

**THE EFFECT OF TANNIC ACID CROSSLINKER ON
THE PROPERTIES OF KENAF FIBRE AND
POLYVINYL ALCOHOL BINDER**

ANIS NAJIHAH BINTI MOHAMMAD

UNIVERSITI SAINS MALAYSIA

2022

**SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
UNIVERSITI SAINS MALAYSIA**

**THE EFFECT OF CROSSLINKER ON THE PROPERTIES OF KENAF FIBRE AND
POLYVINYL ALCOHOL**

By

ANIS NAJIHAH BINTI MOHAMMAD

Supervisor: DR ARJULIZAN RUSLI

Dissertation submitted in fulfilment of the requirements for the degree of Bachelor of
Engineering with Honours

(Polymer Engineering)

Universiti Sains Malaysia

August 2022

DECLARATION

I hereby certify that I conducted, finished, and wrote the dissertation titled "The Effect of Crosslinker on The Properties of Kenaf Fibre and Polyvinyl Alcohol Binder." I further certify that it has never before been presented to any other examination body or university for the granting of a degree, diploma, or other title with a comparable meaning

Name of Student: **Anis Najihah Binti Mohammad** Signature:

Date: 18/08/2022

Witness by

Supervisor: Dr. Arjulizan Rusli Signature:

Date: 18/08/2022

ACKNOWLEDGEMENT

Peace be upon Allah's messenger, Prophet Muhammad SAW, and all praise and thanks be to Allah (SWT). thanks to Allah SWT's grace and generosity. Due to the mercy and generosity of Allah SWT, I was finally able to successfully complete my research. I want to convey my deep gratitude to my supervisor, Dr. Arjulizan Rusli, for all of the insightful counsel, direction, and support she has given me in order to improve the calibre of my work. She demands quality and precision, which is a challenge for me to meet in order to complete my job, and her intelligence and tenacity have been an inspiration. I couldn't finish this arduous road without her encouragement and enlightening direction. I appreciate all your work and the priceless time you invested in my research.

Next, I would like to thank School of Mineral Resources and Materials Engineering, USM Engineering Campus for giving me the opportunity to gain valuable knowledge and practical experience by completing this last-year project. Taking this opportunity, I sincerely thank the School of Materials and Mineral Resources Engineering for providing me with all the necessary facilities for this project.

In addition, all laboratory technicians contributed to this study with their labour of love through their material supply and problem-solving input. This undertaking would never be finished without their direction and assistance. Moreover, I want to express my gratitude to my friends for helping me with this project.

Finally, I would like to dedicate this thesis to my cherished family, and in particular, I would like to express my sincere gratitude to my parents, my sibling, and my friends for their constant support, encouragement, and prayers for my success.

Thank you.

LIST OF TABLES	Error! Bookmark not defined.
LIST OF FIGURES	Error! Bookmark not defined.
LIST OF SYMBOLS	Error! Bookmark not defined.
LIST OF ABBREVIATIONS	Error! Bookmark not defined.
DECLARATION.....	Error! Bookmark not defined.
ACKNOWLEDGEMENT.....	Error! Bookmark not defined.
ABSTRACT.....	1
CHAPTER 1 INTRODUCTION.....	1
1.1 Research Background	1
1.2 Problem Statement	3
1.3 Objective	4
1.4 Outline.....	5
CHAPTER 2 LITERATURE REVIEW.....	6
2.1 Polymer Composites	6
2.2 Natural fiber	8
2.3 Biodegradable polymer	13
2.4 Crosslinking agent.....	21
CHAPTER 3 METHODOLOGY.....	29
3.1 Overview	29
3.2 Process flow	Error! Bookmark not defined.
3.3 Materials.....	29
3.4 Equipment	31
3.5 Formulation and experiment method	32
3.6 Characterization of the Prepared Kenaf Fibre/Polyvinyl Alcohol Samples.....	35

CHAPTER 4	RESULT AND DISCUSSION.....	43
4.1	Effect of Composition of PVA/Kenaf.....	43
4.2	Effect of tannic acid on KF/PVA composites.....	55
CHAPTER 5	CONCLUSION.....	70
5.1	Conclusion	70
5.2	Recommendation for Future Works.....	71

LIST OF TABLE

Table 2.1	Advantages and disadvantages of natural fibres (Alkbir et al., 2016; Jawaid & Abdul Khalil, 2011)	10
Table 3.1	Properties of Poly(vinyl) Alcohol (PVA)	29
Table 3.2	Properties of tannic acid (TA).....	30
Table 3.3	Properties of succinic anhydride (SA) Error! Bookmark not defined.	
Table 3.4	Mecahnical properties and chemical composition of kenaf fibre (Babatunde et al., 2015)	30
Table 3.5	List of equipment	31
Table 3.6	List of samples in stage 1	32
Table 3.7	List of samples in stage 2.....	32
Table 4.1	TGA characterization of pure PVA, pure kenaf fiber, 70KF/30PVA in the temperature range of 100 to 500 °C	48
Table 4.2	DSC analysis of biocomposite materials	58
Table 4.3	TGA Characterization of 70KF/30PVA, 70KF/30PVA/15TA and 70KF/30PVA/20TA in the temperature range of 100 to 500 °C	61

LIST OF FIGURE

Figure 2.1	Composites reinforcement types (Kulkarni, 2021).....	7
Figure 2.2	Classification of natural fibers (Bismarck et al., 2005)	9
Figure 2.3	Kenaf fiber with height 3 to 5 cm (b) Core kenaf fiber (c) Bast kenaf fiber	13
Figure 2.4	Classification of biodegradable polymers (Raghvendra Kumar Mishra, 2015)	15
Figure 2.5	The chemical structure of polyvinyl alcohol (PVA).....	17
Figure 2.6	Manufacturing route to PVA (Rudnik, 2008).....	17
Figure 2.7	Schematic illustration of different cross-linkers used in bone tissue engineering, (A): chemical crosslinking, (B) physical crosslinking, (C): enzymatic cross- linking.	23
Figure 2.8	Chemical structure of tannic acid (TA) (Hussein and Mona, 2017)..	25
Figure 2.9	Chemical structure of succinic anhydride (SAH)	27
Figure 3.1	Process flow of research work	42
Figure 3.2	Grinder machine with sieve 150 μ m.....	33
Figure 3.3	Sieve Machine with Three-tier Filter	34
Figure 3.4	Differential scanning calorimetry machine.....	36
Figure 3.5	Weighing balance.....	37
Figure 3.6	Perkin Elmer Pyris TGA.....	37
Figure 3.7	Optical Microscopy (OM).....	38
Figure 3.8	Zwick Pendulum Impact Tester (Zwick Roell, model 5102, USA). .	39
Figure 3.9	Fourier Transform Infrared spectroscopy (FTIR).....	41
Figure 4.1	DSC cooling curve of pure PVA, 70KF/30PVA and 60KF/40PVA .	44

Figure 4.6	Water absorption percentage of 70KF/30PVA and 60/40PVA composites in 48 hours.....	51
Figure 4.7	Surface fracture of 70KF/30PVA	53
Figure 4.8	Surface fracture of 60KF/40PVA	53
Figure 4.9	Fourier transform infrared (FTIR) spectra of 70KF/30PVA and 60KF/40PVA	54
Figure 4.10	DSC cooling curves for biocomposite of 70KF/30PVA, 70KF/30PVA/15TA and 70KF/30PVA/20TA	56
Figure 4.11	DSC second heating curves for biocomposites of 70KF/30PVA, 70KF/30PVA/15TA and 70KF/30PVA/20TA	57
Figure 4.12	Comparison of TG curves of 70KF/30PVA, 70KF/30PVA/15TA and 70KF/30PVA/20TA.....	Error! Bookmark not defined.
Figure 4.13	Comparison of DTG curves for 70KF/30PVA, 70KF/30PVA/15TA and 70KF/30PVA/20TA.....	60
Figure 4.14	Impact Strength of 70KF/30PVA, 70KF/30PVA/15TA and 70KF/30PVA/20TA.....	63
Figure 4.15	Water absorption percentage (%) of 70KF/30PVA, 70KF/30PVA/15TA and 70KF/30PVA/20TA.....	64
Figure 4.16	Surface fracture of 70KF/30PVA	66
Figure 4.17	Surface fracture of 70KF/30PVA/15TA.....	66
Figure 4.18	Surface fracture of 70KF/30PVA/20TA.....	67
Figure 4.19	Fourier transform infrared (FTIR) spectra of 70KF/30PVA, 70KF/30PVA/15TA and 70KF/30PVA/20TA	68

LIST OF SYMBOLS

X_c	Degree of crystallinity
W_1	The weight of sample after immersed in the water
	W_2
	The initial weight of sample
w	Width of specimens, (mm)
W	Impact energy to break the specimens
T_m	Melting temperature
T_g	Glass transition temperature
T_{cc}	Crystallization temperature
t	Thickness of specimens, (mm)
ΔH_m°	Enthalpy of Heat of fusion
ΔH_m	Enthalpy of Heat release during melting
ΔH_{cc}	Enthalpy of Heat release during crystallization
%	Percentage

LIST OF ABBREVIATIONS

DSC	Differential Scanning Calorimetry
FAO	Food and Agriculture Organization
KF	Kenaf Fiber
OH	Hydroxyl Group
PHA	Polyhydroxyalkanoates
PLA	Polylactic Acid
PMC	Polymer Matrix Composite
PVA	Polyvinyl Alcohol
RTM	Resin Transfer Molding
SA	Succinic Anhydride
SEM	Scanning Electron Microscopy
SMC	Sheet Moulding Compound
TA	Tannic Acid
TGA	Thermogravimetric Analysis
USM	Universiti Sains Malaysia
WA	Water Absorption

LIST OF APPENDICS

Appendix A Calculation for samples preparation

Appendix B Impact strength of samples

Appendix C Water absorption of samples

MENKKAJI KESAN PENYAMBUNG SILANG ASID TANNIC TERHADAP SIFAT-SIFAT SERAT KENAF DENGAN PERIKAT POLIVINIL ALKOHOL

ABSTRAK

Penyelidikan ini bertujuan untuk menentukan kesan komposisi berbeza PVA (30, 40 wt%) dalam kenaf terhadap kekuatan hentaman dan penyerapan air sebagai perikat gentian kenaf (KF) dan untuk mengkaji kesan asid tannic sebagai penghubung silang ke atas sifat-sifat komposit. Walau bagaimanapun, penyerapan lembapan yang ketara dan perubahan dimensi gentian boleh menyebabkan komposit yang dihasilkan membengkak, dan lekatan antara muka yang lemah antara gentian kenaf dan matriks PVA membawa kepada pengurangan dalam parameter kekuatan. Komposit disediakan dengan teknik pengadunan larutan manakala peratusan penyerapan air, kekuatan hentaman, morfologi menggunakan Mikroskopi Optik (OM) dan kestabilan terma komposit dinilai menggunakan Different Scanning Calorimetry (DSC) dan Thermogravimetric analysis (TGA). Peringkat 1 memfokuskan pada sifat 30% berat dan 40% berat PVA dalam komposit KF/PVA. Komposit 70KF/30PVA menyerap lebih sedikit air dan mempunyai kekuatan hentaman yang lebih tinggi daripada 60KF/40PVA. Walau bagaimanapun, kestabilan haba dan keupayaan penghabluran PVA dikurangkan dalam kedua-dua komposit. Dengan kemasukan 15% dan 20% berasaskan PVA penyambung silang asid tannik (TA), peringkat 2 70KF/30PVA telah dipilih untuk menyelidik lebih lanjut sifatnya. Peratusan PVA berdasarkan 15% telah dipilih kerana ia menunjukkan penyerapan air bahan yang sesuai, kekuatan hentaman, dan keupayaan analisis haba.

THE EFFECT OF TANNIC ACID CROSSLINKER ON THE PROPERTIES OF KENAF FIBER AND POLYVINYL ALCOHOL BINDER STUDIES

ABSTRACT

This research aims to determine the effect of different compositions of PVA (30, 40 wt%) in kenaf on impact strength and water absorption as a binder for kenaf fiber (KF) and to examine the effects of tannic acid as crosslinker on properties of the composite. However, significant moisture absorption and fiber dimensional changes can cause produced composites to swell, and poor interfacial adhesion between the kenaf fiber and PVA matrix led to a reduction in the strength parameters. The composites were prepared by solution blending technique while water absorption percentage, impact strength, morphology using Optical Microscopy (OM) and thermal stability of the composites were evaluated using Different Scanning Calorimetry (DSC) and Thermogravimetric analysis (TGA). Stage 1 focuses on the properties of 30 wt % and 40 wt% of PVA in KF/PVA composites. The 70KF/30PVA composites absorbed less water and possessed higher impact strength than 60KF/40PVA. However, the thermal stability and crystallization ability of PVA is reduced in both composites. With the inclusion of 15% and 20% based on PVA of tannic acid (TA) crosslinker, stage 2 70KF/30PVA was selected to further research its properties. The percentage of PVA based on 15% was selected as it showed suitable material's water absorption, impact strength, and thermal analysis capabilities.

CHAPTER 1

INTRODUCTION

1.1 Research Background

The high stiffness and strength characteristics of synthetic fibres like glass, carbon, and aramid make them ideal for use in polymer-based composites. But these fibres have significant shortcomings in terms of their biodegradability, initial processing costs, recyclable nature, energy consumption, machine abrasion, health risks, and other factors (Kabir et al., 2012).

However, due to their appealing qualities, including their light weight, renewability, low density, high specific strength, non-abrasiveness, combustibility, non-toxicity, low cost, and biodegradability, natural fibres have drawn the attention of materials scientists and engineers from all over the world in the last few decades. Additionally, these fibres have great particular qualities like flexibility, impact resistance, and stiffness. These organic materials can be used to create biodegradable composites that can be employed in a variety of applications, including aerospace, building materials, and automobile parts, to help tackle the environmental and ecological issues we are currently facing.

Natural fibre reinforced polymer composites are frequently created by combining natural fibres like kenaf fibre with polymer matrices, which has been the subject of extensive research. In addition to providing numerous environmental benefits, natural fibre bio-composites like kenaf composites promote the growth of industrial crops in Malaysia. In the areas of biomedicine, agriculture, packaging, and other related technical sectors, Bio-composites has several uses. The only drawback to bio-composites is hydrophilicity, or low water or humidity resistance, which can cause early composite disintegration.

Hibiscus Cannabinus L., sometimes known as kenaf, is a warm-season annual fibre that may be grown in a variety of climates (Murphy et al., 2007). Kenaf is known as a cellulosic source with advantages for the environment and the economy that has been discovered to be a significant supply of fibre for composites and other industrial uses (Akil et al., 2011). The fibres of kenaf, which resemble hemp in appearance and have a special combination of long bast and short core fibres, have the potential to be used as filled fibre in thermoset and thermoplastic composites. New opportunities for profitably utilising these natural resources have been made possible by kenaf fibre (Khalil et al., 2013). To increase the mechanical qualities of composite products, however, fibre modification is frequently necessary (Mohd Edeerozey et al., 2007).

PVA is one of the environmentally friendly, biodegradable materials. It is entirely biodegradable, water soluble, and has excellent physical and chemical resistance as well as good film-forming capabilities. Additional additives commonly required to improve properties of PVA-kenaf composites such as crosslinker. According to Chabba et al. (2005), crosslinking agent used to improve the tensile and thermal properties. Teramoto et al. (2001) also reported that the miscibility and mechanical properties of composites were significantly improved after being crosslinked. Previous literature has reported the influence of PVA loading on the water absorption activity of composites for agriculture application. Thus, PVA is a good material for biodegradable mulch film (Tan et al., 2014).

Most of research on PVA/kenaf composites focused on kenaf as filler in PVA matrix to reduce the cost. Research on PVA as binder of kenaf fiber are considered less. In addition, crosslinker such as tannic acid is not well studied in PVA/kenaf compared with crosslinker such as tartaric/succinic acid. The use of PVA as matrix polymeric binders in kenaf fiber would provide biodegradable composites from renewable resources at lower price and reasonable shelf life.

1.2 Problem Statement

In PVA/kenaf composites, a few researchers reported that properties are affected by the composition of the component. According to Abdul Karim *et al.* (2015), when the kenaf content increases, the mechanical qualities such as tensile strength, elongation at break, and compressive strength decrease. In using PVA as a kenaf binder, the ideal concentration of PVA that can bind a specific volume of kenaf must be determined in order to produce reliable qualities. Pang *et al.* (2015) discovered that PVA at a 40 percent concentration is appropriate for usage as snack film.

PVA dissolves readily in water, hence crosslinker is frequently added to improve the mechanical properties of PVA composites. PVA composites have several crosslinker types added to them (Pang *et al.* 2015). Depending on the structure, these crosslinkers have varying degrees of efficacy. Cross-linking can stabilise the structure of a polymer solution. The resulting polymer networks (or gels) behave elastically and, depending on the system, may have good mechanical properties. Polymer networks have the ability to grow by soaking up organic solvents or water. In cross-linked responsive polymers, changes in chain conformation lead to phase transitions that change the macroscopic network's properties include elasticity, swelling behaviour, and turbidity (D. Kuckling *et al.*, 2012).

The fundamental disadvantage of using natural fibres to reinforce synthetic polymers is the interfacial mismatch between the hydrophilic natural fibres and the polymer matrix. Natural fibres made of hydrophilic cellulose typically cause irreversible agglomeration and aggregation in polymer matrices. This may be mainly because more intra- and/or intermolecular hydrogen bonds are being formed between the cellulose molecules. Natural fibres are also hygroscopic in nature as a result of the hydroxyl groups found in the cellulose molecules. The high moisture absorption and dimensional changes of the fibers can result in swelling of the manufactured composites (Ishak *et*

al. 2013). Although both cellulose and PVA have plenty of hydroxyl groups along their molecular chains, direct incorporation of cellulose fibers into PVA matrix cannot produce composites with good mechanical properties (Ozaki et al, 2005). The poor interfacial adhesion between the kenaf fiber and PVA matrix resulted in decreased of strength properties.

Tannic acid is added to improve the mechanical properties, according to Ravindra et al (2020), who claim that the crosslinking process is aided by molecular diffusion across the fiber-matrix interface. Tannic acid's presence is what causes the increase in stiffness and tensile strength (TA). Tannic acid's crosslinking resulted in the formation of a more stable network. The experiment then included succinic acid as a crosslinking agent. Succinic acid (butanedioic acid), which is soluble in water, is found naturally in plant and animal tissues. Due to its non-toxicity and ability to improve the mechanical properties of bio-composite, succinic acid was chosen (Suganthi et al., 2018).

1.3 Objective

The purpose of this study is to explore the potential for tannic acids to act as crosslinking agents in kenaf with PVA polymeric binder. Therefore, the following are the study's objectives:

- I. To determine the effect of different compositions of PVA (20, 30, 40 wt% PVA) in kenaf on density, impact strength and water absorption.
- II. To examine the effects tannic acid as crosslinker on properties of the composite.

1.4 Outline

This dissertation is divided into five chapters. It covers the areas of research interest listed in the Research Objectives section of each chapter:

Chapter 1: Providing background information, a description of the issue, and the dissertation's objective.

Chapter 2: Provides a review of the literature on biodegradable composites and an extensive review of the methods used to introduce the effects of crosslinking agents into composites.

Chapter 3: Explains the experimental techniques used in the fabrication of kenaf fibre/polyvinyl alcohol composites, provides detailed descriptions of the materials and chemicals, and equipment and test procedures, including specifications and parameters used in the study.

Chapter 4: Describe the data and results obtained from the investigation according to its purpose.

Chapter 5: Propose conclusions about current work and ideas for future projects.

CHAPTER 2

LITERATURE REVIEW

2.1 Polymer Composites

Polymer A composite material is a macroscopic fusion of two or more different materials with an obvious interface. However, a typical practical definition of composite materials may be limited to emphasise materials that have a continuous matrix ingredient that combines and gives shape to a variety of stronger, stiffer reinforcement constituents. The combined material has better structural qualities than either constituent material by itself (Miracle & Donaldson, 2008; Das & Pourdeyhimi, 2014). In the composite, the constituent materials retain their distinct identities, but their combination results in qualities and features that are different from those of the constituents.

One of those components creates the matrix, a continuous phase. The addition of reinforcement in the form of fibres or other particles, which generally improves or modifies the matrix's characteristics, is the other important component. The reinforcement creates an intermittent phase that is evenly distributed throughout the matrix. To improve the wetting of the reinforcement by the matrix and to regulate or strengthen the interfacial connection between the reinforcement and the matrix, the reinforcement surface may be chemically treated or coated with a very thin layer (Verma et al., 2012; Madhusudhan & Keerthi Swaroop, 2016). As seen in Figure 2.1, the reinforcement may be made up of fibre, laminar particle, flake, and filled. The surface treatment may also protect the reinforcing surface against environmental deterioration, such as that caused by moisture and chemicals, as well as from undesirable reactions with the matrix at high temperatures (Mitchell, 2004; Zahari, 2017).

Three elements significantly affect the mechanical properties of fiber-reinforced polymer composites: (1) the strength and modulus of the fibre, (2) the strength and modulus of the matrix, and (3) the efficiency of the connection between the fibre and matrix in transferring stress over the interface (S. Saiello et al., 1990). These variables are largely influenced by the materials' microstructure. According to Suherman, while employing low filler content, adding small-sized conductive fillers as secondary filler has the effect of increasing the electrical conductivity of the composite polymer (H. Suherman et al., 2013). The small-sized secondary filler fills the space between the primary fillers, increasing the conductivity networks in the composite polymer matrix and causing the rise in conductivity. In addition, Zhang et al. (2007) reported that for low filler loadings, filler contact and overlap are broken during the system's expansion step that occurs alongside melting. For high filler loadings, however, this effect is negligible.

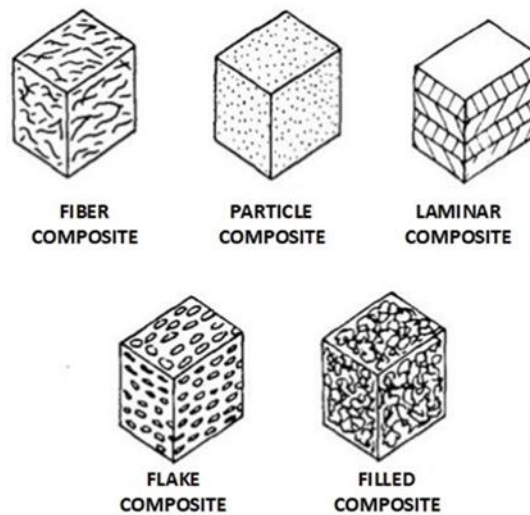


Figure 2.1 Composites reinforcement types (Kulkarni, 2021)

Polymer materials or polymeric matrix composites (PMC) are typically utilised as the composite matrix for fibre reinforced polymers. Due to their various benefits, such as their high strength to mass ratio, excellent longevity, and ease of use in applications, PMC have been widely

used in infrastructure applications (Zaman et al., 2015). Polymer materials or polymeric matrix composites (PMC) are typically utilised as the composite matrix for fibre reinforced polymers. Due to their various benefits, such as their high strength to mass ratio, excellent longevity, and ease of use in applications, PMC have been widely used in infrastructure applications (Zaman et al., 2015).

2.2 Natural fiber

A synthetic fibre with high strength and stiffness is used to make the majority of composite materials on the market today. Carbon and glass fibre stand out among the major synthetic materials used. Given their inexpensive price and superior mechanical characteristics, glass fibres are among the most advantageous (Wambua et al., 2003). There are significant effects on the design of engineering materials as a result of rising understanding of how crucial environmental protection is for human well-being. Because of the enforcement of rules and restrictions by authorities, recyclable and renewable materials are starting to gain appeal among producers.

Because of their advantages over traditional materials, natural fibres as reinforcement have recently attracted a lot of attention from researchers. Simply put, natural fibre is any fibrous plant material created as a result of photosynthesis (Azwa et al., 2013; Cheung et al., 2009). Depending on the context, these fibres may also be referred to as vegetal, biomass, photomass, solar mass, or photosynthetic fibres. They have low density, are completely biodegradable, readily available, renewable, affordable, and are environmentally beneficial (Cheung et al., 2009).

As shown in Figure 2.2, natural fibre can be categorised into a few groups based on where it comes from. The term "plant fibres" also applies to vegetable fibres. Compared to animal fibres, which are made of protein, all plant fibres are composed of cellulose. The additional categorization of plant/vegetable fibres is shown in Figure 2.2 (John and Thomas, 2008; Bismarck et al., 2005).

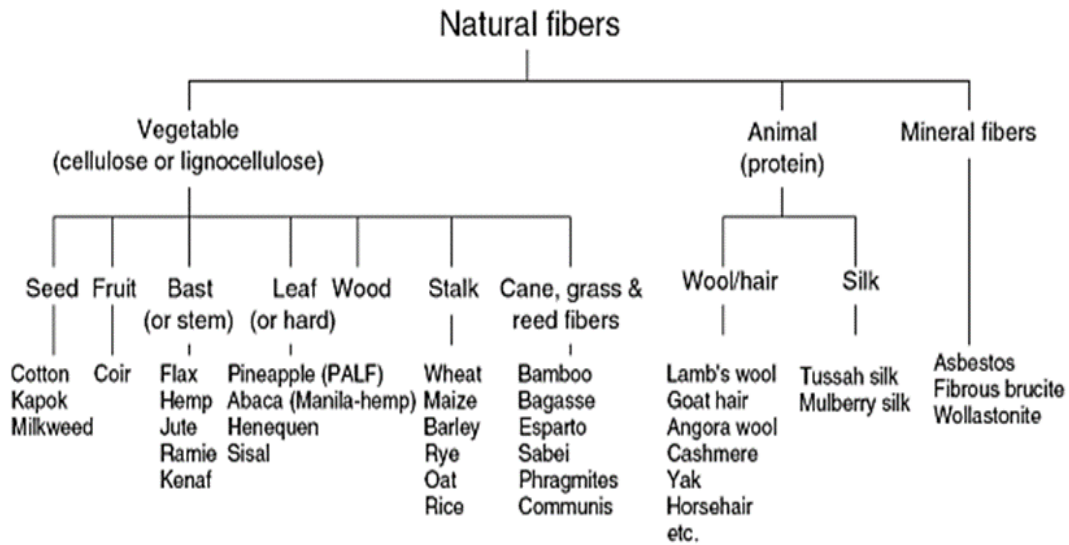


Figure 2.2 Classification of natural fibers (Bismarck et al., 2005)

As a load-bearing component in composite materials, natural fibres have recently made a spectacular comeback. Numerous studies have focused on developing composites with qualities that are similar to those of glass fibre reinforced plastic composites, particularly in the automotive industry (Joshi et al., 2004).

Plant fibres' biodegradability can support a balanced ecosystem, and their high performance and low cost satisfy the commercial needs of industry. The amount of CO₂ emitted when natural fibre reinforced plastics are disposed of in a landfill or burned at the end of their life cycle is equal to the amount assimilated throughout their growth (Girisha et al., 2012). Table 2.1 lists the benefits and drawbacks of natural fibres.

Table 2.1 Advantages and disadvantages of natural fibres (Alkbir et al., 2016; Jawaid & Abdul Khalil, 2011)

Advantages	Disadvantages
Low specific weight results in a higher specific strength	Lower strength especially impact strength
Renewable resources and requires little energy	Variable quality, especially impact strength
Production with low investment at low cost	Poor moisture resistance, which causes swelling of the fibres
Friendly processing, no tools and no skin irritation	Restricted maximum processing temperature
High electrical resistance	Lower durability

2.2.1 Kenaf fiber

Kenaf is one of the most popular natural fibres. Originally from Asia and Africa, kenaf is an annual crop that resembles a cane (Figure 2.3). In three months after the seeds are sown, kenaf can develop under a variety of meteorological circumstances to a height of more than 3 m and a base diameter of 3 to 5 cm, making it a well-known cellulose source with economic and ecological advantages. The stem is straight and unbranched, and it is made up of a core and an outer layer (bast). Kenaf stems are typically rounded and covered with thorns that range in size from small to huge, depending on the variety (Nishino, 2004; Nishino et al., 2003). In kenaf, there are two different fibre types: long fibres in the cortical/outer layer and short fibres in the lignous/core zone. Elementary fibres made of kenaf are polygonal and short (1.5–6 mm).

Their surface is uneven and striated. The lumen's thickness fluctuates significantly throughout the cell, occasionally disappearing entirely. Fibers from kenaf are coarse, brittle, and challenging to process. When wet, they just marginally lose some of their breaking strength, which is comparable to that of low-grade jute (Bismarck et al., 2005). An important instrument in the fight against global warming, kenaf has the largest plant-level carbon dioxide absorption (1 tonne of kenaf absorbs 1.5 tonnes of ambient CO₂). In addition, the photosynthetic rate of kenaf is substantially higher than that of traditional trees. Additionally, it's thought that kenaf can take up nitrogen and phosphorus from waste water and soil (Nishino, 2004; Nishino et al., 2003; Pan et al., 2007).

According to a study by Rouison et al. (2004), kenaf has been actively grown in recent years for two key reasons. The nitrogen and phosphorus in the soil are absorbed by kenaf. The typical nitrogen and phosphorus absorption rates for kenaf are 0.81 g/m² and 0.11 g/m², respectively, and these rates are significantly greater than those under various types of stress. Carbon dioxide is accumulated quite quickly in kenaf. Kenaf photosynthesis occurs at a pace that is far higher than that of a typical tree.

Paper, textiles, and composite materials are just a few of the potential uses for the kenaf entire stalk and outer bast fibres. Regarding environmental friendliness, the utilisation of kenaf fibres is also extremely important (Nishino et al., 2003). Rope, twine, and sackcloth were traditionally made from kenaf fibres. The use of kenaf products is now finding many new uses, such as in paper goods, building materials, absorbents, and feed and bedding for livestock. It is certain that further options will also become available. These alternatives will address everything from fundamental agricultural production techniques to the commercialization of kenaf goods

(Bismarck et al., 2005). Kenaf fibres are intended to be used as polymer reinforcement fibres (Pan et al., 2007; Nishino et al., 2003).

Currently, only a very little amount of kenaf is utilised in the manufacture of paper. It has been investigated how to employ bast fibres in a variety of ways, including the production of woven and non-woven textiles, industrial socks that can absorb oil spills, and more. According to numerous studies conducted by various researchers, kenaf bast fibre has a superior flexural strength that, when paired with its exceptional tensile strength, makes it the material of choice for a variety of extruded, moulded, moulded, and non-woven goods. The kenaf core fibres, meanwhile, are utilised in a variety of products, including potting materials, summer fodder, and animal bedding (Ramaswamy et al., 2003; Aji et al., 2009).



(a)



(b)



(c)

Figure 2.3 Kenaf fiber with height 3 to 5 cm (b) Core kenaf fiber (c) Bast kenaf fiber

Kenaf is also renowned for its excellent mechanical qualities, as well as its resistance to fatigue and corrosion (Maizatul et al. 2013). Due to the widespread use of kenaf in Malaysian industries like furniture, sports and recreation, food packaging, and automotive components, kenaf plantations generate a significant amount of biomass (Meon et al. 2012).

2.3 Biodegradable polymer

Traditional commodity polymers like polypropylene, polyethylene, polystyrene, and polyvinyl chloride have established markets after decades of research and development. However, they are now posing a threat to civilization due to their inability to biodegrade, as well as the fact that they increase pollution from burning and emissions from the usage of plastics (John and Thomas, 2008). The usage of non-biodegradable materials harms the environment severely all over the world. Moreover, the use of biodegradable polymers provides a remedy for this issue that faces humanity.

A polymer that experiences microbially driven chain scission that results in photodegradation, oxidation, and hydrolysis and has the potential to change the polymer's characteristics and/or microstructure can be said to be biodegradable. Another definition suggests

that biodegradable polymers are able to undergo breakdown mostly through enzymatic action of microbes to carbon dioxide, methane, inorganic chemicals, or biomass in a predetermined amount of time (Kolybaba et al., 2003).

The two primary categories of biodegradable materials are those that are made of natural materials and those that are made of synthetic materials (Figure 2.4). Polymers that arise naturally during the growth cycles of all organisms are known as natural biodegradable polymers or biopolymers (Chandra and Rustgi, 1998). Polymers having hydrolysable backbones or polymers that are susceptible to photodegradation typically make up synthetic biodegradable polymers. Aliphatic polyesters, polycaprolactone, polyamides, polyurethanes, and polyureas, as well as polyanhydrides and poly (amideenamine)s, are among them (Chandra and Rustgi, 1998). The interesting thing is that some synthetic biodegradable polymers, including polyvinyl alcohol (PVA), have carbon backbones. Because they are often resistant to hydrolysis, certain polymers (such as vinyl polymers) need to be biodegraded by an oxidation process. Most biodegradable vinyl polymers contain a functional group that is easily oxidizable, and catalysts are added to encourage their oxidation, photo oxidation, or both.

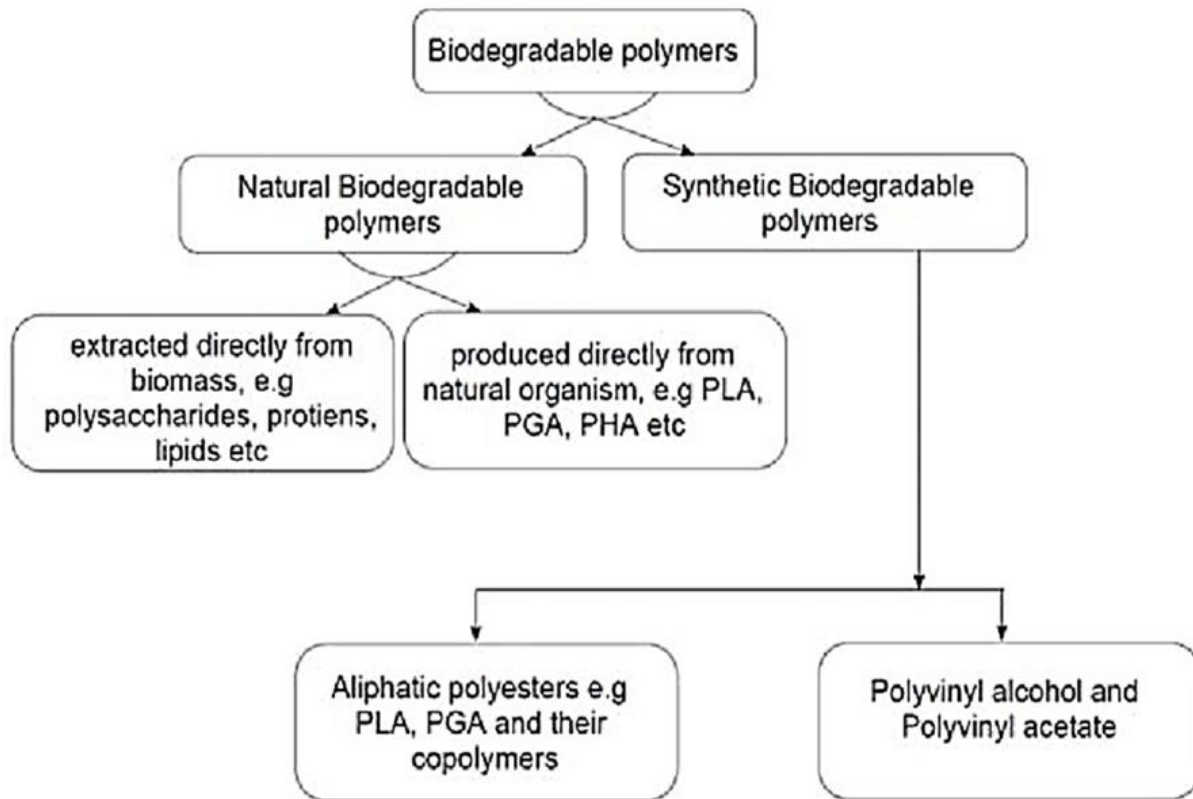


Figure 2.4 Classification of biodegradable polymers (Raghvendra Kumar Mishra, 2015)

In order to create a novel biopolymer with a specific purpose, it is also interesting to combine two or more biodegradable polymers. For instance, mixing starch-based or thermoplastic polymers with other biodegradable polymers like poly (lactic acid), poly (vinyl alcohol), or poly (caprolactone) can help starch overcome its brittle and water-sensitive nature (Chiou et al., 2005). Fillers are frequently mixed with biodegradable polymers to change or lower the cost of the material or modify its qualities. Inorganic compounds like clay, silica, and chalk that are reduced to a fine powder are frequently used as fillers. The presence of the filler alters the material's mechanical properties.

The use of inorganic mineral fillers including talc, calcium carbonate, kaolin, and mica and their effects on the biodegradability of these polymers have also been studied. Recently, a few

researchers have focused on the use of organic natural fillers as reinforcement for biodegradable polymers. Since the properties of particulate polymer composites may differ significantly depending on the polymer additives, manufacturing processes, and test methodologies, it is often challenging to compare separately reported results. All other parameters were kept constant in order to assess the impact of different particle fillers (talc, calcium carbonate, kaolinite, and mica) on the most important mechanical properties of various commercially available biodegradable polymers (PBS, PBSA, PHBH, and PBAT). The effect of particle addition on these polymers' capacity to degrade biologically is also looked at. The summary that results paints a clear picture of how particle fillers can be utilised to modify the mechanical properties of biodegradable polymers to meet the needs of various plastic application (Post et al., 2021).

2.3.1 Poly(vinyl) Alcohol

PVA, or polyvinyl alcohol, is not monomer-based; instead, it is based on a repeating structural unit (Stevens, 2002). This is so that the functional acetate groups can be alkaline alcoholized after the vinyl acetate free radical polymerization, which is the basis for polymerization, takes occurred (Chiellini et al., 2003). PVA has trouble being created by its own monomer, in contrast to other polymers, because of the constraint brought on by the unstable vinyl's propensity to form a stable acetaldehyde tautomer. Figure 2.5 shows the PVA's molecular structure schematically as well as the process for manufacturing PVA in an industrial setting.

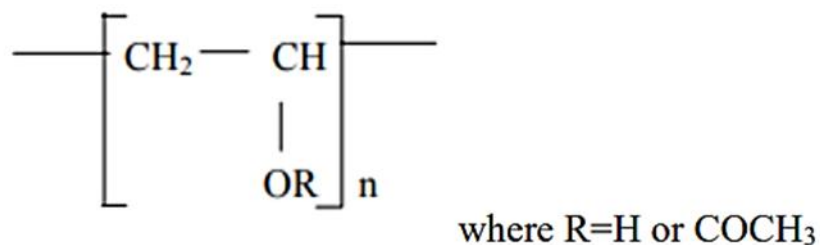


Figure 2.5 The chemical structure of polyvinyl alcohol (PVA)

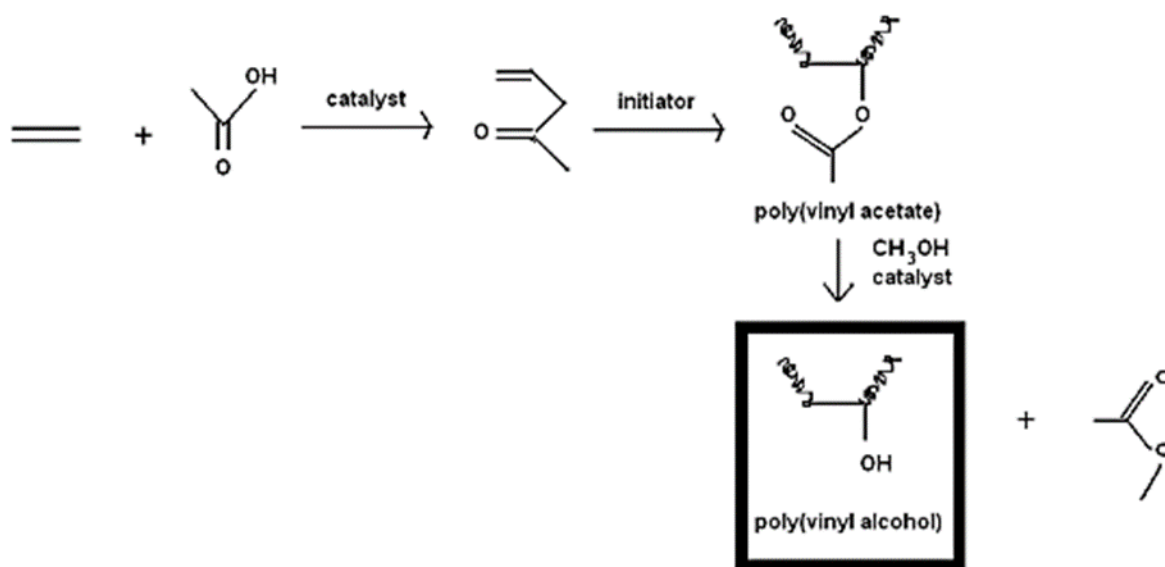


Figure 2.6 Manufacturing route to PVA (Rudnik, 2008)

PVA is a synthetic polymer with exceptional qualities including water solubility, good barrier capabilities to oxygen and oil, good optical and tensile properties, good thermal properties, resistance to organic solvents and oils, non-toxicity, and under some circumstances biodegradability (DeMerlis and Schoneker, 2003; Siddaramaiah et al., 2004; Li et al., 2005, Ramaraj, 2007). PVA can be made using the solution casting method since, according to Siddaramaiah et al. (2004), it is also a water processable polymer. PVA's capacity to create films is

another distinctive quality. As a result, PVA's remarkable qualities have been used in a variety of applications, including dip coating, adhesive, and solution casting film (Zaikov and Lomakin, 1997; El-Shinawy et al., 1998; Seldarik et al., 2007; Ramaraj, 2007).

There is a distinct disadvantage in that there are a limited number of biodegradable polymers that have both the stiffness and impact resistance required for these applications (Barron et al., 2020). This is one of the reasons why these biodegradable polymers are generally not regarded as appropriate alternatives to conventional non-biodegradable plastics. Also important to note is that these polymers are now not widely accepted by industry due to the high costs of production. Using polymer extrusion to blend several biodegradable polymers might be a common method for obtaining relevant polymer characteristics. In order to create plastic formulations with mechanical qualities similar to those of polypropylene (PP), for instance, numerous studies on PBS/PLA blended composites were conducted (Bhatia et al., 2007). Despite the fact that this technology enables the modification of mechanical properties, the biodegradable nature of these immiscible blends will still be determined by the polymer with the lowest intrinsic biodegradation rate (Yang et al., 2015). Another viable approach to improve the mechanical properties is to add fillers to the polymer matrix phase to produce particulate polymer composites (Zhong et al., 2015).

The qualities of the materials were improved by choosing polyvinyl alcohol (PVA) as the blending component with the cassava skin. PVA is the vinyl polymer that biodegrades the quickest (Chandra & Rustgi 1998). This particular class of biodegradable and water-soluble polymers is employed in the processing of textiles, frequently for nylon, and in the creation of fibre as a raw material for PVA fibre (Lin & Ku 2008). The lack of filler in the compound, which prevents flexibility and continuity in the matrix chain, was presumably the cause of the decrease. Without the addition of reinforcement or filler, samples typically exhibit poor physical, high water

absorption, and mechanical qualities (Preechawong et al. 2004). However, the presence of filler component allows the composite to function properly, improving chain flexibility and encouraging PVA ductility. Lower interactions between polymer chains could result from more filler material (Lin & Ku 2008).

Despite the fact that PVA has many advantages, some of its drawbacks include poor water vapour/gas barrier properties and adverse thermal stability, which restrict the amount of time it may be utilised as bioplastics. These limitations have been overcome by researchers using a variety of techniques, including as the development of composites, polymer blends, and nanocomposites with high aspect ratio organic and inorganic fillers. Graphene's outstanding mechanical, electrical, thermal, and optical capabilities have sparked a growing amount of research interest in recent years (Cardinali et al., 2012). It has proven to have enormous promise as fillers in polymer nanocomposite. Often, the properties of polymer nanocomposite are altered as a result of the use of graphene in the manufacturing of polymer materials. The material characteristics can be noticeably improved even at very low graphene concentrations in a polymer matrix. The properties of graphene itself provide an explanation for this. This is evident when a polymer's properties are contrasted with those of a polymer nanocomposite that comprises graphene and nano-filler. Furthermore, it has shown improved mechanical and electrical abilities in comparison to Nano clay and other carbon filler polymer nanocomposites (Chaharmahali et al., 2014).

PVA is the only synthetic polymer with carbon-carbon bonds in its backbone that exhibits biodegradability. This is due to the presence of hydroxyl groups on alternate carbon atoms, which leads to the enzymatic oxidation of hydroxyl groups from carbonyl groups in the polymer backbone, followed by the hydrolysis of two carbonyl groups, which causes polymer chain cleavage and a decrease in the molecular weight of PVA (Kale et al., 2007). PVA's

biodegradability, however, is inferior to that of other biodegradable polymers as poly (lactic acid) and poly (caprolactone) (Ishigaki et al., 1999). Pure PVA degrades quite slowly, especially in anaerobic environments (Pseja et al., 2006), and the pace of degrading greatly depends on the remaining acetate groups (Corti et al., 2002). However, Lenz (1993) observed that PVA with an average molecular weight as high as might be entirely degraded by soil bacteria, especially by Pseudomonads.

2.3.2 Kenaf fiber/Poly(vinyl) alcohol composites

There are several benefits to using kenaf fibre in polymer composites, but a significant disadvantage is that the kenaf and the polymer may not be compatible. In general, polymers are hydrophobic and incompatible with hydrophilic natural fibres. The incompatibility of kenaf fibres with polymer systems may result in composites with subpar qualities. Additionally, the high hydrophilicity of natural fibres frequently results in excessive moisture absorption in polymer composites (Ismail et al. 2010; Noranizan and Ahmad, 2012; Tan et al. 2014). The interactions between natural fibres and the polymer matrix are improved by chemical changes (Ismail et al. 2010). Natural fiber/polymer composites have undergone numerous chemical changes (Malkapuram et al. 2009; Pang and Ismail 2014).

The kenaf fibre (KF)/PVA composites were made and investigated for agricultural applications (Tan et al., 2014). Upon immersion in water, KF/PVA absorbs more water right away. This is because no cross-linking agent was used to the KF/PVA composite to offset PVA's tendency to dissolve in water. The composites are totally hydrophilic, with the KF absorbing the majority of the water while the PVA dissolves more slowly. The application of PVA composites is constrained by the disintegration issue.

The smooth interfacial connection between kenaf and PVA was visible in the kenaf/PVA composites. The strong bond suggested that the molecules of the kenaf/PVA composites may produce additional entanglement because the interfacial bond mostly depends on the number of entangled chains forming connections across the interface (Tan et al., 2014).

2.4 Crosslinking agent

PVA was subjected to a variety of further modifications by functionalization and crosslinking, which improved its thermal and mechanical properties and made it suitable for use in pervaporation systems, biomedical applications, medication delivery, and water soluble photoresists. Independent reports are available in the published literature regarding the properties of PVA membranes that have been crosslinked employing aliphatic and aromatic crosslinkers. To the best of our knowledge, no comparative study conducted in the identical experimental conditions has been done to confirm the precise impact of the geometry and size of the crosslinking agent on the properties of PVA membrane (Sonker et al., 2017).

Due to intermolecular covalent and hydrogen bonds that aid to block free -OH groups, crosslinkers enhance mechanical characteristics and water resistance. Carboxyl groups from acids and hydroxyl groups from PVA are esterified in order to create an ester bridge-group network during crosslinking. Increases in crosslinker concentration and crosslinking time successfully reduce the swelling percentage of PVA, which dissolves quickly in water. The PVA films' ability to absorb large amounts of water molecules is limited by the chains' limited mobility in regard to one another once they have been crosslinked. As a result, the incoming water is unable to make room for itself. In order to control water absorption, crosslinking has two effects: it reduces the number of hydroxyl groups while also limiting chain mobility by covalently connecting them.

Both of them result in less water being absorbed, which reduces swelling. Additionally, the diacid molecule's carbon chain repels water, which further lessens swelling.

A crosslinking agent can be used to link together the functional groups of each polymer in a macromolecular network, which will enhance the network's mechanical properties for a variety of applications. In scaffold technology, crosslinking is crucial for enhancing network bonding and the biomechanical properties of the scaffolds. As shown in Figure 2.7, a crosslink can be created between two functional groups of a polymer chain via either covalent or non-covalent bonding. This type of functional group bonding between polymer chains can regulate the activity, stability, and complex structural assembly of proteins (Reddy et al., 2015). The ideal crosslinker would have a few key characteristics, including enhanced mechanical properties, increased enzymatic resistance, non-toxic behaviour, active cell-material interactions, decreased gas penetration, and the ability to maintain shape memory (Ruini et al., 2015).

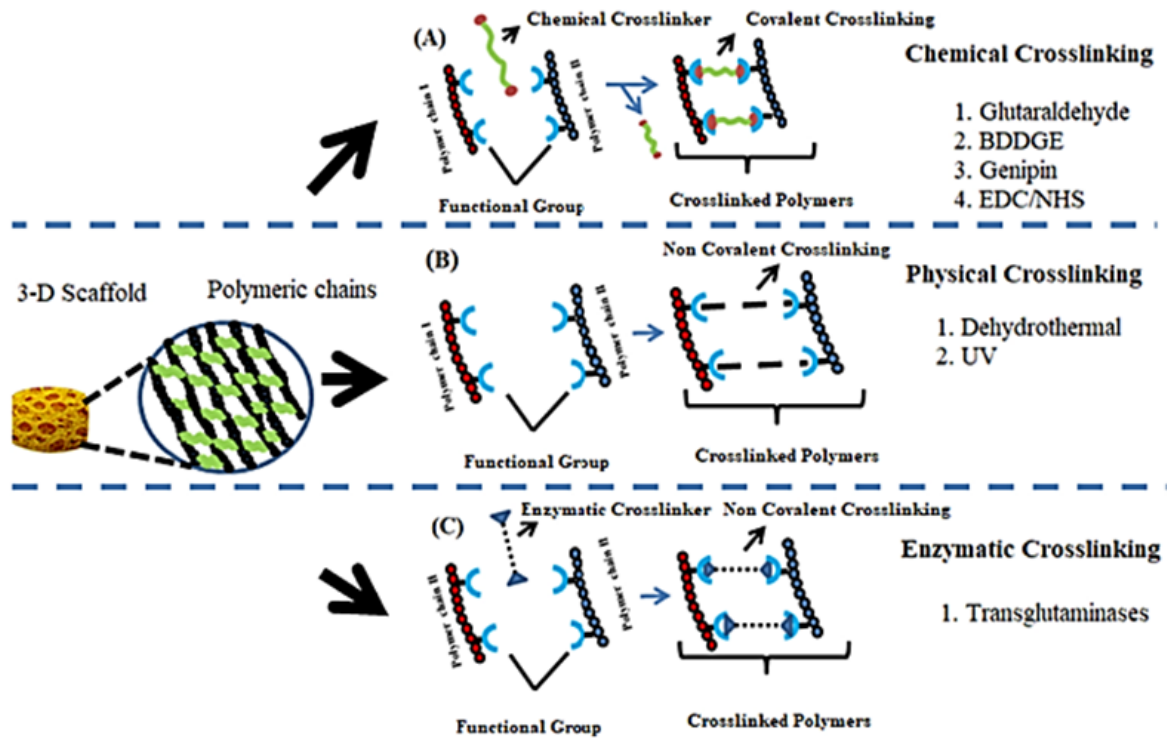


Figure 2.7 Schematic illustration of different cross-linkers used in bone tissue engineering, (A): chemical crosslinking, (B) physical crosslinking, (C): enzymatic cross-linking.

A common method to create supramolecular materials involves the physical crosslinking of functional molecules into 3D networks in a non-covalent manner. This method typically involves the use of polymers or monomers to supply the functional groups that enable the creation of dynamic supramolecular interactions. However, the majority of water-soluble polymers lack certain desirable functional groups in general (M. Cencer et al., 2015). The necessity of physical crosslinking is typically satisfied by a laborious post-functionalization technique that involves covalently attaching the beneficial moieties onto polymer chains. As a result, scientists began looking for natural building blocks, which produced a number of supramolecular materials with benefits such as easy fabrication, robustness, and low cost (Shutav et al., 2005). Numerous studies

have been done on various crosslinker kinds, and they have found that the efficiency of each type vary depending on the type of polymer and crosslinker used.

2.4.1 Tannic acid

Tannic acid (TA) is a naturally occurring polyphenol that appears in a wide range of plants as a colourless to pale yellow solid with an astringent flavour. TA could be extracted from plants, such as plant galls, the leaves of some sumacs, and the bark of trees like oak, chestnut, hemlock, and mangrove (King and Young et al., 1999). After cellulose, hemicellulose, and lignin, TA is the most prevalent natural chemical with a variety of sources, acting as a vital commercial raw material and having historically been used as a tanning agent in leather, coating, adhesive, surgical, pharmaceutical, and food industry uses (Zhao et al., 2018). Numerous catechol and pyrogallol aromatic ring structures are present in the complex polyphenol compound that makes up tannic acid, which allows for the listing of a number of special chemical characteristics. I The solubility of TA in water: TA has a solubility of 300 g L⁻¹ in water, making it appropriate for environmentally friendly chemical modification. Additionally, the TA aqueous solution is air-stable and can be kept in a lab for over 30 days (Moghaddam et al., 2014; Zhu et al., 2019) (ii) The biocompatibility of TA: TA is a naturally occurring polyphenol that is widely accessible, inexpensive, environmentally safe, and generally biocompatible (Wang et al., 2017).

In addition, TA is hydrolysable and biodegradable under specific hydrolytic circumstances, where the disruption of the ester connection between two pyrogallol groups is a key factor (Hagerman et al., 1998) (iii) A TA-derived material has greater skin affinity and underwater adhesion capacity because to the many intermolecular interactions between TA and different nucleophiles (amide bonds, thiols, and amines) on a protein-rich tissue surface (Du et al., 2016) (iv) The metal-chelating capabilities of TA: Through considerable functional metal chelation,