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Intitulée

Elaboration et caractérisation des composites à base de Poly (L-Lactide) et des fibres issues de la biomasse végétale

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Elaboration and characterization of composites based on poly (lactic acid) and biomass fibers

Soutenue le : 09/02/2023   Devant le Jury composé de :

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Dedication

I would like to dedicate my work to several people who have meant and continue to mean so much to me.

First and foremost, I would like to dedicate this work to my parents Ahcene and INAL Zineb who taught me the value of hard work, patience and will to pursue my dreams.

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Last but not least, my deepest gratitude goes, above all, to my beloved parents, brothers and sister; their love goes beyond borders. They have been a constant source of inspiration and support in this long, exciting and worthwhile journey.

Abstract

The aim of this research is to prepare, characterize and evaluate the thermo-physical properties of hybrid bio-composites where Opuntia Ficus Indica flour (OFI-F) as an organic filler and talc as inorganic filler were used as reinforcing agents into PLA matrix, where the matrix is a polymer derived from renewable resources (PLA polymer).

Bio-composites exhibit properties like many petrochemical-based polymers composites. They could be employed in the automobile and decking sector as well as biodegradable packaging.

However, their broad application has been limited because of their expensive cost and poor mechanical and thermal properties. Before bio-composites can be widely employed, there is a number of technological challenges that must be addressed.

In this research, Polylactic acid (PLA) bio-composites, reinforced with organic fillers (OFI- F) and mineral fillers (talc), were investigated. The thermal properties of the bio-composites were studied by means of thermogravimetric analysis (TGA) while the characterization and morphology of the bio-composites were studied by Wide-angle X-ray scattering (WAXS) and Scanning Electron Microscope (SEM).

PLA/Talc/Opuntia Ficus Indica flour (OFI-F) bio-composites were developed by mixing PLA with talc and OFI Flour in different ratios, using a melt compounding process. PLA/Talc (90/10), PLA/OFI-F (90/10), PLA/Talc/ OFI-F (80/10/10).

All TGA curves are sigmoidal in shape whereas the DTG curves show only one peak. This indicates that thermal degradation occurred in a single step for all bio-composites.

The thermal degradation kinetics are studied using non-isothermal multiple heating rate techniques. As a result, model-free methods such as Flynn Wall Ozawa (FWO) and Kissinger Akahira Sunose (KAS) are utilized as well as model-fitting methods such as Kissinger method and Coats-Redfern technique.

The results indicate that compared to neat PLA, the activation energy (Ea) of PLA/Talc bio-composites increases from 157.45 to 160.86 KJ/mol according to the FWO method. The talc distribution into the PLA matrix is homogeneous as observed by SEM. Thermal degradation PLA /Talc bio-composites show compared to neat PLA, that talc particles at 10 wt % into the PLA matrix have a minor impact on the thermal stability of bio-composites.

However, after the addition of OFI-F into the PLA matrix, all thermograms shifted to lower temperatures values. The addition of OFI-F into the PLA matrix reduces the Ea from 157.45 to 151.02 KJ/mol according to the FWO method. The decrease in Ea can be due to the incompatibility between OFI-F and PLA matrix as observed by SEM.

When talc is present with the OFI-F mixture, the activation energy of the bio-composites decreases from 157.45 to is 143.40 KJ/mol according to the FWO method. This result demonstrates that the PLA/Talc/OFI-F hybrid bio-composites have a lower thermal stability; the voids adjacent shown by SEM between OFI-F and talc particles mean that the adhesion between the fillers and the polymer matrix needs to be improved.

In Kissinger method the addition of talc marginally boosts the activation energy (142.33 KJ/mol) similar to what FWO method found.

The Coats-Redfern (C-R) approach yields higher activation energies than the FWO and KAS methods; nonetheless, the C-R method follows the same pattern as the FWO and KAS methods.

Furthermore, in this work, the proposed degradation process of bio-composites utilizing Coats-Redfern and Criado techniques confirms that the F2 reaction model is the most accurate degradation mechanism.

Key words: PLA, bio-composite, biodegradable, talc, activation energy, kinetics, thermal degradation.

Résumé

Le but de ce travail était de préparer, caractériser et évaluer les propriétés thermo-physiques de bio-composites hybrides utilisant la farine des feuilles de figue de barbarie (Opuntia Ficus Indica Flour (OFI-F)) comme charge organique et les particules de talc comme charge inorganique pour renforcement de la matrice PLA où la matrice issue de ressources renouvelables.

Les bio-composites ont des propriétés similaires à de nombreux composites polymères de l'industrie pétrochimique. Ils peuvent être utilisés dans les automobiles et les emballages biodégradables.

Cependant, leur large application était limitée à cause de leur coût élevé et à leurs mauvaises propriétés mécaniques et thermiques. Avant que les bio-composites puisent être largement utilisées, un certain nombre de défis doivent être relevés.

Cette étude a porté sur un bio-composite d'acide poly-lactique (PLA) enrichi de charges organiques (farine de OFI) et de charges minérales (talc). Les propriétés thermiques du bio-composite ont été étudiées par analyse thermogravimétrique (TGA), et la caractérisation et la morphologie du bio-composites ont été étudiées par diffusion des rayons X aux grands angles (WAXS) et microscopie électronique à balayage (SEM).

Le bio-composite PLA / Talc / (OFI-F) a été développé en mélangeant du PLA avec du talc et de la farine OFI dans divers ratios à l'aide d'un procédé de mélange à l'état fondu. PLA/Talc (90/10), PLA/OFI-F (90/10), PLA/Talc/OFI-F (80/10/10).

Toutes les courbes TGA sont de forme sigmoïde, et la courbe de dérivé analyse thermogravimétrique (DTG) ne montre qu'un seul pic. Cela indique que la dégradation thermique s'est produite en une seule étape pour tous les bio-composites.

Les cinétiques de dégradation thermique sont étudiées à l'aide de techniques non isothermes à de vitesses de chauffage multiples. En conséquence, des méthodes model-free telles que Flynn Wall Ozawa (FWO) et Kissinger Akahira Sunose (KAS) sont utilisées, ainsi que des méthodes model-fitting telles que la méthode Kissinger et la technique de Coats-Redfern.

Les résultats indiquent que par rapport au PLA pur, l'énergie d'activation (Ea) des bio-composites PLA/Talc (PLA/T) augmente de 157,45 à 160,86 KJ/mol selon la méthode FWO. La distribution du talc dans la matrice PLA est homogène comme observé par MEB. Les résultats de dégradation thermique sur les bio-composites par rapport au PLA pur montrent que les particules de talc à 10 % en poids dans la matrice de PLA ont un impact mineur sur la stabilité thermique des bio-composites.

Cependant, après l'ajout d'OFI-F dans la matrice PLA, tous les thermogrammes sont passés à des valeurs de températures plus basses. L'ajout d'OFI-F dans la matrice PLA réduit l'énergie d'activation de 157,45 à 151,02 KJ/mol selon la méthode FWO. La diminution de l'Ea peut être due à l'incompatibilité entre la matrice PLA et OFI-F t-elle qu'observée par MEB.

Lorsque le mélange OFI-F est présent avec le talc, l'énergie d'activation des bio-composites passe de 157,45 à 143,40 KJ/mol selon la méthode FWO. Ce résultat indique que les bio-composites hybrides PLA/T/OFI-F ont une stabilité thermique plus faible,

les vides adjacents montrés au MEB entre l'OFI-F et les particules de talc signifient que l'adhésion entre les charges et la matrice polymère doit être améliorée.

Dans la méthode Kissinger, l'ajout de talc augmente légèrement l'énergie d'activation (142,33 KJ/mol) similaire à ce qu'observés par la méthode FWO.

L'approche Coats-Redfern (C-R) donne des énergies d'activation plus élevées que les méthodes FWO et KAS ; néanmoins, la méthode C-R suit le même schéma que les méthodes FWO et KAS, cela indique la validité des résultats et la possibilité d'utiliser la méthode.

De plus, dans ce travail, le processus de dégradation des bio-composites utilisant les techniques de Coats-Redfern et Criado confirme que le modèle de réaction F2 est le mécanisme de dégradation le plus précis.

Mots clés : PLA, bio-composite, biodégradable, talc, énergie d'activation, cinétique, dégradation thermique.

ملخص الأطروحة

الهدف من هذا البحث هو إعداد وتقييم الخصائص الحرارية لمركب طبيعي هجين غير مؤذي للبيئة حيث تم استخدام طحين مستخرج من ورق التين الشوكي كمادة عضوية والطالك كمادة معدنية لتعزيز مصفوفة بولمير متعدد حمض اللبنيك المشتق من موارد طبيعية.

تملك هذه المركبات الطبيعية خصائص مثل العديد من مركبات البوليمرات المستخرجة من المواد البتروكيميائية حيث يمكن استخدامها في قطاعات عدة كقطاع السيارات، التعبئة والتغليف القابلان للتحلل الطبيعي في البيئة ومع ذلك فإن تطبيق هذه المركبات الطبيعية على نطاق واسع كان محدودًا بسبب تكلفتها الباهظة وضعف جودة خصائصها الميكانيكية والحرارية وعليه قبل أن يتم استخدام هذه المركبات بشكل كبير هناك عدة تحديات يجب معالجتها.

تمت دراسة الخصائص الحرارية لهذه المركبات الطبيعية عن طريق التحليل الحراري الوزني كما تمت دراسة توصيفها وتشكلها بواسطة جهاز تشتيت الأشعة السينية بزاوية واسعة وجهازميكروسكوب للمسح الإلكتروني.

تم تحضير المركبات الطبيعية لعديد حمض اللبنيك/طالك/ طحين ورق التين الشوكي عن طريق خلط عديد حمض اللبنيك مع الطالك ودقيق التين الشوكي بنسب مختلفة باستخدام عملية التسخين حتى الذوبان . عديد حمض اللبنيك/طالك (10/90)، عديد حمض اللبنيك ودقيق التين الشوكي(10/90), عديد حمض اللبنيك/طالك/ طحين ورق التين الشوكي (10/10/80).

جميع منحنيات التحليل الحراري الوزني أخذت شكلا سينيا، وهذا دلالة على أن التدهور الحراري حدث في خطوة واحدة لجميع المركبات الطبيعية.

تشير النتائج بالمقارنة مع عديد حمض اللبنيك النقي، أن طاقة التنشيط للمركبات الطبيعية عديد حمض اللبنيك/طالك تزداد من 157.45 إلى 160.86 كيلوجول / مول وفقًا لطريقة فلين وول, كما تظهر الصورة الملاحظة بواسطة الميكرو سكوب ان توزيع الطالك في مصفوفة متعدد حمض اللبنيك موزع بطريقة جد متجانسة .

تظهر نتائج التحلل الحراري للمركبات الطبيعية مقارنةً بـ عديد حمض اللبنيك النقي أن جزيئات الطالك بنسبة 10٪ من الوزن في مصفوفة عديد حمض اللبنيك لها تأثير طفيف على الاستقرار الحراري للمركبات الطبيعية.

بعد إضافة طحين ورق التين الشوكي إلى مصفوفة عديد حمض اللبنيك ، تحولت جميع المقاييس الحرارية إلى قيم درجات حرارة منخفضة بالمقارنة مع عديد حمض اللبنيك النقي. تؤدي إضافة طحين ورق التين الشوكي إلى مصفوفة عديد

حمض اللبنيك إلى تقليل طاقة التنشيط من 157.45 إلى 151.02 كيلوجول / مول وفقًا لطريقة فلين وول، إذ يعود هذا الانخفاض في طاقة التنشيط لعدم التوافق بين عديد حمض اللبنيك طحين ورق التين الشوكي كما لوحظ بواسطة ميكروسكوب المسح الإلكتروني.

عند خلط طحين ورق التين الشوكي الطالك معا في مصفوفة حمض اللبنيك لوحظ أيضا انخفاظ في طاقة التنشيط للمركبات الطبيعية من 157.45 إلى 143.40 كيلوجول / مول وفقًا لطريقة فلين وول , تشير هذه النتيجة إلى أن المركبات الطبيعية الهجينة لعديد حمض اللبنيك/طالك/ طحين ورق التين الشوكي لها ثبات حراري أقل من باقي المركبات، والفراغات المجاورة التي تظهر بواسطة جهاز المسح الإلكتروني بين جزيئات طالك و طحين ورق التين الشوكي تعني أن الالتصاق بين الحشوات ومصفوفة البوليمر يحتاج إلى تحسين اكثر.

في طريقة كيسنجر ، تعمل إضافة جزيئات الطالك بشكل هامشي على تعزيز طاقة التنشيط (142.33 كيلوجول / مول) بشكل مشابه لما وجد بواسطة طريقة فلين وول.

ينتج عن نهج طريقة كوت رادفارن طاقات تنشيط أعلى من طرق فلين وول و كيسنجر أكهيرا سنوز ومع ذلك فإن قيم نتائج طريقة كوت رادفارن تتبع في تغيرها نفس نمط طريقتي فلين وول و كيسنجر أكهيرا سنوزمما يؤكد صحة الطريقة والنتائج المتحصل عليها.

علاوة على ذلك، في هذا العمل، تم التأكد باستخدام طريقة كل من كوت رادفارن وكريادو أن عملية التحلل الطبيعي للمركبات الطبيعية تتبع نموذج تفاعل F2 وهو الأكثر دقة في التعبير على آلية التحلل الطبيبعي.

الكلمات المفتاحية :مركب عضوي طبيعي، عديد حمض اللبنيك، قابلية للتحلل الطبيعي، طاقة التنشيط، التدهور الحراري، الاستقرار الحراري.

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Abbreviations and symbols

PLA	Poly (Lactic Acid)
ROP	Ring Opening Polymerization
Mw	Molecular Weight (g/mol)
PET	Polyethylene Terephthalate
PVC	Polyvinyl Chloride
HDT	Heat Deflection Temperature (K)
V_f	Volume Fraction
TGA	Thermogravimetry Analysis
DTG	Derivate Thermogravimetry
WAXS	Wide Angle X-ray Scattering
SEM	Scanning Electron Microscopy
OFI-F	Opuntia Ficus Indica Flour
T_{max}	Maximum degradation temperature (K)
T_p	Peak degradation temperature (K)
T_g	Glass transition temperature (K)
T_{onset} or T_o	Initial degradation temperature (K)
T_{offset} or T_{end}	Final degradation temperature (K)
W_o	Initial weight of the sample (g)
W_t	Weight of the sample at time (t)

Ea	Activation Energy (KJ/mol)
β	Heating rate (K/min)
k	Rate constant
A	Pre-exponential factor (min^{-1})
α	Conversion rate
R	Universal gas constant ($J.mol^{-1}. K^{-1}$)
FWO	Flynn-Wall- Ozawa
KAS	Kissinger-Akahira-Sunose
g (α)	Integral conversion function
C-R	Coats-Redfern
n	Reaction order
R^2	Regression coefficient
Z (α)	Theoretical master plots

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General Introduction

General introduction

Biodegradable polymers have recently caught the interest of the scientific community since environmental contamination caused by plastics has reached epidemic proportions **[1].**

Biodegradability and bio-recyclability, as well as polymers derived from renewable resources (such as PLA), are viewed as appealing solutions among the various possible routes to eliminate plastic wastes; and it has become widely held belief that biodegradable polymers have a well-grounded role in solving the waste problem **[2].**

Because of its easy availability and strong biodegradability, PLA appears to be one of the most appealing alternatives for film uses in agriculture and as a packaging material **[3].** However, due to a lack of high thermal properties which are required for most applications, its use was limited **[4].** Polymers, fibers, and composites can be used in biomedical systems, disposable containers, plates, cutlery, and especially packaging **[5].**

Despite the fact that PLA is less resistant to breakdown in natural environments than other aliphatic biodegradable polymers like poly-caprolactone (PCL) **[6],** it has been demonstrated that PLA will naturally degrade in soil or compost at a temperature of 60°C in a large-scale operation **[7].** PLA's glass transition temperature is close to 60 °C, hence it does not biodegrade quickly at temperatures below 60 °C **[8].**

PLA is frequently used with natural fillers to improve biodegradability and reduce costs **[9].**

Lignocellulosic fillers are a new strategy to improve the performance of green material with significant economic and ecological sustainability. Among the plant based fibers, OFI-F is identified as one of the most abundant biomasses; its study as a bio-composite will be important because of its availability, and acceptable specific strength and low cost **[10].**

However, the poor interaction between the hydrophobic PLA matrix and hydrophilic natural fillers is a major drawback in many applications. It can reduce the thermal and mechanical properties of the bio-composite **[11].**

On the other hand, the high performance of an inorganic filler can improve the thermal properties of PLA bio-composites reinforced with natural fillers. The addition of inorganic filler like talc to thermoplastics as filler particles is common for the promotion of their efficiency in terms of mechanical and thermal properties **[12].**

A mixture of organic (e.g OFI flour) and inorganic (e.g., talc) fillers in PLA can produce interesting hybrid bio-composite properties. Several authors have described the use of filler mixtures (PLA/newspaper fibers/talc, PLA/cellulose fiber/ montmorillonite, PLA/cellulose fiber and PLA cellulose fiber/clay) **[13].**To further improve the performance of bio-composites Lee et al. examined the mechanical properties of a PLA matrix filled with wood flour and talc. A small decrease in the glass transition of the composites resulted from loading the wood flour and wood flour/talc mixture into the PLA matrix **[14**]. Shi et al. studied the effect of heat treatments on the thermal deformation of PLA/bamboo fiber/talc hybrid bio-composites with 20 wt% bamboo fiber or 20 wt% talc. Significant increases in HDT of PLA hybrid bio-composites were obtained when bamboo fiber and talc were loaded simultaneously **[15].**

Studies have investigated the thermal degradation of PLA. Thus, understanding the impact of reinforcements on the thermal degradation behavior of PLA bio-composites becomes important to make these materials suitable for food packaging applications and to decide how molten PLA should be processed without causing thermal decomposition **[16].** In addition, the thermal degradation kinetics and reaction mechanisms of PLA and its bio-composites need to be understood to better control thermal decomposition, avoid thermal degradation, and maintain mechanical properties. Kinetic analysis of plastics can guide the thermal degradation process from the perspective of reactor design and provide a theoretical basis for industrialization, Xu et al. studied the kinetic analysis of thermal degradation of PLA/BaSO4 according to model free iso-conversional approaches .The kinetic mechanism and reaction order were determined by model fitting in order to prepare eco-friendly PLA bio-composites with excellent thermal properties. Significant increases in activation energy of bio-composite 10wt% BaSO4 compared to pure PLA reveal that inorganic fillers have the inhibition effect on thermal degradation **[17].**

In this context, our interest with this project is to explore biodegradable polymers with natural fillers and inorganic particle reinforcement impacted on thermal properties. The investigation of the thermal behavior of talc and OFI-F reinforced PLA bio-composites was by using TGA in order to determinate the kinetic parameters. Moreover, it aims to evaluate whether Ea is constant with the degree of conversion and the suitability of the proposed methods. Model-free methods such as Flynn-Wall-Ozawa (FWO), KissingerAkahira-Sunose (KAS) and model fitting methods such as Kissinger and Coats-Redfern (C-R) were used to evaluate the activation energy of neat PLA, PLA/Talc, PLA/OFI-F and PLA/Talc/OFI-F.

Master plots methods such as Criado and Coats Redfern were applied to identify possible reaction models of neat PLA and its bio-composites to better understand the thermal degradation mechanism of neat PLA and its bio-composites. In addition, this study highlights the synergy between talc and OFI-F into the PLA matrix.

The present document consists of the following chapters:

Chapter 1: After the general introduction which introduces and describes the scientific, environmental and technological issue, being themselves the motivation behind the present work, chapter one describes the bioplastics and its different classifications, the biodegradable polymers, and the PLA as biodegradable polymer.

Chapter 2: Gives the necessary background on bio-composites materials, different types of bio-composites, bio-fibres and their classification and an overview of Poly (lactic acid) bio-composites.

Chapter 3: Describes the sources of the materials used, the experimental equipments and the preparation methods of bio-composites. In addition, some theoretical kinetics models for thermal degradation of prepared bio-composites are outlined.

Chapter 4: is a discussion of the results issued from the experiments. The final part concludes the thesis with a restatement and recommendations for future work.

The objectives of this thesis are to:

1) Study the thermal degradation properties of neat PLA and PLA bio-composites by TGA.
2) Find a methodology that increases the degradation rate of PLA bio-composites based on the data and results from the study.

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Chapter I

Bioplastics

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Introduction

The awareness of the harms of pollution caused by polymeric materials from petroleum as well as the imminent risk of depletion of oil resources have allowed for the development of a new type of materials i.e. bio-based materials which are environmentally friendly and available in abundance on the earth's surface.

As the bio-polymers, biodegradable polyesters such as poly (lactic acids) (PLA) developed extraordinarily, they established themselves as revolutionary materials in industry.

These materials are expected to play the same role as conventional polymers in the majority of their applications in addition to their new features. It is in this context that the PLA was created.

The purpose of this chapter is review the literature on PLA as biodegradable polymer.

Before going into details, certain words need elucidation.

I.1. Bio-polymers

Bio-polymers can be non-biodegradable or biodegradable when exposed to micro-organisms, water or by aerobic/ anaerobic process; for example, poly-caprolactone (PCL), poly (lactic acid) (PLA), poly-hydroxyalkanoates (PHA) and starch. Biodegradable polymers can be bio-based (PLA, PHA) or non-bio-based (PCL). All the bio-based polymers are not biodegradable like (bio polyethylene) which are produced from renewable resources **[1-3]**.

I.2. Classification of bio-polymers

Polymeric materials come from a variety of renewable and non-renewable sources such as plants, bacteria as well as petroleum **[4, 5].** Biodegradable materials are classified accordingly as natural or synthetic depending on their origin, but bioplastic materials can be divided into three main categories according to their origin as shown in **figure I.1**.

I.2.1. Category 1 (bio-based)

Biopolymers are directly extracted from biomass. Like polysaccharides (starch and cellulose). They are polymers that are produced by biological systems such as micro-organisms, plants, and animals, through metabolic reactions. These are nature's polymers, also called biological polymers or simply biopolymers **[6].**

I.2.2. Category 2 (Bio-derived Polymers)

Polymers are produced by classical chemical synthesis using renewable bio-based monomers. A good example is the poly (lactic acid), a bio-polyester polymerized from lactic acid monomers.

Polymers whose monomers are sourced from biological starting materials such as sugar, natural fats, or oils but are manufactured chemically. This category excludes fossil carbon sources such as crude oil and coal. Bio-derived materials mean materials derived from replenishable natural resources. Inherently bio-derived material has the principal that supply will always meet the demand; a situation that is unlikely to occur in the case of fossil carbon. Bio-derived polymers include aliphatic polyesters which is the center of interest nowadays. Poly (lactic acid) or PLA is the most promising polymers in this group. PLA is an important example of a bio-derived polymer. The monomer, lactic acid, is derived from the fermentation of sugar.

I.2.3. Category 3

Polymers are produced by micro-organisms or genetically modified bacteria. To date, this group of bioplastics consists mainly of the poly-hydroxyalkonoates.

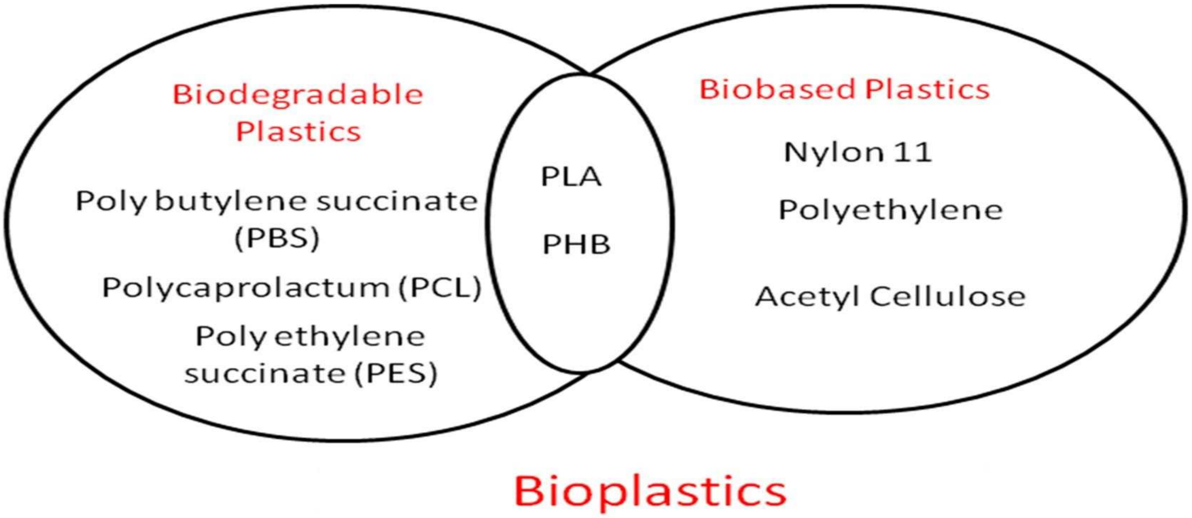

Figure I.1: Classifications of bioplastics **[1]**

I.3. Biodegradable Polymers

Biodegradable materials are those that will degrade completely by the action of micro-organisms. Accordingly, many researchers have discussed biodegradable polymers. All the definitions already in place relate the degradability of a material to a specific disposal environment **[7].** One of the well-accepted definitions reads biodegradable polymers are "materials obtained from nature or by a synthetic route, whose chemical bonds are cleaved at least in one step by enzymes" **[8]**. In addition, we can add to this "according to required conditions". Thus, specific environmental conditions such as favorable pH, humidity and temperature must be met for satisfactory degradation to take place. These factors affect the rate of biodegradation. According to Albertson and Karlsson, biodegradation is defined as "an event which takes place through the action of enzymes and / or chemical decomposition associated with living organisms (bacteria) and their secretion products" **[9]**. **Figure I.2** shows the classification of biodegradable polymers from different sources.

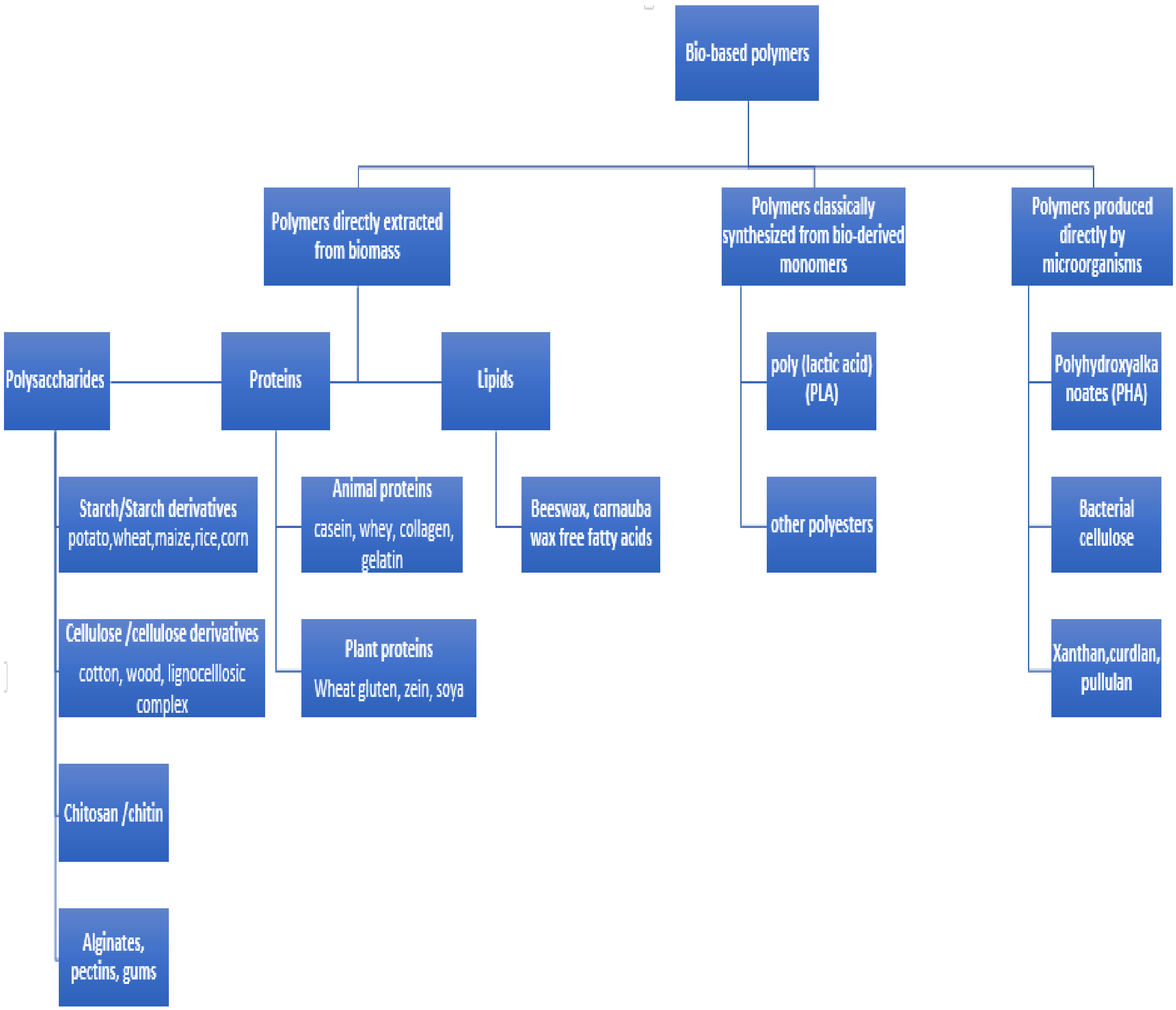

Figure I.2: Classifications of biodegradable polymer from different sources **[10]**

Biodegradable polymers can be divided into 4 different families **[11].**

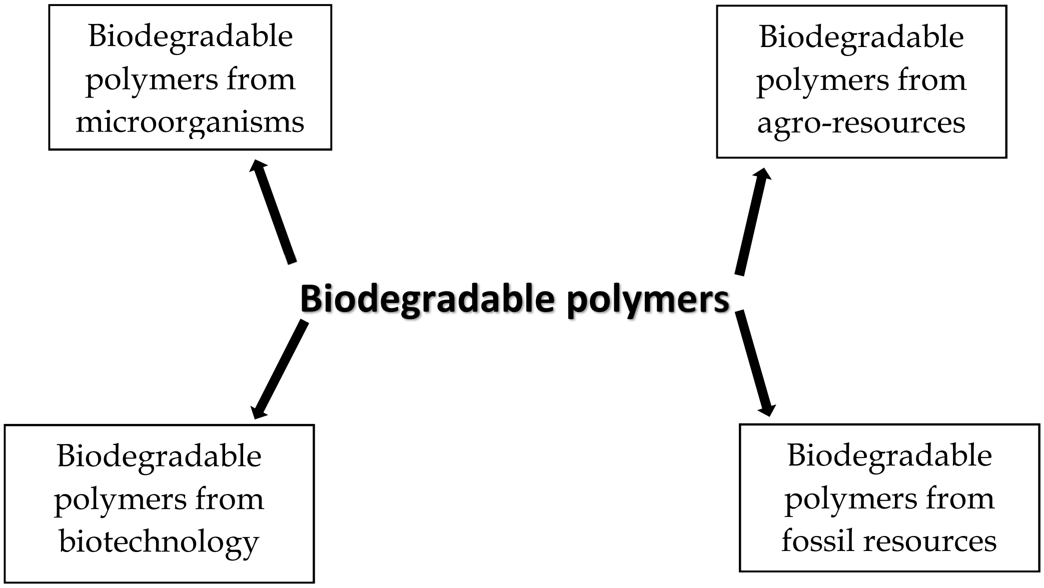

Figure I.3: The different families of biodegradable polymers

I.4. Poly (lactic acid) (PLA)

Poly (lactic acid) sometimes called polylactide has been known since 1845 and was commercialized in 1990 and was the center of attention of many researchers since this time **[12]**.

Polylactide (PLA) is the most promising biodegradable and compostable polymer that belongs to the family of aliphatic polyesters **[13, 14]**.

It is a thermoplastic produced from natural and renewable resources such as corn, wheat, and sugar cane bagasse, starchy materials from potato, tapioca or barley to use in industrial packaging or biomedical applications **[13, 15]**.

PLA may be the polymer with the broadest range of applications because of its ability to be thermally crystallized and its capability to be processed in most common plastics processing equipment.

In spite of its excellent balance of properties, its commercial viability has historically been limited by high production cost. Since the opening of the Nature Works plant in 2003, the industrial production of PLA from renewable resources **[15]** and the significant intention of bringing down the production cost will definitely place PLA as a widely used polymer in the future **[16, 17]**. **Table I.1** presents selected physical and tensile properties of a typical commercial PLA grade.

Table I.1: Physical properties of a typical commercial PLA grade (4 % D-lactide) **[13, 15, 18-19]**

Density at 25 °C (g/cm^3)	1.25
Density of the molten polymer (g/cm^3)	1.07
Glass transition temperature (°C)	55
Melting temperature (°C)	165
Thermal conductivity at 48 °C	0.111 W/ (m°C)
Specific heat capacity at 55 °C	1590 J/ (kg°C)
Tensile strength (MPa)	59
Young's Modulus (GPa)	3.5
Elongation at break (%)	7

I.4.1. PLA Developments

The development of PLA, which began with lactide manufacturing formulas, was published by Bischoff and Walden in 1893. Carothers began producing low molecular weight PLA in 1932 by heating lactic acid under vacuum for coworkers (DuPont). Following that, in 1954, PLA was promoted for medical purposes by E. I. DuPont de Nemours and Ethicon Incorporation, specifically suture, implant, and controlled release medication applications. In 1992, Shimadzu Corporation and Kanebo Gohsen Ltd of Japan began melt spinning PLA fibres, and Kanebo Gohsen Ltd began commercial production in 1994 under the trade name Lactron. Fiber-web France S.A., France, produced another commercial production of PLA fibres under the brand name Deposa in 1997.

Under the trade name Nature Works, Cargill Dow Polymers LLC, USA, a 50:50 joint venture between Cargill Incorporated and Dow Chemical Company, began commercial manufacturing of PLA from starch in 2002. In 2003, Cargill Dow LLC released PLA fibre IngeoTM spun from the Nature Works TM polymer. In 2005, Dow sold its stake in the company to Cargill, which renamed it Nature Works LLC. Nature Works LLC now operates the world's largest PLA plant in Savage, Minnesota **[20, 21].**

I.4.2. Chemical structure

Polylactic acid is aliphatic polyester made from α-hydroxy acid [PLA: (–CH (CH3) –CO–O–) *n*] as shown in **Figure I.3**. The monomer used to polymerize PLA is lactide, a dimer of lactic acid. Lactic acid is the simplest hydroxyl acid with chiral carbon atom. Chemically, lactic acid is 2-hydroxypropanoic acid **[22]**. It has two enantiomeric: L (+)-lactic acid (Laevorotatory) and D (-)-lactic acid (Dextrorotatory) as shown in **Figure I.4.**

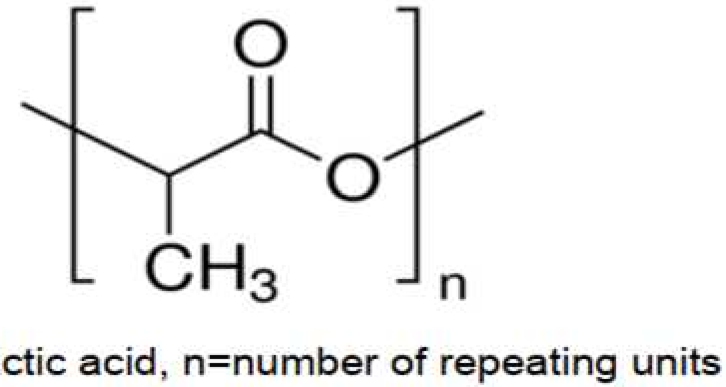

Figure I.4: Chemical structure of PLA **[23]**

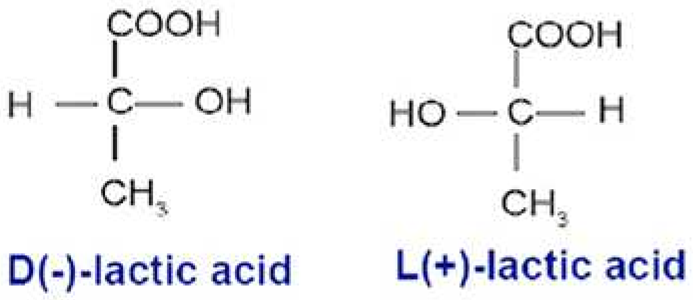

Figure I.5: Shows the two enantiomeric of lactic acid **[24]**

Several distinct forms of Polylactide exist when L (+) & D (-) isomers of lactic acid, same or different isomers are combined with each other, they form lactide. When L & L (+) are combined, they form L (+)-Lactide (PLLA), D & D (-) form D (-) - Lactide (PDLA) and when L (+) and D (-) are combined, they form meso-Lactide (PDLLA) as shown in **Figure I.5 [20].**

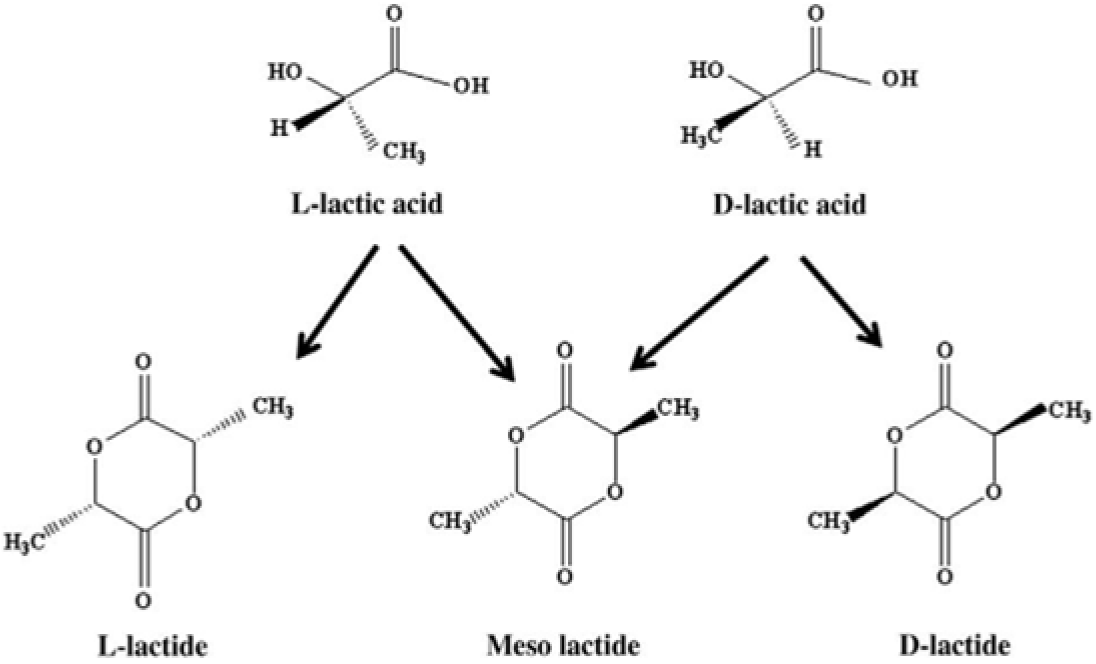

Figure I.6: Stereoforms of lactides **[25]**

One can also have PLA copolymers where the constituents are sequenced of PLLA and PDLA; this category is called stereoblock polylactide (sb-PLA) **[26]** (**Figure I.7**)

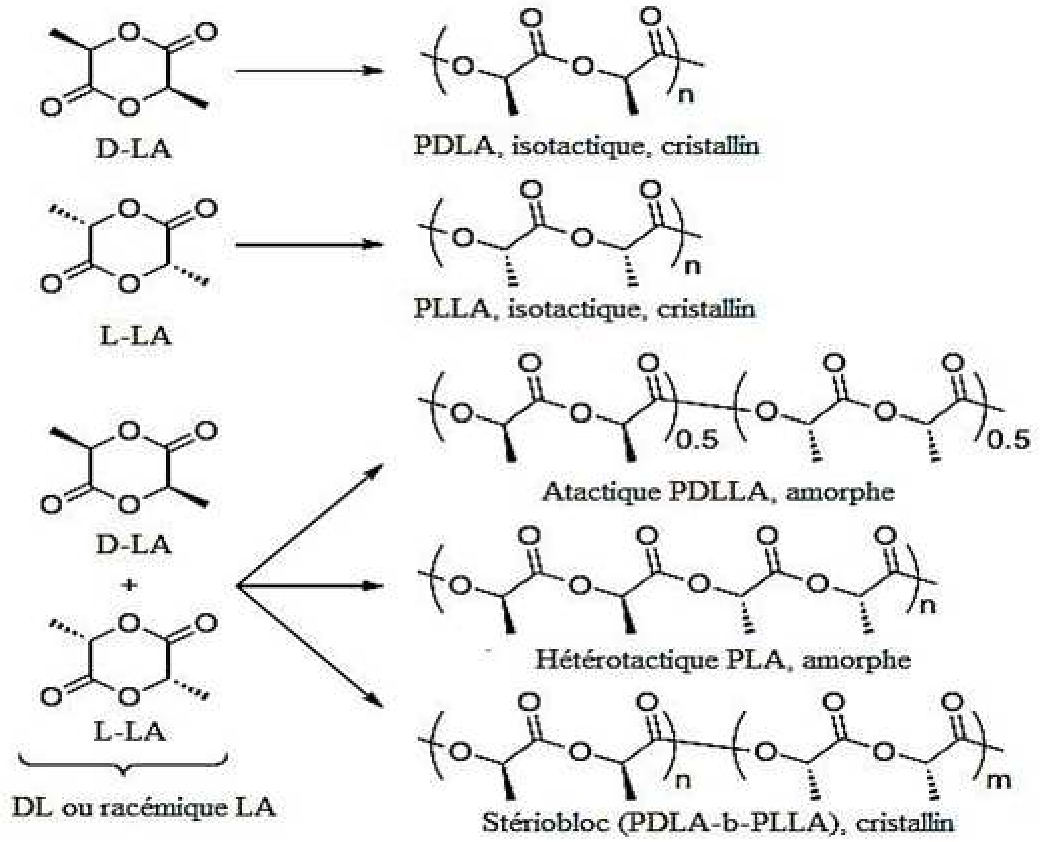

Figure I.7: Possible microstructures of PLA emitted by the polymerization of D or L enantiomers or the D/L racemic mixture of lactic acid **[27]**

I.4.3. Synthesis of PLA

Synthesis of PLA is a multistep process which starts from the production of lactic acid and ends with its polymerization. PLA is synthesized by following three methods which are illustrated in **Figure I.8.**

a. Poly-condensation of lactic acid

PLA can be synthesized by direct condensation polymerization to yield the low-molecular- weight, brittle polymer which for most of the products is unusable.

Condensation polymerization is the least expensive route, but it is difficult in a solvent-free system to obtain high molecular weights, so modifiers like (coupling agent or esterification) are required to increase chain length, but the later causes additional cost and complexities.

- **Solution poly-condensation**

An organic solvent of PLA is introduced to the reaction mixture and refluxed to the reactor during the synthesis process in this method of synthesis. The solvent is not used in the reaction, and the water molecules produced by the polymerization reaction of lactic acid monomers are continually evacuated from the bottom of the reflux condenser.

This aids in the development of a polymer with a larger molecular weight. Due to the difficulty in eliminating contaminants and water in this technique, low molecular weight polymers are produced **[28].**

- **Melt poly-condensation**

There is no requirement for a solvent in this process; however, the reaction temperature should be kept above the polymer's melt temperature (T_m). This method is less complicated than solution poly-condensation, but it is more sensitive to reaction circumstances **[28].**

In general, direct polymerization is a one-step technique that necessitates good reaction factor control in order to produce a polymer with the ideal molecular weight. Water, a by-product of condensation polymerization, has the potential to degrade PLA to low molecular weight oligomers at high reaction temperatures; hence, the reaction kinetics and removal of the generated water are critical in this approach **[16, 28-30].**

b. Dehydration condensation

This route is the azeotropic dehydration condensation of lactic acid. It can yield high molecular weight PLA without employing any chain extender or special additives.

c. Ring Opening Polymerisation (ROP) of lactides

The ring-opening polymerisation (ROP) of lactides to create high molecular weight PLA polymers is the main technique which was patented by Cargill Dow (US) in 1992 **[31]**.

The dimerization of lactic acid monomers and creation of a cyclic intermediate known as lactide is the initial stage of this process. PLA is then made by combining a suitable catalyst with a lactide monomer in a heat and vacuum environment. The critical parameters in the ring opening polymerization process include reaction time, temperature, lactide monomer purity, and the type of catalyst utilized **[28].**

Alternative polymerization methods have been researched since ring opening polymerization of lactide was an expensive and difficult procedure unlike direct polymerization which results in a PLA polymer with a low molecular weight. One option is to add chain extenders to condensation polymers in order to generate high molecular weight polymers **[28, 32].**

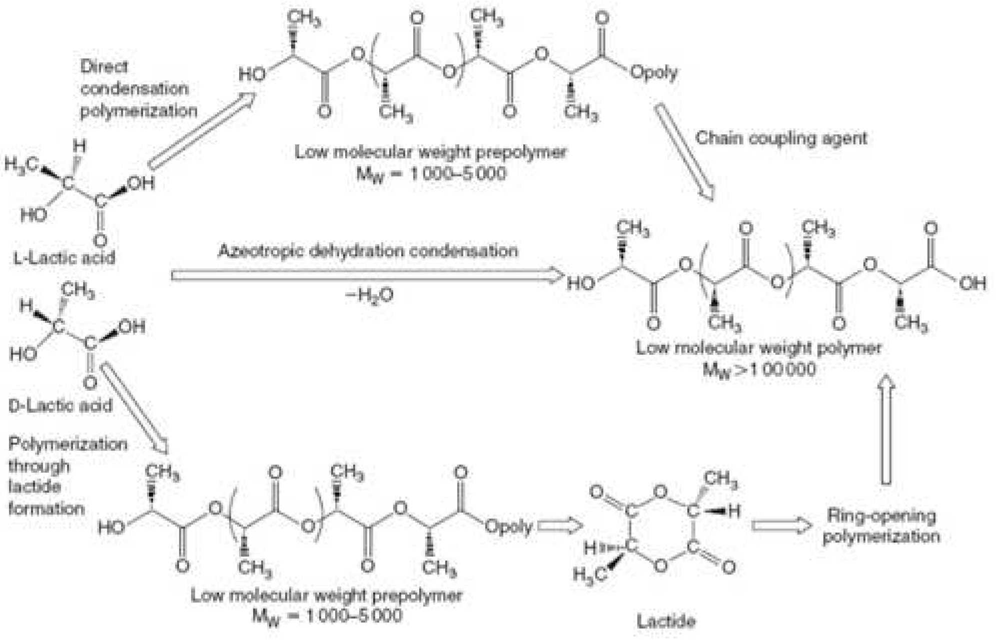

Figure I.8: Direct condensation and ring opening polymerization schema **[6]**

I.4.4. Properties of lactic acid (PLA)

PLA has outstanding qualities such as transparency, eco-friendliness, and non-toxicity, so it does not produce carcinogenic effects on local tissues, making it an excellent biomedical material.

PLA is compostable, renewable, recyclable, and biodegradable **[33]**. PLA has mechanical properties that are equivalent to or better than conventional polymers that is why it is frequently utilized in consumer products.

However, PLA has significant disadvantages that limit its usage in certain applications, such as brittleness and poor crystallization rate, slow degradation by hydrolysis of PLA's backbone ester groups, low thermal stability and thermal resistance, and low toughness **[34, 35].**

PLA polymers' physical properties are determined by molecular characteristics as well as organized structures like crystallinity, spherulite size, morphology, and chain orientation. Depending on the L-to-D lactic acid ratio and thermal history, PLA polymers can be amorphous or semi-crystalline at room temperature **[36].**

PLA's physical, mechanical, and biodegradable properties are all influenced by the monomer's optical purity. PLA is a homo-polymer formed by polymerizing pure L, L- or D, D-lactic acid.

For example, PLLA is a rigid, transparent, and crystalline polymer with a crystallinity of 37%, a melting temperature of 170-180 °C, and a glass transition temperature of 50-60°C [36]. PLA polymers with more than 93% L, L-lactic acid are semi-crystalline whereas PLA polymers with 50 to 93 % L, L-lactic acid are amorphous. The presence of both meso- and D-lactide forms causes crystalline structure imperfections, lowering the percent of crystallinity **[37].**

Amorphous PLA transition from glassy to rubbery occurs above Tg, and when heated further, it behaves like a viscous fluid. PLA behaves like a glass below Tg, with the potential to creep until it reaches its transition temperature of roughly -45 °C. PLA will only behave as a brittle polymer below that temperature **[38].**

For most commercial applications, the glass transition (Tg) specifies the highest usage temperature for amorphous PLAs. The Tg and melting point (Tm) of semi-crystalline PLA are significant for defining the use temperature in various applications **[39].**

The overall optical composition, primary structure, thermal history, and molecular weight have a significant impact on both of Tg and Tm transitions **[38].** The metastable condition of high molecular weight of amorphous and semi-crystalline PLA reacts to different temperatures as seen in the graph below.

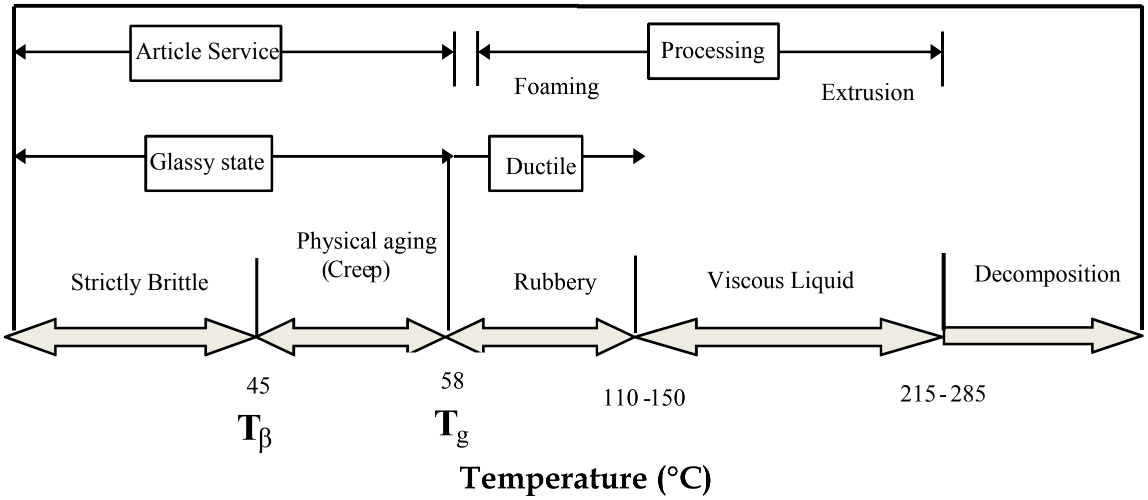

Figure I.9: Metastable state of high molecular weight amorphous Polylactides **[18]**

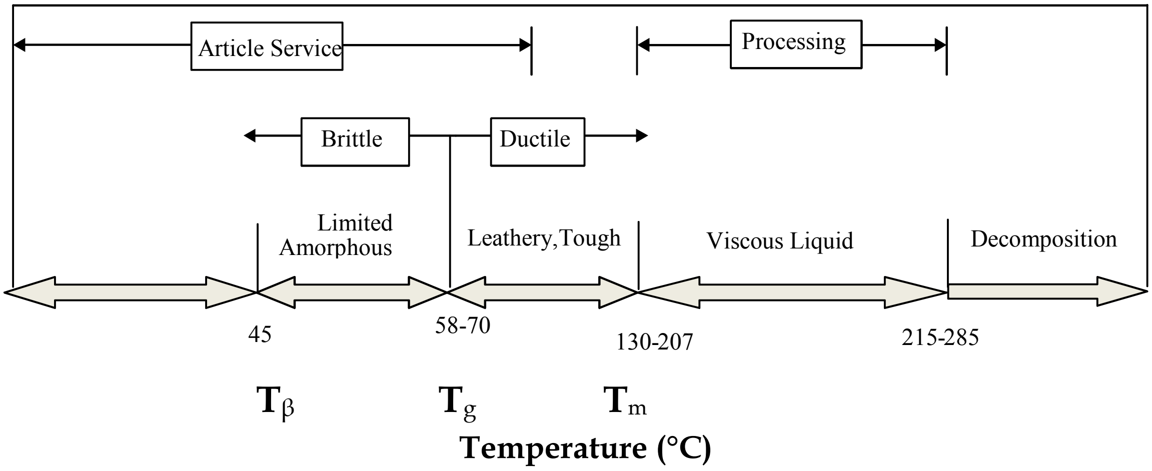

Figure I.10: Metastable state of high molecular weight semi-crystalline Polylactides **[18]**

The temperature of glass transition is also determined by the proportion of the different existing lactides. This results in a PLA polymer with a wide range of hardness and stiffness values. Typical PLA glass transition temperature (*Tg)* ranges from 50 ^{0}C to 80 ^{0}C while the melting temperature ranges from 130 ^{0}C to 180 ^{0}C **[40, 41].** The glass transition temperature (T_g), the melting temperature (T_m) according to the stereo-chemical conformation are shown in **table I.2.**

Table I.2: Changes in T_m and T_g according to the stereo-chemical conformation **[42]**

PLA structure		**T_m (°C)**	**T_g (°C)**
Poly (L-lactide) or Poly (D-Lactide) isotactic	LLLL or DDDD	170 – 190	55 – 65
Random copolymers	Random % of meso or D-Lactide	130 – 170	45 – 65
Stereocomplex PLLA/PDLA	LL mixed with DD	220 – 230	65 – 72
Syndiotactic Poly (meso-lactide)	DLDLDLDL	152	40
Heterotactic (disyndiotactic) Poly (meso-lactide)	LLDDLLDDLLDD	-	40

Glass transition temperature (T_g), melting temperature (T_m) and percentage of crystallinity for the two grades of PLA: (98 % L-lactide), PLA (94% L-Lactide), and PET films are given below in **table I.3**, measured according to ASTM D 3418-9 **[31].**

Table I.3: Physical properties of PLA (98 % L-lactide), PLA (94% L-Lactide) and PET

	PLA (98 % L-Lactide)	**PLA (94 % L-Lactide)**	**PET**
Tg (°C)	71	66	80
Tm (°C)	163	140	245
Crystallinity (%)	40	25	38

When we want to use PLA for long-term applications, especially on a large scale, we need to improve its thermal properties **[43].**

I.4.5. Processing of PLA

For the manufacture of polylactic bio-composites, processing techniques such as extrusion, injection molding, and solvent casting are acceptable. Furthermore, these ways make PLA production easier from small-scale to large-scale and industrial levels, but the twin screw extruder is the preferred method for PLA modification, such as the addition of fibers, plasticizers, fillers, and polymers **[44].**

I.4.6. Limitations

PLA, like all materials, has severe flaws that explain why PLAs are still relatively uncommon on the market and in limited use. To begin with, its cost is relatively higher than that of comparable polymers **[45].**

In addition, PLA has a low deflection temperature (HDT) **[46],** and a low thermal stability during processing due to the presence of heat-sensitive ester groups, restricting its use in industries such as electronics. PLA is also hygroscopic, making it very susceptible to hydrolytic degradation in the molten form **[47].**

All these drawbacks have restricted the use of PLA and forced researchers to use modification methods, by adding substances during processing **[48]**, incorporation of fillers **[49]** and nano-fillers or mixing with other polymers **[50].**

I.4.7. State of the art on PLA bio-composites

Traditional food packaging materials passively protect food products from physical, chemical, and biological contamination when exposed to heat which can result in the deterioration of flavor, odor, color, sensory, and textural properties of foods. Furthermore, with growing environmental concerns, researchers are working to develop and improve the performance of biodegradable biopolymers such as PLA which is a good candidate for a variety of applications **[51].** However, it has a slow decomposition rate, low thermal stability, and low glass transition temperatures below 60°C. PLA can be changed with various additives such as inorganic or organic fillers to widen its application and improve its thermal stability.

PLA has piqued the interest of scientists over the last decade. Recently, naturally available fibers or lignocellulosic materials such as wood, kenaf, jute, ramie, and flax have become popular as cost-effective biofillers and/or reinforcements for PLA. These materials can also make PLA more ecologically friendly by improving the polymer's biodegradability. Biodegradability, eco-friendliness, cost, availability, and low density are all advantages that natural fiber-based polymer composites have over synthetic ones. Natural fiber reinforced polymer composites are rising in popularity and acceptance in food packaging, car, train, and plane interiors, and storage devices. There have been enough studies on PLA/natural filler bio-composites.

The majority of current research projects are centered on manufacturing composites and increasing their mechanical properties **[52].** Sawpan et al. **[53]** studied how to improve the interfacial shear strength (IFSS) of hemp fiber reinforced PLA and unsaturated polyester composites by modifying the surface of hemp fibers. The improved PLA trans-crystallinity and enhanced bonding of the PLA matrix with the treated fibers could explain the greater IFSS.

Shih et al. **[54]** used a melt-mixing procedure to create bio-composites using recycled disposable chopsticks and a PLA matrix. Mechanical tests revealed that the tensile strength of the composites grew noticeably with fiber content, reaching 115 MPa in composites reinforced with 40% fibers, which was roughly three times higher than that of pure PLA.

Alkali-treated industrial hemp fiber (30 %wt) reinforced PLA composites had a Young's modulus of 10.9 GPa and a tensile strength of 82.9 MPa, according to Islam et al. **[55].** Alkali-treated sisal fiber reinforced soy protein resin-based bio-composites were developed by Kim and Netravali **[56]** who found that the treatment increased fracture stress and stiffness in the sisal fiber by 12.2% and 36.2 percent, respectively, while fracture strain and toughness decreased. Gregorova et al. **[57]** found that PLA/spruce wood flour

(40 %wt) bio-composites with various surface treatments of the wood flour had increased Young's modulus (3.73 to 10.247 GPa) and decreased tensile strength (37.2 to 12.0 MPa).

Using scanning electron microscopy, Qin et al. **[58]** investigated the morphological and mechanical properties of polybutyl acrylate (PBA) modified rice straw fiber (RSF) reinforced PLA bio-composites and discovered good interfacial adhesion between PLA and RSF as well as good RSF dispersion in the polymer.

Thermodynamic and mechanical properties of cellulose reinforced PLA bio-composites were investigated by Awal et al. **[59].** Thermo-gravimetric analysis (TGA) was used to study the thermal properties of the generated bio-composites. PLA/wood fibres (WP)/bioadimide bio-composites' heat distortion temperature was somewhat enhanced, perhaps resulting in a longer temperature service life. Short fibres interacted well with PLA, resulting in improved mechanical characteristics. The tensile strength of bio-composites was dramatically enhanced when 1.3 % bioadimide (bioadditive) was added. The impact strength of bio-composites was also significantly boosted as a result of the inclusion of a bio-additive to the mix. This innovative bio-additive was found to be particularly effective for both fibre matrix adherence and bio-composites processability. When compared to plain PLA and PLA/WP composites, the bioadimide composites had better mechanical characteristics. When compared to neat PLA, the tensile modulus of PLA/WP/bioadimide composites improved by 26%. In terms of tensile strength, however, the effect was not as strong. PLA/WP composites with no bioadimide showed weak flexural strength.

Anuar et al. **[60]** showed that adding KF to PLA bio-composites accelerated degradation, resulting in improved biodegradability. Ibrahim et al. **[61]** studied PLA/KF bio-composites and found that tensile qualities improved at 20 and 30 %wt KF when compared to lower (10 %wt) and higher (40–50 %wt) KF loadings; however, the highest properties obtained were still lower than pure PLA. Surprisingly, Yussuf and Massoumi **[62]** found that reinforcing PLA with 20% natural fibres (kenaf and rice husk) enhanced flexural modulus and biodegradability without compromising heat stability.

Furthermore, the experimental results showed that PLA composites incorporating KF had on average better mechanical and thermal properties than PLA composites reinforced with rice husk.

Ait Benhamou et al. **[63]** investigated the effects of alkali treatment and coupling agent on the thermal and mechanical properties of HDPE composites reinforced with Opuntia ficus-indica cladodes fibers. Opuntia ficus-indica (OFI) fibers were employed to reinforce a high-density polyethylene (HDPE) matrix in this study. Extruder and injection molding procedures were used to make composite specimens with varying fiber loadings (2.5, 5 and 10 %wt). All composite systems were investigated for the effects of alkali treatment and coupling agent on thermal and mechanical properties. The alkali treatment was found to be more effective in improving interfacial adhesion between fibers and matrix which positively influences the hardness and Young's modulus properties of composites without SEBS-g-MA whereas the addition of a coupling agent increased composite plasticity and thermal stability due to chemical bond formation at the fiber–matrix interface. Because of the fiber's intrinsic hydrophilicity, various chemical changes are required to provide effective surface adhesion between the polymer and the filler.

The mechanical characteristics of PLA composites made from natural and modified cellulose fibres were shown to be significantly dependent on the mass fraction of fibres **[64].** It's vital to optimize natural fibre-reinforced PLA composites in terms of mechanical and other qualities in order to reduce costs, adjust biodegradability, and expand their applications. The mechanical characteristics of PLA composites reinforced with several types of natural fibres (cotton, hemp, kenaf, and Lyocell) formed by compression molding improved, according to Graupner et al., as compared to neat PLA **[65].**

With alkali treated hemp fibre, a stronger fibre-matrix contact was discovered which increased mechanical qualities **[55].** Masirek **[66]** looked on hemp fiber reinforced PLA composites that were made by batch mixing. The preparation procedures as well as the hemp content in the composites influenced the mechanical characteristics, thermal stability, and morphology of PLA-hemp composites. Mechanical experiments revealed that PLA composites supplemented with 20 %wt hemp fibre increased the composites' modulus of elasticity (to 5.2 GPa). Hu and Lim also looked several other composites **[67].** For hemp fibre reinforced PLA composites made employing hot compression moulding, 40 %vol of alkali treated fibre provided higher adherence and thus gave the best mechanical characteristics.

Moisture absorption and limited heat stability are the main disadvantages of these composites. Natural fibers have been shown to be less thermally stable in the literature **[68].** With the addition of oil palm microcrystalline cellulose (MCC) to PLA, Mohamad et al**. [69]** enhanced the T_{50} decomposition temperature and indicated an increase in the heat resistance of the composites using TGA. In their comparison of PLA/kenaf and PLA/rice husk composites, Yussuf et al. **[62]** discovered that the addition of kenaf and rice husk fibers in the composites lowered thermal stability when compared to the plain PLA. The PLA-rice husk composite showed the greatest reduction. Differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermo-gravimetric analysis (TGA), and thermo-mechanical analysis can all be used to investigate the thermal properties of composites (TMA). Because the TMA study of thermal characteristics has received less attention in the literature, TMA characterization should be carried out in the future to improve knowledge of the impact of integrating natural fiber into PLA composites.

Yu Dong et al. **[70]** looked at the degradation of PLA bio-composites using coir fiber reinforcement. Due to the hydrophilic nature of coir fibers, the bio-composites decomposed faster than plain PLA, with a maximum weight loss of 34.9 percent in treated coir fiber reinforced bio-composites compared to 18 percent in PLA after 18 days of burial. Similar research has been done on ramie, flax, cotton **[71];** hemp **[55];** kenaf, rice husk; and other fibers, indicating that increasing the fiber content of the composites improves biodegradability. PLA is easily processed, biocompatible, and biodegradable in natural settings such as garden soil, compost, and aqueous solution **[54, 72,73].**

Scarffaro et al. **[74]** studied Structure-property relationship of PLA-Opuntia Ficus Indica bio-composites. OFI flour of two different sizes was added to PLA, resulting in a stiffening effect. These bio-composites showed excellent mechanical improvement, with stiffness reaching 135%, indicating a promising potential for the development of sustainable bio-composites. The lower elongation at break and toughness could be attributed to a poor interaction between the hydrophobic PLA matrix and the hydrophilic natural fillers, which limits their compatibility.

The effect of filler concentration and size on the green composites' morphological, rheological, and mechanical properties was investigated. Furthermore, solvent-assisted filler extraction allowed researchers to assess the homogeneity of filler dispersion as well as the impact of processing on the fillers' geometrical properties. Due to the premature failure of the samples, it was discovered that adding OFI to a PLA matrix resulted in a significant increase in stiffness while decreasing tensile strength, elongation at break, and toughness. In terms of the type of OFI, the larger the filler size, the higher the stiffness increase and the more pronounced the brittle behavior. These green composites' outstanding mechanical gains which boosted rigidity by up to 135%.

Tensile and thermal degradation properties of Poly (Lactic Acid)/ Typha Latifolia bio-composites were investigated by Daud, Y. M. et al. **[75].** The presence of natural fiber in the bio-composite raises the glass transition temperature, according to experimental results (Tg). The thermogravimetric analysis (TGA) results showed that adding TLF to bio-composites improved their thermal stability when compared to pure PLA. The thermal properties of PLA biocomposites are improved when 10 wt percent Typha Latifolia fiber is added; however, loading above 10 %wt resulted in lower thermal properties.

Greco et al. **[76]** exploited the wooden backbone of OFI cladodes to produce PLA-based sandwich structures via compression molding, stacking, and impregnation of OFI fiber composites. The cladode backbone provided considerable rigidity to the resultant structures in both situations.

.Malainine et al. studied Lignocellulosic Flour from Cladodes of Opuntia Ficus-Indica reinforced Poly (propylene) composites. They found that when OFI flour was added to polypropylene, it had a weak affinity for the polymer matrix **[77].**

Another way for improving qualities such as stiffness, strength, gas barrier properties, melt strength, and thermal stability is to add fillers to PLA bio-polymers. To change the characteristics of PLA, fillers such as mica, kaolin, calcium carbonate, and talc are commonly utilized. For platelets and flakes, the aspect ratio is defined as the ratio of diameter to thickness. As nucleation agents for PLA, inorganic fillers such as montmorillonite clay, silica, carbon black, and talc have been widely employed **[78,79].**

Using calcium lactate, sodium stearate, and talc as nucleating agents in PLA, Li, H **[80]** et al. examined the influence of nucleation. Talc was discovered to be very effective at nucleating PLA isothermal crystallization.

PLA was also melt blended with various inorganic fillers as $9Al_2O_3$, $2B_2O_3$ and CaCO3, and it was discovered that these fillers improved PLA's mechanical and thermal qualities **[80].**

Uramaya, Ma, and Kimura **[81]** found that **s**train at break increased from less than 5% for neat PLA to 5.1% at 2.5 %wt NPCC content, to 13 % at 5 and 7.5 %wt NPCC, according to research on PLA-nano-sized precipitated calcium carbonate (NPCC) composites and modified montmorillonite (MMT). At 2.5 %wt MMT concentration, MMT demonstrated a strain at break increase to 15.9%.The graphite nano-platelets diffused homogeneously in the PLA matrix in PLA–exfoliated graphite (EG) nanocomposites. With incremental levels of EG up to 3% wt, the thermal stability of the nanocomposites was increased.

The Young modulus increased as the graphite concentration increased **[82].** Another study used mechanical compounding to make PLA blends with acetylated bacterial cellulose. When compared to neat PLA, the composites showed considerable improvements in elastic and Young moduli, as well as tensile strength **[83].**

According to Shakoor and Thomas **[84],** talc functions as a nucleating agent for PLA crystallization at low concentrations, whereas talc content up to 30% in PLA matrix has a considerable reinforcing effect on Young's modulus **[85].**

Lee, C et al. studied the effect of talc content on the thermal properties and tensile performance of the PLA composites. Results showed that the addition of talc ranged from 5 to 30 wt% can enhance the Young’s modulus and thermal stability of the composites but there is no improvement in tensile strength and elongation at break due to poor interfacial adhesion. The addition of talc beyond 30 wt% (i.e., 40 wt%) did not show improvement in thermal stability because at high talc content, the formation of agglomerate and voids allows the oxygen to diffuse into the matrix which lead to decomposition process**[85].**

Saravana, S et al. **[86]** studied effect of Polyethylene glycol on mechanical, thermal, and morphological Properties of talc reinforced Polylactic Acid. Composites Plasticizers polyethylene glycol 1500 (PEG1500) and polyethylene glycol 6000 (PEG6000) were used to strengthen polylactic acid (PLA) with varied talc compositions (PEG6000). The flexural strength of the polylactic acid-talc-PEG1500 composites (PTP1500) has increased from 80 to 140 MPa. When compared to Poly lactic acid fortified with talc and PEG6000, PTP1500 performed better (PTP6000)

Cipriano, T. F et al. **[87]** studied thermal, rheological and morphological properties of Poly (Lactic Acid) (PLA) and talc composites. The impact of talc, a nucleating agent, on the crystallization behavior, rheological characteristics, and morphological qualities of PLA was studied. The addition of mineral fillers to the PLA matrix in the range of 1 to 5%wt increased the degree of crystallinity, according to DSC data. This discovery demonstrates that talc served as a nucleating agent for PLA during the processing stage. A scanning electron microscope was used to examine the morphology of the composites (SEM). The micrographs revealed that all of the formulations studied had good talc dispersion. Thermal study revealed that the addition of 3 wt% talc to the polymer matrix appears to be intriguing in terms of the need for products with good dimension stability.

Hybridization in composite technology has become a widely accepted method for obtaining reinforced polymer composites with good thermal and mechanical properties, and for overcoming the drawbacks of natural fiber, such as poor interfacial adhesion and high moisture absorption.

Several authors have described the use of filler mixtures (PLA/newspaper fibers/talc, PLA/cellulose fiber/ montmorillonite, PLA/cellulose fiber and PLA cellulose fiber/clay) **[88].**

Lee et al. examined the mechanical properties of a PLA matrix filled with wood flour and talc. A small decrease in the glass transition of the composites resulted from loading the wood flour and wood flour/talc mixture into the PLA matrix. The tensile strength of the composites decreases slightly with the addition of talc **[89**]. Shi et al. studied the effect of heat treatments on the thermal deformation of PLA/bamboo fiber/talc hybrid bio-composites with 20 wt% bamboo fiber or 20 wt% talc. Significant increases in the heat distortion temperature (HDT) about 10°C of PLA hybrid bio-composites were obtained when bamboo fiber and talc were loaded simultaneously and this was due to the synergism of BF and talc in PLA composites **[90].**

Nanthananon, P et al. **[88]** studied the reinforcement of Poly (Lactic Acid) by Short-fiber and talc hybrid composite. In this work, the simplified preparation was introduced for the large volume production of 30 wt % short-fiber and talcum reinforced polymer hybrid composite by direct feeding into twin-screw extruder. Multifunctional epoxide-based terpolymer and/or maleic anhydride were selected as in situ reactive compatibilizers. The influence of fiber and talcum ratios and in situ reactive compatibilizers on mechanical, dynamic mechanical, morphological and thermal properties of hybrid composites were investigated. The morphological results showed the strong interfacial adhesion between fiber or talcum and Poly (lactic acid) (PLA) matrix due to a better compatibility by reaction of in situ compatibilizer. The reactive PLA hybrid composite showed the higher tensile strength and the elongation at break than non-compatibilized hybrid composite without sacrificing the tensile modulus. Upon increasing the talcum contents, the modulus and storage modulus of hybrid composites were also increased while the tensile strength and elongation at break were slightly decreased compared to PLA/fiber composite. Talcum was able to induce the crystallization of PLA hybrid composites.

Harmaen, A et al. **[91]** studied the thermal and biodegradation properties of Poly (lactic acid)/Fertilizer/Oil Palm fibers blends bio-composites. Poly (lactic acid) (PLA) and NPK fertilizer with empty fruit bunch (EFB) fibers were blends to produced bioplastic fertlizer (BpF) composites for slow release fertilizer. TGA themogram display that neat PLA, PLA/NPK, and BpF composites degradate at different temperatures. DSC curves of PLA and other composites exhibited same glass transition temperature (Tg) value indicating that both major blend components are miscible. The Tg, crystallization temperature (Tc), melting temperature (Tm) values also decreased with increased amount of fertilizer and fibers. The Tm of BpF composites did not change with an increase in fertilizer content because thermal stability of PLA and PLA/NPK composites was not affected. Soil burial and fungal degradation test of PLA, PLA/NPK, and BpF composites were also carried out. Soil burial studies indicated that BpF composites display better biodegradation as compared with neat NPK. Fungal degradation study indicated that fungi exposure times of BpF composites show higher value of degradation as compared with PLA/NPK. We attribute that developed BpF composites will help oil palm plantation industry to use it as slow release fertilizer.

Valapa, R et al. **[92]** studied thermal degradation kinetics of Sucrose Palmitate reinforced Poly (lactic acid) bio-composites. They focused on investigating the influence of novel bio-filler, “sucrose palmitate (SP)” on the thermal degradation behavior of poly (lactic acid) (PLA) bio-composites in order to render its suitability for food packaging application. Thermal degradation behavior of the PLA bio-composites was investigated by thermo-gravimetric analysis (TGA) using dynamic heating regime. The differential TG analysis revealed that there is no change in the T_{max} value (357 ^{0}C) for PLA and its composites up to 5 wt% of bio-filler loading. This reveals that the sucrose palmitate acts as a protective barrier by decelerating the thermal degradation rate of PLA. In the case of 10 wt% of the filler incorporated in the PLA matrix, Tmax rapidly shifted to lower temperature (324 ^{0}C). This downturn in Tmax at higher loading of the filler is due to the increase in acidic sites and enhancement in the rate of degradation is observed. Differential scanning calorimetry (DSC) analysis revealed unimodal melting peak indicating the α-crystalline form of PLA. Based on the thermal degradation profile of sucrose palmitate, possible mechanism for degradation of PLA composites is proposed. The activation energies (Ea) of thermal degradation of PLA and PLA composites were evaluated by Flynn-Wall-Ozawa and Kissinger methods.

Pal, A et al. **[93]** studied the thermal degradation behavior of nano-amphiphilic chitosan dispersed poly (lactic acid) bio-nanocomposite films. Nano-amphiphilic chitosan termed as chitosan-grafted-oligo l-lactic acid (CHg-OLLA), is synthesized by microwave initiated in situ condensation polymerization. The synthesized CH-g-OLLA becomes hydrophobic in nature due to chemical bond formation between chitosan backbone and OLLA chains. Further, CH-g-OLLA (30%) bio-nanocomposite is used as a nanofiller in poly (lactic acid)/chitosan-grafted-oligo l-lactic acid (PLA/CH-g-OLLA) bio-nanocomposite films. Surface morphology shows a homogeneous dispersion of CH-g-OLLA in the form of spherical aggregates, which vary in the range of ~20 to 150 nm. Non-isothermal degradation kinetics, proposed by Kissinger, Kissinger-AkahiraSunose, Flynn-Wall Ozawa and Augis & Bennett models, are utilized to estimate the activation energies (Ea) for PLA, which are 254.1, 260.2, 257.0 and 259.1 kJ mol^{-1} respectively. The reduction in Ea values of bio-nanocomposite films may be elucidated by intermolecular distance and enrichment in chain mobility. The evolved gaseous products like hydrocarbons, carbon dioxide, carbon monoxide and cyclic oligomers are successfully identified with TG-FTIR analysis.

Huang, Z et al. **[94]** studied the kinetic study of thermal degradation of poly (L-lactide) filled with b-zeolite. The incorporation of b-zeolite has been found to make the onset thermal decomposition temperature of PLA obviously decrease. With the Flynn–Wall–

Ozawa method, the activation energy Ea of the composites has been estimated and the b-zeolite composites have required higher Ea values for thermal decomposition reaction than pure PLA. The pre-exponential factor ln A can be readily obtained so as to establish the thermal conversion curves if the first-order mechanism is taken. Simulated results reflect that the first order reaction mechanism has led to certain large deviations at the low conversion levels. By scanning the well-known 27 mechanism functions, the D5 mechanism of Zhuravlev, Lesokhin, Tempelman equation is found to be the most suitable mechanism for the description of the thermal decomposition of PLA and its b-zeolite counterparts. Along with the Flynn–Wall–Ozawa method, the D5 mechanism has performed excellently to establish all the conversion curves over the whole range, resulting in more satisfactory simulation results than the first-order reaction mechanism.

Pineapple leaf fibers (PALF) and coir fibers (CF) loaded into a polylactic acid (PLA) matrix were examined to generate composite materials with superior mechanical and thermal properties which might be used as a biodegradable food packaging, according to Siakeng et al. **[95].** Mechanical tests revealed that all of the composites outperformed neat PLA in terms of tensile and flexural modulus. In addition, the inclusion of PALF raised strength values while the addition of CF improved strength outcomes in impact testing. The storage and loss moduli of the CF/PALF/PLA hybrid composites increased as compared to the plain PLA, according to DMA data. The use of fiber reinforcements reduced the coefficient of thermal expansion (CTE) of PLA composites. The hybrid composite had the best combination of mechanical qualities and improved heat stability, making it ideal for food packaging applications. It can be concluded that fiber loading at a 1CF: 1PALF ratio, as in hybrid composite C1P1, provides the best mechanical and thermal properties while also permitting adequate distribution within the PLA matrix, and is thus the best fiber hybridization ratio among the choices evaluated in this work.

A comparative study between bio-composites Obtained with Opuntia Ficus Indica Cladodes and Flax Fibers was conducted by A. Grec **[96].** The wooden backbone was employed to substitute flax fibers in the creation of fully consolidated bio-composites in the first option. The results revealed that, despite having lower characteristics than flax fiber composites, Opuntia acts as an effective reinforcement for PLA/wood flour matrix, boosting flexural strength and elongation at break. The cellular structure was used in the second option to create a sandwich bio-composite with a PLA/wood flour skin. In this case, the very high interlaminar adhesion strength between the skin and the core was taken as a sign that this material may be used to make high-strength sandwich constructions. The use of the wooden backbone of Opuntia Ficus Indica cladodes as reinforcement for the fabrication of bio-composites was investigated in this study.

Nonetheless, the mechanical capabilities were found to be inferior to those of a flax fiber composite with a similar reinforcing weight fraction. Alternatively, a PLA coupling film was used to adhere the bio-microcomposite to the opuntia backbone, resulting in a sandwich bio-composite.

Xu et al. **[97]** investigated the kinetics of PLA/BaSO4 thermal degradation using model-free iso-conversional techniques. Model fitting was used to determine the kinetic mechanism and reaction order in order to create environmentally acceptable PLA bio-composites with excellent thermal characteristics. Inorganic fillers have an inhibitory influence on thermal degradation, as evidenced by significant increases in activation energy of bio-composite 10wt% BaSO4 compared to pure PLA. A combination of model-fitting methodologies including the Carrasco method were used to identify the apparent kinetic mechanism and reaction order for the overall thermal deterioration.

Rojas-González, A. F et al. **[98]** studied the thermal degradation kinetic of Polylactic Acid in multiple extrusions in an inert atmosphere with a nitrogen flow for four heating rates, B = 5, 10, 20, and 40°C/min The activation energy (Ea) grows with reprocessing, and the frequency factor (A) increases with the heating rate, according to the findings. When PLA is processed by continuous extrusion, it shows signs of heat deterioration. The average kinetic triplet produced by isoconversional methods is E=147,14 kJ/mol, ln(A)= 26,94 (with A in min^{-1}), and reaction order n = 0,86, whereas the triplet obtained by non-isoconversional methods is E=225,30 kJ/mol, ln(A)= 45,07, and n = 0,91. With activation energies ranging from 137, 82 to 165, 46 kJ/mol and pre-exponential factors (Ln A) ranging from 25, 50 to 30, 86, with A in min^{-1}, the Kissinger technique provided the best accurate description of the thermal decomposition kinetics. The averaged kinetic triplet of PLA extruded in five reprocesses, using isoconversional and non-isoconversional methods, has E values ranging from 147.14 to 225.30 kJ/mol, A values ranging from 26,94 to 45,07 min-1, and n values ranging from 0,86 to 0,91, respectively.

Guida, M et al. **[99]** studied the thermal behavior of sawdust wood (SW) wastes samples was examined at different heating rates (β) in inert atmosphere using the technique of thermogravimetric analysis (TGA). Eight methods: Friedman (FR), Ozawa-Flynn-Wall (OFW), Vyazovkin (VYA), Kissinger Akahira-Sunose (KAS), Starink method (ST), Avrami theory (AT), Coats-Redfern and Criado methods were used in this work to evaluate the kinetic parameters, including apparent activation energy (Ea), reaction order (n) and the appropriate conversion model f (α). For the range of conversion degree (x) investigated (20 – 80 %), the mean values of apparent activation energy for Sawdust wood waste were 168 KJ/mol, 153 KJ/mol and 164 KJ/mol for FR, OFW and VYA methods respectively. While for KAS and ST methods were 158 KJ/mol and 156 KJ/mol. With varied temperature (300-700 °C), the corresponding values of reaction order (n) was increased from 0.1072 to 0.2587, along with a decrease to .1635. The pyrolysis model f (α) of SW is described by reaction order (Fn), first order (F1) for the degradation of the studied wastes samples.

Borkotoky, et al. **[100]** studied the thermal degradation behavior and crystallization kinetics of poly (lactic acid) and cellulose nanocrystals (CNC) based microcellular composite foams. The investigation addresses the thermal degradation and non-isothermal crystallization behavior of the fabricated poly (lactic acid) foam (nPLA) and poly (lactic acid) (PLA)/cellulose nanocrystal (CNC) based foams at three different loadings of CNC (i.e. 1%, 2% and 3%) as PLA/CNC 1, PLA/CNC 2 and PLA/CNC 3 having highly porous, interconnected and microcellular morphology. The formation of various gaseous products at two different conversions (α=0.3 and α=0.7) are investigated by using thermogravimetric analyser hyphenated Fourier transmission infrared spectroscopy (TGA-FTIR) analysis in isothermal condition. Effect of porosity and CNC reinforcement towards thermal degradation and crystallization of the PLA is thoroughly investigated by using mercury intrusion porosimetry (MIP). "Model-free" and "modelistic" approaches like Friedman, Flynn-Wall Ozawa (FWO), Kissinger-Akahira-Sinouse (KAS), Kissinger and Augis & Bennet have been utilized for non-isothermal degradation kinetics of the fabricated foams. Non-isothermal melt crystallization kinetics of fabricated foams reveals that both primary and secondary crystallization process taking place. The apparent activation energy calculated from FWO are ~175.8 kJ/mol, ~198.6 kJ/mol, ~175.5 kJ/mol and ~174.7 kJ/mol for nPLA, PLA/CNC 1, PLA/CNC 2 and PLA/CNC 3 respectively. It is also observed that at higher conversions, complex three dimensional diffusion mechanism of degradation might be taking place in accordance with Criado plots.

Li, J et al **[101]** studied the thermal degradation kinetics of poly (l-lactide) (PLA) and hydroxyapatite nanoparticle that was surface-grafted with l-lactic acid oligomer (g-HA) in a nitrogen atmosphere. The kinetic models and parameters of the thermal degradation of PLA and the g-HA/PLA composite were evaluated by the invariant kinetic parameters (IKP) method and Flynn–Wall–Ozawa (FWO) method based on a set of TGA data obtained at different heating rates. It was shown that the conversion functions calculated by means of the IKP method depend on a set of kinetic models. The g-HA particle slowed down the thermal degradation of PLA polymer matrix.

Dhar, P et al. **[102]** studied the thermal degradation kinetics of Polylactic Acid/ Acid fabricated cellulose nanocrystal based bio-nanocomposites. The resulting acid derived CNC are melt mixed with Polylactic acid (PLA) using extruder at 180 °C. Thermogravimetric (TGA) result shows that increase in 10% and 50% weight loss (T_{10}, T_{50}) temperature for PLA-CNC film fabricated with HNO_3, H_3PO_4 and HCl derived CNC have improved thermal stability in comparison to H_2SO_4-CNC. Non isothermal kinetic studies are carried out with modified Coats-Redfern (C-R), Ozawa-Flynn Wall (OFW) and

Kissinger method to predict the kinetic and thermodynamic parameters. Subsequently prediction of these parameter leads to the proposal of thermal induced degradation mechanism of nanocomposites using Criado method. The distribution of Ea calculated from OFW model are (PLA-H_3PO_4-CNC: 125-139 $kJmol^{-1}$), (PLA-HNO_3-CNC: 126-145 $kJmol^{-1}$), (PLA-H_2SO_4-CNC: 102-123 $kJmol^{-1}$) and (PLA-HCl-CNC: 140-182 $kJmol^{-1}$). This difference among Ea for the decomposition of PLA-CNC bio-nanocomposite is probably due to various acids used in this study. The Ea calculated by these two methods are found in consonance with that observed from Kissinger method. Further, hyphenated TG-Fourier transform infrared spectroscopy (FTIR) result shows that gaseous products such as CO2, CO, lactide, aldehydes and other compounds are given off during the thermal degradation of PLA-CNC nanocomposite.

Sajna, V et al. **[103]** studied the thermal degradation kinetics and flammability properties of Poly (lactic acid)/Banana Fiber/Nanoclay hybrid bio-nanocomposites. The bio-nanocomposites were prepared using melt blending technique followed by injection molding. The reinforcing effect of silane treated banana fiber (SiB) and Closite 30B (C30B) nanoclay on the thermal stability and fire retardancy of PLA has been studied. Isoconversional kinetic analysis using Friedman and Flynn-Wall-Ozawa method as well as analysis based on parameters at the maximum degradation rate (Kissinger method) were employed to understand the thermal degradation kinetics in the bio-nanocomposites. The results from thermogravimetric analysis (TGA) revealed that bio-nanocomposites have improved thermal stability.

According to the scientific literature, only few studies report the use of OFI for preparation bio-composites. For the first time the kinetics and mechanism of thermal degradation of a PLA matrix filled with 10 wt% talc and 10 wt% OFI-F will be studied.

This work aims to investigate the thermal behavior of talc and OFI-F reinforced PLA bio-composites using TGA and to determinate the kinetic parameters. Moreover, it aims to evaluate whether Ea is constant with the degree of conversion and the suitability of the proposed methods. Model-free methods such as Flynn-Wall-Ozawa (FWO), Kissinger-

Akahira-Sunose (KAS) and model fitting methods such as Kissinger and Coats-Redfern (C-R) were used to evaluate the activation energy of neat PLA, PLA/Talc, PLA/OFI-F and PLA/Talc/OFI-F. Master plots methods such as Criado and Coats Redfern were applied to identify possible reaction models of neat PLA and its bio-composites to better understand the thermal degradation mechanism of PLA and its bio-composites.

Conclusion

Bioplastics are being developed as a solution for the accumulation of waste plastics, and so are an important research topic in the plastics sector. Poly (lactic) acid is a polymer that can be used for both general and technical purposes. It has received a lot of attention because of its renewable resources, biodegradability, thermal performance, and ultimate material transparency.

This literature review shows that it is possible to optimize the final properties of PLA bioplastics.

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Chapter II

Bio-composites

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Bio-composites

Introduction

Sustainability is transforming the dynamics of industries' materials, providing new opportunities and prospects to the scientists of materials. The materials industry is being pushed to develop the next generation of materials by industrial ecology and eco-efficiency. Bioplastic innovations are providing a portfolio of sustainable and environmentally friendly products to compete in a market currently dominated by synthetic plastics. Concerns about petroleum resource depletion and disposal have arisen as a result of the development and usage of synthetic polymers.

These two major problems have prompted efforts to develop fossil fuel based products alternatives. One of these endeavors is the development of bio-composites where there are potentials to investigate 'green' materials and produce sustainable products. Over the last decade, bio-composites have seen significant expansion **[1].**

II.1. Bio-composites

The composite comprises of two or more different parts or phases, when one or more discontinuous phases (reinforcements) or reinforcing material are distributed in another continuous phase (matrix) to get tailor-made features or properties. The composite material should be designed to achieve qualities that none of the components could accomplish on its own. Bio-composites are composite materials that contain one or more phases that are generated from biological sources. **[2, 3].** Green composites, which are fully sustainable bio-composites created from bio/natural fibers and biodegradable polymers, are the center of attention due to environmental concerns and legislation. **Figure II.1 s**hows diagram of composite material.

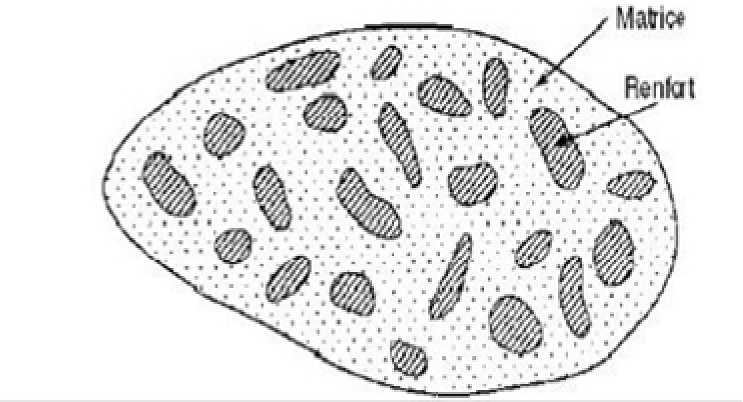


Figure II.1: Diagram of composite material **[4]**

II.1.1. Matrix

The matrix is the weaker phase that is bolstered by the stronger reinforcing phase. The matrix serves as a bulk material that distributes loads between the reinforcements.

The matrix also serves to protect the reinforcement, shielding it from the impact of environment. The matrix serves three main purposes:

- To keep the reinforcement in the proper orientation;
- To avoid damage to the reinforcement;
- Transferring applied loads to reinforcing agents.

The classification of commonly encountered matrix types is given **in figure II.2**

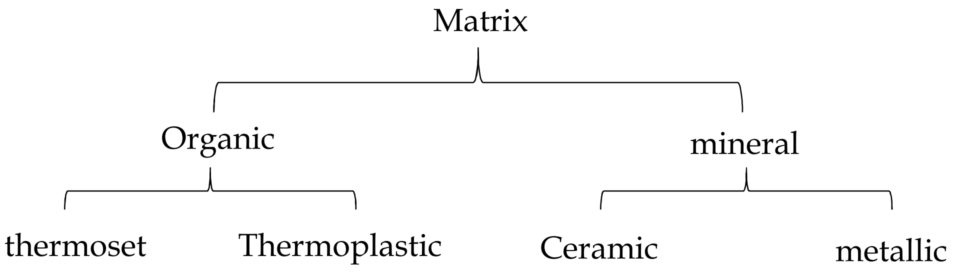


Figure II.2: Matrix types **[5]**

II.1.2. Reinforcement

Various geometry particles, fibers, flakes, and fillers can all be used as reinforcements. The reinforcement provides the strength and stiffness properties to the bio-composites. As the fillers are supplied to the mold, their shape and arrangement can vary significantly. They can be arranged in a variety of ways, including short strands of randomly oriented whiskers, a bundle of fibers, a unidirectional fabric, a woven fabric, and so on. A variety of composite properties can be achieved by combining different reinforcing elements. Depending on the use and production technique, reinforcement can take a number of different shapes or combinations **[6].**

II.2. Polymer composites

Nowadays polymer matrix composites are the most common commercial composites. Polymer composites are increasingly popular due to their low weight, comparatively high stiffness and strength, thermal and chemical resistance, and ease of production.

In many areas such as the automobile and aerospace industries, composites are replacing metal components **[7].** The resins used to make composites are either thermoplastics or thermosets.

II.2.1. Thermoplastics

Thermoplastics have a linear or branching molecular structure that cannot be crosslinked to form a three-dimensional network.

In thermoplastics, weak van der Waals connections between polymer chains are broken by applying high temperatures under stress, causing the polymer to flow. Thermoplastics solidify when they cool, allowing them to be heated, molded, and cooled repeatedly. The following are some of the most often used thermoplastic resins: polyethylene, polyethylene trephtalate (PET), polyvinyl chloride (PVC) and polystyrene **[8].** Thermoplastics become more popular than thermosets because no curing reaction is necessary; they can be processed more quickly than thermoset composites. Heating, shaping, and chilling are all that is required of thermoplastic composites. They have a high level of hardness, low moisture absorption and low toxicity, among other properties **[9].**

II.2.2. Thermosets

Thermosetting polymers have a three-dimensional cross-linked structure. Curing causes the polymer to get cross-linked. An irreversible curing reaction is triggered by the addition of a catalyst (curing agent) or the application of heat and pressure. The thermosetting polymers are unable to be molded when heated due to strong covalent bonds within the cross links. To put it another way, thermosets do not flow or melt by reheating. Cured thermosets often have higher heat resistance than thermoplastics. Due to their low viscosity thermosets are often processable at room temperature **[10].** Among thermosets, unsaturated polyesters, epoxies, vinyl esters and phenol resins are the most common in composites **[9, 11].**

II.3. Types of composite materials

As indicated in **figure II.3**, composite materials are widely categorized into groups.

II.3.1. Fiber-reinforced composites

Because of their inherent high specific strength and stiffness, reinforced-composites are being utilized in a variety of industrial applications. Fiber reinforced composite materials are made up of high-strength, high-modulus fibers attached to a matrix having different interfaces **[12].**

Both the fibers and the matrix retain their physical and chemical uniqueness in this state. Despite this, they provide a mix of qualities that would be impossible to achieve if one of the parts acted alone. Fibers are the main load-bearing candidates, with the surrounding matrix ensuring that they remain in the proper position and orientation. Fibrous composites can be divided into two categories: continuous (long) fiber composite and discontinuous (short) fiber composite.

a. Continuous or long fiber composite

The matrix of a continuous composite is reinforced by a dispersed phase in the form of continuous fibers. A continuous fiber is geometrically identified as having a very high length-to-diameter ratio. They're usually more rigid and stronger than matrix material.

It is classified into two types based on the orientation in which the fibers are placed within the matrix:

- Unidirectional reinforcement;
- Bidirectional reinforcement.

The fibers in unidirectional reinforcement are only orientated in one direction whereas in bidirectional reinforcement, they are directed in two directions, either at right angles to each other (cross-ply), or at a chosen angle (angle-ply) **[13].**

b. Discontinuous or short fiber composite

The matrix of short-fiber reinforced composites is reinforced by a dispersed phase in the form of discontinuous fiber. Short fiber composites are a good solution to large-scale production due to the easiness of making their complex parts and also due to their reduced costs. As a result, light loaded component manufacturing has benefited from the use of short-fiber reinforced composites. The discontinuous fiber reinforced composite is further classified into the following categories:

- Biased or preferred oriented fiber composite;
- Random oriented fiber composite.

The fibers in the first category are orientated in predetermined places whilst in the second category are randomly organized. Short fibers can be oriented by sprinkling the fiber on a specific plane or adding a matrix in a liquid or solid state before or after the fiber is deposited **[14].**

II.3.2. Laminate composites

Laminate composites are made up of many layers of materials held together by a matrix. In most cases, these layers are alternated to improve the bonding between the reinforcement and the matrix. The fiber reinforcement in these laminates can be oriented either unidirectionally or bidirectionally. Unidirectional, angle-ply, cross-ply, and symmetric laminates are the many forms of composite laminates. A hybrid laminate can be made from a variety of constituent materials or from the same material with a variable reinforcing pattern **[15].**

II.3.3. Flake composites

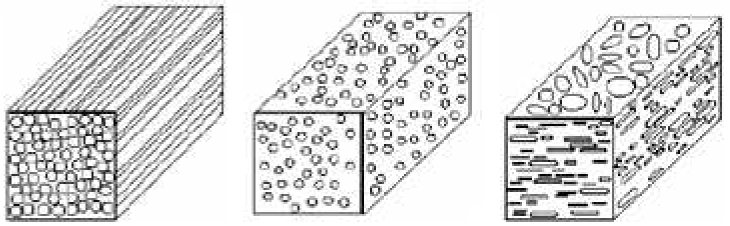
Flakes are frequently substituted by fibers because they can be densely packed. Flakes are less expensive to manufacture than fibers. However, they fall short in areas such as size, control, and shape, their final product also has flaws.

II.3.4. Particulate composite

Filled polymers are more commonly referred to in the plastics industry as particle reinforced polymer matrix composites. Particulates, also referred to as fillers, are low-cost, micrometer-sized solid particles that have traditionally been used to lower material costs. Fillers, on the other hand, affect the mechanical and thermal properties of polymers, and in some situations can even act as reinforcing agents **[16].**Particulates are divided into two types: inorganic fillers and organic fillers.

The most commonly used inorganic fillers are low-cost minerals like talc and mica, which are abundant in nature. Solid glass microspheres and other synthetic inorganic fillers are also available, but they are significantly more expensive than naturally occurring mineral fillers.

Organic additives such as wood floor, powdered peanut shells, and rice hulls are also used in the plastic industry. The main drawbacks of organic fillers are their low temperature stability and high moisture absorption; both of which limit their use. One of the most exciting elements of the topic of particle filled-polymer composites is the wide range of materials used as fillers.



(a) Continuous fiber composite **(b) Particulate composites** **(c) Flake composites**

(d) Random fiber (short fiber) Composite **(e) Laminate Composite**

Figure II.3: (a-e) Schematic figure of different types of composites **[17]**

II.4. Bio-fibers and their classification

Natural fibers have been used for 3000 years in composites, for example in ancient Egypt, where straw and clay were mixed to build walls. Over the past decade, natural fiber reinforced composites have received increasing attention from both academia and various industries. There is a wide variety of natural fibers that can be used for reinforcement or as fillers **[18].**

Green composites are made up of a biodegradable polymer matrix with bio-fibers as reinforcement (e.g. wood, hemp, flax, jute, etc.). Because both components are biodegradable, the bio-composite, as the integral part, should be biodegradable as well **[19].**

Depending on their origin, as well as their physical, chemical, and structural composition, these bio-fibers improve the strength and stability of the resulting composite structures **[20].**

The properties of bio-fibers vary depending on whether they are extracted from plant stems or leaves, the quality of plant sites, the plant's age, and preconditioning, among other factors **[21].**

Natural fibers offer the benefits of low cost and biodegradability. Natural fibers are categorised based on their origin. The first is animal-based, the second is plant-based, and the third is mineral-based.

The animal based fibers are split into three categories: hair based fibers (wool), silk fiber (bugs) and avian fibers (birds).

Plant based fibers are subdivided into fruit based, stalk based and leaf based. Flax, jute, hemp, and wood fibers are the most common stalk-based fibers. Depending on where it comes from, wood is classified as hardwood or softwood **[22, 23].** The most common plant-based natural fibers used as reinforcing natural fibers are flax, jute, hemp, and wood. Plant-based natural fibers are also made from the leaves of plants such as sisal, pineapple, banana, and agave. Fruit-based fibers such as coconut, cotton, and coir, as well as mineral-based reinforcing materials such as asbestos or inorganic whiskers, are utilized as hard reinforcing fibers. **Figure II.4** shows natural fibers classification.

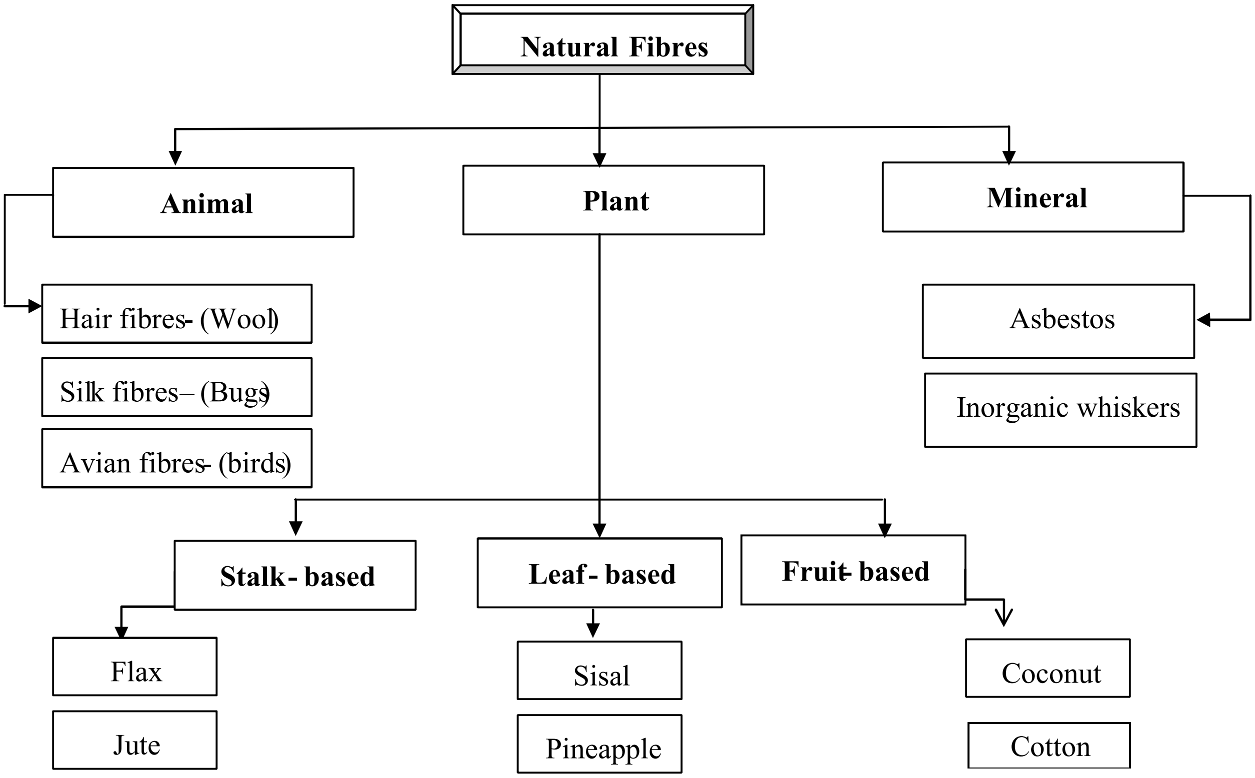


Figure II.4: Natural fibres classification **[24]**

Natural fibers derived from plants are lignocellulosic in nature. The most abundant renewable biomaterial is lignocellulosic materials. Bio-fibers are made up mostly of cellulose, hemicelluloses, and lignin which is a kind of natural composite itself **[19, 25].**

In lignocellulosic systems, the amount of cellulose varies depending on the age of the plant/species. The chemical compositions and structural properties of several natural fibers are shown in the **table II.1** which reveals that all three principal constituents differ significantly.

Table II.1: Chemical composition and structural parameters of natural fibers **[26]**

Type of fibers	Cellulose	Lignin	Hemicellulose	Pectin	Wax	Moisture content
	(wt %)	(wt %)	(wt %)	(wt %)	(wt %)	(wt %)
Stalk **Jute**	61 - 71.5	12 - 13	13.6 – 20.4	0.2	0.5	12.6
Flax	71	2.2	18.6 – 20.6	2.3	1.7	10.0
Hemp	70.2 – 74.4	3.7 – 5.7	17.9 – 22.4	0.9	0.8	10.8
Ramie	68.6 – 76.2	0.6 – 0.7	13.1 – 16.7	1.9	0.3	8.0
Kenaf	31 - 39	15 - 19	21.5	--	--	--
Leaf **Sisal**	67 - 78	8 – 11	10.0 – 14.2	10.0	2.0	11.0
Fruit **Cotton**	82.7	- -	5.7	- -	0.6	--
Coir	36 - 43	41 -45	0.15 – 0.25	3 - 4	- -	8.0

II.4.1. Structure of natural fibers

The phrase "elementary fiber" refers to the tiniest strand of vegetable fiber that can be identified with an optical microscope. These fibers have different properties and natures depending on where they are grown and extracted **[27,28].** 'Technical fibers,' which have 10-40 elementary strands, usually naturally bonded together. Technical fibers can be as long as a meter and as wide as 50-100 meters in length and diameter.

Technical fibers have been used as reinforcement in composite manufacture because of their easy extraction processes and overall qualities **[29].**

a. Cellulose

Cellulose is the major component of natural fibers, with a ratio ranging from 40 to 70% depending on the kind of fiber **[30].** Cellulose is a homopolysaccharide consisting primarily of -D-glucopyranose units coupled to (1→ 4) glycosidic linkages to produce cellulose units at the molecular level. The smallest repeating unit in cellulose is shown in **Figure II.5 [31].**

The molecular structure of cellulose determines its macromolecular structure, chemical characteristics, and physical qualities. Furthermore, cellulose is the load-bearing component of natural fibres, and its degradation causes mechanical characteristics to deteriorate **[30].** The length of the cellulose chain (DP) in living natural fibers is not well established; nonetheless, native molecules are between 5000 and 10,000 glucopyranose units in size **[31].** The end-to-end chains are connected by strong hydrogen bonds between the three hydroxyl groups in each unit and their positions.

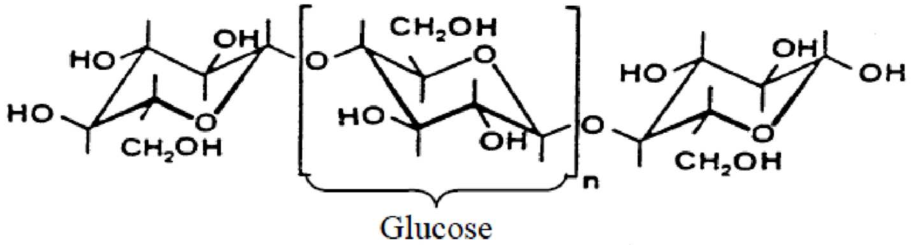


Figure II.5: Chemical structure of cellulose **[31]**

b. Hemicellulose

Hemicellulose refers to any of the heteropolymers (matrix polysaccharides) found in natural fibers **[3031].** The bulk of hemicelluloses, like cellulose, serve as a supporting element in the cell wall and are very hydrophilic **[28, 32, 33].** Xylan, glucuronoxylan, arabioxylan, glucomannan, and xyloglucan make up the chemical composition of hemicellulose **(Figure II.6).** Hemicellulose has a lower molecular weight (MW) than cellulose and a density profile (DP) of 50-300 **[34].**

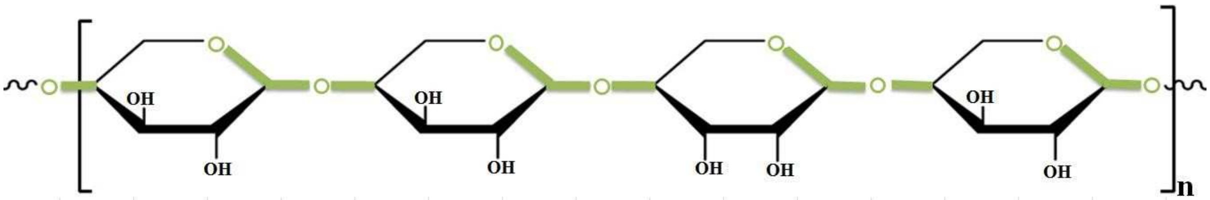


Figure II.6: Most common molecular motif of hemicellulose **[33]**

c. Lignin

The stiffness of natural fibers is provided by lignin, a complicated three-dimensional (aromatic hydrocarbon polymer) molecule with an amorphous structure. In other words, without lignin, natural plants cannot grow tall (**Figure II.7**) **[30].** Due to the technological challenges of isolating lignin in its natural condition, the chemistry of lignin is not completely understood. According to Mohanty et al. **[32],** lignin is a thermoplastic polymer that melts around 170 °C. It works as a chemical glue within and between stem fibres, as well as increasing natural fibers' resistance to microbes **[31].** Lignin has a large molecular weight and is less polar than cellulose **[32],** hence it is considered hydrophobic.

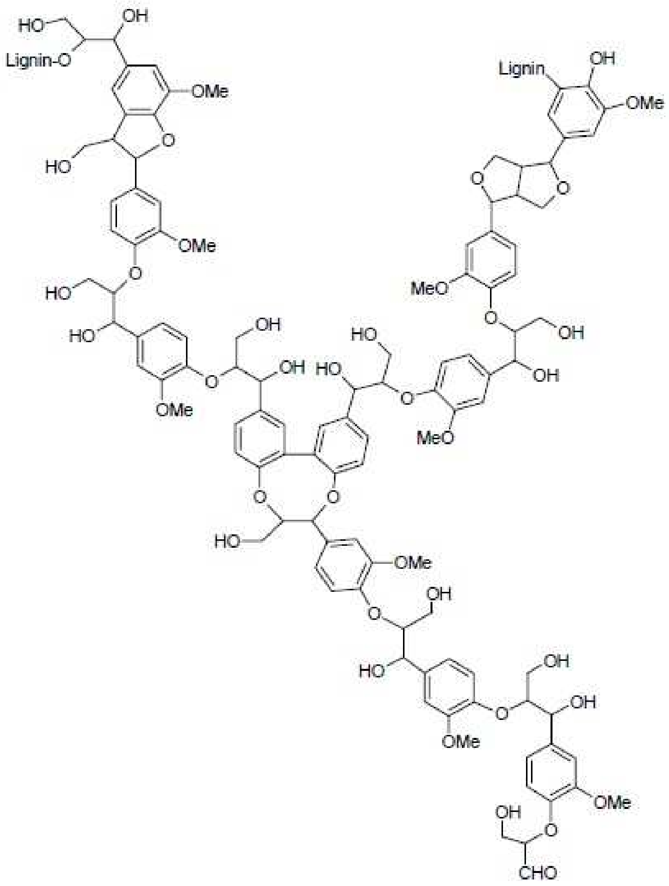


Figure II.7: Chemical structure of lignin **[31]**

II.5. Factors affecting composite properties

The proportion and qualities of the matrix and reinforcement have a big impact on the composites' properties. The stiffness and strength behavior of composites determine the desirable qualities of fibers. Appropriate fiber reinforcement is determined by a number of factors, including: **[35, 36]**

- **a.** Thermal and mechanical properties ;
- **b.** Adhesion between fibers and matrix;
- **c.** Dynamic behaviour ;
- **d.** Long-term behaviour ;
- **e.** Price and processing costs.

All of these aspects interact to influence the properties of composite materials, but the intrinsic properties of the constituents control composite properties. The following are the two most important properties that determine the mechanical and thermal properties of composites **[22]:**

- **Fibre architecture**
  (Geometry / Aspect ratio, Orientation, Volume fraction)
- **Fibre-matrix interface**

II.5.1. Fiber architecture

a. Fiber volume fraction

One of the most critical parameters regulating the strength, stiffness, and many other physical properties of composites is the fiber volume fraction. There are two possible failure regimes for a composite system where matrix failure strain is greater than fiber failure strain, depending on whether the fiber volume fraction (V_f) is above or below a minimum value (V_{min})

The polymer matrix can carry the applied load following fiber breakage when V_f is less than V_{min}. The failure of the fibers does not result in the failure of the composite, but rather increases the stress in the matrix. The failing fibers can be thought of as holes in the polymer matrix because they no longer bear any load.

Failure of the fibers leads to failure of the entire composite when V_f exceeds V_{min}, because the polymer matrix is insufficient to withstand the increased load transmitted into the matrix of the fibers.

As a result, the critical volume fraction (V_{crit}) for the composite system is the number of fibers required to ensure that the composite strength is at least equal to the matrix strength. The strength of composites begins to deteriorate at a very high volume fractions due to insufficient loading by the matrix material **[37].**

b. Fiber Aspect ratio

In composite materials, the fiber aspect ratio (length/diameter or thickness) is an important parameter. For effective composite strengthening and stiffening, a crucial fiber aspect ratio is required. This critical fiber length is the shortest length of fiber required for the tension to reach the fiber's fracture stress. Fibers that are less than the crucial length cannot bear the maximum load and so cannot function effectively **[37, 39].**

c. Fiber Orientation

The length of the fibers is not as important as the orientation of the fibers. The fiber orientation is determined by the processing method. When continuous fibers are employed, the orientation can be regulated to give the composite predictable strength and stiffness and output qualities. Short fiber reinforced composites feature randomly aligned fibers; however, they frequently have preferred fiber alignment in the matrix flow direction or a layered structure with distinct fiber alignment in different layers. The viscoelastic properties of the fiber filled matrix, mold design, and the change in shape of the material created by the processing operation are all factors that influence fiber orientation **[38].**

II.5.2. Composite (fiber –matrix) interface

The "composite interface," which is a region of considerably modified chemical composition that forms the bond between the matrix and the reinforcement, is the most important phenomenon in composite theory. This contact region is critical for transferring load from the matrix to the fibers. In general, a weak contact results in low strength, stiffness, and less resistance whereas a strong interface results in high strength, stiffness, and a high resistance **[38].**

The bonding mechanism at the contact is another important phenomenon. Different sorts of bonds may form once the matrix and reinforcement are exposed to one other; some of which may occur at the same time. Inter-diffusion, electrostatic attraction, chemical bonding, reaction bonding, and mechanical bonding are the five main mechanisms involved in interfacial bonding **[39].**

Aside from these, there is a number of other elements to consider in order to maximize the benefits of fiber reinforcement. The homogenous dispersion of fibers into the matrix and the optimization of processing parameters (i.e temperature, rpm, etc.) are two of them.

II.6. Overview of Poly (lactide) – composites

The market for PLA composites has been expanding for some years. Polymer composites with filler reinforcement have shown to be effective. This section introduces the PLA matrix as well as the various fillers that are used as reinforcement.

PLA – Natural fiber reinforcement
PLA - Synthetic fiber reinforcement
PLA – Mineral filler reinforcement

II.6.1. PLA natural fiber reinforcement

Organic fibers are less abrasive than inorganic fibers which gives them a processing advantage **[40].** Natural fibers are preferred over synthetic fibers because of their long-term vitality, low cost, competitive mechanical properties, and lower ash output after burning **[41].**

Wood fillers, fibers, and derivatives are the most well-known and regularly used organic fillers. Other natural fillers such as cellulose, cotton, jute, flax, and hemp are employed in a variety of applications in addition to wood derivatives **[42].**

Several research articles on lignocellulosic - PLA composites have been published. There has been tremendous progress in the production of biodegradable PLA composites, according to a number of studies. Hemp-PLA, kenaf PLA, flax-PLA, jute-PLA, PLA-Wood **[43].** Satyanarayana et al. **[44]** provided an overview of biodegradable composites made from lignocellulosic fibers.

Because of its incompatibility, plant-fiber reinforced PLA composites are still a challenge. The following are a few of these difficulties **[2];**

Poor interfacial adhesion between the hydrophilic fiber and the hydrophobic PLA matrix causes difficulties in mixing.

Plant fiber composites are processed at temperatures of less than 200 °C or less because plant fiber degrades at higher temperatures.

Natural fibers absorb a lot of moisture which causes swelling and presence of voids at the interfaces, resulting in poor mechanical characteristics and dimensional stability of composites.

In terms of size and mechanical qualities, there is no uniformity (even between individual plants in the same cultivation).

Opuntia Ficus Indica (OFI) is a cactus widespread in the Mediterranean region and represents one of the most abundant biomasses.

According to the scientific literature, only few studies report the use of OFI for preparing bio-composites. Greco et al. used the wooden backbone of OFI cladodes to prepare PLA-based sandwich structures by compression molding plus stacking and consolidated OFI fibers composites by impregnation **[45].** In both cases, the cladode backbone imparted high stiffness to the resulting structures. According to the work of Malainine et al., OFI flour was added to polypropylene, revealing a poor affinity to the polymer matrix **[46].**

II.6.2. Synthetic Fiber Reinforcement

Synthetic fiber reinforcement is commonly used to reinforce polymer matrices to develop structural composites with improved properties. Therefore, synthetic fiber reinforced PLA composites need to have favorable characteristics like **[47]** high strength to weight ratio, good dimensional stability, good resistance to heat, resistance to moisture and corrosion, and good processability.

II.6.3. PLA mineral filler reinforcement

Utilization of mineral fillers as a reinforcement is one of the approaches used to improve the mechanical and thermal properties of thermoplastics in the development of particulate composites. Fillers or additives are used to produce particulate composites, by modifying properties like flexural modulus and temperature resistance. Therefore, these fillers are often called functional fillers, mineral additives or reinforcing agents.

Mineral additives- matrix composites are made of two very dissimilar materials. The matrix or resin is covalently bonded organic in nature, and the filler is inorganic in nature with ionic interactions between the atoms. Differences in the nature of the matrix and fillers can be exploited to develop composites for specific desired properties by blending various amounts of different components.

There are certain issues that need to be considered during the use of mineral filler as a reinforcement material. Processing of the mineral additives is critical to the end-use performance; having the best filler and then dispersing or processing it poorly into the resin will not lead to desired results. In general, the physical properties of the fillers, like average particle size, particle size distribution, particle shape and surface properties have the greatest influence on the mechanical and thermal response of the composites.

Different types of functional fillers can be used to improve the mechanical performance, but talc, calcium carbonate, mica and kaolin are the most common and are frequently incorporated into thermoplastics to reduce the end-product cost and improve mechanical and thermal properties of the virgin material **[48].**

Interests in using talc as reinforcing filler is mounting due to its unique properties.

Talc is a hydrated magnesium silicate with the formula Mg_3SiO_{10} (OH) **[44].** The elementary sheet is composed of a layer of magnesium/ (oxygen-hydroxyl) octahedra, trapped between two layers of silicon-oxygen tetrahedrons, hence its name type 2 phyllosilicate. **Figure II.8** shows the classification of clays. **Figure II.9** (a) and (b) show the structure and morphology of talc, respectively. Talc platelets can be dispersed at low shear pressures and are easy to scatter because they have a plate-like structure kept together by weak van der Waal's forces **[49].**

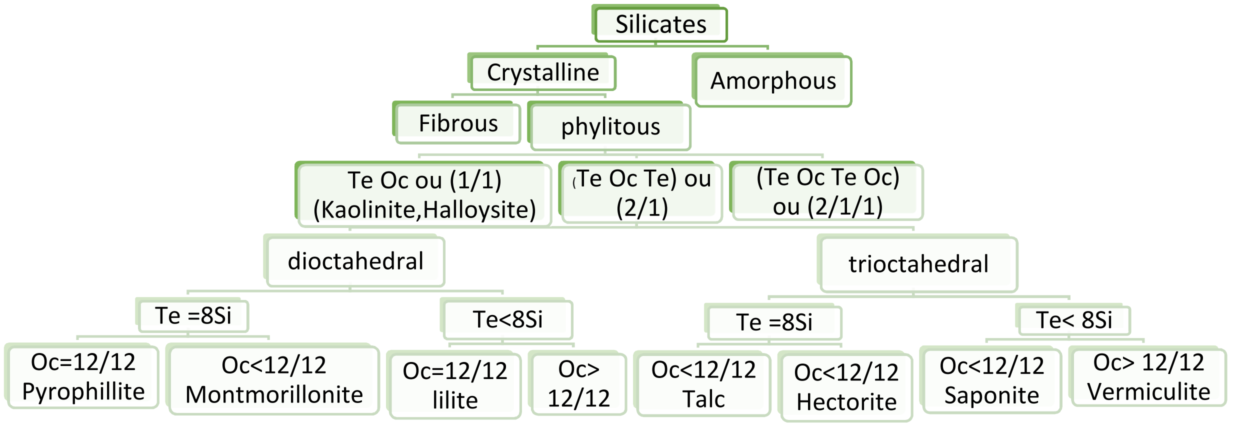


Figure II.8: Simplified classification according to Caillère and Hénin **[50]**

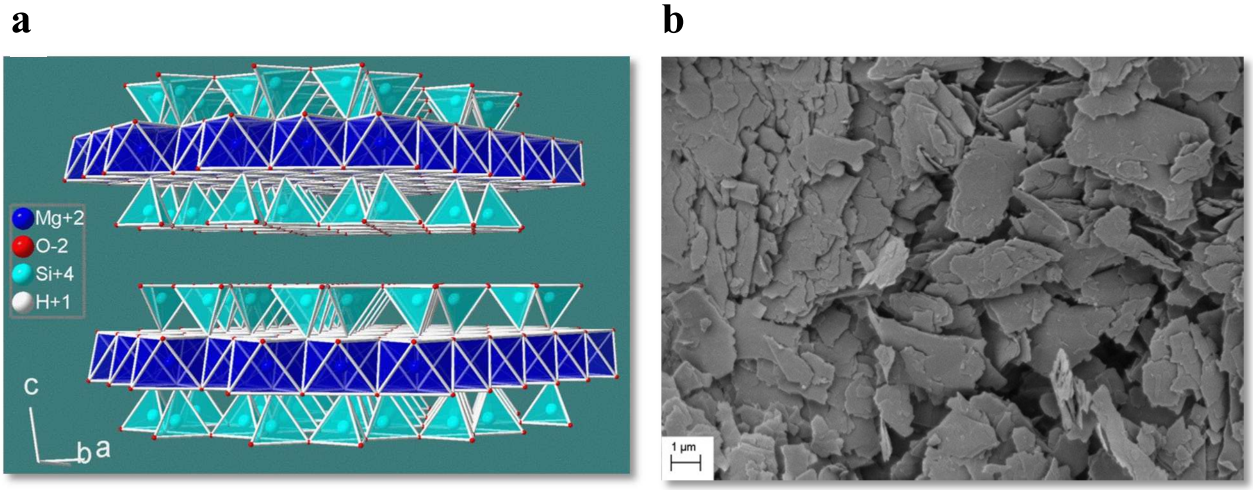


Figure II.9: (a) the structure of talc, **(b)** morphology of talc **[47]**

Talc is one of the softest naturally occurring minerals which is beneficial because it reduces abrasion on polymer processing equipment. Natural talc comes in a variety of colors, including white, colorless, green, and brown. Talc has a high thermal stability of up to 900°C, therefore using it as a filler can help decrease product shrinkage. Talc is also chemically inert, meaning that it is insoluble in water, dilute mineral acids **[51].**

The addition of talc to PLA to form a bio-based polymer composite could be used as a sustainable packaging material that can be reused, recycled, and disposed of in a composting facility. Furthermore, because talc powder is less expensive than PLA resin, the inclusion of talc as a filler is projected to result in a cost-effective packaging material. There are also few research papers or publications on the study of high-dose talc-filled PLA composites (> 30 wt %).

Previous studies **[52-55]** used talc at modest concentrations (<30 wt %) to improve the characteristics of PLA. According to Shakoor and Thomas **[56]**, talc at low concentrations functions as a nucleating agent for PLA crystallization whereas talc content up to 30% in PLA matrix has a considerable reinforcing effect on Young's modulus. As a result, the study's target is to close a knowledge gap by examining how the addition of talc, particularly talc with a high talc content (> 30 wt %), affects the properties of composites. The scanning electron microscope was used to look at the dispersion of the high talc content in the PLA matrix. As previously stated, there are few investigations on high talc content PLA and no comparative studies on the consequences of low to high talc content PLA composites.

Due to the reinforcing ability of the talc particles, the tensile test found that the talc greatly increased the Young's modulus by 10–66%. The PLA/talc composites, on the other hand, showed no improvement in tensile strength or elongation at break due to weak interfacial adhesion between the talc filler and PLA matrix. The maximum Young's modulus was achieved by including 30 wt% talc, which also enhanced the thermal stability of the neat PLA by 7.6 °C, but at the cost of reduced tensile strength and elongation at break. At high talc concentration, SEM micrographs revealed the creation of voids and agglomerates. The optimal formulation for talc filled PLA bio-based polymer composite is 5 wt% talc, with an increase in Young's modulus of 1358 MPa and the highest onset degradation temperature of 309°C, based on overall tensile and thermal characteristics data. The 5 wt% talc had slightly poorer tensile strength and elongation at break qualities than neat PLA. The addition of 5% talc to the material could eventually lower the cost, and it could be used as a long-term packaging material with good thermal stability.

II.7. Applications of polylactid acid (PLA)-composites

PLA is used in biomedical applications. PLA composites produce partial degradable bone plates. The development of PLA composite-based biodegradable porous structure represents a promising alternative for bone grafting **[57].**

PLA based bio-composites are fully biodegradable and biocompatible and have shown potential growth for developing polymeric scaffolds for tissue engineering applications **[19].**

Another development is applications of biodegradable composites in the automotive industry. Developing biodegradable composites for interior and exterior uses in the automotive sector has gained a lot of momentum. There are a lot of potential benefits of using the PLA-based composites in car design, as a concept of “green car” which is appealing from both the consumer and manufacturer point of view. Automotive manufacturers are exploring various applications of PLA composites. **[58].**

On the other hand, various films, molds (trays, cups, etc.), and bottles are made for food packaging and used as biodegradable, short shelf-life plastic products, useful for producing loose-fill packaging, compost bags, and disposable tableware, etc,.

Recently another PLA-based composite has been developed to be used in the electronic industry which is still in the developmental phase **[24].** While numerous opportunities exist for PLA composites to enter into new markets, the future growth and sustainability of PLA composite is reliant on continued research which will help in producing technically viable and economically feasible PLA composites in the future to widen its application spectrum.

Conclusion

The analysis of this literature review has shown that the tendency to use materials made from renewable materials has expanded into the growing bio-composite market.

In this chapter, the focus was on the integration of bio-composites with natural and mineral fibers in the field of bio-composites which represent an interesting alternative to plastics derived from petrochemicals. We have also tried to highlight the use of PLA composites with various fillers like natural or mineral fillers that are used as reinforcements and whose main advantages are: biodegradability, renewability, abundance and recyclability. These advantages overweigh the drawbacks which consist in, inter alia, weak thermal properties, allowing bio-composites to enter real competition with petrochemicals composite materials.

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Chapter III

Materials, experimental methods, characterization techniques and kinetics study

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Materials, experimental methods, characterization techniques and kinetics study

Introduction

This chapter details the materials and methods used in this research. The details of methodologies and techniques adopted have been clearly outlined in this chapter.

This study conducted the following experiments:

OFI-F preparation;
PLA/PLA hybrid bio-composite fabrication;

The thermal and morphological properties of bio-composites were evaluated using a variety of characterization methods. Hence, the following techniques, thermogravimetry (TGA), wide angle X-ray scattering (WAXS) and scanning electron microscopy (SEM) are used. In addition, the kinetics of non-isothermal degradation of OFI flour and talc-filled PLA are studied. The Coats-Redfern and Criado methods are also used to explore the degradation mechanism of bio-composites.

III.1. Materials

III.1.1. Poly (lactic acid)

The poly-lactide (PLA) used in this work as the base polymer was supplied by Nature Works LCC as shown in **Figure III.1**. It is a semi-crystalline grade (PLA 4032D) with D isomer < 2%, $Mn_{(PLA)}$ =51.400g.mol^{-1}.

Figure III.1 PLA in pellet form

III.1.2. Opuntia Ficus Indica Flour (OFI-F)

a. Origin

It is a plant native to the arid and semi-arid regions of Mexico and the southern United States which was introduced into Europe and North Africa around the 16th century by shippers **[1].**

b. Appellation of Opuntia Ficus Indicas

The nopal is the Mexican name of the plant comes from the name nochtili in Nahuatl, the classic language of the Aztecs. Opuntia its scholarly name comes from the Latin Opuntius of Oponte.

c. Classification

Table III.1: Classification of Opuntia Ficus Indicas

Reign	plant
Branch	Mangnoliphyta
Class	Magnoliopsida
Order	Cayophyllide
Family	Cactaceae
Gender	Opuntia
Species	Ficus-Indica

OFI flour used as a reinforcing filler were gently prepared in a laboratory following a procedure reported earlier.

III.1.3. Talc powder

Talc powder was obtained from Sigma Aldrich (Algeria). Talc is widely known for its barrier qualities which make it an excellent healer for bio-composites found in nature. As a result, talc was chosen as a reinforcing filler for PLA bio-composites in this investigation. **Figure III.2** shows the photo of talc powder.

Figure III.2: Photo of talc powder

III.2. Samples preparation

III.2.1. Preparation of OFI Flour

OFI cladodes were collected from Skikda pilot plantation (480 Km from Algiers, Algeria) shown in **figure III.3**. Spines were removed manually from the cladodes, and then they were cleaned, boiled in water for 2 hours and dried under room condition for 3 months, as shown in **figure III.4.a.** OFI wooden backbones were mashed and sieved after the drying period to move through 0.125 mm sieve. **Figure III.4.b**, shows photography of floured OFI cladodes. OFI-F is used without surface treatment because such method is time consuming and hard to scale up for large manufacturing **[2].** OFI-F has a real density close to 1.54 ± 0.002 g/cm^3 which resembles most of lignocellulosic fillers **[3].**

Figure III.3: OFI plant in the town of Beni Bechir, Skikda

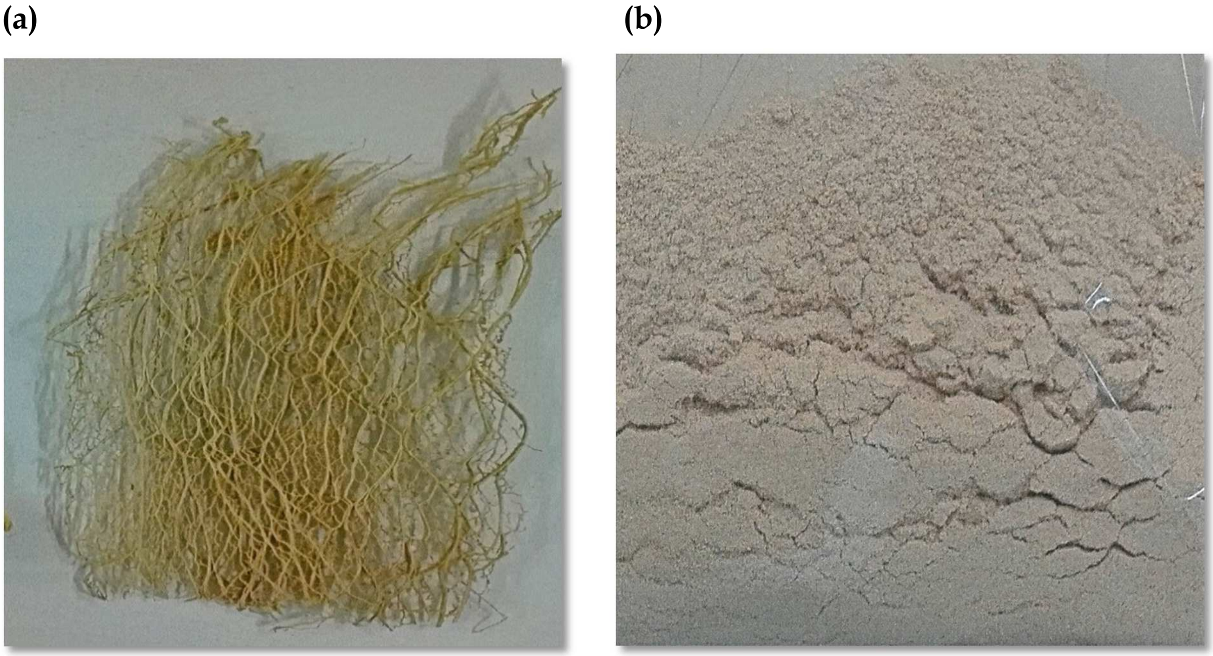

Figure III.4: **(a)** photography of wooden backbone extracted from cladode, **(b)** Powdered OFI cladodes

III.2.2. Mixing and processing of bio-composites

All samples were vacuum-dried overnight at T = 60 °C to reduce water content during processing in order to devoid them of any moisture. **Figure III.5** shows photo of vacuum oven (vacuum dried).

Figure III.5: Vacuum Oven University of Setif

PLA-Talc-OFI flour bio-composites were prepared by melt blended using a Brabender internal mixer with rollers (W50 EHT, Brabender GNbH, and Germany) under a nitrogen atmosphere as displayed in **Figure III.6:** For all bio-composites, the mixing time was performed for 4 min at 64 rpm and 190 °C. The mixtures were cooled at room temperature and cut to produce pellets.

Figure III.6: Brabender University of Setif

Table III.2 lists the mixture formulations of the hybrid bio-composites. Sample identification follows the PLA/weight percentage-name of filler, for example PLA/10-T code alludes to the bio-composite of PLA filled talc of 10 % by weight (wt%).

Table III.2: Formulation of samples

Samples	PLA (wt %)	Talc (wt %)	OFI-F (wt %)
Neat PLA	100	0	0
PLA /10-T	90	10	0
PLA/10-OFI-F	90	0	10
PLA/10-T/10-OFI-F	80	10	10

III.3. Characterization techniques

III.3.1. Structure and phase analysis (Wide-Angle X-ray Scarttering (WAXS))

X-ray diffraction is a technique for acquiring information at the molecular level, specifically for distinguishing between the states of order and structural disorder of a material. This technique is commonly used in the field of polymers to characterize the crystalline phase or other ordered phases (e.g. orientation) in a qualitative or quantitative manner.

This method is based on the idea that the number of diffracting atoms in the crystalline phase and scattering atoms in the amorphous phase are directly proportional to the intensities diffracted and scattered by the material. As a result, it is possible to obtain, among other things, the "absolute" crystallinity rate of the considered material. This is a widely used method for studying crystallinity in given materials, such as polymers. This method provides quantifiable results on the crystal structure of polymer mixes to be obtained.

The wide angle x-ray scattering experiments were performed on an Empyrean Were X-ray diffractometers were from Bruker D8 ECO operating at 40 KV and 20mA in Guelma, Algeria (figure). This apparatus is equipped with a copper anticathode tube, emitting a light wave of length $K\alpha_1$= 0154 nm, step-size 0.02° at 2°/min scanning rate and the angle 2θ goes from 5 to 50°.All X-ray diffractograms were processed using the EVA software.

III.3.2. Morphological properties (Scanning Electron Microscopy)

Scanning electron microscopy (SEM) is an electronic microscopy technique that uses the principle of electron-matter interactions to produce high-resolution images of a sample's surface.

Scanning electron microscopy (SEM) experiments were performed on a JOEL 840 A LOGS apparatus at an accelerating voltage of 1-5KV. Observations are made from the metal-coated surface of samples broken in liquid nitrogen for about 1 to 2 min to have brittle fracture sufaces. The examination is carried out using the accelerating voltage of 12.0 kV so as to avoid any risk of degradation of the samples.

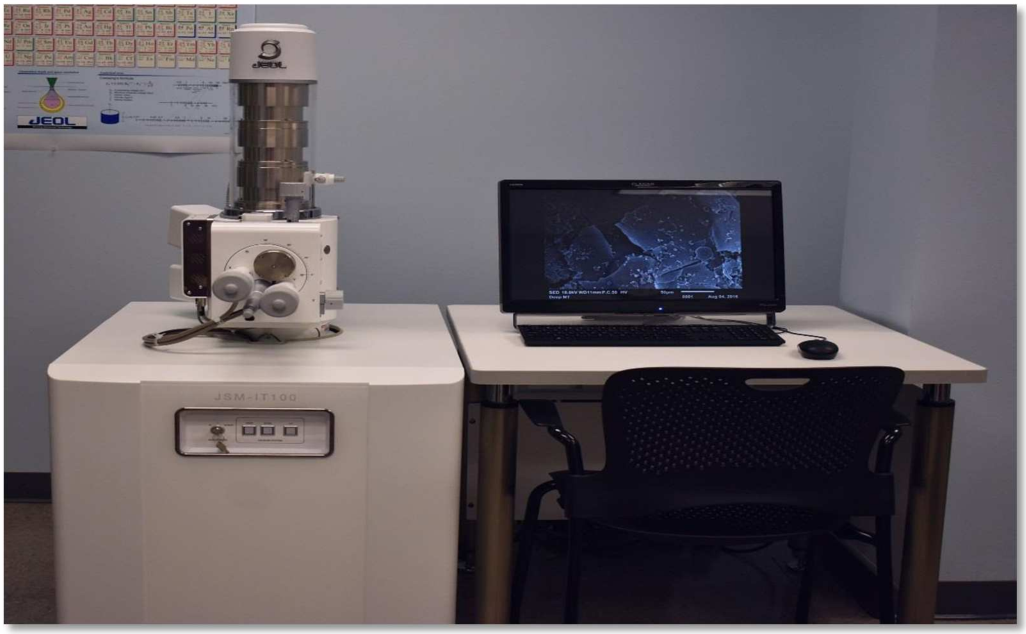

Figure III.7: SEM, JEOL, JSMIT 100, Scanning Electron Microscope

III.3.3. Thermal properties (Thermogravimetry (TGA))

It is of two types:

- **a. Isothermal thermogravimetry**: In this technique, the change in mass of the sample is monitored as a function of time at a constant temperature.
- **b. Non-isothermal/Dynamic thermogravimetry**: The change in mass of the sample is measured as a function of time or temperature while the temperature of the sample is raised at a fixed heating rate.

The TG curve shows the thermal stability of a substance as well as the concept of a product formed while heating. Thermal stability, activation energy, reaction order, and frequency factor all influence the form of the TG curve, which is often sigmoidal.

The data gathered by these methods is made up of:

1. The number of breakdown stages;
2. A quantitative measure of the mass loss at any stage;
3. The temperature at which the processes begin and end as well as the temperature at which the maximum rate of mass loss occurs.

Thermogravimetric analyses were performed using a TGANETZSCH STA 449 F3 Jupiter, Germany. The measurements were carried out at different heating rates (β) 5, 10, 20 and 40 °C/min in the temperature range 293-773 K. The ovens were purged with dried nitrogen at a flux rate of about 20 mL. The samples weight was about 10-15 mg.

The mass loss of a substance as a function of temperature is measured during the heating process.

The initial degradation temperature (T_{onset} or T_0), and the final degradation temperature (T_{offset} or T_{end}) were determined by finding the intersection of the baseline and the extrapolated tangent at the inflection point of the weight loss curve **Figure III.8**.

The related derivative thermogravimetric analysis (DTG) curves were explored to evaluate peak temperature (T_p) (the maximum degradation temperature (T_{max}), the initial degradation temperature (T_{onset} or T_0) and the final degradation temperature (T_{offset} or (T_{end}) **Figure III.9**.

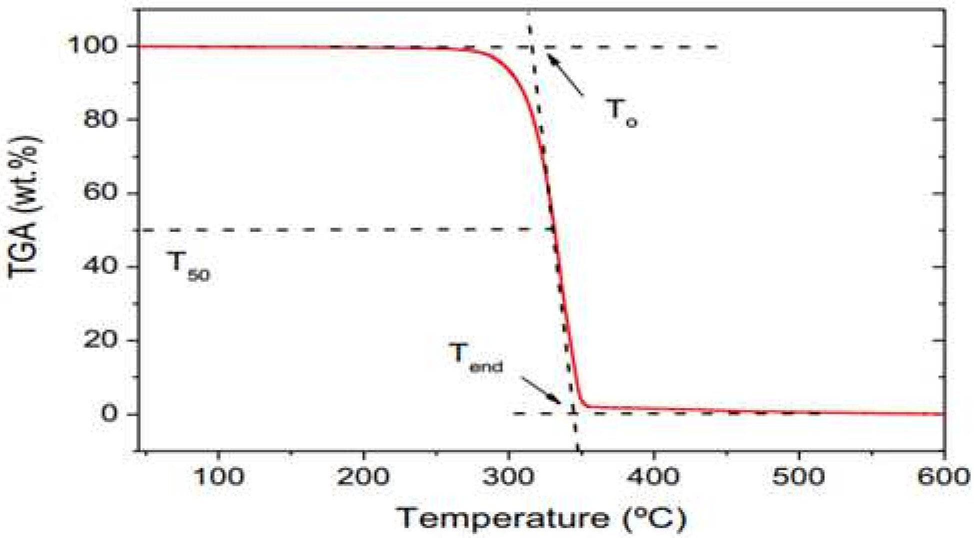

Figure III.8: Determination of thermogravimetric parameters of PLA from TGA curve

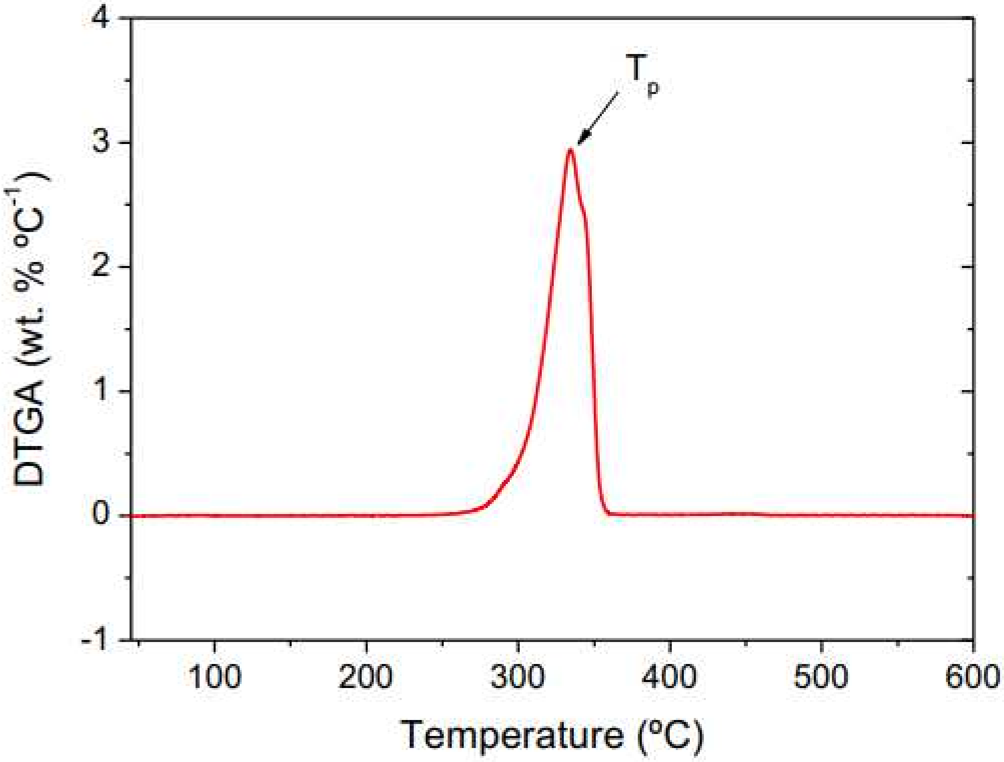

Figure III.9: Determination of T_p from the first derivative of TGA curve

The thermal analysis experiments were carried out at the LSPN laboratory of the University of Guelma, on a STA 449 (F3) -Jupiter device. (**Figure III.10**). It is composed of an integral structure containing:

- An ATG microbalance associated with a DSC sensor.
- A sensitive thermocouple which measures the temperature of the system (temperature of the sample and of the reference).
- A metal resistor furnace that can rise up to 1600°C.
- A multitasking computer that allows you to control the different modules and record the results.
- A circulation of water which is permanently maintained in the furnace of the apparatus during the test and the cooling.
- A purge gas circuit (N2 or He) is also present in order to protect the interior of the furnace.

Figure III.10: Device (ATG/DSC) STA 449 (F3) –Jupiter

A comprehensive understanding of the PLA bio-composites can be obtained through exploring the results of these experiments. The results will be presented and discussed in next chapter.

III.4. Non-isothermal degradation kinetics of OFI flour and talc filled PLA

An adequate of thermal degradation kinetics and mechanism may help us to better understand the various aspects of industrial processes which can be profitably applied for process design and optimization, in particular.

Kinetic examinations of the thermal degradation process of PLA and its bio-composites have looked into the effects of talc and OFI-F on the degradation behavior of PLA and its bio-composites. The kinetics of thermal deterioration were determined using thermodynamic analysis (TGA).

The degradation response for all types of non-isothermal kinetics investigations can be described by equation (1) **[4].**

$$\frac{d\alpha}{dt} = kf(\alpha) \qquad (1)$$

Where, k (T), f (α), α denote the rate constant, reaction model and conversion rate (degree), respectively. The conversion(α) of bio-composites can be calculated by equation (2)

$$\alpha = \frac{W_0 - W_t}{W_0 - W_f} \qquad (2)$$

Where, W_0, is the initial weight of the sample, W_t is the weight of the sample at time (t) and W_f is the final weight of the sample.

The rate constant k (T) in equation (1) obeys the Arrhenius equation: **[5]**

$$k = Aexp\left[\frac{-E_a}{RT}\right] \quad (3)$$

Where, E_a is the activation energy (KJ/mol), R is the universal gas constant (8. 314J.mol^{-1}. K^{-1}), T is the absolute temperature (K) and A is the pre-exponential factor (min^{-1}).

For the dynamic analysis of the non-isothermal data obtained from the TGA experiments, the constant heating rate (β) is defined as follows: **[5]**

$$\boldsymbol{\beta = \frac{dT}{dt}} \quad \textbf{(4)}$$

By combining the value of k (T) and (β) in equation (1), we can rewrite equation (4)

$$\boldsymbol{\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) exp\left[\frac{-E_a}{RT}\right] f(\alpha)} \quad \textbf{(5)}$$

Equation (4) represents the degradation rate expression of analytical methods to estimate the activation energy (E_a) based on TGA kinetics data **[6].**

To better understand the decomposition behavior of bio-composites, the activation energy can be calculated using different techniques. There are generally two approaches: the model-free (isoconversional) approach and the model-fitting approach. The latter is generally more popular because the kinetic triplets are found directly. Nevertheless, the inability to predict a unique reaction model is the weakness **[7].**

Isoconversional methods can predict activation energies by a model independent of different heating rates at a constant degree of conversion **[8].** The model-free methods include Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS).

III.4.1. Model-free methods (isoconversional)

a. Flynn, Wall and Ozawa (FWO) method

The FWO method is one of the most widely accepted linear integral isoconversional methods for calculating E_a at different heating rates **[9].** In this method, temperatures corresponding to fixed values of α are calculated from experiments at different (β), **[10]** as follows:

$$\ln(\boldsymbol{\beta}) = \boldsymbol{ln}\left[\boldsymbol{A}\frac{\boldsymbol{F_\alpha}}{(\frac{\boldsymbol{d_\alpha}}{\boldsymbol{dt}})}\right] - \left[\frac{\boldsymbol{E_a}}{\boldsymbol{RT}}\right]$$

Moreover, based on the corrected Doyle's linear approximation proposed by Flynn, **[11]** the formula is given by equation (6):

$$\ln(\boldsymbol{\beta}) = \left[\ln(\frac{\boldsymbol{AE}}{\boldsymbol{g(\alpha)R}}) - \boldsymbol{5.331}\right] - \frac{\boldsymbol{1.052E_a}}{\boldsymbol{RT}} \qquad \textbf{(6)}$$

Where, E_a is the activation energy, g (a) is the integral kinetic function or integral reaction model, A is the preexponential factor and R is the universal gas constant. Accordingly, plotting ln (β) against (1/T) should give straight lines and from the slope (1.052Ea/R), we can measure the activation energy.

b. Kissinger-Akahira-Sunose (KAS)

Akahira et al., proposed an improved approach that provides a significant development in the activation energy values **[12]**. The KAS method is based on the numerical approximation of the Arrhenius integral **[13].** It is used for the calculation of the apparent activation energy at multiple heating rate values mainly for lignocellulosic materials and bio-composites **[14]**. The final form of the equation can be expressed by equation (7):

$$\ln\left(\frac{\boldsymbol{\beta}}{\boldsymbol{T^2}}\right) = \boldsymbol{ln}\left(\frac{\boldsymbol{AR}}{\boldsymbol{E_a\,g(\alpha)}}\right) - \frac{\boldsymbol{E_a}}{\boldsymbol{RT}} \qquad \textbf{(7)}$$

Where, E_a, g (α), A, R refer to the activation energy, integral conversion function, pre-exponential factor and universal gas constant, respectively.

Similarly, using equation (7), plotting ln (β /T^2) against 1/T at constant conversion α and the slope gives the apparent activation energy.

III.4.2. Model-fitting approach

a. Kissinger method

The activation energy is the only parameter that can be calculated by the model-free methods, while the model fitting approach can calculate the activation energy and consider the reaction mechanism. In addition, more kinetic parameters can be obtained, such as pre-exponential factor and the fittest reaction mechanism function **[15].** The Kissinger method is one of the most recognized model-fitting approach **[10].** In this method, it is not necessary to calculate the E_a for each conversion value to evaluate E a. The activation energy is given by equation (8): **[16]**

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E_a}\right) + \ln\left(-\frac{df(\alpha)}{d\alpha}\right) - \frac{E_a}{RT_m} \quad (8)$$

Where β , T_m are the heating rate and the maximum degradation temperature respectively.

The activation energy can be determined at constant heating rate by plotting ln (β /T^2_m) against (1/T_m).In the Kissinger method, the plot of ln (β /T^2_m) against (1/T_m) at different heating rates.

III.4.3. Reaction order and mechanism

The kinetic study is a mathematical and theoretic explanation of what is happening experimentally **[17, 18].**

In solid-state reactions, a model can explain a specific reaction type and translate it mathematically into a rate equation. Several models are based on certain mechanistic assumptions **[19].**

To find the degradation mechanism and kinetic model for the thermal degradation of composites, the Coats-Redfern and Criado methods are two most important methods that can used.

a. Coats-Redfern (C-R method)

C-R equations have the following form **[18].**

$$\boldsymbol{ln}\left[\frac{-\ln(1-\alpha)}{T^2}\right]=\boldsymbol{ln}\left[\frac{AR}{\beta E_a}\left(1-\frac{2RT}{E_a}\right)\right]-\frac{E_a}{RT} \qquad \textbf{For n=1} \qquad \textbf{(09)}$$

$$\boldsymbol{ln}\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right]=\boldsymbol{ln}\left[\frac{AR}{\beta E_a}\left(1-\frac{2RT}{E_a}\right)\right]-\frac{E_a}{RT} \qquad \textbf{For n}\neq\textbf{1} \qquad \textbf{(10)}$$

Where, n, β are the reaction order and the heating rate, respectively.

This method is used to compute the kinetic triplet (E_a, A, and reaction order n) **[17].**

The activation energy and pre-exponential factor can be measured by plotting ln (-ln (1-α)/T^2) against 1/T. In equations (9) and (10), the value of 2RT/E_a is very small and less than 1. Therefore, the entire term can be regarded as constant **[20].**

The slope and intercept give the values of Ea/ R and Ln (AR/βE)) respectively. In the C-R method, a unique value of Ea is obtained, which is not the case for the FWO and KAS methods where the E a values depend on (α). It is noteworthy that the FWO and KAS methods are reliable for evaluating Ea without prior information about the reaction model, but they are complex for determining the reaction order (n).

In C-R method, the choice of (n) is confirmed when regression coefficient (R^2) of equations (9) and (10) is close to 1.

It is noteworthy that the FWO and KAS methods are reliable for evaluating Ea without prior information about the reaction model, but they are complex for determining the reaction order (n). In C-R method, the choice of (n) is confirmed when regression coefficient (R^2) of equations (9) and (10) is close to 1.

The summary of kinetic methods used in calculating activation energy is given in **table III.3.**

Table III.3: Kinetic methods used in calculating activation energy in this study

Methods	Finals Equations	Plots
Flynn, Wall and Ozawa (FWO)	$\ln(\beta) = \left[\ln(\frac{AE}{g(\alpha)R}) - 5.331\right] - \frac{1.052E_a}{RT}$	ln (β) against (1/T)
Kissinger–Akahira–Sunose (KAS)	$\ln\left(\frac{\beta}{T^2}\right) = ln\left(\frac{AR}{E_a\, g(\alpha)}\right) - \frac{E_a}{RT}$	ln (β /T^2) against 1/T
Kissinger method	$ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E_a}\right) + \ln\left(-\frac{df(\alpha)}{d\alpha}\right) - \frac{E_a}{RT_m}$	ln (β /T^2_m) against (1/T_m).
Coats-Redfern (C–R)	$ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = ln\left[\frac{AR}{\beta E_a}\left(1-\frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT}$ For n=1 $ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right] = ln\left[\frac{AR}{\beta E_a}\left(1-\frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT}$ For n≠1	ln (-ln (1-α)/T^2) against 1/T

b. Degradation mechanism by C-R method

It is not easy to explain the reaction model using isoconversional methods like FWO and KAS. The model fitting equations can be useful for mechanism analysis by defining a reasonable reaction model. Thus, the integral form of the C-R method is used to determine the most probable model. The integral form of the C-R method in equation (11) is widely used to determine the degradation mechanism, **[18]** as follows:

$$\boldsymbol{\ln\left(\frac{g(\alpha)}{T^2}\right) = -\frac{E}{R}.\frac{1}{T} + ln\frac{AR.(1-\frac{2RT}{E})}{\beta.E}} \qquad \textbf{(11)}$$

Table III.4. Lists the theoretical functions of f (α) and g (α).

Table III.4. theoretical functions of g (α) and f (α) for the most common reaction mechanisms of solid state process **[21]**

Mechanism	Solid state process	$f(\alpha)$	$g(\alpha)$
Diffusion D_n	One-dimensional diffusion D1	$\frac{1}{2\alpha}$	α^2
	Two-dimensional diffusion (Valensi model) D2	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
	Three dimensional diffusion (Jander model) D3	$(1-\alpha)^{2/3}\left[1-(1-\alpha)^{1/3}\right]^{-1}$	$\left[1-(1-\alpha)^{1/3}\right]^2$
Reactin order Fn	First order F1	$(1-\alpha)$	$-\ln(1-\alpha)$
	Second order F2	$(1-\alpha)$	$-\ln(1-\alpha)$
	Third order F3	$(1-\alpha)^2$	$[(1-\alpha)^{-2}-1]/2$
Avrami-Erofe've A_n	Avrami- Erofe've A1	$\frac{1}{2}(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	$[-\ln(1-\alpha)]^{2/3}$
	Avrami- Erofe've A2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
	Avrami- Erofe've A3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
Contraction Reaction R_n	Contraction sphere R2	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
	Contraction cylinder R3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$

Based on the C-R equation, the straight lines ought to be given by the linearity fitting of the logarithmic term of g (α) over $1/T$ **[21].**

The best regression coefficient (R^2) should identify the most probable function.

c. Degradation mechanism by Criado method

Equation (12) can be used to determine the experimental values, as follows:

$$Z(\alpha)_{exp} = \frac{E_a}{R}\frac{d\alpha}{dT}e^{\frac{E_a}{RT}}p(x) \qquad \textbf{(12)}$$

Where, p(x) can be expressed from equation (13), with minimal error level of 105% for x > 20: **[22]**

$$p(x) = \frac{e^{-x}}{x}\frac{x^3+18x^2+86x+96}{x^4+20x^3+120x^2+240x+120} \qquad \textbf{(13)}$$

Where, x is E_a/RT. Theoretical master plots Z (α) against (α) for various reaction mechanisms were plotted according to equation (14), using the g (α) and f (α) values from **Table III.4.** Based on the mechanism assumptions, these functions could be grouped into reaction order, diffusion, geometrical contraction, and nucleation, **[23]** as follows:

$$Z(\alpha)_{theortical} = g(\alpha)f(\alpha) \qquad \textbf{(14)}$$

The experimental curves are then compared with different theoretical master plots to decide the correct thermal degradation mechanism. The E_a and A obtained by the C–R method are used to plot the master curves of PLA and its bio-composites to show the thermal degradation mechanism

III.5. Summary protocol of kinetic study

Kinetic modeling is a mathematical procedure for giving an adequate explanation to experimental data. In the case of a thermal analysis, the complexity of the mechanisms involved makes modeling difficult and delicate, requiring a judicious procedure.

The non-isothermal kinetics were studied with four heating rates: 5, 10, 20 and 40°C/min. The calculations and simulations were carried out at using Microsoft Excel 2013 and Originlab Pro 2017 software. **Figure III.11.** Shows the flow chart for the development and processing of PLA bio-composites as well as the characterization approach applied and the procedure followed in this thesis.

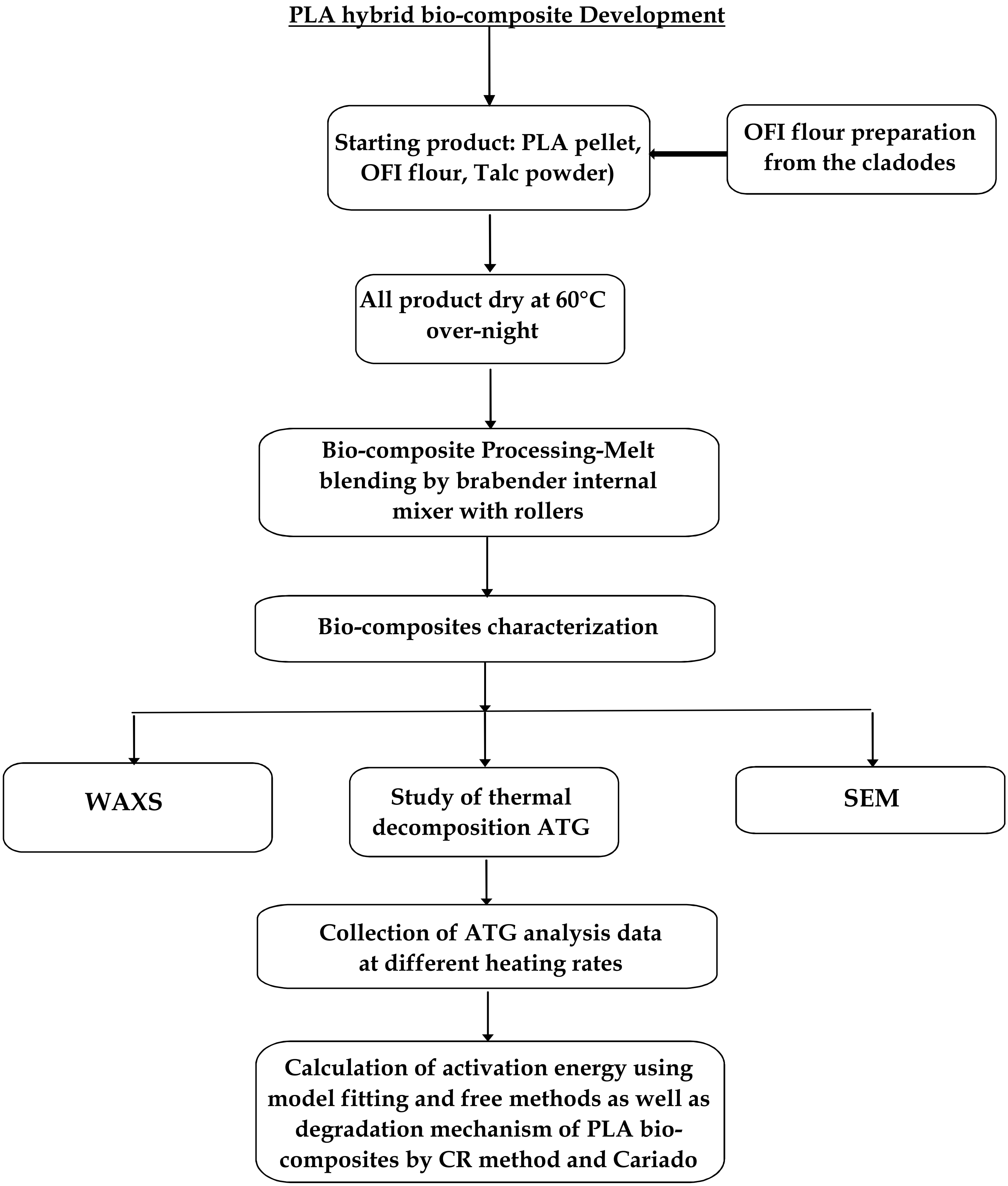

Figure III.11: Flowchart for experimental procedures followed

Conclusion

This chapter covers the materials used, the preparation procedures and the experimental equipments employed in this research. The non-isothermal degradation kinetics of OFI flour and talc-filled PLA are investigated. For calculating activation energy, isoconversional methods (FOW and KAS) and models fitting (Kissinger and CR) were used respectively. In this chapter also the degradation mechanism of bio-composites is investigated using Coats-Redfern and Criado methods.

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Chapter IV

Results and Discussion

Chapter IV

Results and Discussion

Introduction

In this chapter, the intrinsic properties of PLA bio-composites were studied through characterization.

This chapter provides the main experimental results of produced bio-composites as well as highlights, analyses and compares their significant attributes to neat PLA.

IV.1. Microstructural characterization

The WAXS of the various samples is shown in **Figure IV.1**. The results of neat PLA are displayed by a broad band with maximum at 2θ = 16.66°, suggesting an amorphous structure. The same results are found by **[1].** The narrow peak at 2θ = 16.66°, is indicative of the crystalline nature of PLA material**.** The same results are obtained by **[2].** In addition, the presence of the reticular plans, (002), (020) and (006) at 2θ = 9.42, 18.92 and 28.56° respectively is observed which signifies that its final output is pure talc. Similar results are observed by **[3].** The PLA/T bio-composites containing 10 wt % of talc shows the presence of the three talc peaks, and a new high-intensity diffraction peak at 16.66°, designating a crystalline structure of PLA. Similar results are found by **[4].**

The peak position at 2θ= 22.2° on the WAXS indicates the crystalline phase of which cellulose is responsible. Similar observations are recorded with the utilization of wood flour **[5].** The PLA/T/OFI-F bio-composites with 10 wt % of talc and 10 wt % of OFI-F show a decrease in the peaks' intensity in comparison with PLA/T.

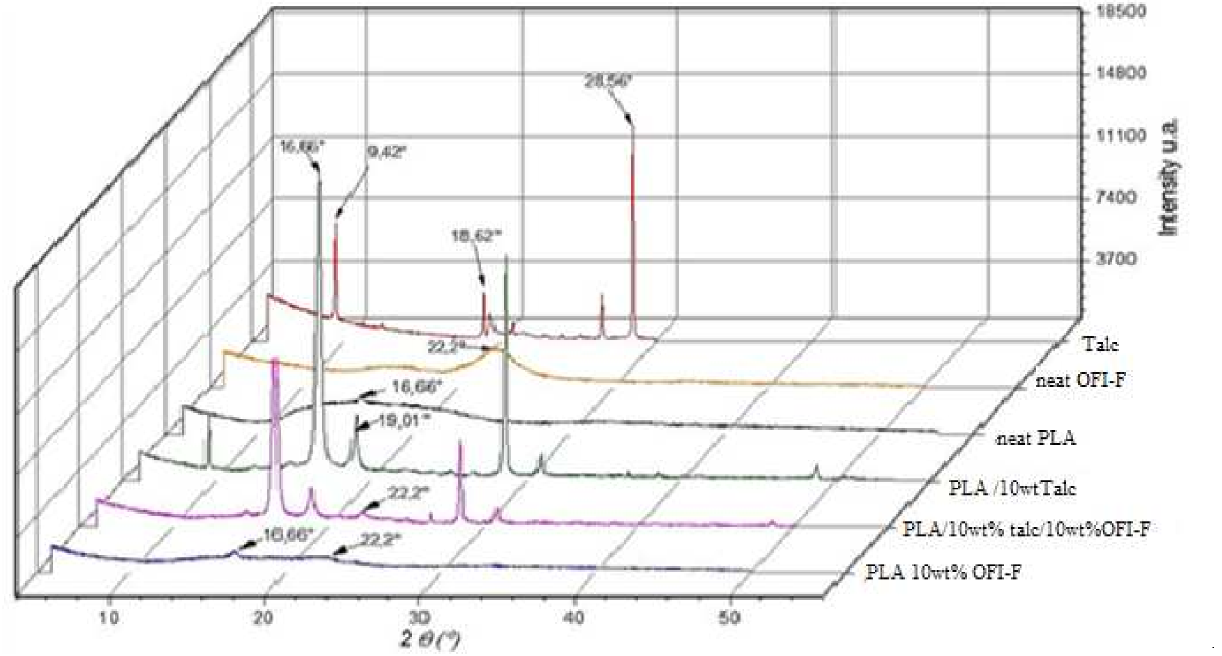

Figure IV.1 Diffractogram (WAXS) of neat PLA, OFI-F, Talc, PLA/T, PLA/OFI-F, and PLA/T/OFI-F.

IV.2. Morphological properties

Figure IV.2 Represents the SEM images of the neat PLA and its bio-composites. **Figure IV.2.a** represents the captured image of fracture surface of neat PLA. The image covers clear surface corresponding to the fracture in PLA. The distribution of talc in the PLA matrix is homogeneous as indicated in **figure IV.2.b**. **Figure IV.2.d**, shows that there are voids adjacent to OFI-F and talc particles, meaning that the adhesion between the fillers and the polymer matrix needs to be further improved. There is a formation of an agglomerate of fillers and voids (indicated in **figure. IV.2.c**. and **figure IV.2.d**) and this could be due to the incompatibility between OFI-F and the PLA matrix. The multiple agglomerates and voids can engender early breakdown and weak thermal stability of the bio-composites.

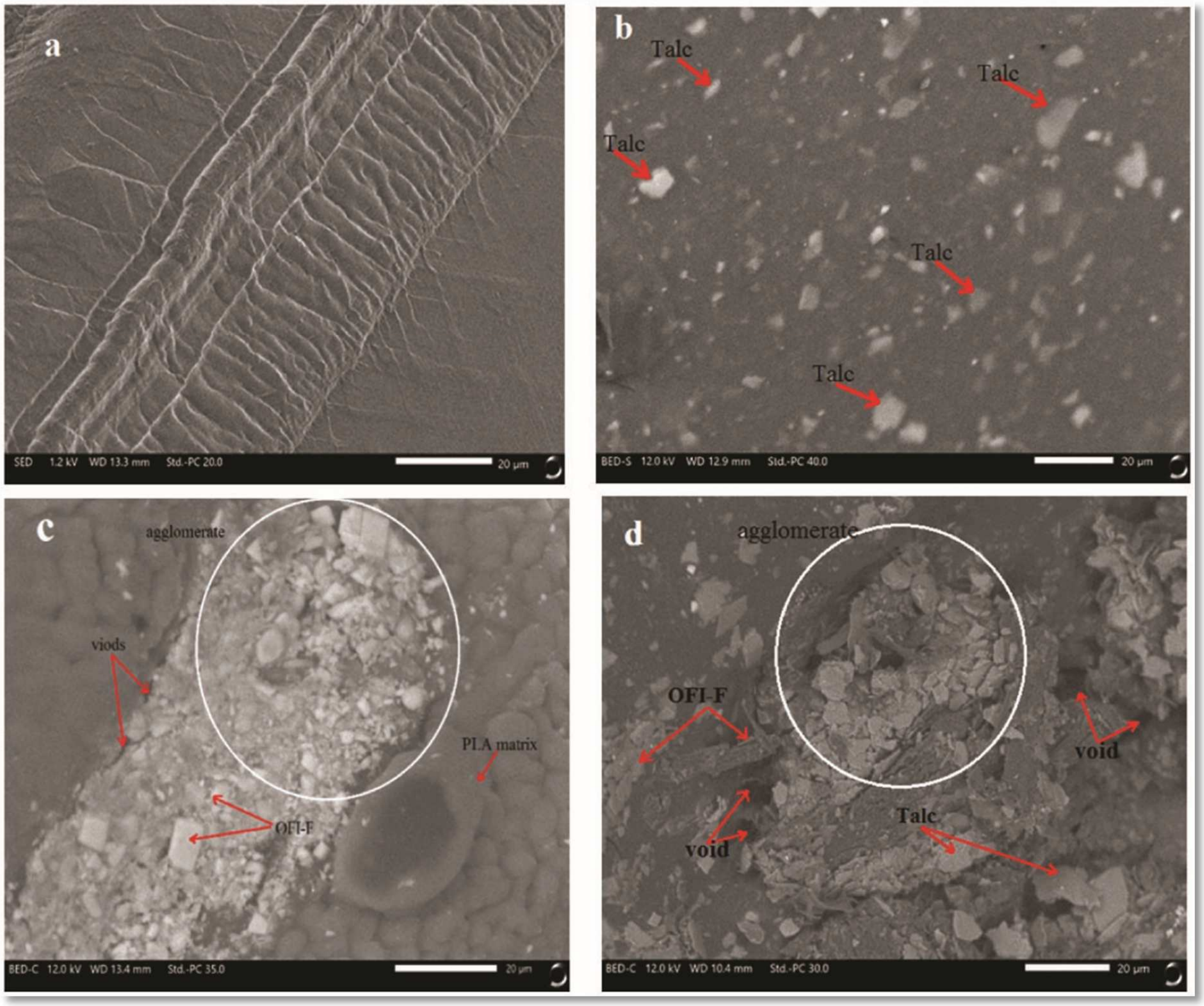

Figure IV.2. SEM photographs of bio-composites: **(a)** Neat PLA, **(b)** PLA/T, **(c)** PLA/OFI-F and (**d**) PLA/T/OFI-F

IV.3. Thermal properties (Thermogravimetric Analysis)

To get a better understanding of thermal decomposition characteristics of neat PLA and its bio-composites, TGA method is adopted to study the thermal decomposition behaviors of neat PLA, PLA/T, PLA/OFI-F and PLA/T/OFI-F bio-composites. The thermal degradation kinetics were analyzed using the data obtained from TGA under nitrogen atmosphere to protect the environment of the equipment at high temperature. Generally, the heating rate has great influence on thermal degradation kinetics and products distribution; therefore, it is important to investigate the degradation characteristics under different heating rates.

Figure IV.3 shows the TGA and the DTG of neat PLA and its bio-composites at various heating rates (β): 5, 10, 20 and 40 K.min^{-1}.

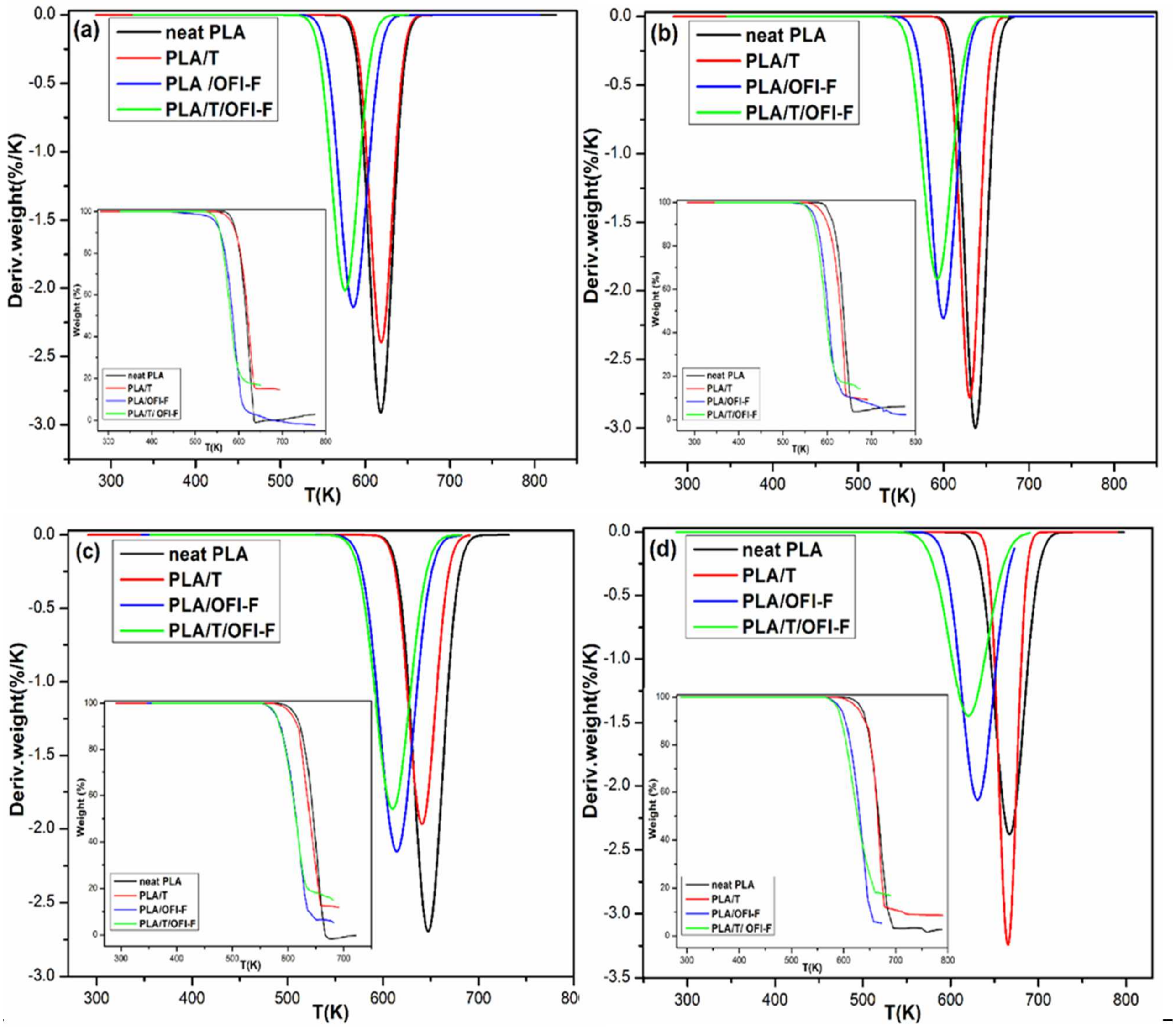

Figure IV.3. Representative TGA and DTG curves at various heating rates **(a)** 5, **(b)** 10, **(c)** 20 and **(d)** 40 K/min of neat PLA, PLA/T, PLA/OFI-F and PLA/T/OFI-F

All the TGA curves are sigmoidal shaped while DTG curves show only one peak. This indicates that thermal degradation happened as a single-step degradation for all bio-composites. Similar observations are recorded with **[6].**

All TGA curves start with perfect flat plateau; this is mainly caused by the removal of moisture.

As expected, TGA plots moved to the higher set value of temperature as (*β*) increases which affirms that less time is required to attend a given temperature at a higher (*β*). Similar findings are observed with. **[7].** This pattern might be attributed to the fact that the sample has more retention time at low heating rates, causing so more weight loss than at high heating level. Similar observations are registered with **[8].**

The onset degradation temperature (T_{onset}), the maximum (peak) degradation temperature (T_m) and the offset degradation temperature (T_{offset}) are summarized in **table IV.1**.

These parameters are fundamental to predict the effects of OFI-F and talc on PLA bio-composites decomposition.

Table IV.1. DTG parameters of samples at various heating rates

Samples	**β ($K.min^{-1}$)**	**T_{onset} (K)**	**T_m (K)**	**T_{offset} (K)**
Neat PLA	5	573.3	618.4	668.0
	10	591.7	637.5	682.1
	20	594.5	647.3	697.8
	40	614.9	667.2	722.1
PLA/10-T	5	574.5	618.9	664.8
	10	588.7	630.9	668.5
	20	590.6	640.8	689.3
	40	631.8	665.3	701.9
PLA /10-OFI-F	5	526.6	586.0	641.8
	10	551.0	599.7	645.9
	20	554.5	614.5	682.1
	40	569.9	630.7	672.8
PLA/10-T/10-OFI-F	5	521.9	576.3	690.0
	10	534.5	592.8	648.8
	20	552.4	610.1	670.7
	40	551.2	620.3	690.1

As seen in **figure IV.3** and **table IV.1** talc and OFI-F effect the thermal decomposition of the PLA matrix. Neat PLA taken as a reference point shows single stage degradation which is mainly due to the hydrolysis of amounts of water traces in PLA Similar findings are recorded with. **[9]**.

In case of heating rate is 5 K/min, neat PLA shows initial degradation temperature (T_{onset}) at 573.3 K and maximum degradation temperature (T_m) at 618.4 K. The incorporation of talc within the PLA matrix increases slightly the initial degradation temperature and the maximum temperature of degradation to 574.5 K and 618.9 K respectively which means that talc decreases the degradation rate. For heating rates 10 and 20 K/min the maximum temperature of degradation is observed at 630.9 K and 640.8 K respectively. It can be seen that the addition of talc in this range of temperature does not much alter thermal stability. The loading of talc at 10 wt % level causes a small shift of DTG curves to lower temperature which means that the bio-composite does not have observable improvement in thermal properties than the neat PLA. Same results are saved with **[10].**

The incorporation of OFI-F within PLA matrix decreases the (T_{onset}) and (T_m) in PLA/OFI-F bio-composites to 526.6 K and 586.0 K for heating rate 5 K/min. The OFI-F decreased the decomposition temperature of the PLA/OFI-F bio-composites. The (T_m) of neat PLA is 618.41 K, and the one of PLA/OFI-F is 32 to 37K lower than neat PLA. This low value may be due to the decomposition of OFI-F parts. OFI flour's components (cellulose, hemicellulose and lignin) degradation are usually from 473 K to 673 K **[1].**

The lower PLA/OFI-F bio-composite decomposition temperatures suggest that the bio-composites are less thermally stable than that of the neat PLA. The incompatibility of hydrophobic PLA with hydrophilic nature of OFI-F (because of free OH groups) contributes to weakened interfacial adhesion between the PLA matrix and the OFI-F. PLA/T/OFI-F bio-composites exhibit lower (T_{onset}), (T_m) and (T_{offset}) than PLA/OFI-F bio-composites which means that PLA/T/OFI-F bio-composites have less thermal stability. It is observed that PLA/talc/OFI-F hybrid bio-composites show T_{onset} at 521.9 K and T_m

at 576.3 K at heating rate 5 K/min. The addition of talc to PLA/OFI-F hybrid bio-composites shows no significant effect on the thermal decomposition process. There is no synergism between talc and OFI-F. Same observation are recorded with **[1].**

IV.4. Non-isothermal degradation kinetics

IV.4.1. Model-free methods

a. Flynn, Wall and Ozawa (FWO) and Kissinger–Akahira–Sunose methods (KAS)

The activation energy of non-isothermal degradation of neat PLA, PLA/T, PLA/OFI-F and PLA/T/OFI-F bio-composites was calculated using FWO and KAS methods. **Figures IV.4** and **figures IV.5** display the FWO and KAS plots for different (α) values of neat PLA, PLA/T, PLA/OFI-F and PLA/T/OFI-F, respectively.

Using equations (7) and (8) mentioned in previous chapter, plotting ln (β) against (1/T), plotting ln (β/T^2) against 1/T at constant conversion α, the slopes give the apparent activation energy.

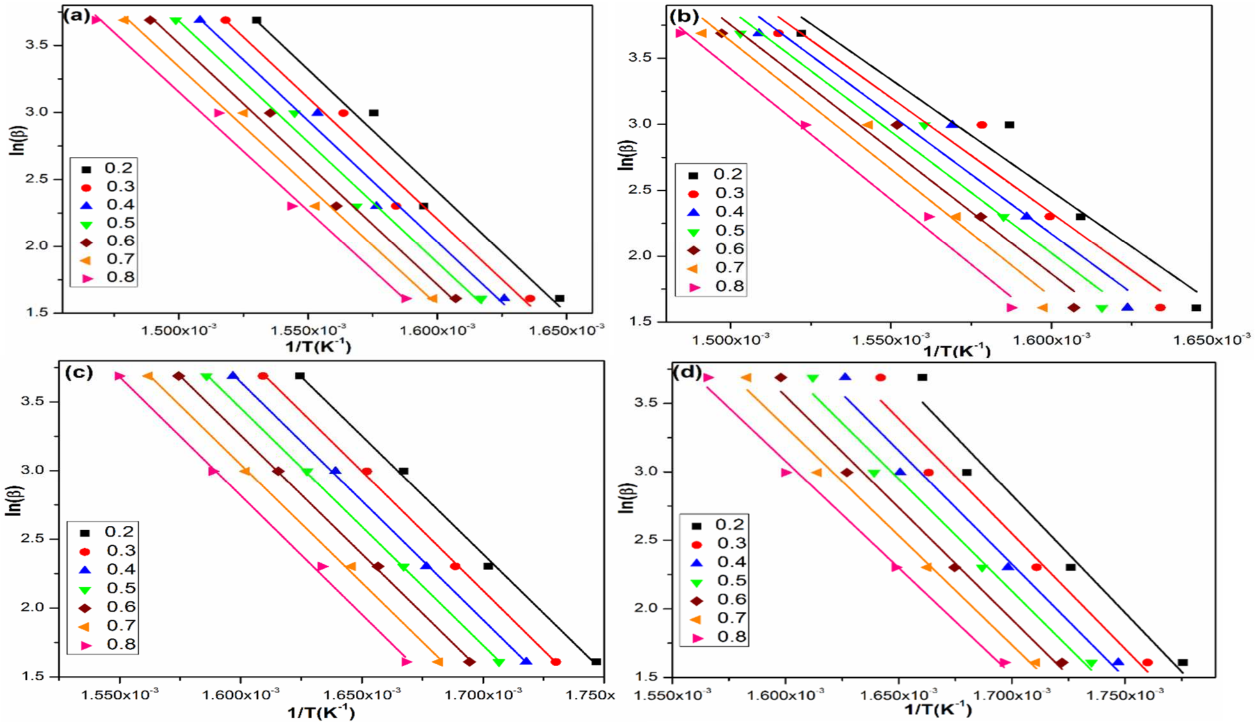

Figure IV.4. FWO plots at different conversion rates: (a) neat PLA, (b) PLA/T, (c) PLA/OFI-F and (d) PLA/T/OFI-F

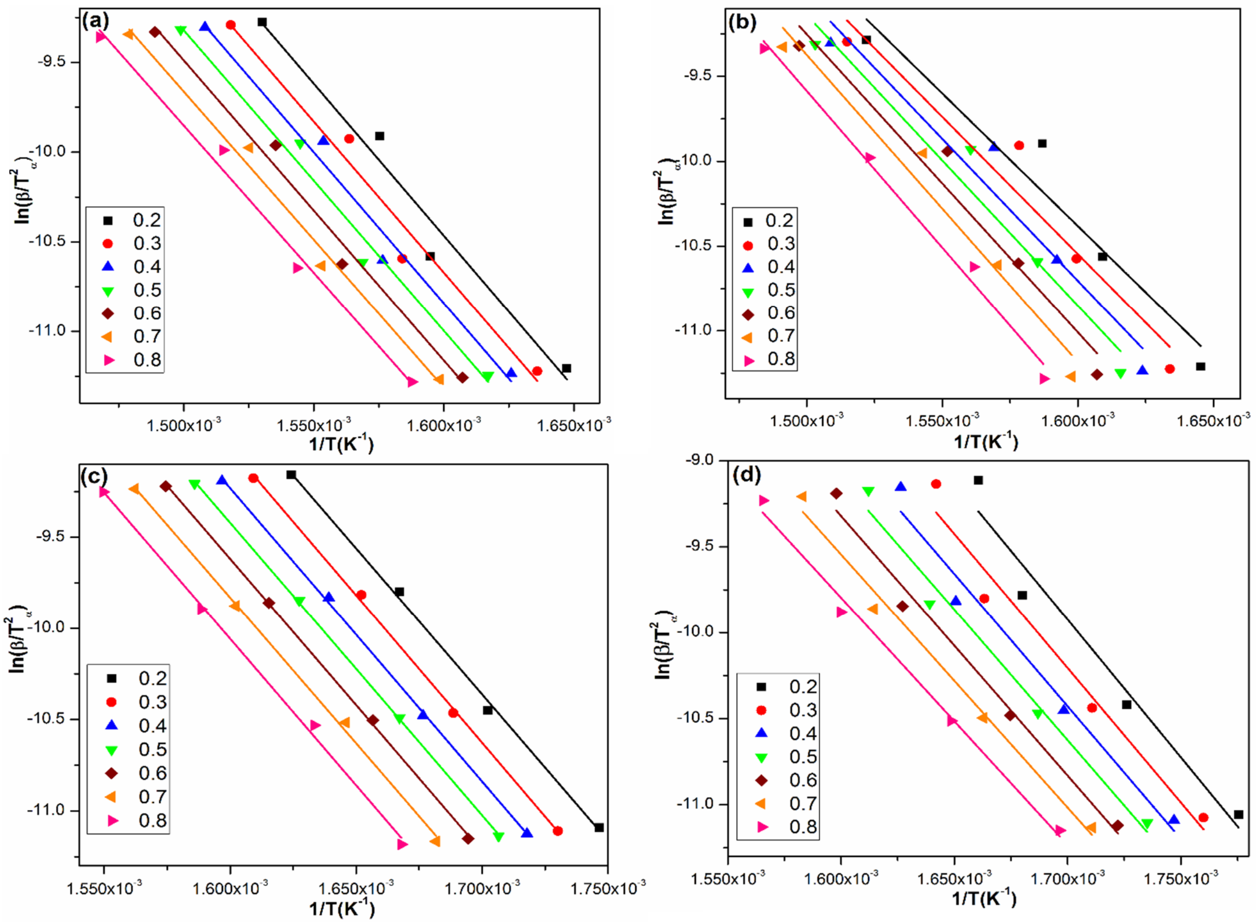

Figure IV.5. KAS plots at different conversion rates: (a) neat PLA, (b) PLA/Talc, (c) PLA/OFI-F, (d) PLA/T/OFI-F

It can be noticed that in both cases, the straight lines obtained are almost parallel to the conversion (a) range (from 0.2 to 0.8) which means that there are similar behaviors for all samples and a possibility of a simple reaction mechanism. The same results are fonud by **[11].** The suitability of the models is assessed according to the R^2 values of the FWO and KAS plots. The R^2 values as obtained from FWO and KAS are found to be 0.9827 and 0.9799, respectively (**figures IV.4** and **figuresIV.5**). This result confirms that both approaches are appropriate for exploring the thermal degradation kinetics of these systems. **Table IV.2**: gives the relationship of E_a as a function of conversion rate (α) obtained by these isoconversional methods (FWO and KAS).

Table IV.2. Variation of activation energies and average activation energies of samples determined from FWO and KAS methods at different *(α)*

Samples	**α**	**FWO method Ea (KJ/mol)**	**R²**	**KAS method Ea(KJ/mol)**	**R²**
Neat PLA	0.2	159.19	0.9732	140.85	0.9693
	0.3	158.34	0.9762	139.97	0.9726
	0.4	158.43	0.9825	139.98	0.9897
	0.5	157.76	0.9851	139.29	0.9827
	0.6	157.66	0.9883	139.12	0.9864
	0.7	155.75	0.9913	137.24	0.9898
	0.8	155.00	0.9916	136.44	0.9901
Average		**157.45**	**0.9840**	**138.98**	**0.9816**
PLA/10-T	0.2	147.69	0.9546	129.87	0.9470
	0.3	152.51	0.9515	134.39	0.9437
	0.4	157.52	0.9561	139.10	0.9492
	0.5	160.98	0.9628	142.34	0.9570
	0.6	164.88	0.9674	146.00	0.9623
	0.7	169.70	0.9710	150.53	0.9665
	0.8	172.74	0.9916	153.37	0.9903
Average		**160.86**	**0.9650**	**142.23**	**0.9594**
PLA /10-OFI-F	0.2	150.50	0.9982	133.20	0.9979
	0.3	151.85	0.9991	134.38	0.9990
	0.4	151.26	0.9995	133.75	0.9994
	0.5	150.87	0.9999	133.31	0.9998
	0.6	151.01	0.9999	133.37	0.9995
	0.7	150.43	0.9987	132.73	0.9984
	0.8	151.20	0.9977	133.38	0.9973
Average		**151.02**	**0.9990**	**133.44**	**0.9988**
PLA/10-T/10-OFI-F	0.2	150.23	0.9684	133.12	0.9639
	0.3	146.90	0.9728	129.86	0.9688
	0.4	145.06	0.9797	128.03	0.9768
	0.5	143.23	0.9850	126.22	0.9828
	0.6	142.62	0.9887	125.58	0.9870
	0.7	139.34	0.9910	122.36	0.9896
	0.8	136.40	0.9942	119.46	0.9933
Average		**143.40**	**0.9828**	**126.37**	**0.9801**

The plots of E_a versus *(a)* of neat PLA, PLA/T, PLA/OFI-F and PLA/T/OFI-F are graphically shown in **figure IV.6**. In the case of neat PLA, E_a values with *(a)* ranging from 0.2 to 0.8 have found stabilization which confirms that it has similar types of bond breaking during the degradation process. This behavior reveals presence of single-process reaction. This results confirmed by **[12].** For neat PLA, the average values of activation energies are 157.44 and 138.98 KJ/mol according to FWO and KAS equations respectively, the KAS method shows lower values than FWO, but the results have similar trend. The FWO method used gross estimation of the integral temperature; various corrections are suggested **[13, 14].** As Flynn observed, the error related to the approximation of the Doyle is less than 1%, for reduced temperature values, $x = Ea / RT$ comprising between 21 and 81**[14].** The reduced temperature values (x) are between 32, 08 ($\alpha = 0.2$) and 32, 97 ($\alpha = 0.8$) at various heating rates, so that the expected error in the FWO method was under 1 %. The apparent activation energy is observed ≈ 157. KJ/mol by FWO method, similar value is observed by Xu YX et al. **[15].** The KAS method uses a more precise solution for integral temperature; therefore, it provides values that are more precise.

The average activation energy of bio-composites after the incorporation of talc increases from 157.45 to 160.86 KJ/mol according to FWO method. The E_a of PLA/T is greater than the neat PLA in the range of *(α)* from 0.5 to 0.8; more energy is needed to break the bonds at the last level of conversion because of the homogenous dispersion of talc powder as observed by SEM (**figure III.2b**). The addition of OFI-F into PLA matrix reduces the E_a from 157.45 to 151.02 KJ/mol according to FWO method. The decrease in E_a can be due to the incompatibility between OFI-F and PLA matrix. The addition of OFI-F in the PLA matrix causes an increase in the degradation rate of the PLA bio-composites because the activation energy is an obstacle which must be overcome before a chemical reaction is made and a lower value of activation energy means easier reaction can occur. PLA /OFI-F has more acidic sites which accelerate degradation due to auto-catalytic effect. Similar behavior is also reported **[16].**

When talc is present with OFI-F mixture, the activation energy of the bio-composites decreased with (α). The average activation energy of hybrid bio-composites is 143.40 KJ/mol according to FWO method. This implies less energy is required to sever the bond. This result indicates that PLA/T/OFI-F hybrid bio-composites have a lower thermal stability, probably due to the existence of talc which is non-degradable in the temperature range. The PLA content which used energy during the thermal degradation decreased meanwhile talc consumed no energy below 873.15 K; that is why thermal degradation energy decreased. Similar behavior is reported **[17].** The loading of T/OFI-F simultaneously decrease the thermal stability of PLA hybrid bio-composites.

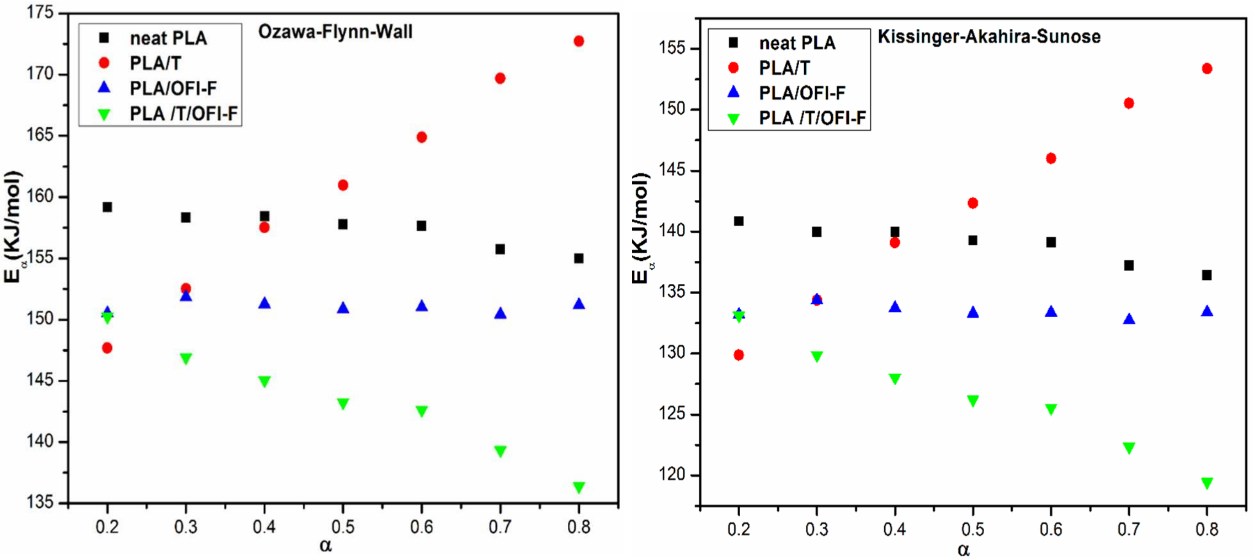

Figure IV.6. Variations of activation energy values as function of *(α)* of neat PLA, PLA/T, PLA/OFI-F and PLA/T/OFI-F obtained from the FWO and KAS methods

IV.4.2. Model fitting methods

a. Kissinger method

The activation energy can be determined at constant heating rate by plotting ln (β/T^2_m) against $(1/T_m)$ **[18].** In the Kissinger method, the plot of ln ln (β/T^2_m) against $(1/T_m)$ at different heating rates shows the aligned fit for all samples as shown in **figure IV.7.**

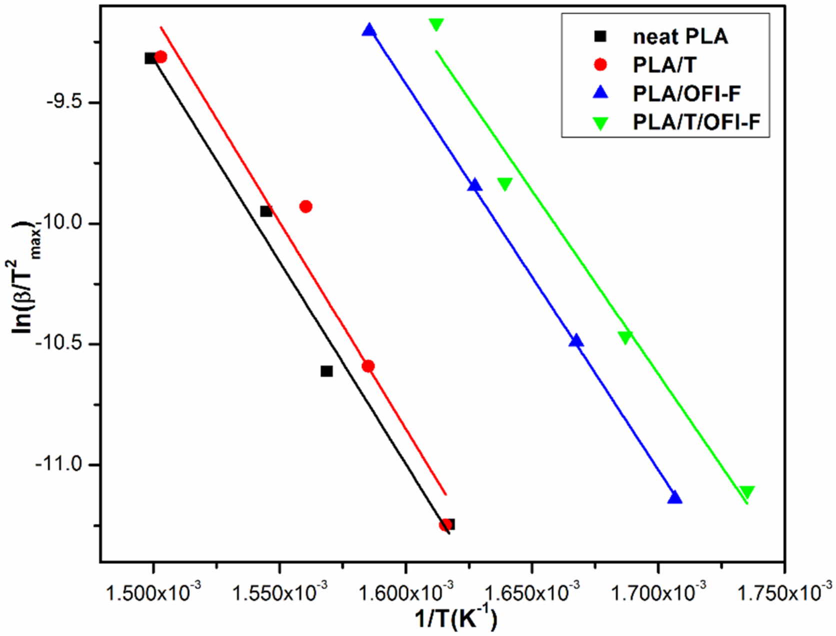

Figure IV.7. Kissinger fitting plots of: neat PLA, PLA/T, PLA/OFI-F, and PLA/T/OFI-F

The smooth linear fitted lines prove the feasibility of Kissinger method **[19].** The straight relationship cannot be assumed if the term $\frac{(-df(\alpha))}{d\alpha}$ is reliant on the heating rate; thus, restricting the technique **[20].**

The E_a by this method shows only the average value of activation energy called apparent energy for the whole process, without giving information about the variation of activation energy during the thermal degradation; that is why FWO and KAS method are also employed. The activation energy is calculated for each sample shown in **table.IV.3.**

Table IV.3. Apparent activation energies, coefficient regression (R^2) of samples determined by Kissinger method

Samples	Kissinger method E_a(KJ/mol)	R^2
PLA	139.31	0.9827
PLA/10-T	142.33	0.9569
PLA /10-OFI-F	132.77	0.9997
PLA/10-T/10-OFI-F	126.27	0.9828

The E_a values estimated from Kissinger method are in good agreement with FWO and KAS methods for PLA and its bio-composites. The E_a for neat PLA by Kissinger method is 139.31 KJ/mol which shows the comparable value obtained by Dai et al. (140.7-146.3 KJ/mol) **[21].**

The adding of talc increases slightly the activation energy 142.33 KJ/mol. **Table IV.4** recapitulates the results obtained in relation to (T_m) and the conversion for each (T_m) value (α_m).

Table IV.4. Summary of the maximum temperature of degradation (T_m), and its corresponding conversion (α_m) and conversion rate $(d\alpha/dT)_m$ values, for the thermal degradation of PLA and its bio-composites at various heating rates

Samples	β ($K.min^{-1}$)	T_m (K)	α_m	$(d\alpha/dT)_m$
Neat PLA	5	618.4152	0.501	0.029
	10	637.4556	0.500	0.032
	20	647.3399	0.499	0.026
	40	667.1752	0.500	0.024
PLA/10-T	5	618.921	0.500	0.03
	10	630.88	0.501	0.035
	20	640.84	0.501	0.028
	40	665.311	0.503	-

PLA /10-OFI-F	5	585.9815	0.499	0.024
	10	599.7046	0.500	0.027
	20	614.4944	0.500	0.022
	40	630.7173	0.503	0.022
PLA/10-T/10-OFI-F	5	576.3283	0.500	0.025
	10	592.8203	0.501	0.024
	20	610.0533	0.501	0.022
	40	620.3177	0.501	0.018

The conversion of all samples at the maximum temperature is approximately identical to a mean value of 0.500 ± 0.001 for the various heating rates. One of the Hypotheses of this approach is that $f(\alpha)$ does not change with α. In reality, Kissinger method gives activation energy at a particular conversion $\alpha_m = 0.500$. It provides a dependable value of E_a if α_m does not change significantly with β. The systematic error decreases as the reduced temperature $x = E_a/RT$ increases. In this situation, x is included between 24.483 and 27.659 for the corresponding (T_m) values. As stated, x values greater than 10 lead to an error in E_a less than 5% **[22, 23].**

However, the Kissinger system, because of its simplicity, can only describe a single stage kinetic process. Further tests are required to validate the applicability of the Kissinger method as showed by Farjas et al. **[24]**, the peak width of the degradation rate $d\alpha/dT$, is an extremely responsive parameter to the existence of multiple transformations.

IV.5. Reaction order and mechanism

IV.5.1. Coats-Redfern (C–R) method

a. Reaction order

In this study, different reaction orders are supposed from n = 0.1 to 2.0 used in equations (9, 10) mentioned in the previous chapter. In C-R method, the choice of (n) is confirmed where regression coefficient (R^2) of the above mentioned equations is close to 1. **Figure IV.8** shows the plotted graphs for neat PLA and its bio-composites, for different

(n) values at a heating rates 10 K.min^{-1}. The same trend for all curves is observed at all heating rates. The comparison of E_a of neat PLA and its bio-composites is shown in **table IV. 5**.

Table IV.5. Activation energies, average activation energies, reaction orders (n) of samples determined by C-R method at various heating rates

Samples	**Coats Redfern method**				
	5 K.min^{-1}	**10 K.min^{-1}**	**20 K.min^{-1}**	**40 K.min^{-1}**	**Ea average**
Neat PLAn	345.75 (1.75)	419.67 (1.83)	353.49 (1.83)	337.88 (1.77)	364.20 (1.8)
PLA/Tn	375.61 (1.88)	463.48 (1.9)	383.83 (1.88)	578.97 (1.91)	450.47 (1.90)
PLA/OFI-Fn	266.34 (1.8)	301.76 (1.77)	272.37 (1.85)	277.99 (1.77)	279.62 (1.8)
PLA/T/OFI-Fn	263.13 (1.77)	267.67 (1.8)	256.65 (1.75)	219.18 (1.8)	251.66 (1.78)

It is clear that the activation energy values obtained by C-R method are greater than those obtained by FWO and KAS methods; however, it is noticed that the C-R method follows the same pattern like FWO and KAS methods. The explanation behind such contrast is that in model fitting approach, different models are fitted to conversion versus temperature curve, and then activation energy and pre-exponential factor are calculated **[25].** The disadvantage of this method is that it provides extreme differences in parameters of Arrhenius if a system obeys a complex thermal degradation mechanism **[26].**

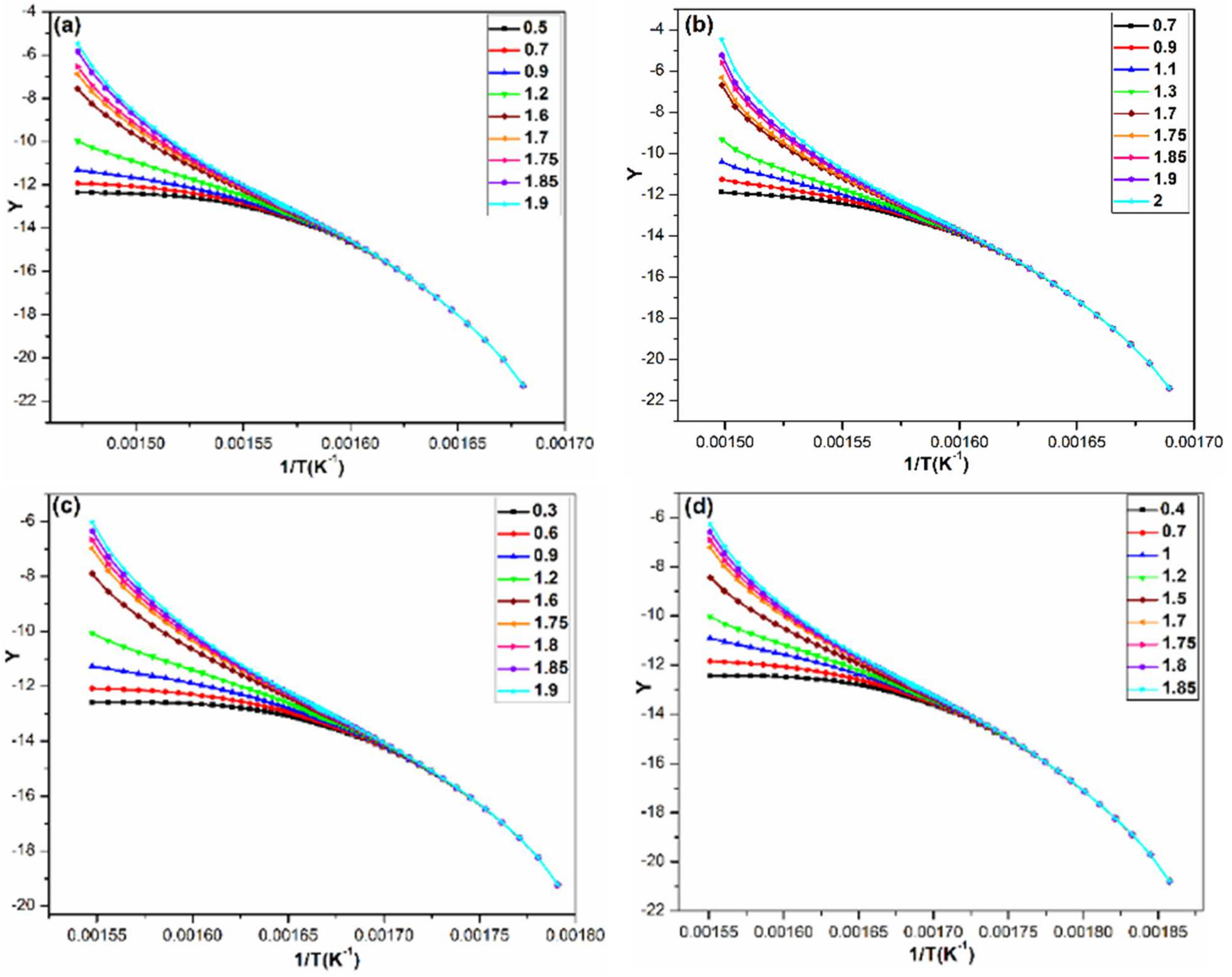

Figure IV.8. Determination of activation energies using C-R method for : **(a)** neat PLA, **(b)** PLA/T, **(c)** PLA/OFI-F and **(d)** PLA/T/OFI-F at a heating rate: 10K/min

b. Degradation mechanism by C-R method

The fitted plots including varied theoretical functions according to Coats Redfern equation (equation 11 mentioned in the previous chapter) are shown in **figure IV.9**. **Figure IV.9** shows the plotted graphs for neat PLA and its bio-composites, at a heating rates 10 K.min^{-1}. The same trend for all curves is observed at all heating rates. Only F2 kinetic models show the great level of straight fitting with (R^2) equal to 0.999. F2 reaction model means random nucleation with two nuclei in each individual particle. In this mechanism, nuclei are developed at imperfection sites of samples due to impurities and edges within **[8].**

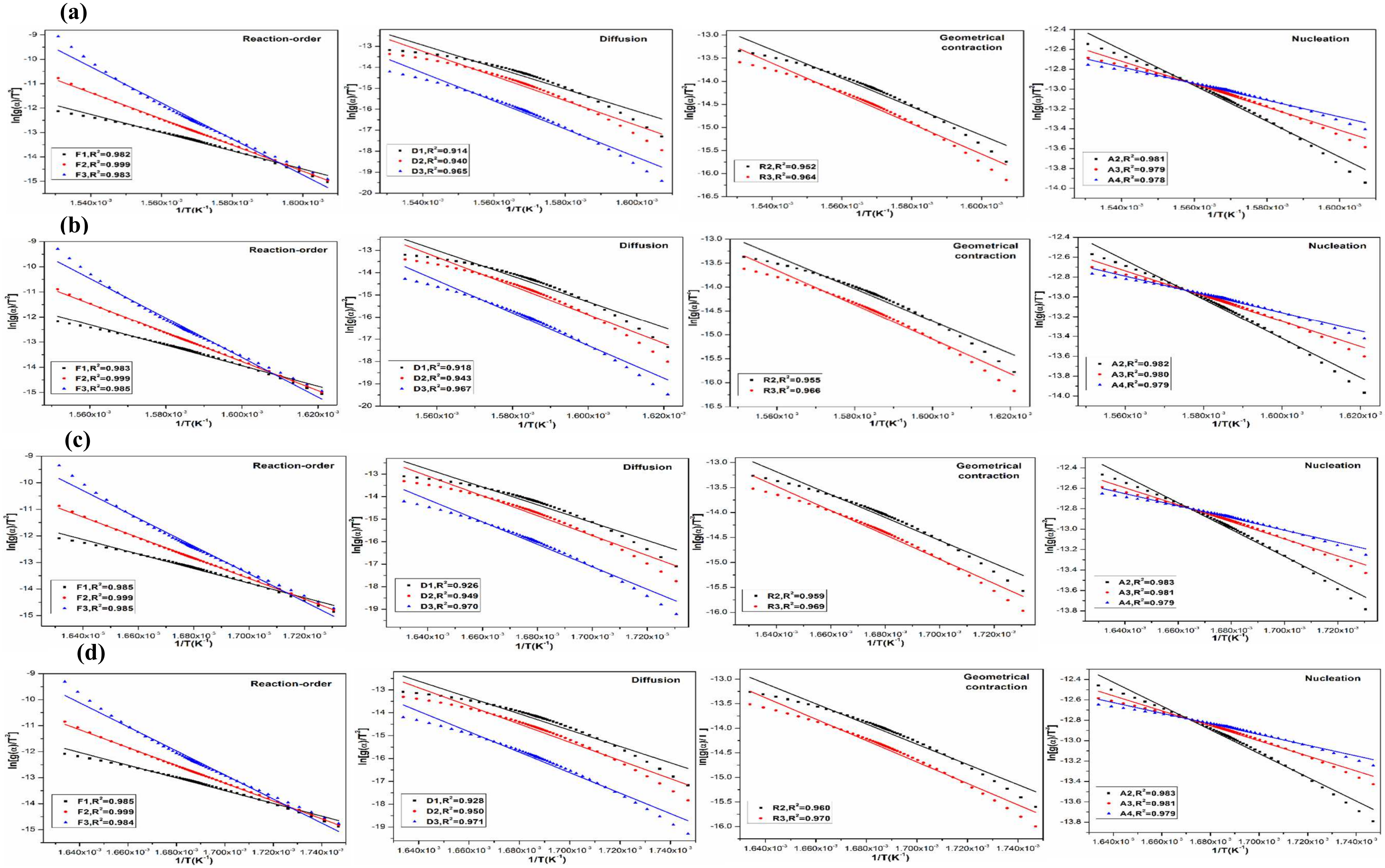

Figure IV.9. Fitted results according to integral form of Coats Redfern method for **(a)** neat PLA, **(b)** PLA/T, **(c)** PLA/OFI-F, **(d)** PLA/ T/ OFI-F at a heating rate: 10K/min

IV.5.2 Confirmation of degradation mechanism by Criado method

The E_a and A got form C-R method, are utilized to trace master curves of PLA and its bio-composites to exhibit thermal degradation mechanism. The $Z(\alpha)_{exp}$ plots calculated are showed in **figure IV.10**. **Figure IV.10** shows the plotted graphs for neat PLA and its bio-composites, at a heating rates 10 K.min^{-1}. The same trend for all curves is observed at all heating rates. This experimental plot provides a simple and exact determination of the degradation mechanism when matched with the master plots. It is clear that F2 is the matching point. For advanced conversion rates, there was a slow alternation to the F3 mechanism. For these conversion rates, the temperature was higher than 623 K.

Therefore, the higher temperature accelerates the cellulose polymer chain into shorter chains. These chains with lower molecular weights may serve as sites for random nucleation and growth for degradation mechanism .Similar finding are seen by **[27].**

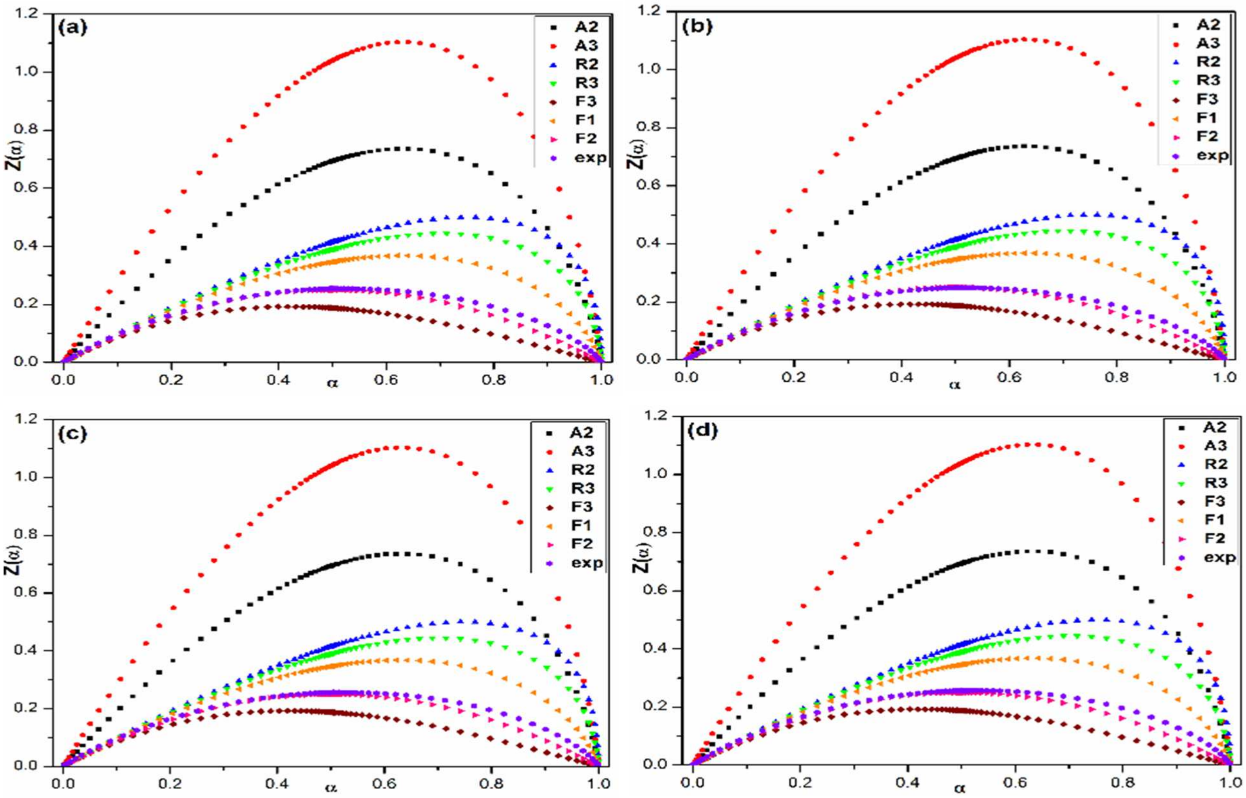

Figure IV.10. Reaction mechanism plots using Criado method for **(a)** neat PLA , **(b)** PLA/T , **(c)** PLA/OFI-F , (d) PLA/T/OFI-F at a heating rate :10K/min

Conclusion

The results of thermal degradation kinetics studied by model-free (isoconversional) approach and the model-fitting approach based on thermogravimetric analysis (TGA) at different heating rates are clearly outlined in this chapter.

From the results of the kinetic study, it can be seen that the inorganic fillers improve thermal properties by increasing the activation energies. PLA/OFI-F and PLA/Talc/OFI-F reveal a decrease in thermal stability due to the poor interaction between natural fillers and PLA matrix, and there are no synergism between PLA talc particles and OFI-F fillers.

The kinetic model of neat PLA and its bio-composites is determined using the Coats-Redfern and Criado methods. All bio-composites follow the second order kinetic model (F2).

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General conclusion and perspectives

General conclusion and perspectives

The objective of this research was to investigate PLA as a matrix in a bio-composite system where natural fibres (OFI-F) and mineral particles (talc) are used as reinforcement to reduce the cost of PLA and improve its properties while maintaining its biodegradability. Neat PLA and its bio-composites were generated using melt processing. In addition, the thermal degradation kinetics at multiple heating rate approaches of neat PLA and its bio-composites were analyzed by model-free like Flynn Wall Ozawa (FWO) and Kissinger Akahira Sunose (KAS) and model-fitting approaches methods like Kissinger and Coats-Redfern.

From the research results and discussion in previous chapters, the following conclusions are summarized:

Talc has been used as a reinforcing filler in the PLA matrix in order to investigate the thermal and the morphological properties of PLA/talc bio-composites. These bio-composites were studied at weight ratios of 90/10. The following conclusions have been drawn.

The results indicate that, compared to neat PLA, the activation energy of PLA/T bio-composites increases. Thus, the experimental findings demonstrate that the presence of 10 wt% talc improves the thermal stability of PLA bio-composites. Furthermore, they reveal that the presence of inorganic fillers has an inhibiting effect on the thermal degradation of the PLA matrix. With improved thermal stability of PLA/Talc bio-composites, they could be suitable for a range of applications including packaging. SEM images suggest that talc is homogeneously mixed within the PLA matrix, and most of the fibers show good adhesion with the PLA matrix.

After the addition of OFI-F as a natural filler into the PLA matrix, all thermograms shifted to lower temperatures values. Compared to neat PLA, the activation energy of PLA/OFI-F bio-composites decreased, revealing that the presence of OFI-F accelerated the thermal degradation due to the formation of aggregates and voids into the PLA matrix. The morphology of the bio-composites was observed by scanning electron microscopy (SEM). OFI-F was seen to be uniformly distributed. The voids accelerate the movement of oxygen, leading to the acceleration of the thermal degradation.

The results denote that the addition of the talc/OFI-F mixture does not enhance the thermal properties of PLA bio-composites.

The average Ea of the PLA/T/OFI-F hybrid bio-composites obtained by the FWO method is 143.3965 KJ/mol while that of PLA/OFI-F is 151.0167 KJ/mol. The decrease in Ea signifies that the addition of talc causes a decrease in thermal properties which means that there is a synergy between talc and OFI-F and also that in this temperature range talc does not consume energy. It can be inferred that the activation energy of thermal degradation can be used as an efficient tool to understand thermal stability.

The kinetic model was confirmed by Coats-Redfern and Criod methods. The thermal degradation for neat PLA, PLA/T, PLA/OFI-F and PLA/T/OFI-F follows the second-order reaction (F2) with the integral form $g(\alpha) = (1-\alpha)^2$ and the differential form $f(\alpha) = [1/(1-\alpha)]^{-1}$. The findings provide useful insights to understand the thermal degradation mechanism of neat PLA and its bio composites.

Further Work

We believe that OFI-F flour and talc are promising fillers for PLA bio-composites manufacturing.

For future work, intensive investigations will be conducted in order to:

1. Understand the mechanical properties of bio-composites to make them suitable for food packaging and other applications.
2. Study the environmental impact on the degradation of the PLA and its bio-composites (hydrolytic and soil bio-degradation). The environnemental factors include humidity and soil conditions.

Research Work and Activities

Research Work and Activities

International Publications

1. Gharsallah, A., Layachi, A., Louaer, A., & Satha, H. (2021). Thermal degradation kinetics of Opuntia Ficus Indica flour and talc-filled poly (lactic acid) hybrid biocomposites by TGA analysis. Journal of Composite Materials, 55(22), 3099-3118.https: DOI: 10.1177/00219983211008202 journals.sagepub.com/home/jcm.

International Communications

2. Gharsallah, A., Layachi, A., & Satha, H. (2021). Inverstigation on thermal degradation of Opuntia Ficus Indica flour and talc filled Poly (lactic acid) hybrid bio- composites. International Seminar on Material Sciences (Physics and Chemistry) organized by Algerian Journal of Engineering, Architecture and Urbanism. (Poster presentation).

1. Gharsallah, A., Layachi, A., & Satha, H. (2019). Non isothermal crystallization kinetics of poly (lactic acid) polymethyl methacrylate (PMMA) copolymer). The fifth international conference on bio-based materials and composites (ICBMC). (Poster presentation).

National communications

1. Gharsallah, A., Layachi, A., & Satha, H. (2018). Kinetics crystallization of PLA/PMMA. National day “Study of materials: Elaboration and modeling. (Poster presentation).