6.3.1 Influence of di, tri, tera carboxylic acids as crosslinker

Films fabricated with a 30% concentration of di, tri, and tetracarboxylic acids were used to evaluate the impact of varying the number of carboxyl groups on CV dye adsorption. All four crosslinked films showed dye removal efficiencies greater than 70% at equilibrium. Among these, the PVA-TETRA film exhibited the highest removal efficiency, exceeding 90%, as illustrated in Fig.6.1. The dye removal efficiency followed the trend: PVA-TETRA (BTCA) > PVA-DI (OA) > PVA-TRI (CA) > PVA-DI (MA).

The superior performance of the PVA-TETRA (BTCA) film may be attributed to its higher number of surface carboxyl groups, which provide more binding sites and enhance electrostatic attraction between the positively charged CV dye and the negatively charged carboxyl groups. However, it is noteworthy that the PVA film crosslinked with oxalic acid performed better than the CA crosslinked film, despite OA having fewer carboxyl groups. This suggests that factors beyond the number of carboxyl groups are at play. Similar results were reported in a previous study.[18]

In Chapter 3, SEM analysis revealed (Section 3.3.4 and Fig.3.4) that the OA crosslinked film had a rougher surface with pores, in contrast to the relatively smoother surfaces observed in the CA and MA crosslinked films (discussed in chapter 5, section5.3.7 and Fig.5.6). The rougher surface morphology likely contributed to enhanced dye adsorption by increasing surface area and providing additional sites for dye capture. Therefore, both the number of binding sites and surface morphology are crucial factors influencing the efficiency of dye adsorption.

Given its superior adsorption capacity, the PVA-TETRA (BTCA) film was identified as the best adsorbent and was selected for further adsorption experiments.

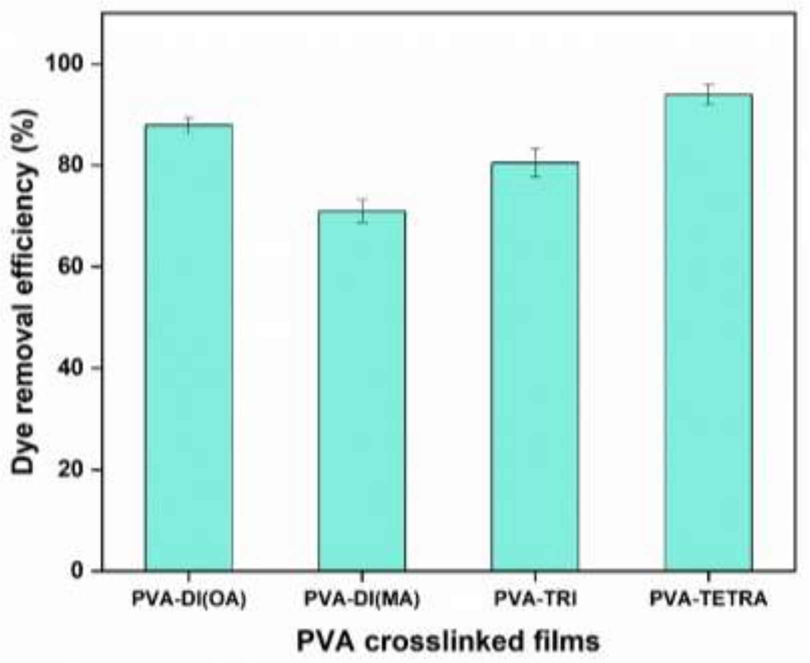


Fig. 6.1: *Influence of di, tri and tetracid crosslinked films on dye removal*

6.3.2 Influence of % of crosslinker

To examine the effect of the amount of tetracarboxylic acid as a crosslinker on CV dye adsorption, five different films with varying crosslinker concentrations (10-50%) were fabricated and tested. Fig.6.2 displays that the dye removal percentage was below 90% at lower crosslinker concentrations. However, it sharply increased to over 93% when films containing 30-50% crosslinker were used. For concentrations between 30-50%, the change in removal efficiency was almost constant. The increase in dye removal at 30% and above may be associated with the increased availability of adsorption sites at high doses of crosslinker, resulting in increased removal efficiency. However, at even higher concentrations, although more adsorption sites are available, increased agglomeration between the adsorbent particles causes many sites to be covered or overlap, thereby reducing the overall adsorption efficiency.

Nevertheless, the dye removal percentage of PVA-TETRA (BTCA) already exceeded 90 with a film containing 30% tetracarboxylic acid, and further increases in crosslinker concentration showed no substantial improvement in the removal percentage. Therefore, the PVA-TETRA (BTCA) film containing 30%

tetracarboxylic acid was chosen for adsorption kinetics and adsorption isotherm studies.

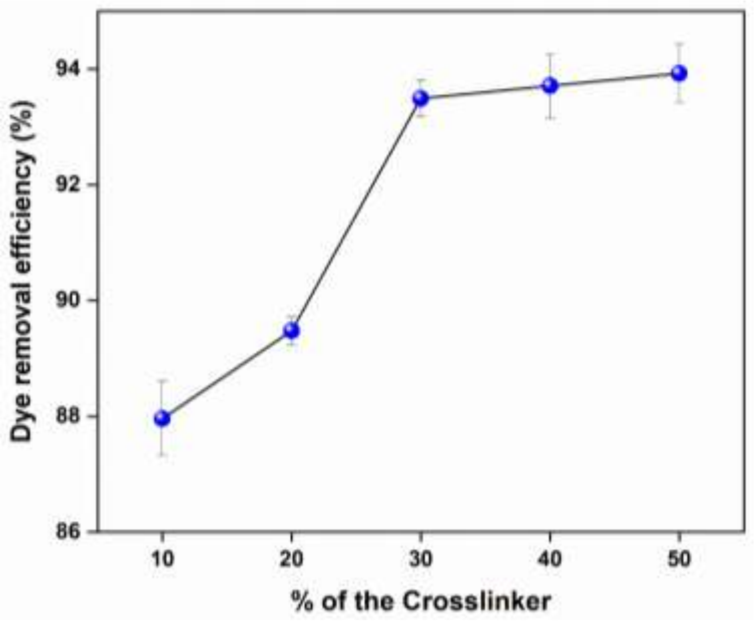


Fig. 6.2: *Influence of amount of crosslinker on dye removal*

6.2.3 Influence of adsorbent mass

From an economic perspective, investigating the impact of adsorbent dosage on dye removal from wastewater is crucial for future large-scale applications. Experimental results depicted in Fig.6.3 demonstrate that the CV dye removal efficiency is strongly dependent on the adsorbent dosage. As shown in Fig.6.3, variation in the adsorbent doses (0.05- 0.2 g) significantly impacts dye removal efficiency. When the adsorbent dose was increased from 0.05 to 0.15 g, by keeping the volume of the dye solution 100 mL and concentration 20 PPM, CV adsorption efficiency on PVA-TETRA (BTCA) surface sites increased from 79.39% to 93.70%. However, increasing the adsorbent dose beyond 0.15 g did not result in a significant improvement in CV removal efficiency. Therefore, considering both the adsorption performance and cost-effectiveness, an optimal adsorbent dose of 0.15 g was selected for subsequent experiments. In conclusion, for cost-effective and efficient CV removal, 0.15 g of PVA-TETRA (BTCA) film was determined to be the optimal adsorbent dosage and was used for all adsorption experiments.

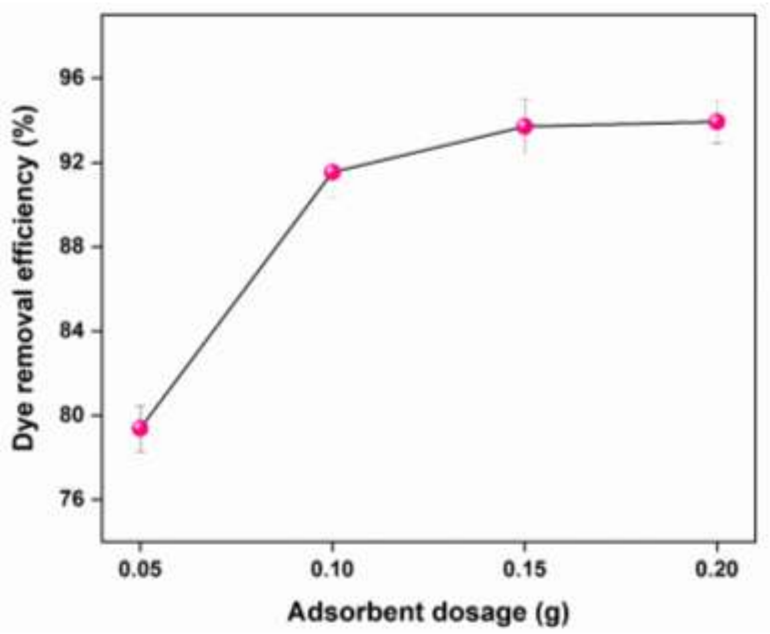
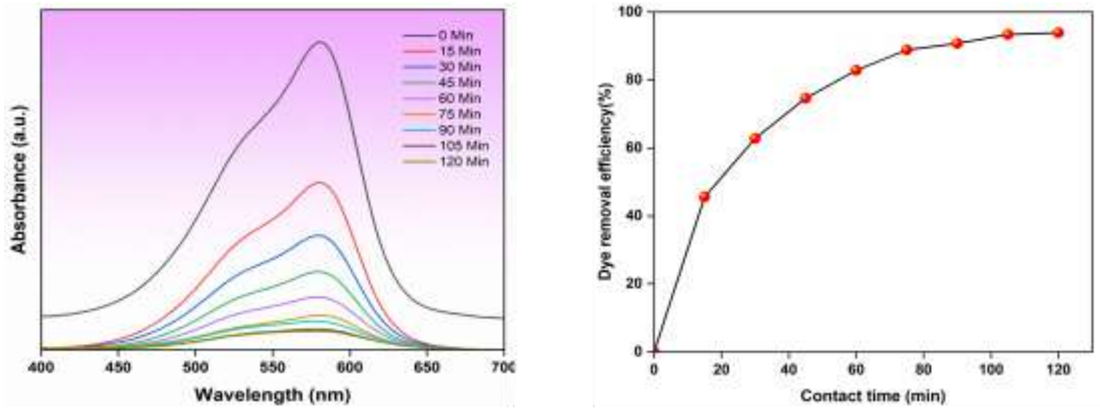


Fig. 6.3: *Influence of adsorbent mass on dye removal*

6.3.3 Influence of Contact Time

The impact of contact time on the adsorptive removal of CV dye using PVA-TETRA (BTCA) film with an initial CV concentration of 20 PPM was evaluated. As presented in Fig. 6.4(a-b), the adsorption of CV by the PVA-TETRA (BTCA) film increased steadily with time. Initially, the adsorption capacity of PVA-TETRA (BTCA) increased rapidly during the first 60 minutes, reaching nearly 90% within 90 minutes, after which the adsorption rate slowed down and then reached equilibrium at 105 min. The initial rapid increase in adsorption was primarily due to the abundant availability of initially free adsorption sites on the surface of PVA-TETRA (BTCA) film and the elevated concentration of CV in the solution, which resulted in a stronger attraction between the dye molecules and the film.

With the progress of the adsorption process, the availability of adsorption sites on PVA-TETRA (BTCA) film slowly reduced, and the catalyst for dye adsorption, due to the concentration difference between the liquid phase and the adsorbent, diminished. Consequently, the adsorption rate of CV onto PVA-TETRA (BTCA) slowed down as the system approached equilibrium.



(a) (b)

Fig. 6.4: *Influence of variation of time on dye removal*

6.3.4 Influence of initial concentration of dye

The initial dye concentration significantly affects dye removal efficiency, as it provides the driving force necessary to overcome mass transfer resistances between the liquid and solid phases. To examine the effect of initial CV concentration on the adsorption potential of the PVA-TETRA (BTCA) film, experiments were performed at different CV concentrations of 20, 30, 40, 60, and 100 PPM. In each experiment, 0.15 g of adsorbent was placed in 100 mL of CV dye solution and agitated in a shaker at 150 rpm for 120 min until adsorption equilibrium was reached. The solution was subjected to centrifugation, and the obtained supernatant was examined using a UV-Vis absorption spectrophotometer. The dye removal efficiency of CV dye decreased with increasing dye concentration. The PVA-TETRA (BTCA) film demonstrated high dye removal efficiency at a dye concentration of 20 PPM. However, as the dye concentration increased from 20 to 100 PPM, the removal efficiency decreased (Fig.6.5). This reduction in efficiency at higher dye concentrations is attributed to the saturation of adsorption sites on the PVA-TETRA (BTCA) film and the increased competition for these sites between CV dye molecules. At equilibrium, the adsorption capacity of PVA-TETRA for CV was determined to be 38.53 mg g^{-1}.

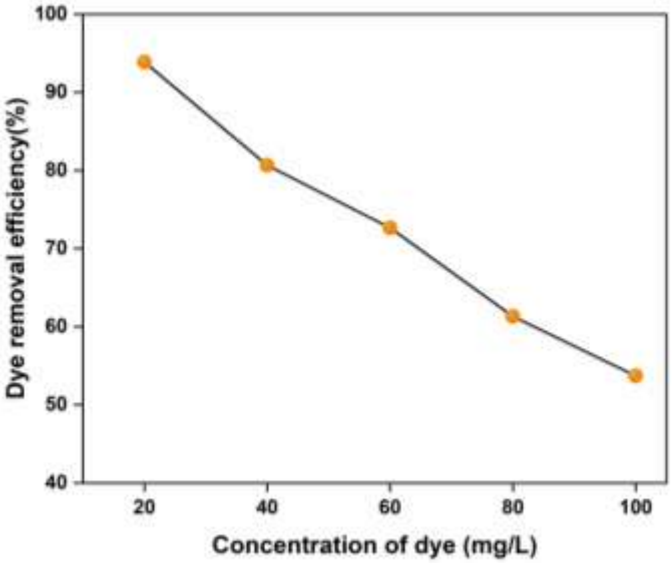


***Fig. 6.5**: Influence of initial dye concentration*

6.3.5 Influence of pH

During adsorption, the pH of the solution significantly affected the adsorbent's performance. To examine the impact of pH on the adsorption capacity of the PVA-TETRA film, different pH levels (2-9) were tested, and removal efficiency values were determined under identical conditions, The ideal pH value is affected by the molecular structure of the dye molecules and the functional groups present on the adsorbent surface. The effect of pH on the adsorption performance of PVA-TETRA (BTCA) is shown in Fig.6.6.

From Fig.6.6, it is noticeable that the removal rate increased from 19.11% to 95.72% when transitioning from an acidic to a basic medium. At low pH levels, the solution contains a high concentration of H^+ ions, which actively compete with the cationic CV dye molecules for the available adsorption sites on the PVA-TETRA (BTCA) film. As a result, many of these sites are occupied by H^+ ions rather than CV dye, leading to reduced adsorption efficiency. Additionally, when the pH of the solution falls below 7.0, the surface of the PVA-TETRA (BTCA) film becomes protonated, meaning that the carboxylate ions (COO-) on the surface are converted into neutral carboxylic acid groups (COOH). This protonation process not only decreases the number of negatively charged sites available for electrostatic attraction with the positively charged CV dye molecules but also creates an electrostatic repulsion between the protonated surface and the cationic dye molecules. This combined effect of site competition and electrostatic repulsion at low pH levels significantly reduces the overall dye adsorption capacity of the PVA-TETRA (BTCA) film.

Conversely, at pH levels above 7.0, the surface of the PVA-TETRA (BTCA) film undergoes deprotonation, where the carboxyl groups (COOH) lose their hydrogen ions and convert them into negatively charged carboxylate ions (COO^-). This deprotonation process significantly enhances the electrostatic attraction between the negatively charged surface of the PVA-TETRA (BTCA) film and the positively charged CV dye molecules. As a result, the adsorption of CV dye onto the film is facilitated, leading to a substantial increase in dye removal efficiency. However, after the pH exceeds 7.0, the increase in adsorption removal rate becomes very marginal, rising only from 93.88% to 95.72%.

Therefore, a solution with pH 7.0 was selected for all the adsorption experiments.

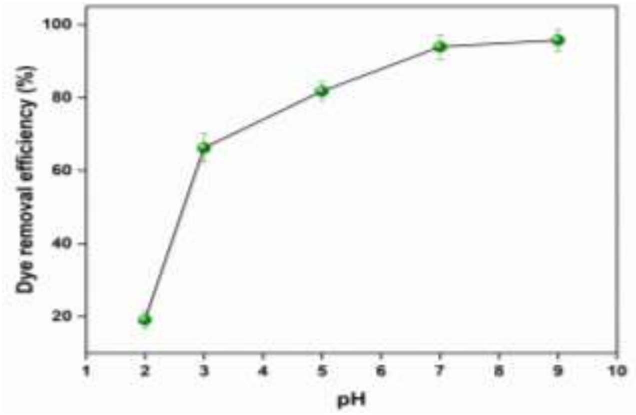


***Fig. 6.6:** Influence of pH variation on dye removal*

6.3.6 Adsorption kinetics

To explore the kinetics of adsorption mechanism of the PVA-TETRA film, two mathematical models were applied: the pseudo-first-order and pseudo-second-order models, as shown in Fig.6.7. The pseudo-first-order model is the simplest and has been extensively used to study the adsorption characteristics in solid/liquid systems. This model postulates that the rate of adsorption is directly proportional to the number of available adsorption sites, making it a straightforward approach for analyzing adsorption kinetics. However, it is essential to compare this model with the more complex pseudo-second-order model, which accounts for chemisorption and assumes that the adsorption rate depends on the square of the number of available sites.

The linear expression of the pseudo-first-order is given as follows:

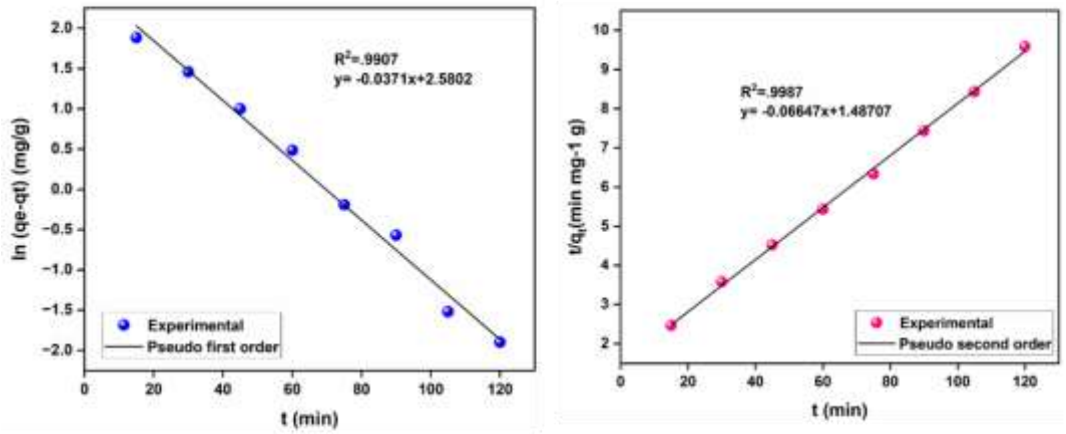
$$\ln(q_{e-}\, q_t) - K_1 \mathrm{t} \qquad 6.4$$

Here, q_t and $q_e$represent the amounts of dye adsorbed in mg g^{-1} at time t (min) and at equilibrium respectively, while K_1 (min^{-1}) is the pseudo-first-order rate constant. The rate constant K_1 and $q_e$were obtained from the slope and the intercept of the plot of $\ln(q_{e-}\, q_t)$ vs t.

The pseudo-second-order model in its linear form is represented as:

$$\frac{t}{q_t} = \frac{1}{K_2 {q^2}_e} + \frac{t}{q_e} \qquad 6.5$$

A plot of $\frac{t}{q_t}$ vs t produces a straight line through which the second-order rate constant, K_2 and equilibrium adsorption capacity $q_e$can be calculated. The linear plots of both the pseudo-first-order and pseudo-second-order models regarding adsorptive removal of CV dye on the PVA-TETRA (BTCA) film are displayed in Fig 6.7. Notably, the correlation coefficient value of the pseudo-first-order model (0.9960) was found to be lower than compared to the pseudo-second-order model, which has a higher correlation coefficient (0.9987). This proposes that, for the present adsorption data, the pseudo-second-order model offers a better fit. Consequently, the results suggest that the adsorption kinetics of CV by PVA-TETRA (BTCA) film follows the pseudo-second-order model, implying that the process of chemisorption is probably contributing in the adsorption process.



(a) (b)

Fig. 6.7: *Adsorption kinetics of PVA-TETRA (BTCA)films (a) Pseudo first order (b) Pseudo second order*

6.3.7 Adsorption isotherm

To understand the adsorption behaviour of the PVA-TETRA (BTCA) films, two established isotherm models: viz; Langmuir and Freundlich isotherm models have been employed. The Langmuir isotherm model gives information about monolayer adsorption on a uniform, homogeneous surface. The Langmuir equation is expressed as:

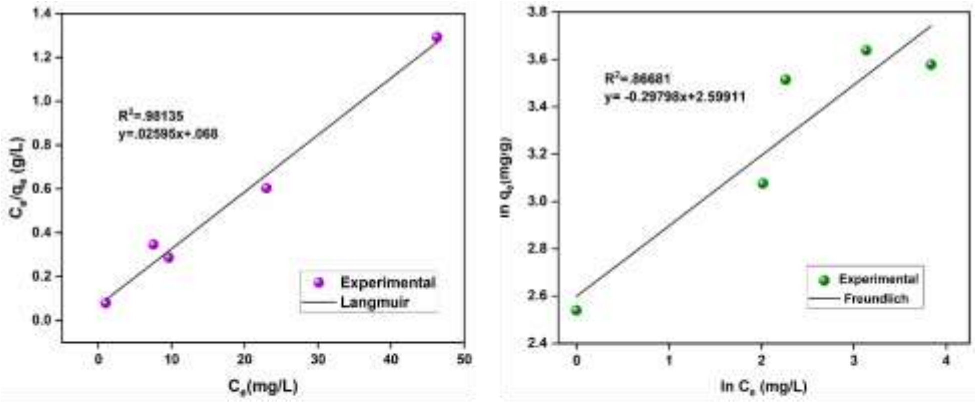
$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}K_L} \qquad 6.7$$

In this model, C_e represents the equilibrium concentration of the adsorbate (the crosslinked film in mg/L, q_e denotes the equilibrium adsorption capacity of the adsorbent in mg/g, the parameter q_{max} is the maximum adsorption capacity in mg/g and K_L the Langmuir constant in L/mg. The values of $q_{max}$and K_L are calculated from the slope and the intercept of the plot between Ce/qe and Ce (Fig. 6.8a) respectively.

The Freundlich isotherm model is use to describe a heterogeneous system where adsorption may occur in multiple layers. It assumes the presence of non-uniform adsorption sites with varying adsorption energies. This model is expressed as

$$\ln q_e = lnK_f + \frac{1}{n} lnC_e \qquad 6.8$$

where K_f and n are Freundlich adsorption constants, determined from the plot between $\ln q_e$ and lnC_e (Fig.6.8b). K_f represents the maximum adsorption capacity in mg/g while ‘n’ gives the adsorption intensity. The experimental data for the adsorption of CV dye over the PVA-TETRA (BTCA) film was fitted with both the isotherms, as displayed in Fig.6.7. From the graphs, it was found that the correlation coefficient of Langmuir model is much closer to unity (0.981) and is greater than the Freundlich model (0.866); indicating that the adsorption process involves a single layer of dye molecules binding to a limited number of uniform sites on the surface of the film. The film eventually reaches a point where no more dye can be adsorbed, indicating that the surface is uniform in its binding properties and that adsorption is limited to monolayer coverage.



(a) (b)

Fig. 6.8: *Adsorption isotherms of PVA-TETRA(BTCA)films(a)Langmuir(b) Freundlich*

6.3.8 Reusability

As displayed in Fig.6.9, the adsorption-desorption cycles of PVA-TETRA (BTCA) reveal a progressive decline in adsorption capacity with each successive cycle. This gradual decrease may be linked with the reduction in functional groups responsible for binding the dye, diminishing the material's adsorption efficiency. Furthermore, some of the molecules of CV dye may remain adsorbed on the surface of the PVA-TETRA (BTCA) film after the desorption process, resulting in partial blockage of available adsorption sites. By the end of the fifth cycle, PVA-TETRA (BTCA) retained an impressive 80.9% adsorption efficiency for crystal violet dye, starting from an initial 93%. This highlights its remarkable recyclability and ability to maintain high removal performance above 80% even after multiple reuse cycles, demonstrating its durability and effectiveness for sustainable wastewater treatment.

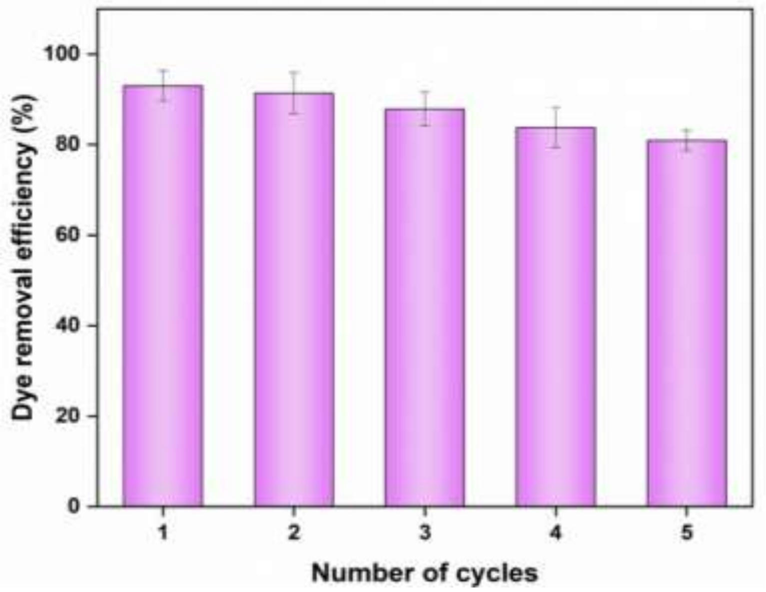


***Fig. 6.9:** Regeneration cycles of PVA-TETRA film on dye removal.*

6.3.9 Proposed adsorption mechanism

The adsorption experiments demonstrated that PVA films crosslinked with PVA−TETRA (BTCA) exhibited strong performance in adsorptive removal of crystal violet (CV) dye from aqueous solutions. The kinetic analysis revealed that chemisorption is likely to be more significant than physisorption in this process, which may contribute in the following ways: (1) Electrostatic interactions occurred when the carboxyl groups in the PVA−TETRA (BTCA) films deprotonated and generated carboxylate ions that attracted the positively charged CV dye molecules. Furthermore, (2) Electron donor-acceptor interactions between the oxygen atoms in the hydroxyl and carbonyl groups present over the surface of PVA and the benzene rings in the CV dye molecules played a pivotal role in the adsorption process [19]. These combined mechanisms, as shown in Fig.6.10, including electrostatic attraction and electron interactions, may contribute to the high dye removal efficiency of the PVA−TETRA (BTCA) films, making them effective adsorbents for water treatment applications.

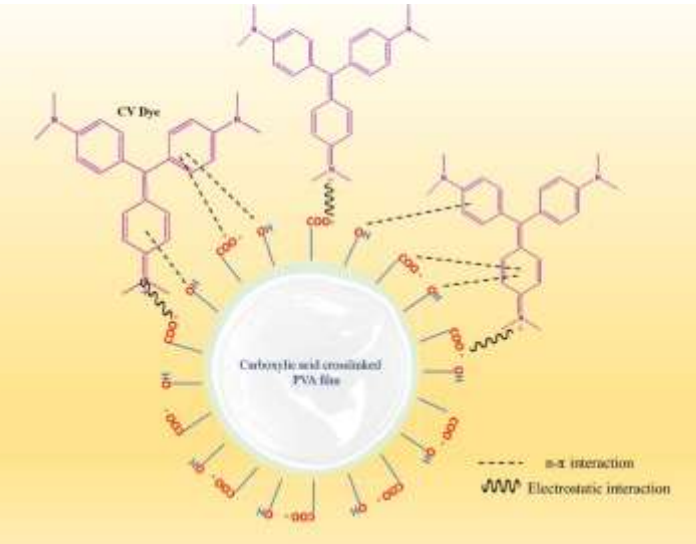


Fig. 6.10: *Proposed mechanism of adsorption of CV dye on PVA-TETRA films.*

6.4 Conclusion

This chapter investigated the use of PVA films crosslinked with four different carboxylic acids containing di, tri and tetracarboxyl groups for removing the cationic dye crystal violet (CV) from aqueous solutions. Results showed that the number of carboxyl groups in the crosslinker and the morphology significantly affected the adsorption capacity of the films. Among the films tested, film crosslinked with tetracarboxylic acid, which has the highest number of carboxyl groups, exhibited the best adsorption performance. Additionally, increased surface roughness, observed in SEM images was associated with enhanced dye adsorption. The optimal conditions for dye removal were found with a film crosslinked with 30 wt% tetracarboxylic acid, which achieved a dye removal efficiency of over 90% and an adsorption capacity of 38.53 mg/L with a 20 ppm CV solution over 105 minutes. Adsorption isotherms were analyzed using the Langmuir and Freundlich models, where the Langmuir model ($R^2 = 0.98135$) provided a better fit than the Freundlich model ($R^2 = 0.86681$), indicating uniform adsorption sites and monolayer adsorption. Kinetic analysis showed that the pseudo-second-order model ($R^2 = 0.998$) best described the adsorption process, suggesting that chemisorption, probably involving the formation of chemical bonds between dye molecules and the functional groups of the film, could be the primary mechanism for CV removal. These findings suggest that tetracarboxylic acid crosslinked PVA films have strong potential for use in environmental remediation, particularly for treating wastewater containing cationic dyes.

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Chapter 7

Conclusion, Future Scope & Social Impact

7.1 Conclusion

Crosslinking is a versatile method to modify the properties of polymers like PVA. The tailored properties of PVA depend on experimental conditions and the choice of crosslinker. This thesis is dedicated to investigating the impact of various carboxylic acids as crosslinkers and analyzing the influence of their molecular structural differences on the physicochemical properties of PVA. The study was conducted by taking various factors such as carbon chain length, the nature of carboxylic acids, bonding types, and the number of functional groups.

In a homologous series of dicarboxylic acids, solubility and crystal packing exhibit alternating trends, known as the odd-even effect, which arises due to the odd or even number of carbon atoms. The impact of this odd-even trend was also observed on the physicochemical properties of PVA. Even-numbered acids, characterized by lower solubility and symmetrical structures, demonstrated higher crosslinking efficiency, leading to significant changes in morphological, swelling, and crystalline properties. Morphological analysis revealed that even-numbered acids (OA and SA) produced rough, porous surfaces, whereas odd-numbered acids (MA and GA) formed smoother, non-porous surfaces.

A comparison of saturated (single bond, SA) and unsaturated (double bond, MAL) carboxylic acids showed that the double-bonded crosslinkers, with their smaller molecular size and higher reactivity, resulted in greater crosslinking density. These films exhibited enhanced thermal and mechanical properties, reduced hydrophobicity, and smoother surfaces.

Additionally, the number of carboxyl groups in the crosslinker was found to have a significant impact on crosslinking. Polycarboxylic acids, such as diacids (OA and MA), triacid (CA), and tetraacid (BTCA), were evaluated and films crosslinked with tetraacid showed the highest crosslinking density, minimal swelling, and superior thermal and mechanical properties, including maximum modulus. CA, with an extra hydroxyl group, notably influenced the swelling behaviour.

Furthermore, the synthesized crosslinked films were employed for the adsorptive removal of the cationic dye, crystal violet, from aqueous solutions. Adsorption experiments demonstrated that these films exhibited high efficiency in dye removal, which was influenced by the number of carboxyl groups present and the surface roughness of the films. Notably, films crosslinked with tetraacid showed superior adsorption performance, achieving a maximum adsorption capacity of 38.53 mg/g. This enhanced adsorption capacity can be attributed to the increased availability of functional groups for binding interactions and the improved surface area provided by the rough texture, facilitating greater contact with dye molecules. These findings highlight the potential of PVA-carboxylic acid crosslinked films as promising materials for effective and eco-friendly dye removal applications in wastewater treatment.

In conclusion, this study provides valuable insights into how PVA properties can be tailored by selecting appropriate crosslinkers, enabling the design of materials for specific applications.

7.2 Future scope

Future research on PVA crosslinked with carboxylic acids can be further developed by incorporating simulation studies to gain a detailed understanding of the precise molecular interactions involved. Computational techniques, such as molecular dynamics (MD) simulations and density functional theory (DFT), can be used to investigate how specific carboxylic acid molecules interact with PVA chains, including the formation of hydrogen bonds, ionic interactions, and covalent bonds. These studies provide valuable insights into selecting the most suitable acids and optimizing the conditions necessary for efficient crosslinking, ultimately improving the material’s performance and application potential.

In addition, crosslinking can also be achieved using physical methods, such as freeze-thaw cycles or irradiation, which can then be compared with chemical crosslinking to determine the most cost-effective method without compromising the quality of the films.

The crosslinking of PVA with carboxylic acids not only enhances its mechanical strength and thermal stability but also improves its water resistance, making it suitable for diverse applications. The utility of these films can be further increased by incorporating nanoparticles, both inorganic (such as silica and metal oxides) and organic (such as graphene oxide), into the crosslinked matrix. This addition may further improve the films' properties, such as barrier performance, chemical resistance, and functionality. Therefore, future research can focus on developing smart nanocomposite films made from crosslinked PVA for applications in biomedical devices, where their biocompatibility, non-toxicity can be utilized. In packaging, crosslinked PVA-nano films can provide superior moisture and gas barrier properties, while in electronics, they can serve as flexible substrates for wearable devices. Additionally, their potential for use in energy storage systems, water purification membranes, and antimicrobial coatings underscores their promise for sustainable, high-performance material solutions.

7.3 Social Impact

The increasing need for sustainability and environmental protection is a driving force to explore innovations in material science. By creating materials like, PVA films crosslinked with carboxylic acids, which are both environmentally friendly and functional, industries can adopt more sustainable practices. This helps reduce plastic waste, conserve resources, and promote better care for the environment.

The sustainability and environmental benefits of crosslinked PVA with carboxylic acids are particularly noteworthy due to both the inherent eco-friendly properties of PVA and the green nature of carboxylic acids. PVA is a water-soluble and biodegradable polymer, making it a more sustainable alternative to conventional, non-biodegradable plastics. When crosslinked with carboxylic acids, PVA's properties are further enhanced without compromising environmental friendliness.

Carboxylic acids are naturally occurring and environment-friendly substances. They can be sourced from natural products such as plant-based materials and agricultural by-products, which significantly reduces the environmental impact of the crosslinking process. By using carboxylic acids in the crosslinking process, the overall sustainability of the material is enhanced, as these acids do not introduce toxic or harmful substances into the environment.

Crosslinking PVA with carboxylic acids increases the material's water resistance and durability, extending its lifespan and making it suitable for a broader range of applications. This enhanced performance enables PVA to serve as a viable substitute for synthetic, non-biodegradable polymers that are often used in packaging, medical devices, and other industries. The ability to use a biodegradable, renewable material for crosslinking not only reduces reliance on petroleum-based plastics but also helps alleviate the long-term environmental issues associated with plastic waste.

Furthermore, carboxylic acids contribute to the "green" nature of the material by promoting a process that is free from toxicity and does not produce harmful by-products, supporting a circular economy where materials are used, reused, and disposed of safely. As a result, crosslinked PVA with carboxylic acids offers a sustainable, eco-friendly alternative to traditional plastics, addressing environmental concerns and the demand for greener materials. Moreover, these films effectively remove dyes from wastewater, providing an eco-friendly solution to industrial pollution.

LIST OF PUBLICATIONS AND THEIR PROOFS

Journal Articles:

1. Leela Gautam, Syed Ishraque Ahmad, S.G.Warkar, Ravikant, Manish Jain. A review on carboxylic acid cross-linked polyvinyl alcohol: Properties and applications. Polymer Engineering and Science, Wiley 2022. DOI: https://doi.org/10.1002/pen.25849

2. Leela Gautam, S.G Warkar, Manish Jain. Physicochemical evaluation of polyvinyl alcohol films crosslinked with saturated and unsaturated dicarboxylic acids: A comparative study. Polymer Engineering and Science, Wiley 2024. DOI: doi:10.1002/pen. 26806.

3. Leela Gautam, Manish Jain, S.G. Warkar. Influence of Odd-Even Effect of Dicarboxylic Acids as Crosslinker on the Physicochemical of Polyvinyl Alcohol. Journal Of Applied Polymer Science, Wiley 2024.DOI: 10.1002/app.56046

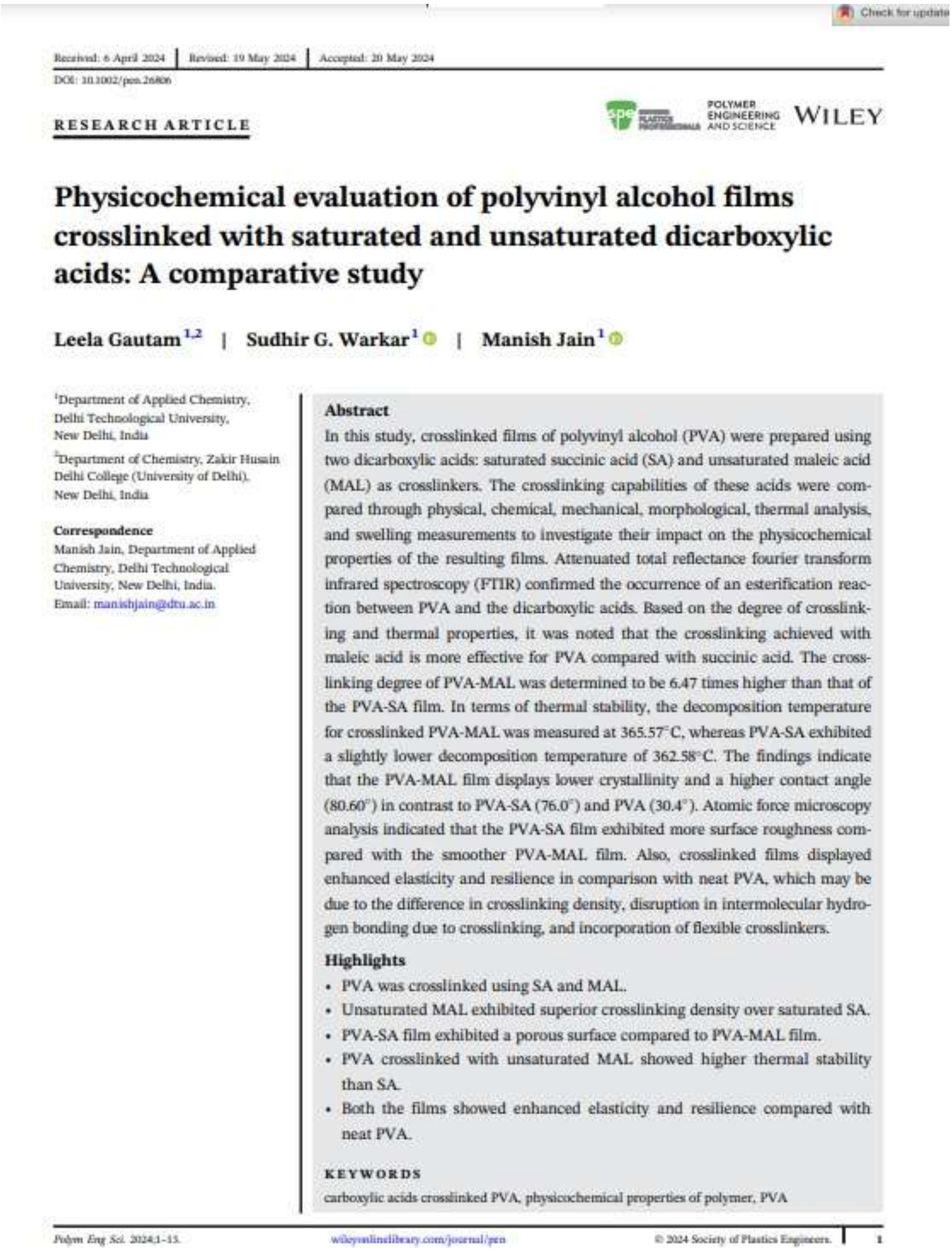
4. Leela Gautam, Manish Jain, S.G. Warkar. Crosslinking of polyvinyl alcohol with di, tri, and tetracarboxylic acids: An experimental investigation. Colloid and polymer Science, Springer 2024. DOI: https://doi.org/10.1007/s00396-024-05313-3

Conferences:

1. Presented paper at 3rd Indian Analytical Congress (IAC-2024)-An International Analytical conference and Exhibition, jointly organized by ISAS-Delhi chapter and IIP-Dehradun, held on 5-7th June 2024. (Oral Presentation)

2. Presented paper at International Conference on "Advancement in chemical sciences and Nanocomposites" (ACSN-2022), organized by Zakir Husain Delhi College, University of Delhi and ISAS, Delhi Chapter held on 1st–2nd April 2022 (Oral Presentation) (Received Best Oral Presentation Award)

PROOF OF PUBLICATIONS



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RESEARCH ARTICLE

POLYMER ENGINEERING AND SCIENCE
WILEY

Physicochemical evaluation of polyvinyl alcohol films crosslinked with saturated and unsaturated dicarboxylic acids: A comparative study

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Abstract

In this study, crosslinked films of polyvinyl alcohol (PVA) were prepared using two dicarboxylic acids: saturated succinic acid (SA) and unsaturated maleic acid (MAL) as crosslinkers. The crosslinking capabilities of these acids were compared through physical, chemical, mechanical, morphological, thermal analysis, and swelling measurements to investigate their impact on the physicochemical properties of the resulting films. Attenuated total reflectance fourier transform infrared spectroscopy (FTIR) confirmed the occurrence of an esterification reaction between PVA and the dicarboxylic acids. Based on the degree of crosslinking and thermal properties, it was noted that the crosslinking achieved with maleic acid is more effective for PVA compared with succinic acid. The crosslinking degree of PVA-MAL was determined to be 6.47 times higher than that of the PVA-SA film. In terms of thermal stability, the decomposition temperature for crosslinked PVA-MAL was measured at 365.57°C, whereas PVA-SA exhibited a slightly lower decomposition temperature of 362.58°C. The findings indicate that the PVA-MAL film displays lower crystallinity and a higher contact angle (80.60°) in contrast to PVA-SA (76.0°) and PVA (30.4°). Atomic force microscopy analysis indicated that the PVA-SA film exhibited more surface roughness compared with the smoother PVA-MAL film. Also, crosslinked films displayed enhanced elasticity and resilience in comparison with neat PVA, which may be due to the difference in crosslinking density, disruption in intermolecular hydrogen bonding due to crosslinking, and incorporation of flexible crosslinkers.

Highlights

- PVA was crosslinked using SA and MAL.
- Unsaturated MAL exhibited superior crosslinking density over saturated SA.
- PVA-SA film exhibited a porous surface compared to PVA-MAL film.
- PVA crosslinked with unsaturated MAL showed higher thermal stability than SA.
- Both the films showed enhanced elasticity and resilience compared with neat PVA.

KEYWORDS
carboxylic acids crosslinked PVA, physicochemical properties of polymer, PVA

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REVIEW ARTICLE

POLYMER ENGINEERING AND SCIENCE
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A review on carboxylic acid cross-linked polyvinyl alcohol: Properties and applications

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Abstract

Polyvinyl alcohol (PVA) is a nontoxic, biodegradable, and biocompatible polymer and has been used extensively in various fields. Indeed, important features of PVA such as its film-forming ability, high tensile strength and flexibility, high viscosity, solvent tolerance ability, thermostable nature have made it vital and drawn the attention of scientific community. However, being a water-soluble polymer, some chemical modifications are required to alter this property of PVA. Cross-linking is the most attractive and widely used method to change the properties of PVA to make it more valuable material. Different carboxylic acids have already been used for PVA cross-linking in various applications such as pervaporation, reverse osmosis (RO), wound dressing, drug delivery, and fuel cells. However, a comprehensive study on structure–property correlation of carboxylic acids as PVA cross-linker is not available. In this review, different available studies on carboxylic acid cross-linked PVA are summarized and are used to develop structure–property correlations of carboxylic acids as cross-linker on the properties of cross-linked PVA. Advantages and limitations of different carboxylic acids as PVA cross-linker are also summarized for various fields such as tissue engineering, wound dressing, drug delivery, fuel cell/solid polymer electrolyte, pervaporation, desalination and RO solid polymer electrolytes, and food packaging.

KEYWORDS

carboxylic acids, cross-linked PVA, cross-linking, films, membranes, water-soluble polymers

1 | INTRODUCTION

Polyvinyl alcohol (PVA) is a synthetic, linear, semicrystalline polymer that is composed of carbon chain as backbone and hydroxyl group as a functional group. It is obtained by the hydrolysis of polyvinyl acetate, and its physical properties are affected by its degree of hydrolysis, that is, complete or partial. Therefore, PVA is available commercially in two grades, namely, fully hydrolyzed and partially hydrolyzed. It is also available in different molecular weights mainly due to the variation in length of polymeric chain.[1,2]

PVA exhibits many important features such as it is readily available, having low cost, biodegradable, biocompatible, nontoxic, water soluble, excellent film-forming ability, thermostable, good chemical resistance, and adhesive. All these features make it a very valuable material in a wide range of applications.[3–7]

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RESEARCH ARTICLE

Applied Polymer SCIENCE WILEY

Influence of the odd-even effect of dicarboxylic acids as crosslinker on the physicochemical properties of polyvinyl alcohol

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Abstract

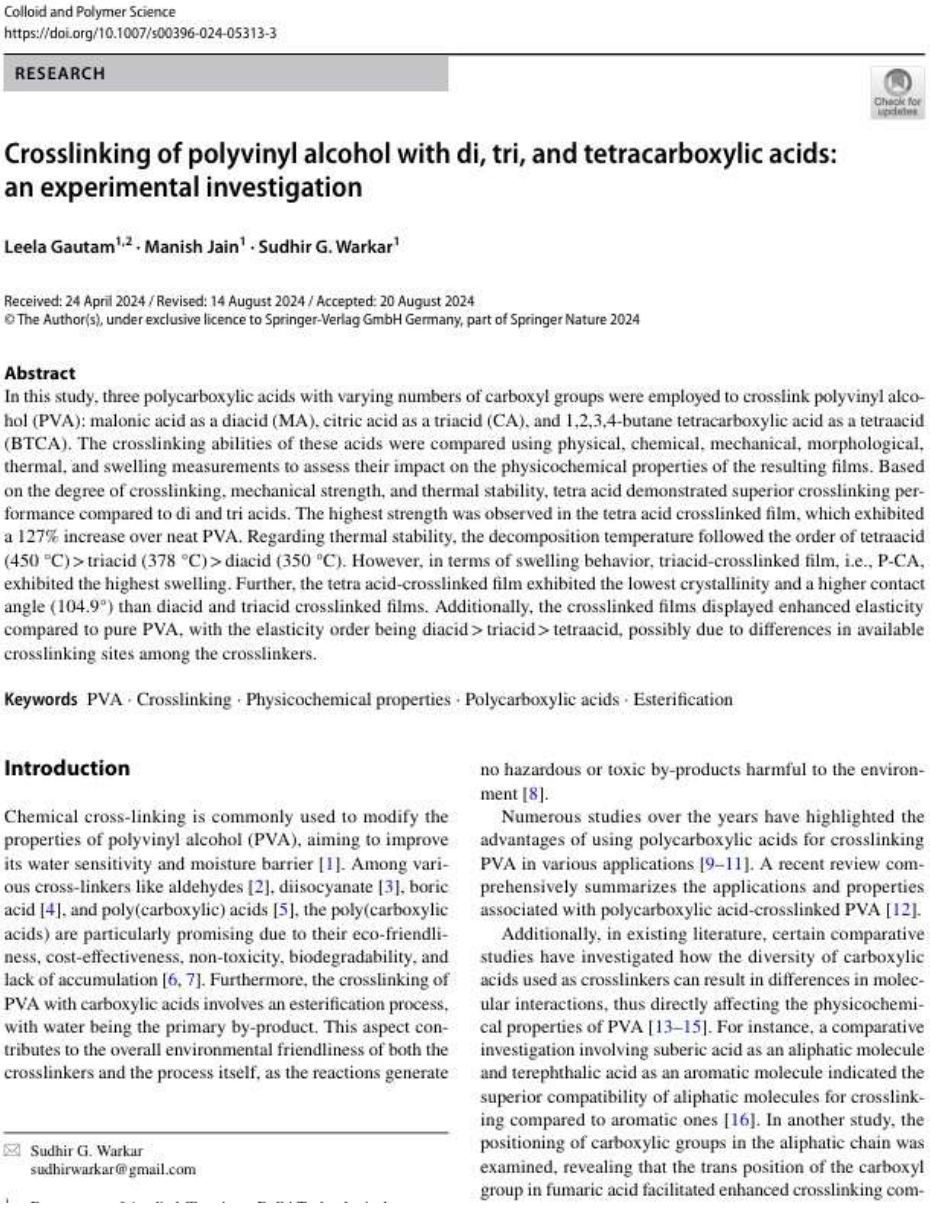
Polyvinyl alcohol (PVA) was crosslinked with a homologous series of four different dicarboxylic acids, $HOOC(CH_2)_{n-2}COOH$ ($n = 2$ to 5) viz. oxalic acid (OA; C2), malonic acid (MA; C3), succinic acid (SA; C4) and glutaric acid (GA; C5) containing odd and even number of carbon atoms. The characterization and assessment of synthesized crosslinked films were done using ATR-FTIR, XRD, SEM, AFM, DSC, rheology, percent swelling and sessile drop contact angle. The odd-even effect of dicarboxylic acids was observed to significantly influence the physicochemical properties of PVA when employed as a crosslinker. PVA films crosslinked using dicarboxylic acids containing an even number of carbon atoms, displayed translucency, roughness, and an irregular matrix. In contrast, films incorporating an odd number of carbon atoms were transparent, homogenous, and densely packed. Furthermore, films containing even acids exhibited relatively lower crystallinity, lower melting temperature (T_m) and displayed an unexpected irregular trend in swelling as crosslinker concentration increased compared to films containing dicarboxylic acids with an odd number of carbon atoms which exhibits a consistent swelling with increasing crosslinker concentration. These results are attributed to the difference in the solubility and crystal structures of the odd-even series of dicarboxylic acids.

KEYWORDS
crosslinking, dicarboxylic acids, odd-even effect, physicochemical properties, PVA

1 | INTRODUCTION

In recent years, carboxylic acids have gained attention as potential crosslinking agents due to their easy accessibility, lack of odor, environmentally friendly nature, cost-effectiveness, non-toxicity, biodegradability, and non-accumulative properties, earning them the designation of green crosslinkers.[1–9] Over the past decades, numerous studies have highlighted the advantages of crosslinking polyvinyl alcohol (PVA) with carboxylic acids in various applications.[10–17] A recent review comprehensively summarizes the applications and properties associated with carboxylic acid-crosslinked PVA.[18]

Some of the studies have compared the effect of different carboxylic acids as a crosslinker with PVA and investigated their effects on the properties of the PVA cross-linked films. These studies showed that the molecular structure of carboxylic acids also affects the extent of crosslinking with PVA and the properties of cross-linked



Colloid and Polymer Science
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RESEARCH

Crosslinking of polyvinyl alcohol with di, tri, and tetracarboxylic acids: an experimental investigation

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Abstract

In this study, three polycarboxylic acids with varying numbers of carboxyl groups were employed to crosslink polyvinyl alcohol (PVA): malonic acid as a diacid (MA), citric acid as a triacid (CA), and 1,2,3,4-butane tetracarboxylic acid as a tetraacid (BTCA). The crosslinking abilities of these acids were compared using physical, chemical, mechanical, morphological, thermal, and swelling measurements to assess their impact on the physicochemical properties of the resulting films. Based on the degree of crosslinking, mechanical strength, and thermal stability, tetra acid demonstrated superior crosslinking performance compared to di and tri acids. The highest strength was observed in the tetra acid crosslinked film, which exhibited a 127% increase over neat PVA. Regarding thermal stability, the decomposition temperature followed the order of tetraacid (450 °C) > triacid (378 °C) > diacid (350 °C). However, in terms of swelling behavior, triacid-crosslinked film, i.e., P-CA, exhibited the highest swelling. Further, the tetra acid-crosslinked film exhibited the lowest crystallinity and a higher contact angle (104.9°) than diacid and triacid crosslinked films. Additionally, the crosslinked films displayed enhanced elasticity compared to pure PVA, with the elasticity order being diacid > triacid > tetraacid, possibly due to differences in available crosslinking sites among the crosslinkers.

Keywords PVA · Crosslinking · Physicochemical properties · Polycarboxylic acids · Esterification

Introduction

Chemical cross-linking is commonly used to modify the properties of polyvinyl alcohol (PVA), aiming to improve its water sensitivity and moisture barrier [1]. Among various cross-linkers like aldehydes [2], diisocyanate [3], boric acid [4], and poly(carboxylic) acids [5], the poly(carboxylic acids) are particularly promising due to their eco-friendliness, cost-effectiveness, non-toxicity, biodegradability, and lack of accumulation [6, 7]. Furthermore, the crosslinking of PVA with carboxylic acids involves an esterification process, with water being the primary by-product. This aspect contributes to the overall environmental friendliness of both the crosslinkers and the process itself, as the reactions generate no hazardous or toxic by-products harmful to the environment [8].

Numerous studies over the years have highlighted the advantages of using polycarboxylic acids for crosslinking PVA in various applications [9–11]. A recent review comprehensively summarizes the applications and properties associated with polycarboxylic acid-crosslinked PVA [12].

Additionally, in existing literature, certain comparative studies have investigated how the diversity of carboxylic acids used as crosslinkers can result in differences in molecular interactions, thus directly affecting the physicochemical properties of PVA [13–15]. For instance, a comparative investigation involving suberic acid as an aliphatic molecule and terephthalic acid as an aromatic molecule indicated the superior compatibility of aliphatic molecules for crosslinking compared to aromatic ones [16]. In another study, the positioning of carboxylic groups in the aliphatic chain was examined, revealing that the trans position of the carboxyl group in fumaric acid facilitated enhanced crosslinking com-

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PLAGIARISM VERIFICATION

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