

École polytechnique de Louvain

Environmentally friendly thermoplastic composite from natural banana fibers and recycled PET

**Influence of epoxy chain extender, fiber
treatments and fiber content**

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Abstract

Today's society faces the accumulations of considerable amounts of plastic waste. This waste can be managed in several ways, and one of them is recycling. In this work, the design of a composite is made from recycled PET and natural banana fibers (BF) with an environmentally friendly mindset. Unfortunately the melting temperature of PET is around 250-260°C and the thermal stability of a banana fiber is around 200°C. PET is therefore chemically modified to lower its melting temperature. This modification consists of a depolymerisation by glycolysis with 1,3-propanediol (1,3-PD). Followed by a repolymerisation, with a chain extender made of 1,3-PD and succinic anhydride (SA), which contributes to the reduction of the melting temperature while increasing the molar mass. 1,3-PD and SA can be produced in a bio-sourced way. The next step is solid state polymerization (SSP) to further increase the molar mass. Finally the influence of tetraglycidyl 4,4 diaminodiphenyl methane epox (TGDDM) as chain extender is studied in different proportions and for different reaction times. However, a higher concentration of TGDDM does not further increase the molar mass as expected. It may rather react with small chains to make a branching structure or react with water molecules and gender degradation by transesterification.

Before addition of BF in the matrix, acid and alkaline treatments on BF were studied. Alkaline treatment of the fiber increases the thermal stability by 20°C compared to untreated fiber and allows a good cohesion with the matrix. Acid treated fibers have residues on the surface that must be removed by cleaning. Otherwise, these residues mix and react with the matrix during extrusion and make the matrix brittle. This leads to low mechanical properties for the composite. Influence of BF loading content in the matrix corresponding to 5, 10 and 20% was done for alkaline treated BF. The amount of fiber improves the mechanical properties but renders the material brittle, whereas the matrix has a strain at break exceeding 110%. The highest Young's modulus is observed for 20wt.% BF and has a value of 4.75 GPa. Influence of annealing temperatures has been done to show the behavior of the composite and the increase of crystallinity that it generates.

The techniques used for the characterisation are the Ubbelohde viscometer to determine the molar weights, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) for thermal characterization, tensile tests for the mechanical analysis, dynamic mechanical analysis (DMA) for thermomechanical characterization, and at last, scanning electron microscopy (SEM) for morphologic characterization.

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Liste of acronymes

1,3-PD	1,3-propanediol
BF	banana fiber
BHET	bis-(2-hydroxyethyl)-terephthalate
CoPS	co-polyester saturated
CoPS1	CoPS obtained after repolymerisation
CoPS2	CoPS obtained after SSP
CoPS3	CoPS obtained after chain extension with TGDDM
DEG	diethylene glycol
DMA	dynamic mechanical analysis
DMT	dimethyl terephthalate
DP	degree of polymerization
DTG	derivative thermogravimetry
DSC	differential scanning calorimetry
DSM	DSM is the name of the discontinuous extruder
EG	ethylene glycol
GPET	glycolised polyethylene terephthalate
HFIP	hexafluoroisopropanol
PET	polyethylene terephthalate
PDI	polydispersity
PLA	polylactic acid
PP	polypropylene
RPET	recycled polyethylene terephthalate
SA	succinic anhydride
SEM	scanning electron microscopy
SP	saturated polyester
SSP	solid state polymerisation
STP	standard temperature and pressure
TBF	treated banana fiber
TGDDM	tetraglycidyl 4,4 diaminodiphenyl methane epoxy
TGA	thermogravimetric analysis
TPA	terephthalic acid
UBF	untreated banana fiber
UP	unsaturated polyester

Introduction

Global warming is one of the main concerns that the world has yet to tackle. The successive intergovernmental panel on climate change (IPCC) reports have shown that the amount of carbon dioxide (CO_2) contained in the atmosphere had strongly risen in recent decades due to human activities. Anthropogenic greenhouse gas emissions is increasing for more than 2.2%/yr since 2000 [1]. In addition, today's society faces the accumulations of considerable amounts of solid waste. In countries with poor sorting infrastructures, tons of trash and waste may be stored in inappropriate places. The most common waste is plastic bottles because of its massive worldwide production. These bottles and many other plastics are made of polyethylene terephthalate (PET). Moreover, the increasing population induces a larger demand of PET. PET correspond to a third of the actual plastic waste.

Despite the useful application of PET, this material creates serious environmental concerns. Approximately 300-450 years are necessary to naturally decompose the final product obtained from PET [2]. Therefore, it is important to give a new life to this valuable waste. PET is well known to be easily recyclable. There are a many ways to recycle PET bottles [3], three possibilities could be : (a) making new bottles from existing bottles. Unfortunately, in this case, the properties of the new made material are decreased and the plastic is less valuable. After multiple recyclings, it becomes harder to fulfill the market requirements a plastic bottle must have [4]. (b) combining some pre-recycled PET with virgin PET to get rid of the bad properties. (c) incorporating fibers in the recycled PET matrix to totally change the physical properties of the material, thereby, making a composite.

When the purpose is to make bottle to bottle recycling, only methods (a) and (b) are possible. Indeed, addition of fibers to make a composite give the material some inappropriate properties for bottle application. However, making a composite (c) may result in an end product being light, strong, tough, and stiff. These properties come from different materials combined together. E.g., polymers are low density and fibers are stiff. A wide range of fibers can be used in recycling, and the choice of the fiber is important as it provides the properties of the end product. While some fibers are known to be strong (e.g. glass, carbon), other are from natural and renewable origin (e.g. pineapple, banana). For example, banana fibers comes form the pseudo stem of the banana plant. This part of the plant is expected to be available in large quantities since the banana fruit is widely cultivated, and that pseudo stems of banana trees have a lifetime of 1 only year (they are cut and regrow every year) [5]. These features would make of banana fibers a great candidate for the synthesis of composites, even at a large scale.

Banana fiber can be incorporated in PET to make a composite. However, the association of those materials is not that simple, when incorporation into the melted PET matrix, banana fibers may degrade thermally. Unfortunately the melting temperature of PET is around 250-260°C and the thermal stability of a banana fiber is around 200°C [6]. This means that a banana fiber suffer degradation when

exposed to temperatures exceeding 200°C. Consequently, working with banana fibers as reinforcement in the composite involves that the melting temperature of the matrix must be below the thermal stability temperature of the fibers. This can be achieved by chemically modifying the PET to lower its melting temperature.

The chemical modification of PET involves several successive stages. The first step is a glycolysis depolymerization. The second step consists in a repolymerization with the incorporation of impurities in the chain extension in order to ensure a lower melting temperature. And the third stage is an extension of the polymer chains to ensure good mechanical properties. Tetraglycidyl 4,4 diaminodiphenyl methane epoxy (TGDDM) is a tetrafunctional epoxy resin used in this work as a chain extender. The objective of this resin is to react with at least two chain ends to bond them together, and that way, increase the global molar mass of the polymer. On the other hand, banana fibers are also studied. Banana fibers undergo a treatment before being incorporated into the matrix and form a composite. Banana fibers can be treated in different ways, either by an alkaline treatment using NaOH or by an acid treatment using succinic anhydride. These treatments aim to improve the thermal stability of the fibers and to optimize the cohesion with the chemically modified PET matrix.

The main objective of this work is to develop a composite with good mechanical and sufficient thermal properties. To achieve this, several parameters have been studied. The amount of TGDDM as chain extender and its reaction time were studied to optimize the properties of the matrix. Then the influence of fiber content in the composite and the different acid treatments on the mechanical properties were considered. Finally, the influence of different temperatures of annealing on the composite was studied.

Here, the mindset is to give a second life to PET waste and to use only elements of natural origin such as banana fibers and alternatives to the standard chemicals reagent from petroleum. Therefore, 1,3 propane diol is used instead of ethylene glycol. Although, TGDDM is of industrial origin but is very available and very efficient. This is why it is used instead of other bio-sourced chain extenders such as polyglycidyl methacrylate (PGMA) for example.

The first chapter contains an introduction to the knowledge of plastics, and more particularly thermoplastics. It then reviews the current knowledge on PET and its different synthesis, recycling, and degradation methods. A review on natural and banana fibers is also provided. The origin, composition, and different types of treatments to improve the compatibility of these fibers into a matrix are explained. The second chapter presents the materials used and the experiments carried out within this framework. The study of various parameters as well as characterization techniques are also presented in this section. These techniques of characterization allow to analyse and discuss results obtained from the experiments. The results and discussion are presented in the third chapter followed by a conclusion including the possible prospects.

Chapter 1

State of the art

The purpose of this chapter is to make a global review of the knowledge required to better understand the research presented in this thesis. The university course of "polymer science and engineering"[7] has been used as main reference for the thermoplastic review. This section also briefly describes the properties, applications and manipulations of polyethylene terephthalate, banana fibers and PET/banana fibers composite.

1.1 Thermoplastic review

Plastic consumption is about 38 million tons per year in Europe, whereof the majority are used in packaging [9]. A thermoplastic is a type of plastic widely used in industrial applications. Other types of plastics include thermoset and elastomer. These polymers can be differentiated by their intermolecular links, which leads to differences in properties between them. An elastomer is very elastic and turns back into its initial shape after huge deformations. Thermosets are very hard because the plastic molecules are strongly linked by crosslinking bonds, and these molecules do not relax completely when heated. This means that thermosets do not melt and are limited in terms of recycling. Finally, thermoplastics are composed of molecules that relax at a certain glass transition temperature (T_g), and a second time at melting temperature (T_m). Thermoplastics are therefore reformable and well known for their easy recycling.



Figure 1.1 Bali's iconic surf beach in Kuta littered with Coke bottles, thongs, crumpled plastic water cups and drinking straws [8].

1.1.1 Molecular Weight Distributions

Plastics are synthetic polymers. These polymers are composed of macromolecules which themselves are made of monomers linked together by covalent bonds. We can define the degree of polymerisation (DP) as the number of monomers linked

together. The degree of polymerisation is generally a high number, e.g. it is not uncommon to find 10^4 or 10^5 monomers linked together in a single polymer [7]. In addition, one polymer may be composed of macromolecules of different lengths, i.e. containing different amounts of monomers. The distribution of different degrees of polymerisation is called polydispersity.

There are several ways to measure the average molecular weight [10]. The number-average-molecular-weight is noted $\bar{M}_n$. This average consists of measuring the number of polymer molecules in a given sample weight.

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i} \quad (1.1)$$

Where M_i is the molecular weight of the molecule of length i , and N_i is the number of molecules of size M_i .

The weight-average-molecular-weight, $\bar{M}_w$ is the mean of the weight distribution with $W_i = N_i M_i$:

$$\bar{M}_w = \frac{\sum W_i M_i}{\sum W_i} \quad (1.2)$$

Polydispersity is also denoted PDI.

$$PDI = \frac{\bar{M}_w}{\bar{M}_n} \quad (1.3)$$

1.1.2 Role of crosslinking

Thermoplastics are polymers with reversible (or physical) linear links between chains. They differ from thermosets which form irreversible chemical bonds during the curing process. This means that thermoplastics can be molten and shaped repeatedly by heating while thermosets do not melt when heated. Polystyrene, polyamides, polyethylene terephthalate, polypropylene, polyethylenes, etc. are different types of thermoplastics.

Elastomers are polymers with irreversible chemical cross-links. The deformation of elastomers is essentially reversible over a wide range of deformations, up to several hundreds of percents, whereas most other materials are limited to a few percents. The capacity to reverse deformations comes from the cross-links between chains. Figure 1.2 shows the force versus elongation of a sample of natural rubber, before and after crosslinking. Elastomers without crosslinking have a large irreversible deformation. This is due to the relaxation of chains, which gently slide over each other during the tensioning process. The chains are all entangled, so this process is slow. But when the elastomer has crosslinks, sliding of the chains over each other during deformation does not take place anymore and the initial shape is recovered at the end of the cycle. To create crosslinks, it is useful to have double bonds in the molecular chains of the elastomer, so they can react by radical polymerisation.

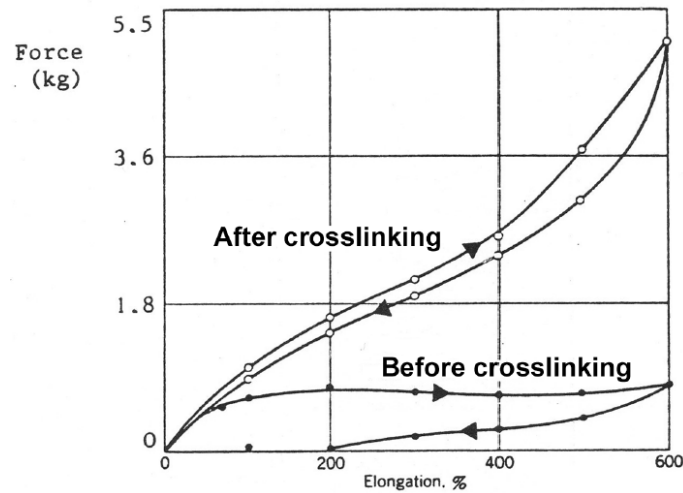


Figure 1.2 Force versus elongation for natural rubber before and after crosslinking [7].

Standard elastomers are chemically crosslinked, meaning they can not be reshaped after processing, and hence can not be recycled. At the end of their life, most of them are thrown away or disposed off. To avoid this problem, alternatives to chemical binders are studied. For example, reversible binders that can be broken at very high temperatures, which would lead to a reshapable material.

1.1.3 Crystallization

Some polymers can partially crystallize. This happens when the polymer moves from liquid to solid phase relatively slowly to give the chains time to re-organise themselves. This requires the chains to be fairly regular (e.g., isotactic). Figure 1.3 represents the microstructure of a semi crystalline polymer.

To facilitate the creation of a crystalline phase in the material, nucleating agents may be used. These agents are usually inorganic materials added to the polymer but fibers in a composite tend to play this role as well [11]. Other classic nucleating agents are fillers like talk, chalk, kaolin, etc. A high crystallinity content induces a higher Young's modulus (*the Young's modulus measure the stiffness of solid material*) because the chains have less facility to move but it also changes the properties such as clarity and density.

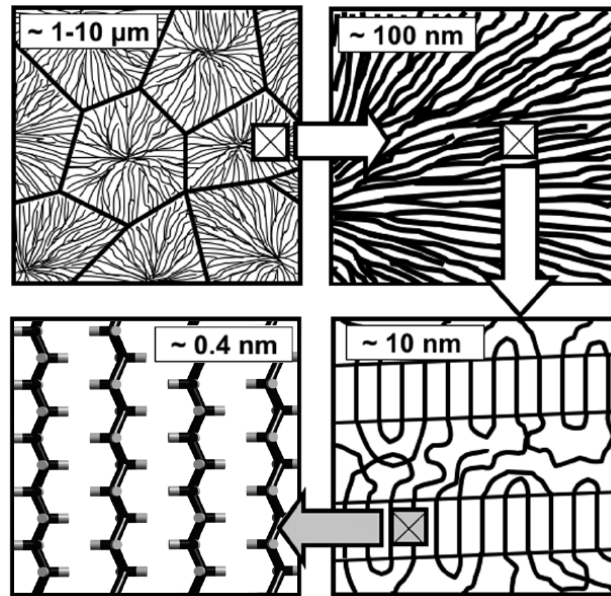


Figure 1.3 Scheme of the microstructure of a semicrystalline polymer crystallized from a quiescent isotropic melt. The material is made of spherulites (top left), which are aggregates of crystalline lamellae separated by amorphous interlayers, forming fibrillar stacks growing more or less radially from the spherulite center (top right). The lamellae comprise segments of chains in an extended straight conformation (bottom left), whereas amorphous regions contain sharp and loose folds, chain ends, bridging tie molecules, and chain defects (bottom right) [7].

Whitening is a sign of the presence of crystals and, on the contrary, a polymer which is quenched will be much more amorphous because the chains do not have time to reorganize and the appearance is much less opaque.

Due to amorphous regions interspersed between the crystalline regions, crystalline polymers have a heterogeneous structure (Figure 1.4). In contrast, amorphous polymers have a homogeneous structure.

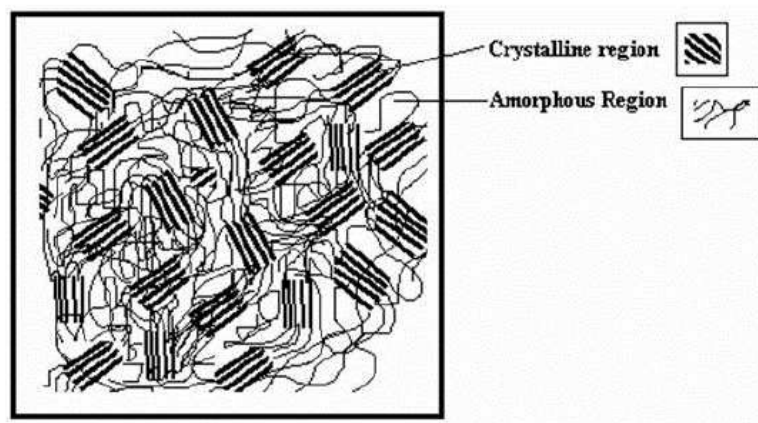


Figure 1.4 Mixed amorphous/crystalline polymer structure [12].

1.1.4 Glass transition and melting temperature

The glass transition temperature, also noted as T_g , is the temperature at which amorphous materials gradually change from a brittle (*easily breakable*), glassy state to a viscous and rubbery state. From an application point of view, it is important to consider this transition because mechanical properties vary widely over a relatively small temperature range by motion of molecular chains in free volume. The melting temperature is noted as T_m .

At the melting point, polymers are like a rubber-liquid. For crystalline polymers, the relationship between T_g and T_m is described as follows [12] :

$$T_g \rightarrow \frac{2}{3}T_m \quad (\text{for unsymmetrical chains}) \quad (1.4)$$

and

$$T_g \rightarrow \frac{1}{2}T_m \quad (\text{for symmetrical chains}) \quad (1.5)$$

The glass transition temperature can vary according to a series of parameters such as cooling or heating rate, chemical nature of the polymer, topology and microstructure of the chains or composition and morphology of the material. Hereafter, the effects of volume, cooling rate and molar mass on the glass temperature T_g will be described

1.1.4.1 Free volume and specific volume

Except for water, amorphous materials tend to have a lower density than their crystalline counterparts. This is due to irregular positions of the atoms compared to the organized chains in the crystalline material. The excess volume in amorphous materials is called the free volume v_f . An amorphous material may have a density of about 10% lower than for the material in its crystalline phase.

We can thus define the specific volume v , which is the addition of the volume occupied by the atoms v_{occ} and the free volume v_f . These volumes are directly dependent on temperature T [7].

$$v(T) = v_{occ}(T) + v_f(T) \quad (1.6)$$

1.1.4.2 Effect of the cooling rate

Figure 1.5 shows the variations of the specific volume for two different cooling rates. It is observed that for a high cooling rate q_1 , the transition temperature and the free volume are higher. This can be explained by the amorphous state of the material, as the chains in amorphous materials have less time to evacuate the free volume, and thus reach the glassy state at a higher temperature T_{g1} .

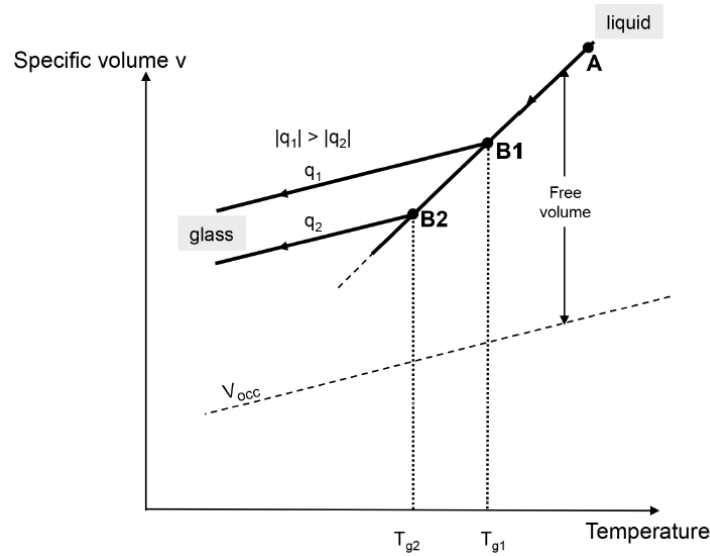


Figure 1.5 Variation of the specific volume of a polymer cooled at different rates q_i [7].

1.1.4.3 Effect of the molar mass and degree of crystallinity

The molar mass of a polymer also affects the glass transition temperature. Indeed, T_g decreases with the molar mass. This directly results from the ability of a short-chained polymer to relax earlier than a long-chain polymer during heating [7]. This effect appears to be strongest when n is low. One could consider that T_g is only affected by the molar mass below a mass of 10^5 g/mol.

1.1.4.4 Methods to measure T_g and T_m

There are several methods for measuring glass transition temperatures [7]. One of them is dilatometry. It measures the volume of a sample as a function of temperature. Upon heating the specific volume increases more rapidly after the glass transition temperature has been crossed (Figure 1.5). In addition, there is a large expansion of the volume during melting. These specific reactions of the material to heating enable to (precisely) determine its melting and transition temperatures.

Beyond dilatometry, other techniques include differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). DSC has a technology to measure the heat transfer of a sample during heating and cooling. In contrast, DMA is based on the measurement of temperature while applying a sinusoidal deformation of low amplitude. DSC and DMA techniques will be further explained in the experimental chapter.

1.1.5 Mechanical properties

What gives a polymer good mechanical properties are mainly its molar mass and its degree of crystallinity. A thermoplastic with high molar mass will have a high Young's modulus and especially a high tensile strength (*maximum stress that a*

material can withstand) because the polymeric chains will be highly entangled. Furthermore, the crystallinity enhances the hardness at the expense of making the material more brittle and decrease its toughness (*ability of a material to absorb energy and plastically deform without **fracturing*** [13]). Figure 1.6 shows the typical stress-strain curves of different polymers.

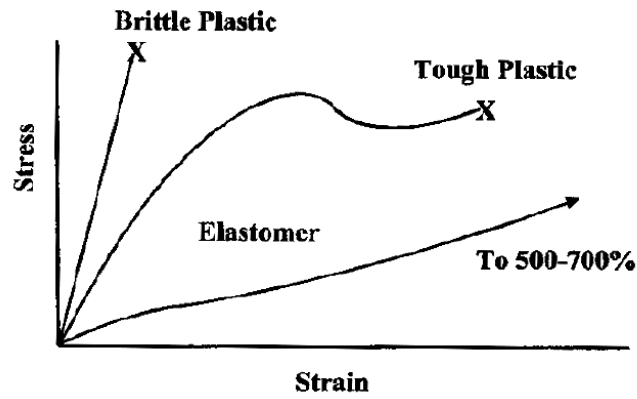


Figure 1.6 Curve of stress versus strain for different polymers[14]

1.2 Polyethylene terephthalate (PET)

Most plastic bottles available in grocery stores are made of polyethylene terephthalate. Figure 1.7 illustrates its chemical structure and Figure 1.8 is a 3-dimensional representation of the atomic space-filling model. This material is a semi-crystalline thermoplastic with good properties for the synthesis of soft drink bottles. This section resumes the synthesis method, characteristics, and applications of PET. The recycling and depolymerisation are then discussed, followed by the description of some relevant chain extension methods.

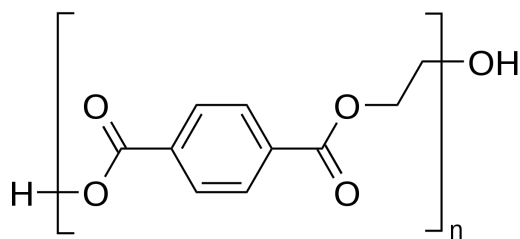


Figure 1.7 Chemical structure of PET.



Figure 1.8 Space-filling model of a section of PET. Colour code: Carbon: black; Hydrogen: white; Oxygen: red [15]

1.2.1 Synthesis of PET

Two monomers are used for the synthesis of PET. These are terephthalic acid (TPA) and ethylene glycol (EG).

The process of synthesis of PET consists of two main steps [16–18] :

1. The first step is esterification of TPA with EG (Figure 1.9). This forms a pre-polymer containing BHET (2-hydroxyethyl)terephthalate and short-chain oligomers having a degree of polymerisation (DP) of approximately 2 to 4. The esterification reaction gives water as by-product.
2. In a second step, polycondensation leads to a DP of 150. This reaction is carried out using a catalyst, i.e. usually antimony oxide (Sb_2O_3).

After the second stage of the reaction, solid state polymerisation (SSP) is realized to increase rapidly the DP from 150 to a higher degree to have good mechanical properties for current applications.

The first step of PET synthesis can also be done by transesterification, which involves the synthesis of bis (2-hydroxyethyl)terephthalate (BHET) by dimethyl terephthalate (DMT) and EG molecules. Transesterification is more efficient than direct esterification and is often used to make PET fibers. However, DMT has to be synthesized beforehand from TPA and EG at high temperature and pressure. This reaction takes place in the presence of a catalyst (below 0.5wt.%). The synthesis by transesterification is illustrated in Figure 1.10.

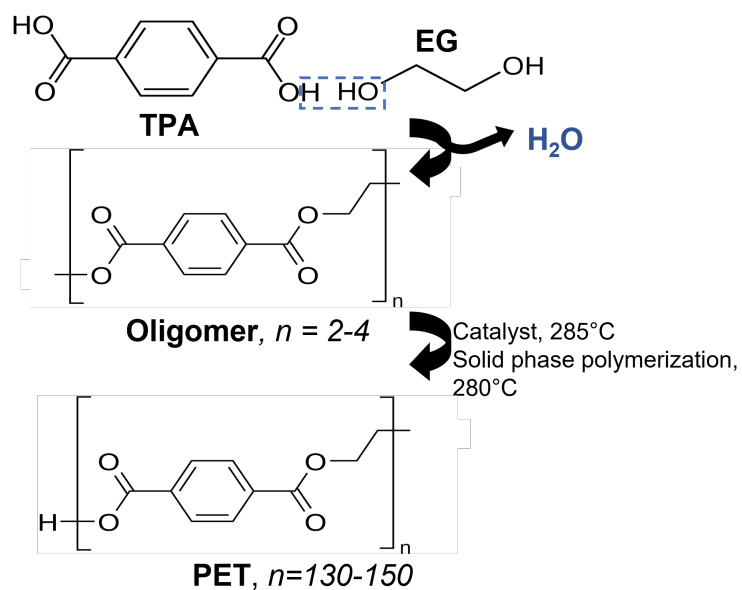


Figure 1.9 Synthesis of PET by direct esterification of TPA and EG. Modified from *PET Chemistry* [16].

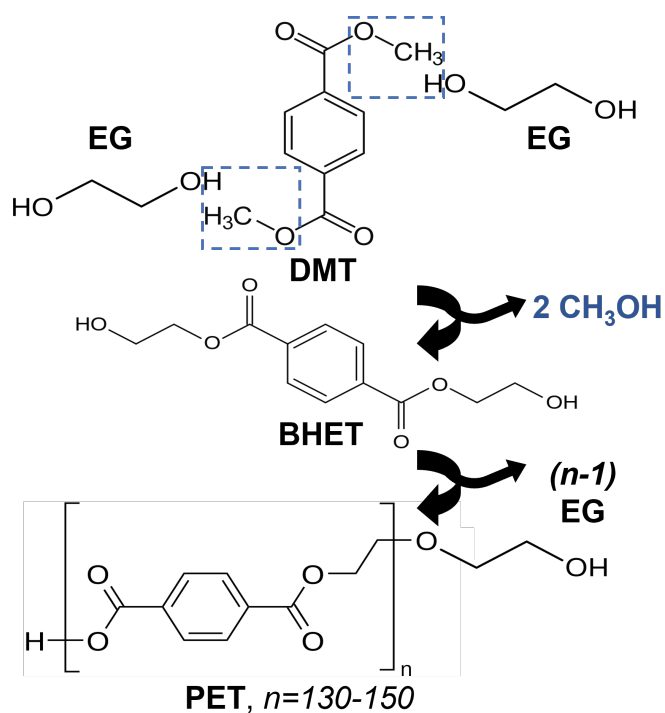


Figure 1.10 Synthesis of PET by transesterification of DMT and EG. Modified from *PET Chemistry* [16].

The production of EG and TPA can be done in a sustainable way, as it is described in Table 1.1. However, it involves limitations, such as the limited amount of resources, high cost or harsh conditions. Therefore, few of these processes are feasible on a commercial scale and their production almost only takes place in laboratories for research.

Table 1.1 Comparison of sustainable processes for obtaining the two monomers useful for the PET synthesis, namely EG and TPA [17].

Monomer	Feedstock	Yield	Selectivity	Criticalities	Feasibility
EG	Ethanol	High	High	High costs	Commercial
	Glycerol	Medium-Low	-	Limited feedstock	-
	Sorbitol	Medium-Low	-	Limited feedstock	Commercial
	Biomass	High	High	Diluted conditions	Laboratory
Terephthalic acid	Ethanol	Medium	Low	Harsh conditions	Laboratory
	HMF	High	-	High costs	Laboratory
	Isobutanol	Low	-	High costs	Pilot Plant
	Biomass	Low	Low	-	Demonstration
	Isoprene/Acrylic acid	High	-	Limited feedstock	Laboratory
	Limonene	-	-	Limited feedstock	-
	Furfural	Low	-	Harsh conditions	Laboratory

So far, only two methods to produce EG have reached an acceptable feasibility for commercial purposes [17]. Firstly we have the production from ethanol thanks to the Coca-Cola brand which has made bio ethanol plants (PlantBottleTM) available in Brazil and Asia. Secondly, there is the production of EG from sorbitol in China by Changchun Dacheng Industrial Group Comapny Ltd. For the production of TPA, only the process using biomass has reached the demonstration scale. This is by a pyrolysis-reforming technique to obtain para-xylene and consequently TPA by oxidation (Figure 1.11).

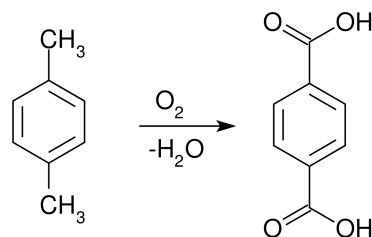


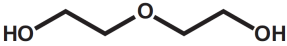
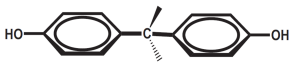
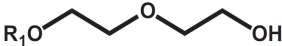
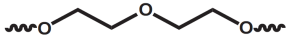
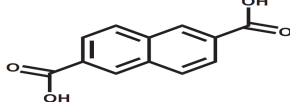
Figure 1.11 Oxydation of p-xylene for TPA synthesis [19]

1.2.2 Characteristics of PET

PET thermoplastic has excellent mechanical and thermal properties. Furthermore, it has good chemical resistance, dimensional stability, transparent and light weight, economic availability and processability, low adsorption and low moisture absorption [16]. These properties justify why plastic bottles are usually made of PET. In addition, the energy consumption during the production of PET bottles is much lower than that of glass bottles.

Table 1.2 includes a large part of the reagents for the synthesis process of PET. The nature of diols, diacid and additifs used in PET could modify properties of PET for specific application like describe in table below :

Table 1.2 Reagent for PET synthesis[16].

Type	Molecule	Molecular Structure	Influencing property
Diols	Ethylene glycol		Fiber grade PET formation
	Diethylene glycol		Improves dye ability of fiber grades and lowers melting temperature
	Bisphenol A		Improves melt stiffness
	EG end group		Decrease in hydroxyl value which improves thermal stability
	DEG end group		Decrease in hydroxyl value which improves thermal stability and flexibility
	bDEG repeat unit		Improve in mechanical property
	Vinyl end group		End group functionalization of PET
Diacids	Terephthalic acid		Formation of carbonyl end groups and acetaldehyde results in yellowing of polymer and reduction in the hydrolytic and thermal stability
	Isophthalic acid		Stress cracking resistance and melting temperature
	2,6-Naphthalene dicarboxylic acid		Improves mechanical properties and reduce gas permeability
	TPA repeat unit		Improves the hydrolytic and thermal stability as acid value reduces

1.2.2.1 Thermal properties of PET

Polymers are generally semi-crystalline, given that is impossible to have 100% crystalline PET under normal processing conditions. Usually, they have less than 90% of crystallinity.

Tabarin [20] used Avrami's expression for crystallization kinetics to develop a method to predict the slowest cooling to get a completely amorphous PET. The results show that the obtention of an amorphous material depends on the molar mass, but also on the catalysts used in the synthesis and the cooling rate. A typical differential scanning calorimetry (DSC) thermogram of PET is shown in figure 1.12.

PET has a T_g between 67°C to 80°C and a T_m of 267 °C.

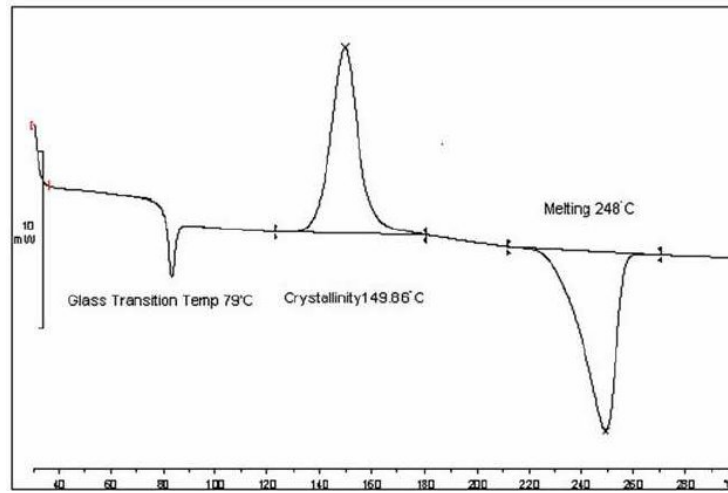


Figure 1.12 DSC thermogram of PET [12].

1.2.2.2 Physical and mechanical properties of PET

Table 1.3 shows a summary of the main physical properties.

Table 1.3 Summary of PET properties (STP : standard temperature and pressure).

Name	PET
Phase at STP	solid
Density	1.3-1.4 g/cm³
Young's Modulus	3 GPa
Melting Point	267°C
Thermal conductivity	0.3 W/mK
Heat capacity	1250 J/gK
Price	0.8 \$/kg

As we can see in the study of Amborski et al.[21], the average molecular weight (M_w) of the commercial polymer is 20,000 to 30,000 g/mol. Considering M_w of an

ethylene terephthalate monomer :

$$m_{monomer} = 192 [g/mol],$$

with a DP between 130 and 150 units as mentioned earlier in the synthesis section, we obtain a global molar mass situated between 24 960 and 28 800 g/mol.

Viana et al. [22] studied the morphology and mechanical behavior of PET after injection molding with different mold temperatures. They highlighted that mechanical properties change depending on the thermal process applied (Table 1.4). The mold temperature varied from 30°C to 150°C, for 100°C the material is the more brittle but for 30°C the modulus and the yield stress are good. The mold temperature influences decisively the morphological development of slowly crystallizing PET of very low degree of crystallinity.

Time and temperature are major influencing factors of the crystallization mechanism for PET, although they are not the only ones. There is, for example, the pressure, the degree of molecular orientation and the environment. Note that nucleating agents also affect the crystallization by facilitating the appearance of crystals on them. These factors directly influence the morphology and final properties of PET [12].

Table 1.4 Tensile tests at $8.33 \times 10^{-4} \text{m.s}^{-1}$ and 23°C. T_w - mold temperature, E - initial modulus, σ_y - yield stress, ε_y - yield strain, ε_b - strain at break of PET after injection molding process with different temperature mold [22].

T_w (°C)	E (MPa)	σ_y (MPa)	ε_y (mm/mm)	ε_b (mm/mm)
30	1353	56.5	1.65	5.57
50	1334	51.2	1.99	5.67
80	1373	53.1	1.46	4.39
100	1269	56.5	0.89	0.98
120	1187	56.4	2.34	4.29
150	1294	56.8	6.91	1.96

1.2.2.3 Moisture absorption behavior of PET

First, let's define the general term *water sorption* as the relative water content of a material on water activity of the surrounding medium at a given temperature. This includes absorption and desorption. We will use the term absorption of water by a material when the surrounding water activity is high compared to the material water content.

It is important to study the trend of water absorption for PET because it has several applications such as based material for coatings or bottles where it has the role of containing liquids. Indeed, water molecules react at high temperature with PET by hydrolysis and decrease the molar mass [3, 23, 24]. The hydrolysis reaction (Figure 1.13) is a reaction of transesterification where a water molecule reacts with

an ester linkage and gives chains of lower molecular weight containing hydroxyl and carboxyl end groups.

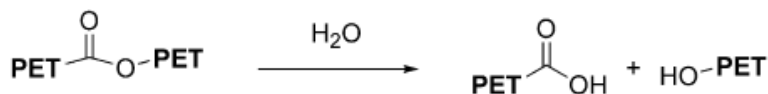


Figure 1.13 Hydrolysis : reaction of chain scission leading to degradation in the presence of contaminant water [25].

1.2.3 PET waste management

PET is the most recycled plastic in the world. Recycled PET is called RPET. In 2012, PET was recycled at a rate of 31% in the US and 52% in Europe. This rate can be increased in the US because Americans tend to throw their bottles with the garbage rather than in the recycling bin. In fact, the recycling rate fell to 29% in 2016. These informations are taken from PET Resin Association - PETRA[26]. In contrast to the decreasing recycling rate, the global production of PET is on an increasing trend and was estimated at 64.4 million tons in 2008 [4]. For example, between 2016 and 2019, the production of PET for packaging was expected to grow by more than 20Mt according to a study by Drah et al [27].

The different plastics are identified by a symbol that is called the coding system of identification of resins (SPI) in French and International Resin Identification Coding System (ASTM) in English which is often abbreviated by RIC. The code for PET is 1, 2 is for HDPE, 3 for PVC, etc. Figure 1.14 shows the code for PET materials. The presence of a code on a plastic product does not necessarily mean that it is recyclable, nor does it mean that the plastic object is not recyclable [28].

Recycled PET (RPET) is employed for different kind of products[29] :

- Polyester carpet fiber
- Fabric for T-shirts
- Long underwear
- Athletic shoes
- Luggage, upholstery
- Sweaters and fiberfill for sleeping bags and winter coats
- Industrial strapping
- Sheet and film
- Automotive parts
- New PET containers



Figure 1.14 SPI code 1: for PET materials.

Replacing virgin PET with RPET is mainly about reducing energy consumption, cutting costs and reducing environmental impact.

1.2.3.1 PET Collection and Sorting

The collection of PET waste is done via programs. These programs have either a single stream or a double stream approach. In addition, other PET recycling programs are set up for special events where there is a high concentration of bottles or other PET waste. Recyclable materials such as PET are first sent to sorting centers and then compressed to be sent to shaping plants.

At Valtris in Belgium [30], the sorting center has a very high capacity. Steel, aluminum and plastics are separated. The different types of plastics such as PET, HDPE, TetraPak, PP, PS, trays are sorted via optical sorting. In addition, PET are separated by color (colorless, blue, colored). This sorting is done by machines using all types of detectors. But an over-sorting is realized by humans to check-up with eventual machine related mistakes or unidentified materials.

The sorted and stored materials are transported to the baler. There, they are compacted and bound to form bales of about 1 m³. Each bale weights between 250 kg and 800 kg depending on the material. These bales are then weighted, labeled and stacked by product family before being loaded onto trucks and bound for the recycling channels.

1.2.4 Recycling of PET

1.2.4.1 Contaminants

It is very important to remove contaminants from post-consumer waste PET as these are the major causes of physical property deterioration. Contaminants include water, acid producing contaminants, dyes, acetaldehyde, but also pesticides and detergents in some cases. Different contaminants will have different effects, e.g. some will decrease the molar mass by chain scission, others may have an impact on health if they are still present in the RPET [3].

1.2.4.2 Mechanical recycling

Mechanical recycling of PET is the main recycling system for PET due to its non-biodegradable character. This recycling is done in different steps which are illustrated in Figure 1.15. The advantage of this type of recycling is that it is inexpensive, simple to perform and environmentally friendly [3, 23]. Mechanical recycling of PET follows several consecutive steps:

Plastic collection and plastic sorting : These steps have been discussed in the previous paragraph but they are crucial to end with a PET of high purity. This will reduce the problems caused by the presence of impurities in the following stages.

Chipping : The sorted PET is sent to a cylindrical oven which will cut the plastic in small pieces with the help of gyratory blades. The aim is to form small PET chips.

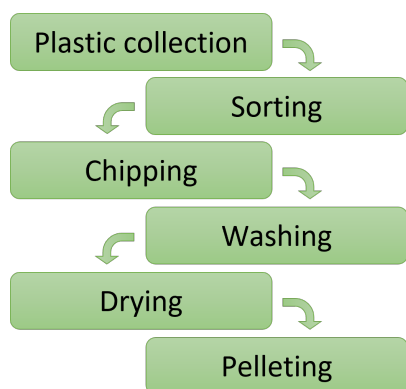


Figure 1.15 The different steps involved in mechanical recycling [23].

Washing : There are two ways to wash the post-consumer PET. Either in two steps in a 2% NaOH solution at 80 °C followed by a cold wash with water. Or washing by solvent, for which tetrachloroethylene has been reported as being approved for washing PET flakes.

Drying : Drying is an essential step as it minimizes the risk of moisture content and degradation by hydrolysis. In most cases, drying conditions are found to be in the 140°C-170°C range for a period of 3-7 hours. Typically, no more than 50 ppm of water are allowed in the PET before extrusion.

Pelleting : Finally the PET chips can be extruded into pellets. Unfortunately, due to the contaminants mentioned above, the molar mass of this recycled PET is greatly reduced compared to virgin PET.

1.2.4.3 Chemical recycling

Chemical recycling means depolymerisation into oligomers and monomers. There are several chemical recycling processes and these lead to different products. Figure 1.16 shows the different products obtained from PET by the mentioned chemical process of complete PET depolymerisation. These processes are methanolysis, hydrolysis, glycolysis, aminolysis and ammonolysis.

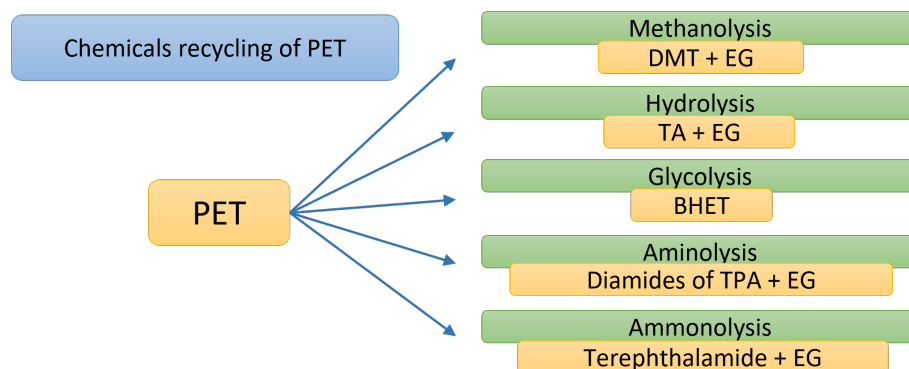


Figure 1.16 The various processes of chemical recycling of PET

Glycolysis is the most used method and the chemical reactions it includes are presented in Figure 1.17. In short, it consists of adding ethylene glycol to PET to obtain BHET which can be reused directly for PET synthesis. This process generally takes place at temperatures between 180°C and 250°C with an excess of EG. In addition, a catalyst such as zinc or lithium acetate or others are added [31].

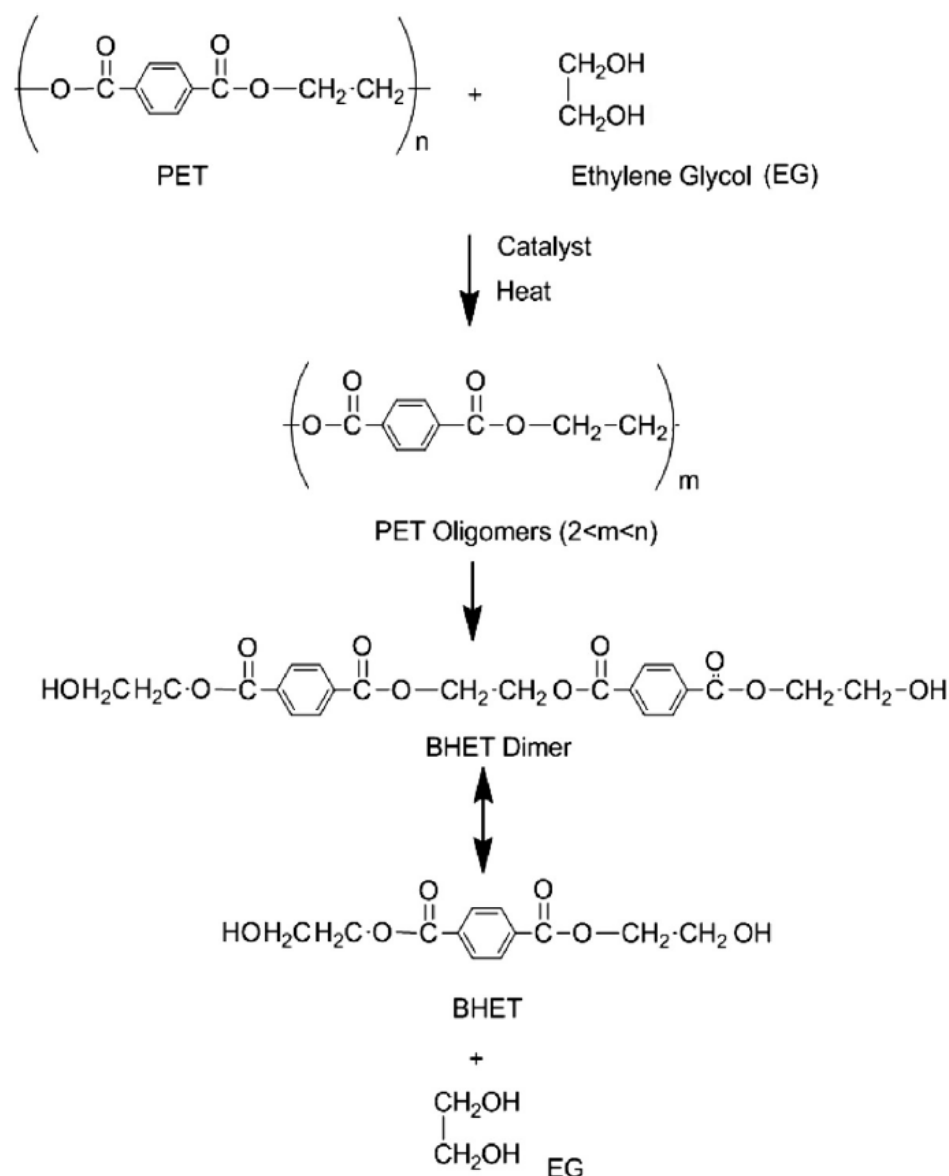


Figure 1.17 Glycolysis : Chemical depolymerisation with EG that breaks the ester linkages [31].

1.2.5 Degradation of PET waste

PET is known to have good resistance to its environment and to degradation. But even on a small scale, it is important to avoid decomposition in order to keep the materials uniform[23]. The degradation process is due to molecular chain splitting and discoloration. We can have thermal degradation, biodegradation and degradation because of radiation such as photodegradation. These three degradation modes are described hereunder.

1.2.5.1 Thermal degradation

The degradation by heating generally occurs at the ester function. As it can be seen in Figure 1.18, the $C - O$ (α) bond and the $C - H$ (β) bond are partially broken

and an $O-H$ bond is formed with a thermal contribution. Then the electrons move again to form a $C=C$ and $C=O$ double bond and the molecule splits in two. Thermal degradation of PET does not occur below 280°C . [32]

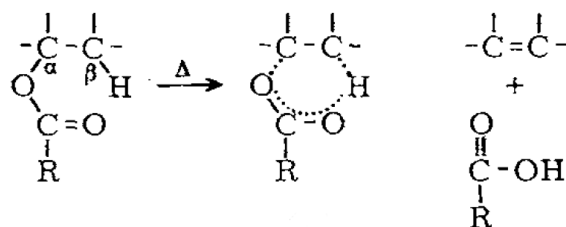


Figure 1.18 Thermal degradation of a carboxylic ester [32]

1.2.5.2 Biodegradation

Taniguchi et al. [33] shows the biodegradation of PET by a microbial consortium and its bacterial resident, *Ideonella sakaiensis*. The mechanism of PET degradation into monomers is shown in Figure 1.19. This technique uses PET hydrolase (PETase) and mono(2-hydroxyethyl)terephthalic acid (MHET) hydrolase (MHETase). The recovery of an intermediate TPA and MHET could be possible by modifying genes in the bacteria, which would allow recycling without undergoing thermal degradation. Biodegradation could find an application to degrade PET oligomers present in industrial wastewater streams due to water cleaning during recycling.

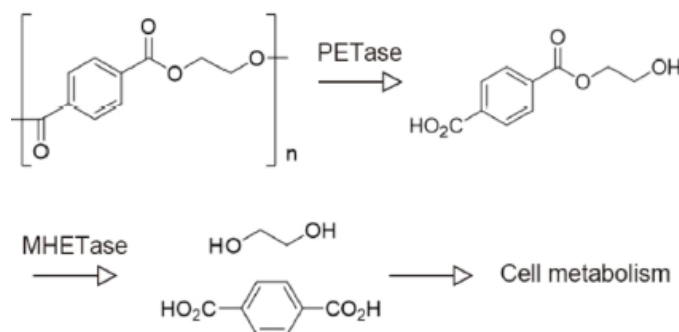


Figure 1.19 Microbial (*ideonella sakaiensis*) biodegradation pathway[33]

1.2.5.3 Photocatalytic degradation

PET naturally undergoes photodegradation in the environment due to exposure to solar UV radiation. The ultraviolet radiation provides the activation energy needed to initiate the incorporation of oxygen atoms into the polymer chains of PET waste. This process makes the PET waste brittle and breaks it down into smaller pieces. This process continues until the polymer chains reach a sufficiently low molecular weight. In fact, PET is very stable to light until the wavelength reaches ultraviolet [34]. The fastest degradation occurs during exposure to wavelengths of 300-330 nm [32]. The process of photodegradation can then be followed by biodegradation. However the complete degradation will take more than 50 years[23].

1.2.6 Increasing intrinsic viscosity

1.2.6.1 Solid state polymerisation

It is not easy to do bottle-to-bottle recycling with all the possible degradations. Indeed, as seen previously, PET is put in contact with many agents that can cause its degradation, such as water, high temperature or UV. Many studies have tried to make this possible and overcome the molar mass decrease. Solid state polymerisation (SSP) is a well known technique to increase the molar mass of virgin PET. This technique is also applicable to recycled PET.

The increase in molar mass is achieved via esterification and transesterification reactions by post condensation in the solid state.[24] Figure 1.20 shows the reactions. To do this, the polymer is heated below its melting temperature but beyond the glass transition temperature. It is at this stage that the condensation phenomenon appears and the molar mass increases while co-products are removed by the inert gas flow or by the applied vacuum. Agarwal et al. [35] studied the SSP conditions in their work and reported that under vacuum the chain extension was faster than under inert gas flow of nitrogen.

Esterification



Transesterification

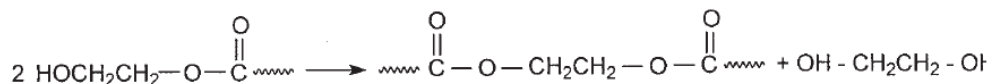


Figure 1.20 Esterification and transesterification reactions occurring during SSP [24]

1.2.6.2 Chain extension

PET chain extension is the reaction between a chain extender and the PET hydroxyl or carboxyl end-groups. A chain extender is a low mass molecule having at least two functional groups. This can link two chains together that have been split during melt processing. There are several chemical molecules that can be used for chain extension to ultimately increase the intrinsic viscosity.

Zhao et al.[36] studied the effect of chain extension of PET with a trifunctional isocyanate chain extender on the mechanical properties and viscosity. They obtained a maximum viscosity for a content of 1.4% and a clear decrease for 1.6%. An isocyanate is a molecule containing $-N=C=O$ end-groups as shown on Figure 1.21. Figure 1.21 shows the molecular structure of a tetra functional epoxy that is the TGDDM and an isocyanate trimer molecule. Raffa et al.[25] studied chain extension with different epoxy resins and isocyanate additives. The results show that for the

same content, the viscosity increases drastically when going from a bi-functional chain extender to a multi-functional chain extender and this difference is even more marked for the epoxy resin which has more functional groups per molecule. But overall, the isocyanate additives have a higher reaction rate than the epoxy thus have a more pronounced effect on molar mass increase. The reaction of PET with epoxides function is shown in Figure 1.22.

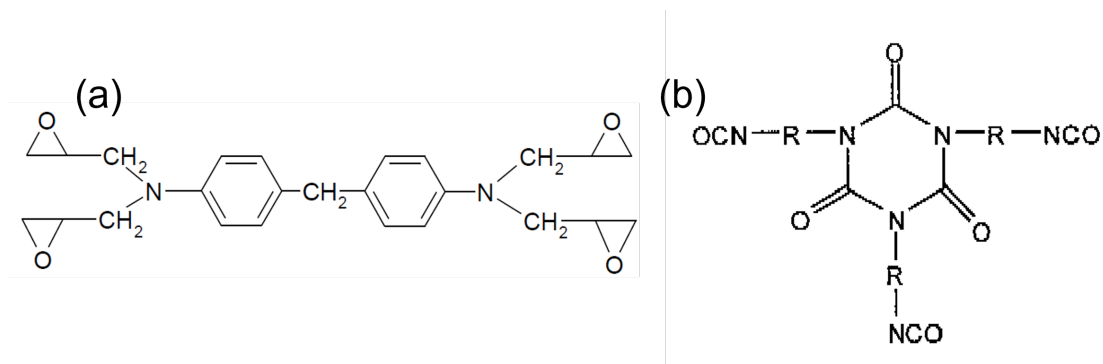


Figure 1.21 TGDDM (a) and Isocyanate trimer (b).

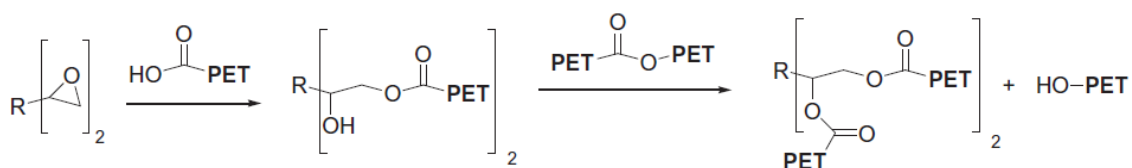


Figure 1.22 Chain extension and secondary branching reactions of PET with di-epoxides [25].

It can be seen on the Figure 1.23 that epoxy functions of TGDDM react between 177°C and 250°C. MY720 is the resinous form of TGDDM and boron trifluoride-ethylamine ($\text{BF}_3 \cdot \text{NH}_2\text{Et}$) is a catalytic curing agent. In the study of K. Hodd [37], they analysed the GPC of a 25% TGDDM/DDS mixture at 177° (Figure 1.24) where it could be observed the evolution of the reaction between TGDDM and DDS for different reaction times.

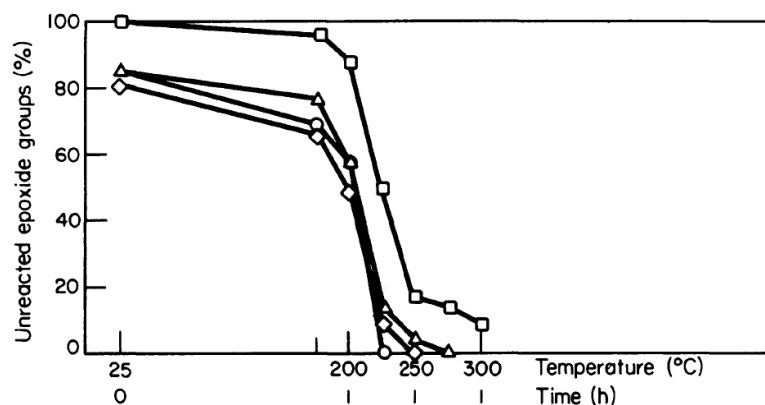


Figure 1.23 Percent of unreacted epoxide groups vs. cure conditions for pure TGDDM (□), MY720 (△), MY720 + 0.4 wt % $\text{BF}_3 \cdot \text{NH}_2\text{Et}$ -nonacetone mixed (◇), MY720+0.4 wt% $\text{BF}_3 \cdot \text{NH}_2\text{Et}$ -acetone mixed (○) [37].

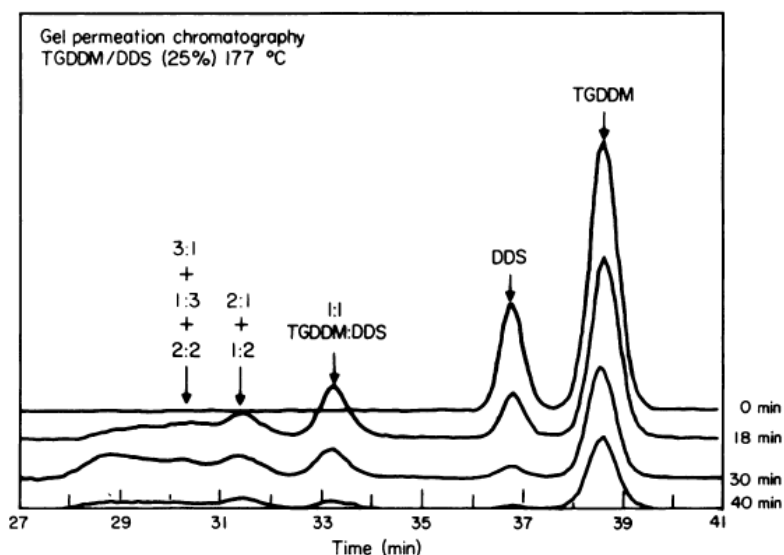


Figure 1.24 GPC analysis of the TGDDM/DDS (25%) reaction at 177° [37].

However, chain extension by branching and chemical crosslinking increases molar mass but may lead to the creation of a gel which is not desired. In addition, the decrease in crystallinity is a side effect of chain extension because of the entanglement of the chains and their difficulty to organize themselves to form crystals [3].

1.3 Banana fibers

1.3.1 Natural fibers review

The set of natural fibers is very broad. There are fibers of animal, mineral or vegetable origin [38–40]. We will focus on the fibers of plant origin. Natural fibers have different advantages such as low cost, low density, renewable resource, biodegradability, and minimum health hazards. Such fibers as banana, coir or sisal are very available but not widely used in developing countries [41].

Vegetable fibers are composed of cellulose, hemicellulose and lignin. Figure 1.25 shows a SEM image of a section of banana fiber. On this image, the multi-cellular structure is clearly distinguished. It is in fact a trunk of multiple fibers and the morphology of the individual fiber is shown in Figure 1.26. We can see the center of the fiber which is called the lumen and the different walls. The primary wall and the secondary wall in 3 layers (S1, S2 and S3). These walls are composed of fibrils. The fibrils are composed of hemicellulose and cellulose molecular chains which have crystalline parts interspersed with amorphous parts (Figure 1.27). Lignin is the main component of the amorphous part around the fibrils.

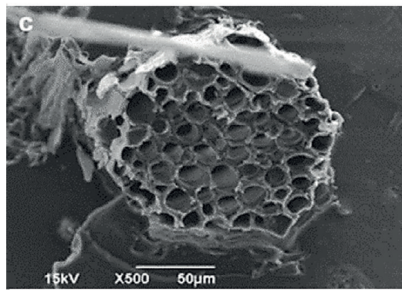


Figure 1.25 Cross-section of a pseudo-stem banana fiber [42].

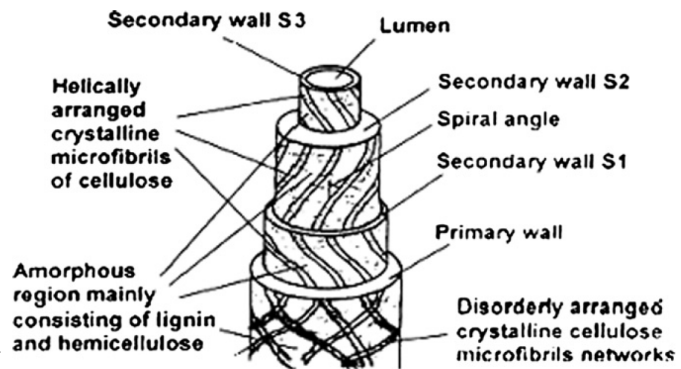


Figure 1.26 Biofiber structure [38].

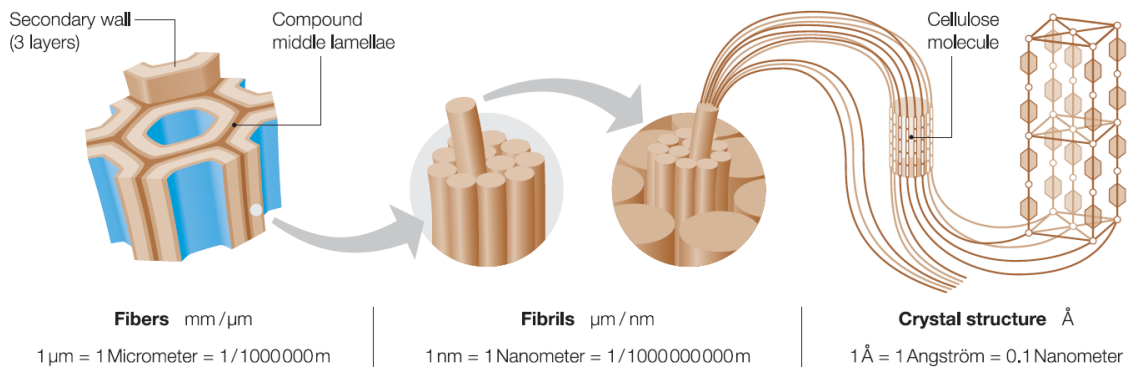


Figure 1.27 Scheme of a wood cell wall showing the compound middle lamella (middle lamella and primary wall), and three layers of the secondary wall. Cellulose, the principal component of the cell wall, exists as a system of fibrils. Parts of the fibrils are arranged in an orderly fashion and provide crystalline properties to the wall [43].

1.3.1.1 Cellulose

Cellulose is the material at the base of the composition of plant fibers. It is a macromolecule of D-anhydroglucopyranose linked by β -1,4-glycosidic molecules. In the native cellulose we can have a DP up to 14000 [44]. It can be seen on Figure 1.28 that it is exclusively composed of carbon, hydrogen and oxygen atoms. The different cellulose molecules can form hydrogen bridges between them which makes appear crystalline regions as shown in Figure 1.27. In addition the hydroxyl groups give the fiber a hydrophilic nature [45].

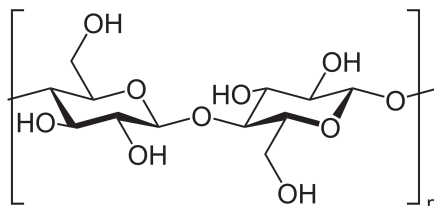


Figure 1.28 The chemical structure of cellulose [46]

1.3.1.2 Hemicellulose

Please note that hemicellulose is not a form of cellulose. Hemicellulose is the constituent of the walls of natural fibers that has a bridging role between the cellulose fibers. Unlike cellulose, the composition of hemicellulose differs from plant to plant. In addition, hemicellulose has a DP ten to one hundred times lower and it has a high rate of branching where cellulose is a linear chain.[44]

1.3.1.3 Lignin

As can be seen in Figure 1.29, lignin is a very complex molecule that is in fact a combination of aromatic and aliphatic functions linked together. It is a totally amorphous thermoplastic that has an approximate T_g of 90°C and a T_m of 170°C. Lignin has a hydrophobic nature.[44]

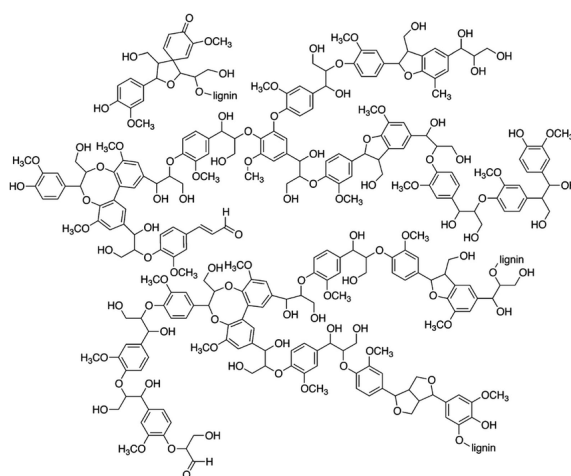


Figure 1.29 A possible chemical structure of lignin [47]

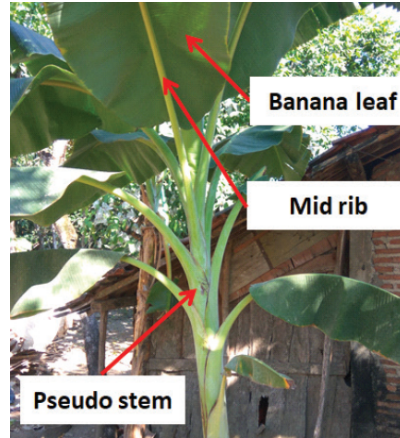


Figure 1.30 The different parts of a banana tree [42].

1.3.2 Banana fibers properties

Banana fibers (BF) are fibers that come from the trunk of the banana plant (*Musa sapientum*) as shown in Figure 1.30. The pseudo stem of the banana tree is very little exploited, for the moment, it is a waste product of the banana production. Banana fiber is a natural fiber and is composed mainly of lignin, cellulose and hemicellulose. The composition of natural fibers varies from one to another. Table 1.5 shows the composition of banana fiber.[40, 48]

Mechanical properties and density are presented in Table 1.6 for some natural fibers compared to glass, carbon and aramid fibers. We can easily see that the ultimate tensile strength of the natural fibers cannot compete with the other fibers in the table which are widely used for performance objects.

Table 1.5 Components composition of banana pseudo-stem [42].

Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractives (%)	Ash content (%)	Moisture content (%)
49	12	14	5	5	12.5

Table 1.6 Properties of natural fibers, glass, carbon and aramid fibers[49] + ajouter des détails de [50]
+ regarder sur edupack

Fibers	Width or diameter (μm)	Density (kg/m^3)	Cell l/d ratio	Initial modulus (GPa)	Ultimate tensile strength (MPa)	Elongation (%)
Banana	80-250	1350	150	7.7-20	54-754	10.35
Coir	100-450	1150	35	4-6	106-175	17-47
Pineapple leaf	20-80	1440	450	34.5-82.5	413-1627	0.8-1
Palmyra	70-1300	1090	43	4.4-6.1	180-215	7-15
Sisal	50-200	1450	100	9.4-15.8	568-640	3-7
E-glass	-	2540	-	70-73	2000-3450	-
Carbon	-	1800	-	230-400	2500-6350	-
Aramid	-	1440	-	63-131	3000-4100	-

1.4 Banana fiber reinforced composite

1.4.1 Composite materials

A composite is a material that has at least two phases. One phase is continuous and is called the matrix, and the other phase is discontinuous and is called the inclusion or the reinforcement. The matrix is generally more ductile and less hard than the inclusion. It can be polymer, metal and ceramic matrices. The inclusions are generally harder and stronger than the matrix. The goal of creating a composite from several materials is to obtain a material with better properties than the components separately. The reasoning to decide the design of a hybrid material is represented on the diagram (Figure 1.31).

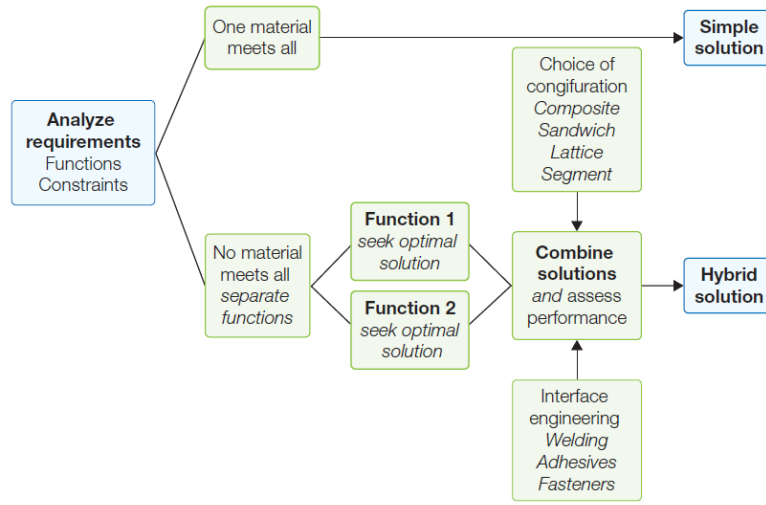


Figure 1.31 The steps in designing a hybrid to meet given design requirements [51].

We can find the density and the modulus of the composite knowing some properties of the two phases separately [51]. The density of the composite ρ is given by :

$$\rho = f\rho_r + (1 - f)\rho_m \quad (1.7)$$

Where f is the reinforcement volume fraction and ρ_r and ρ_m are the densities of the reinforcement and the matrix respectively.

For the estimation of the modulus (E), we calculate an upper bound E_u and a lower bound E_L :

$$E_u = fE_r + (1 - f)E_m \quad E_L = \frac{E_r E_m}{fE_m + (1 - f)E_r} \quad (1.8)$$

Where E_r and E_m are the modulus of the reinforcement and the matrix respectively.

We can also estimate the bounds for the strength but it is less satisfactory because of the multitude of failure mechanisms and the sensitivity of the toughness and strength against impurities and processing defects.

As seen above, the volume fraction of the fibers is one of the factors influencing the properties of the composite other than the nature of the material. The volume fraction is not the only parameter, but it is a parameter that can easily be modified by producers to alter the properties of the material. Orientation and geometry (size, aspect ratio, etc.) also affect properties [40]. Figure 1.32 shows different types of fibers geometries and orientation in the composite.

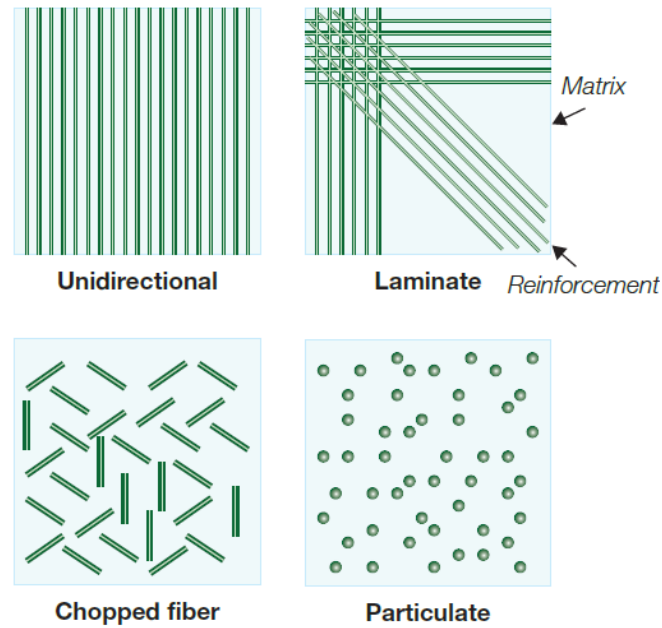


Figure 1.32 Schematic of hybrids of the composite type: unidirectional fibrous, laminated fiber, chopped fiber, and particulate composites [51].

There are different cracking modes for composite materials. Under tension, the load is redistributed between the components until one yield or crack. As it can be seen on Figure 1.33, either the matrix cracks first or the fibers fractures before the matrix. The strongest composite has the two components that reach failure simultaneously.

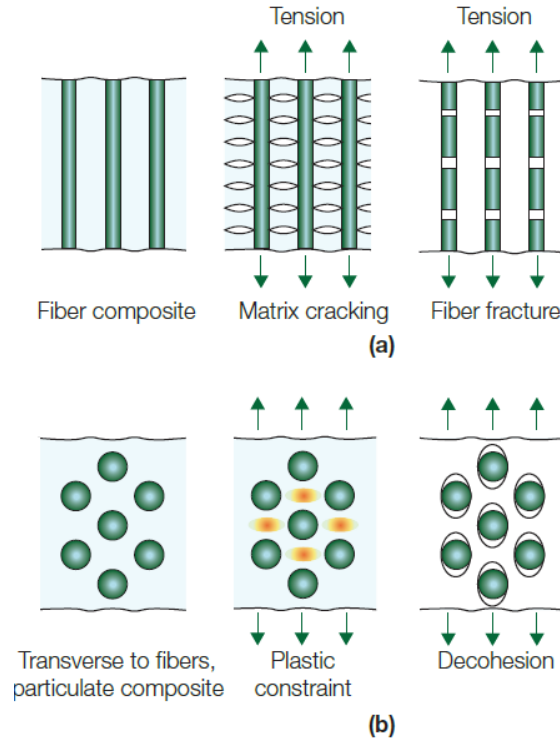


Figure 1.33 Failure modes in composites [51].

1.4.2 Fiber compatibility with the polymer matrix

The presence of hydroxyl groups and other polar groups, dead cells, waxes and oils, and low fire resistance make the virgin natural fibers incompatible with the polymer and lead to the formation of aggregates. In addition, the high water absorption of natural fibers results in lower interfacial strengths than glass or carbon fiber composites. Developing environmentally friendly composite applications requires a proper understanding of the fundamental properties and composition of natural fibers to make the appropriate treatments. Some disadvantages of natural fibers, such as biocompatibility and hydrophilicity, can be overcome by various surface modification and chemical treatment methods for sufficient applications [52].

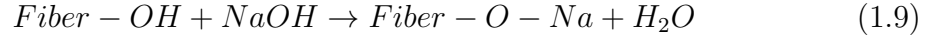
1.4.3 Fiber treatments and their effect

Banana fibers have good mechanical properties such as high modulus, high tensile strength and low elongation at break compared to other natural fibers. Unfortunately, banana fibers also have some disadvantages, such as low thermal stability and poor compatibility with hydrophobic polymers. These disadvantages can be improved by a chemical treatment on the surface of the fiber and thus improve the cohesion between the fibers and the matrix [53]. Treatments for natural fibers, such as alkaline treatment or acid treatment, are common. These two treatments are further described hereunder.

1.4.3.1 Alkaline (NaOH) treatment

Sodium hydroxide is an alkaline solution that can be used for the treatment of BFs. Komal et al. studied the effect of this treatment which consists of soaking the BFs in the solution for some time before rinsing to remove the collected impurities and recover a neutral pH. Drying is then important to avoid a high level of moisture in our material [53].

The reaction that takes place between the fiber and the sodium hydroxide is as follows:



A NaOH treatment removes everything that is not cellulosic from the surface of the fiber, including lignin, hemicellulose, waxes, and oils. This allows a better compatibility with the matrix thanks to the availability of hydroxyl groups. It also increases the roughness and therefore the grip of the fiber in the matrix.

Thermal analysis of the treated and untreated fibers (Figure 1.34) shows different stages of fiber degradation at the indicated temperatures. Up to 150°C, we have a degradation due to the evaporation of moisture. Then up to 300°C with a peak at 245°C, there is the degradation of hemicellulose and non-cellulosic compounds. Then the narrow peak corresponds to the degradation of cellulose at 322°C for UBF and 343°C for TBF, which proves an improvement of the mechanical properties. Finally, the degradation between 400 and 500°C is due to lignin undergoing pyrolysis. The peaks appear at the temperatures where the degradation has the highest rate.

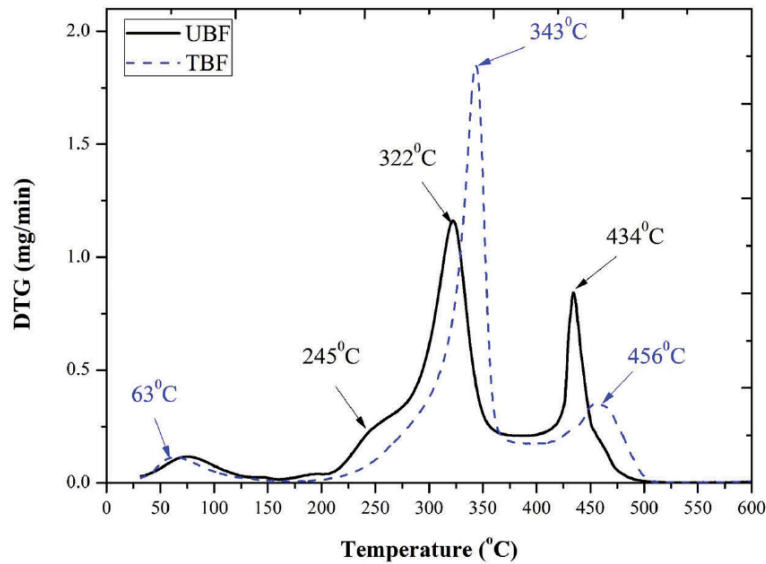


Figure 1.34 DTG thermograph of UBF and TBF [53].

1.4.3.2 Acid treatment

Acid is used to make bonds between the fiber and the matrix that contains hydroxyl end chains [54]. The influence of citric acid treatment on natural fibers for rein-

forcement of composite has been studied by Sujito et al. [55]. For different acid concentrations ranging from 3 to 7%, the 4% treatment gives the highest mechanical tensile properties to the ramie fiber/polylactic acid (PLA) composite [55]. This is due to the interfacial attraction between the fiber and PLA. The addition of acid groups on the fiber creates chemical bonds between the fiber and the matrix. This results in a better tensile strength.

Chapter 2

Experimental part

This chapter describes all the experimental part of this study starting with the materials used, the fiber treatments, the chemical modification of PET, the injection molding process, and finally the techniques of characterisation. As a reminder, the study is about the incorporation of banana fibers in a PET thermoplastic matrix. The main problem is that the degradation temperature of the banana fibers occurs at lower temperature than the melting temperature of PET. This is why PET has to be chemically modified to obtain a lower melting temperature. This modification includes a series of steps which are described below.

2.1 Materials

2.1.1 PET thermoplastic matrix

The initial idea was obviously to recycle plastic bottles as a source of PET. But to avoid additional washing and crushing steps, the PET used is an industrial PET provided by *Dow Chemical* in the form of pellets *LIGHTERTM C88* as trade name [56]. This polymer is typically used for bottles conception. The main physical properties of this PET is resumed in the Table 2.1.

Table 2.1 *Dow LIGHTERTM C88 PET* [56].

Density [g/cc]	0.88
Glass transition [°C]	78
Melting temperature [°C]	247
Clarity of the pellets	Opaque
Moisture content	<=0.40%
Crystallinity	>= 50%

2.1.2 Reagents for PET chemical modification

This PET was modified before processing. Chemicals were used for the different reactions. These reagents are 1,3 propandiol, succinic anhydride, zinc acetate, antimony trioxyde and dichloromethane.

2.1.3 Banana fiber reinforcement

The fiber reinforcement used for the composite are banana fibers from Cameroon. Figure 2.1 shows the raw banana fibers. These come from the *Plantations du Haut Penja* (P.H.P.) which is the first producer in the world of fairtrade certified bananas [57]. Chemicals used for the surface treatment were caustic soda (NaOH) and succinic anhydride (SA).

2.2 Fibers treatment

The banana fibers used in this study were those on Figure 2.1. It was therefore necessary to prepare them for incorporation into the PET matrix.

First, fibers are cut and ground to a suitable size. Then, they are sieved and only the fibers with a diameter between 300 and 500 microns are kept.

2.2.1 Alkaline (NaOH) treatment

Fibers were immersed in a caustic soda (0.25N) solution of 5wt.% concentration. Sodium hydroxide (0.25N) is a standard volumetric solution of 0.25mol/L. And then washed with distilled water until it reaches a neutral acidity or a pH equal to 7.

2.2.2 Acidification treatment

The purpose of the acidification treatment is to add acid functional groups to the fiber surface to react with the alcohol end-groups of the polymer matrix. These chemical bonds could highly increase the mechanical properties. The acid solution for the treatment is a mixture of water and succinic anhydride (SA) with different contents corresponding to 2, 4 and 6wt.% SA. After this treatment, the fibers were not washed afraid that the cleaning removes the acid molecules from the fiber surface.

2.3 Chemical modification of PET

The sample preparation includes several steps of depolymerisation by glycolysis followed by a chain extension incorporating some defaults that reduces the melting temperature but gives good mechanical properties. Several pictures were taken during experiments and are shown in the appendix. The chemically modified PET obtained is a co-polyester saturated (CoPS).



Figure 2.1 Raw banana fibers.

2.3.1 PET depolymerisation

PET is depolymerized by glycolysis in order to incorporate the polyester chain extender from 1,3-PD and SA, and lower its melting temperature. PET has to be prepared to the chemical reaction first. Thus there are several steps including extrusion and grinding before the chemical reaction of glycolysis.

2.3.1.1 Extrusion of industrial PET

The initial PET used in this experiment come from Dow chemical industry : *LIGHTER C88* . At this state, the polymer is too crystalline so it has been extruded and directly quenched in cold water to get it more amorphous. The polymer in amorphous state will be more capable to undergo the chemical reactions because the crystalline phases fix the chains and prevent their mobility and thus prevent them from reacting. The extrusion simulate the starting point with recycled PET as we obtain PET in amorphous state as for PET bottles.

Figure 2.2 shows the inside of an extruder. We can see 3 zones indicated by red numbers. First the solid PET is fed by the hopper and is in the solids conveying area. Then the polymer melts and its volume decreases and finally the molten polymer is pushed to the die. The main objective of the extruder is to produce a well mixed and homogeneous polymer. Plunging the polymer at the die exit directly into a cold water basin solidifies the polymer while keeping it amorphous.

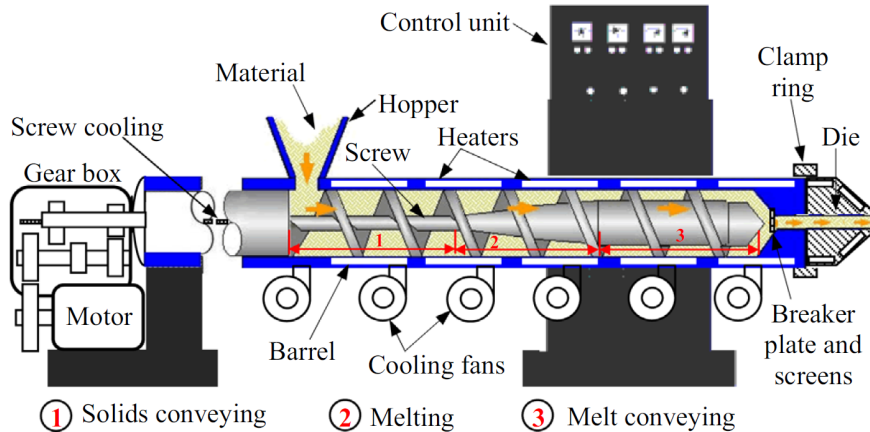


Figure 2.2 Basic components of a single screw extruder [58]

The extruder used is a *thermo scientific process 11 twin screw extruder*. This one is on the right on Figure 2.3, in the center, the elongated tank is the water basin to quench the polymer at the die exit. And on the left is the *VariCut Pelletizer* to cut the PET filament into pellets with a collecting bag just in front. The parameters controlling the extruder are the different temperatures but also the speed of rotation of the screws and the torque which can be found in the Table 2.2.

Table 2.2 Extrusion temperature profile, rotation speed and torque.

T_2 [°C]	T_3 [°C]	T_4 [°C]	T_5 [°C]	T_6 [°C]	T_7 [°C]	T_8 [°C]	T_{die} [°C]	Rotation speed [rpm]	Torque [%]
220	245	250	255	255	260	260	260	100	50-60

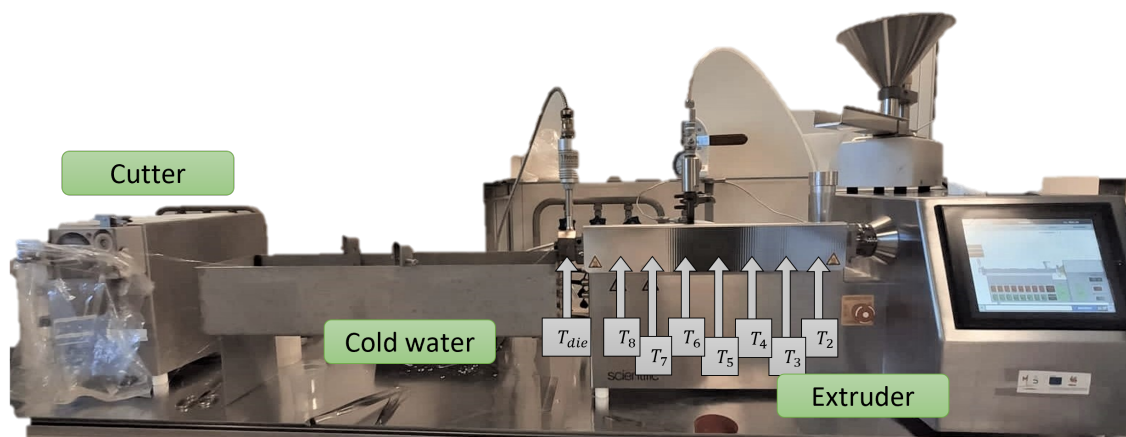


Figure 2.3 Thermo Scientific Process 11 Twin-screw Extruder and VariCut Pelletizer.

2.3.1.2 Crushing of pellets of PET

The extruded polymer is cooled down at -195°C with the help of liquid nitrogen so that it gets very brittle. We put it then directly in a rotating machine that crush it in a small powder. The powder shape is useful because for the polymerisation it has to react with liquid chemicals so this improves the reaction exchange between the different phases.

2.3.1.3 Glycolysis with 1,3-propanediol

1,3-propanediol (1,3-PD), crushed PET, Zinc acetate as catalyst and methanol (as solvent for 1,3-PD) are first mixed all together at 35° . The proportions can be found in Table 2.3. As it is shown on Figure 2.4, EG and 1,3-PD have a very similar structure and can thus act as equal for the glycolysis reaction. This step lasts until all the solvent has evaporated. The solution is agitated with a magnetic bar at 150 rpm. The quantities

of 1,3-PD and catalyst are that small compared to the amount of PET that it is important to add enough solvent so that these can be well dispersed in the solution. Methanol is used for slurring to increase dispersion of reactant. Furthermore, it has a very low boiling temperature compared to other solvents such as water for which the sample should have been heated at more than 100°C . And staying at that temperature would have modified the crystallinity of PET.

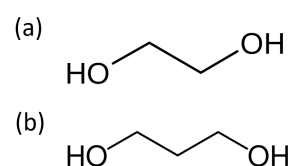


Figure 2.4 (a) Ethylene glycol (EG) and (b) 1,3-Propanediol (1,3-PD).

Next to the dispersion of the reactant comes the glycolysis depolymerisation. This reaction occurs at high temperature, the polymer is heated at 180°C for around 30 min for the well dispersion of the 1,3-PD in the solution. And finally, the sample is heated to 200°C for 2h for the reaction of glycolysis.

At the end of this part the polymer is washed in water then filtered and put under vacuum at 170°C until it is well dried. It is always important to have a well dried polymer before making the reactions. Because water molecules could promote the chain scission in the next reaction.

Table 2.3 Reactant quantities for glycolysis depolymerisation.

Material	Quantity [mg]
PET	50 000
Catalyst (Zinc acetate)	54.73
1,3-PD	8160
Methanol	enough to submerge all the sample

The glycolysis reaction is represented by the first arrow in Figure 2.7 (a summary diagram of the different steps realised for the chemical modification of PET).

2.3.2 Polymerisation of the co-polyester saturated (CoSP)

This section include three stages. First, 1,3-PD is mixed with succinic anhydride (SA) and antimony trioxide (Sb_2O_3) as catalyst that is normally already present in plastic bottles of PET. This mixing takes around 2h. And creates in fact a molecule with a carbocyclic and an alcohol end-group. This molecule is the chain extender (red bullet on Figure 2.7) to product the saturated polyester (SP). The ester chain extender has a low melting temperature [59] and it permits to lower the melting temperature of the global CoPS.

Table 2.4 Data for the chemical depolymerisation.

material	1,3-PD	succinic anhydride	antimony trioxide
quantity [mg]	1560	3161	29.5

The choice to take succinic anhydride instead of succinic acid is because during the reaction with 1,3-PD, the succinic acid would release a water molecule and moisten the solution.

Further more the proportion of reactants are not chosen without a good reason. During the depolymerisation using 1,3-PD, there was a lot of alcohol end-groups incorporated to the polymer. Thus the reaction with succinic anhydride and 1,3-PD for making a chain extendere has to contain twice more acid end-groups. That is why more succinic anhydride is put in the reaction.

Secondly, we can add to it the PET oligomers (40 mg) and agitate during approximately 20 hours in an inert environment (under a flux of nitrogen gas) at 200°C. This gives saturated chains of modified PET (Figure 2.5). This reaction is represented by the second arrow of Figure 2.7, where the chain extender is represented by the red bullet point.

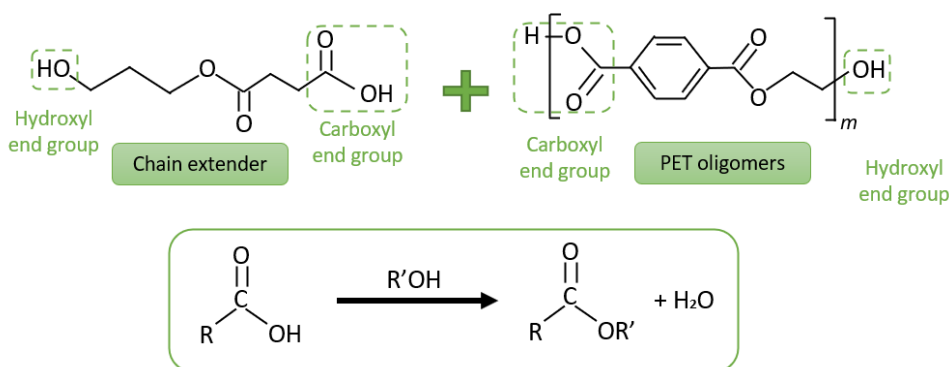


Figure 2.5 Esterification of carbonyl with hydroxyl end-groups to form a saturated polyester with water as by-product.

Finally, the polymer is dissolved in dichloromethane to extract it from the beaker. The liquid solution is poured drop by drop into methanol in order to precipitate the polymer. Indeed, the polymer is non soluble in methanol but methanol and dichloromethane are two miscible liquids. Thus it gives the polymer as precipitate that can be collected by filtering the solution. The filter also allows to keep the heaviest molecules because a fraction of the small molecules with small molecular weight pass through the filter.

2.3.3 Solid state polymerisation (SSP)

As we have seen in the previous section, solid state polymerisation (SSP) is a way to extend the chain just by letting the polymer at high temperature for a certain amount of time. The energy given by the heat allows the carboxylic end-groups of the chains to react with the alcohol end-groups of other chains giving a combination of chains.

In the present work, the saturated polyester (SP) has been dried at 70°C to avoid hydrolysis and then heated at 170°C under vacuum for 15h. The goal is that a very little fraction of the material composed of the low molar mass particles melts first and react with other chains by condensation. The by-products (water, EG) are released and evacuated by the vacuum pump of the oven due to their higher volatility. And the condensed SP has a higher new molecular weight. Finally, the temperature is increased to melt another fraction of SP.

At the previous stage, the molar mass could have reached almost 10 000 g/mol. But this molar mass is still very low to reach good mechanical properties. Thus with SSP we could reach a mass higher than 20 000 g/mol.

2.3.4 Addition of the tetrafunctional epoxy chain extender

Tetraglycidyl 4,4 diaminodiphenyl methane epoxy (TGDDM) is a well known molecule used for chain extension in PET. The epoxy groups react with the end of the chains of the polymer and this create a big network of chain. In order to have a thermoplastic polymer and not a thermoset, the amount of TGDDM was very small. The amounts used in the experiment were 0,5%, 1% and 2% of TGDDM in the polymer.

The reaction between the SP and TGDDM was performed in a discontinuous extruder (*DSM - Xplore conical twin-screw extruder*) shown in Figure 2.6. The other paramater studied was the time of reaction between TGDDM and the SP in the extruder that varied between 10, 15 and 20 min. The general sheme of the chemical modification of PET is shown in Figure 2.7.

For the conception of the composite PET/banana fibers, the fibers were injected with the PET in the DSM to have a homogeneous dispersion of the fibers in the material.



Figure 2.6 DSM - Xplore conical twin-screw extruder. Equiped of a recirculating valve which allows to vary the residence time in the DSM [60].

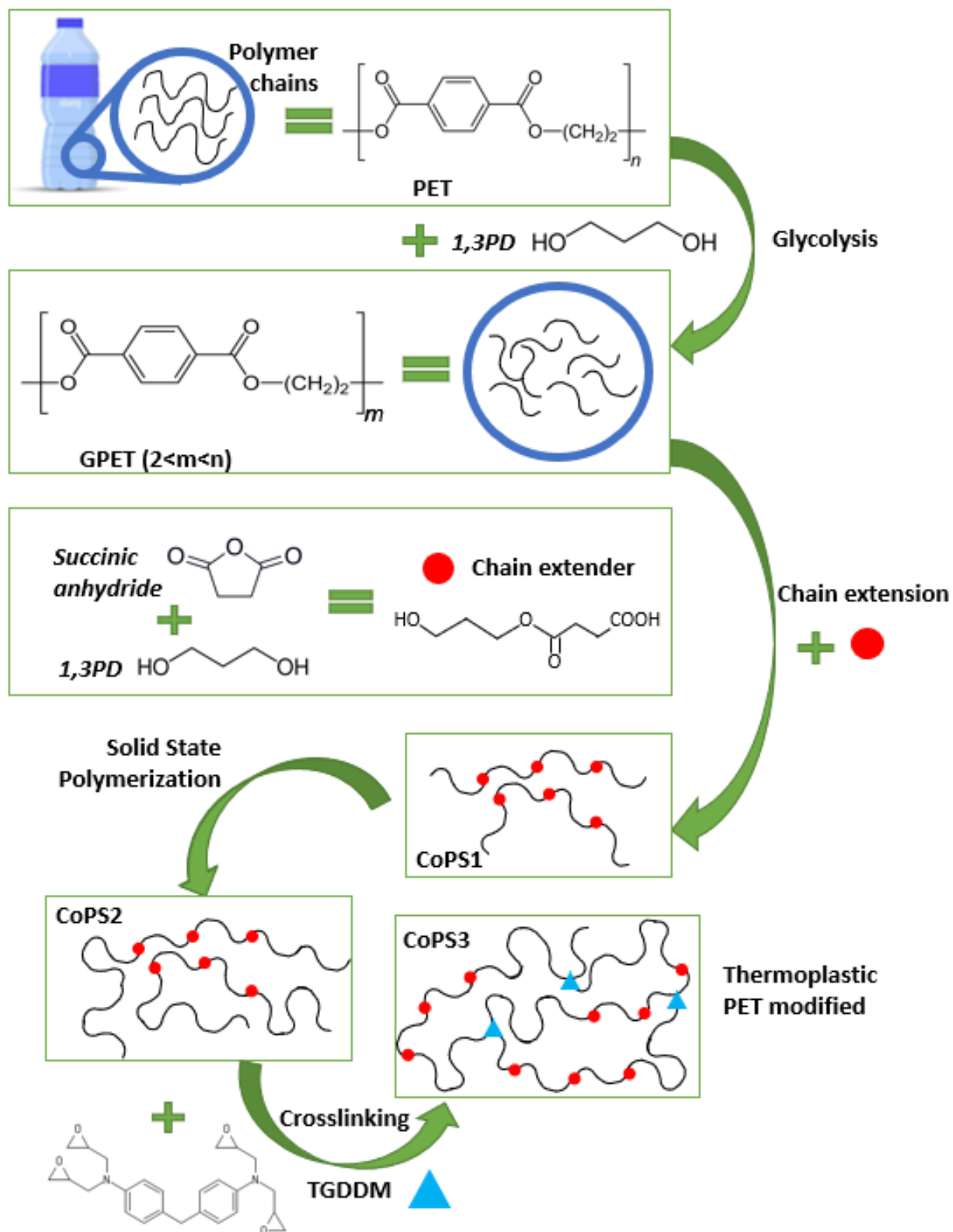


Figure 2.7 Summeryed diagramme illustrating the different steps followed for the obtention of the modified thermoplastic.

2.4 Injection molding

The material composite extracted from de DSM is molded by injection using the *Thermo ScientificTM HAAKE MiniJet Pro*. The mold has a standard dog-bone shape (Figure 2.8). The dimensions are given in Table 2.5. Once more, before injection, the sample is dried at 90°C under vacuum for 2h.

The injection pressure is 600 bar, the injection temperature is 180°C and the mould temperature is set at 47°C.

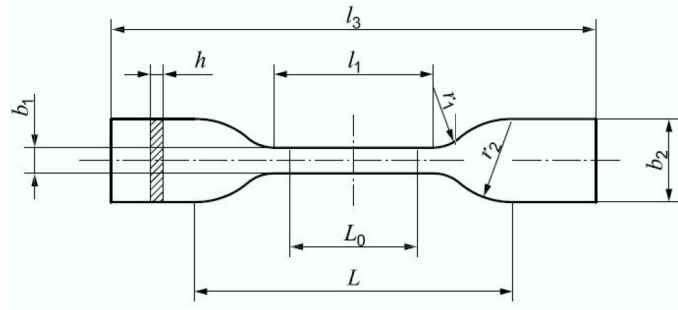


Figure 2.8 ISO 527-2 type 5A test specimen [61].



Figure 2.9 Injection molding machine of the lab : *Thermo ScientificTM HAAKE MiniJet Pro*.

Table 2.5 Test specimen dimensions according to ISO 527-2 type 5A [61].

Variable	Description	Dimension (mm)
l_3	Total length	75
b_2	Width at ends	12.5
l_1	Length of narrow parallel-sided portion	25
b_1	Width of narrow parallel-sided portion	4
r_1	Small radius	8
r_2	Large radius	12.5
h	Thickness	5
L_0	Length of narrow portion, spacing of the extensometer used as reference for the tensile test	20

2.5 Characterisation techniques

To characterize the experiments results, several analysis techniques are used. These techniques are described below.

2.5.1 Determination of intrinsic viscosity and molar weight

«The viscosity of a fluid is a measure of its resistance to deformation at a given rate. For liquids, it corresponds to the informal concept of "thickness": for example, syrup has a higher viscosity than water.» [63]

To measure the intrinsic viscosity, a small amount of sample was dissolved in a solution of hexafluoroisopropanol (HFIP) and chloroform. These are strong solvents that are hydrogen-bonds acceptor, and dissolves substances such as amides and ethers. The mixture of chloroform/HFIP was 98:2 vol %. The concentration of the polymer was 25%. The viscosity test was performed using the Ubbelohde viscometer (Figure 2.10) at 30°C. The solution of dissolved PET must be added to the viscometer and sucked into the capillary tube. The time it takes for the liquid to flow from bar *A* to bar *B* must be measured and this time is used to find the viscosities using the following equations [36] :

$$\mu_r = \frac{t}{t_0} \quad (2.1)$$

$$\mu_{sp} = \mu_r - 1 \quad (2.2)$$

$$[\mu] = \frac{1}{c} \sqrt{2(\mu_{sp} - \ln \mu_r)} \quad (2.3)$$

Where μ_r , μ_s and $[\mu]$ are the relative, specific and intrinsic viscosities respectively.

The molecular mass can be obtained from the intrinsic viscosity using the Mark-Houwink equation [36] :

$$[\mu] = K \bar{M}^\alpha \quad (2.4)$$

Where K and α are the Mark-Houwink constants and depend on the solvent and the polymer. For the system chloroform/HFIP, constants K and α are $1.91 \cdot 10^{-4}$ dL/g and 0.734 respectively [64, 65].

2.5.2 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is the most widely used thermal analysis technique [66, 67]. It measures the enthalpy differences in samples as a result of the evolution of chemical and physical properties as a function of temperature and time.

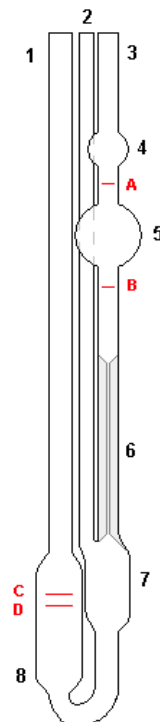


Figure 2.10 Ubbelohde viscometer. 1)Filling tube 3)Capillary Tube 5)Measuring Bulb 6)Capillary 8)Reservoir A-B)Timing Marks [62].

The DSC1 of brand *Mettler Toledo* was used for the experiment (Figure 2.12) and the inner parts are represented on Figure 2.11.

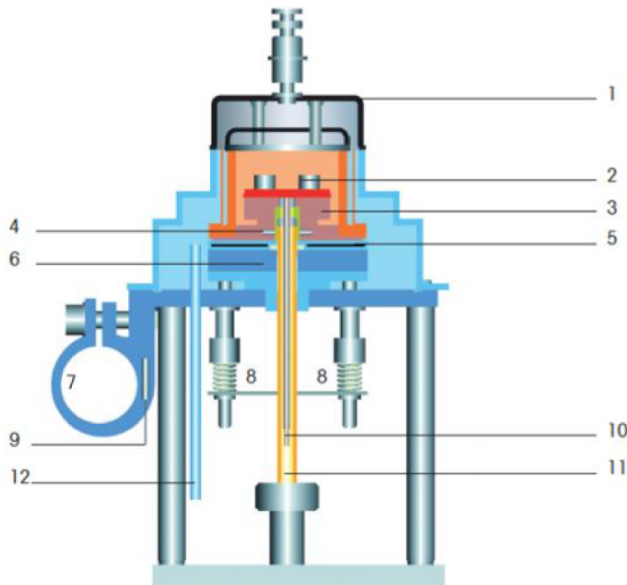


Figure 2.11 Schematic principle of a Differential Scanning Calorimetry (DSC). Furnace lid (1); Crucible on the DSC Sensor (2); Silver furnace (3); Pt100 temperature sensor of furnace (4); Flat heater between two insulating disks (5); Thermal resistance for cooler (6); Cooling flange (7); Compression spring construction (8); Cooling flange Pt100 (9); DSC raw signal for amplifier (10); Purge gas inlet (11); Dry gas inlet (12). [68]



Figure 2.12 DSC1 from *Mettler Toledo*.

Differences in heat flux occur when a sample absorbs or releases heat due to thermal effects including melting, crystallization, chemical reactions, polymorphic transitions, vaporization and many other processes. Specific heat capacities and heat capacity changes, for example during a glass transition, can also be determined from the heat flux difference.

A typical DSC curve is shown on Figure 1.12. We can see on this curve a first decrease which represents the passage of the temperature of the glass transition. At this temperature the polymer chains tend to relax, which is why there is an exothermic heat exchange. We then observe an endothermic peak which means a reorganization of the chains, corresponding to a cold crystallization. Finally, the melting temperature is visible by a second exothermic peak. At this temperature the chains relax completely. It happens to see more or less concentrated peaks, these changes are due to the polydispersity of the polymer where some chains relax before others and this flattens the extremes.

Thermal properties of thermoplastics are of primary importance in this study since the objective is to decrease the melting temperature. Therefore, thermal analyses allows to follow the evolution of chemical modification on T_m , T_g and also on the degree of crystallinity. For the measurements, the samples are placed in a nitrogen flow and the heating rate is set at 10°C/min. After the addition of the chain extender,

the PET is less able to relax, so the heating rate is decreased to 5°C/min to observe the characteristic peaks on the graphs.

Using DSC, it is possible to find the degree of crystallinity of the PET semi crystalline material. During the first heating, we can thus potentially see that the material will further crystallize with a endothermic peak. The enthalpy exchange is given by the surface integral of the peaks. Knowing that the endothermic melting enthalpy for a 100% crystalline PET (ΔH_m^0) is 140 [J/g] [69], the following equation gives the degree crystallinity χ_c :

$$\chi_c = \frac{\Delta H_m + \Delta H_c}{\Delta H_m^0} \quad (2.5)$$

Where ΔH_m and ΔH_c are respectively the endothermic melting enthalpy and the exothermic enthalpy of crystallization.

Furthermore, annealing of the composite were simulated using DSC. At a temperature above T_g , polymer chains can move and organize themselves slowly. The method consists to heat the material until the annealing temperature where it stays for 20 minutes. We can then observe if some crystallization occurs during this isothermal stage. The different annealing temperatures studied were 60, 70, 80, 90, 100, and 110°C.

2.5.3 Dynamic mechanical analysis (DMA)

DMA is an analysis technique where a mechanical vibration is applied during a temperature change. The machine measures the force, strain and phase difference between these two as a function of temperature.

The DMA machine used is a *DMA/SDTA861* from *mettler toledo*. The complex modulus E^* can be calculated from the geometries of the sample and thanks to the phase shift δ between force and deformation, it can be directly separated into a storage modulus E' and a loss modulus E'' [70]:

$$E^* = \frac{l^3}{16bh^3} \frac{F^*}{A^*} \quad (2.6)$$

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos \delta \quad (2.7)$$

$$E'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta \quad (2.8)$$

Where F^* and A^* are the complex force and deflection, and σ_0 and ε_0 are the stress and the strain amplitude respectively. l , b and h are the geometry parameters. $\tan \delta = \frac{E''}{E'}$ is called the damping factor.

We can have a better view of the glass transition so this technique is complementary to DSC analysis. In addition, it is possible to observe mechanical behaviour under thermal changes and viscoelastic properties of the material. The parameters of the DMA are listed in Table 2.6.

Table 2.6 Parameters for DMA.

Temperature range	10-160°C
Applied strength	0.5 N
Maximum displacement	10 μm
Frequency	1 Hz
Pre-stress	3N



Figure 2.13 DMA/SDTA861 from mettler toledo

2.5.4 Tensile test

Traction machines measure the displacement and the applied force. This has to be converted into strain and stress. There is a true stress and an engineering stress. The difference and the link between these two are explained in the equations [71]:

- $\sigma_n = \frac{F}{A_0}$ [MPa] engineering stress
- $\varepsilon_n = \frac{L-L_0}{L_0}$ [-] engineering strain
- $\sigma = \frac{F}{A} = \frac{F}{A_0} \frac{L}{L_0} = \sigma_n \cdot (1 + \varepsilon_n)$ [MPa] true stress
- $\varepsilon_{true} = \ln\left(\frac{L}{L_0}\right) = \ln(1 + \varepsilon_n)$ [-] true-logarithmic strain
- Relation between true stress and strain: $\sigma = K\varepsilon^n$ with K the strength coefficient and n the strain hardening coefficient.

Where $l - l_0$ is the displacement and F is the force measured. Figures 2.14 and 2.15 represent typical tensile curves for a ductile and brittle polymer respectively. σ_0 is called the yield strength and represents the maximum stress that can be applied without deforming the material plastically (or irreversibly). It is considered that beyond a deformation of 2%, the deformation is irreversible. We can therefore say that the yield strength corresponds to the stress applied for a deformation of 0.2%.

σ_f represents the stress at failure. For a ductile material such as PET, the strain at break is greater than 100%. For small deformation, the curve is almost linear. The slope of the curve at this point corresponds to Young's modulus $E = \frac{\sigma}{\epsilon}$. The Young's modulus measures the stiffness of the material. So a very stiff material, such as diamond will have a Young's modulus of 1000GPa while industrial PET has a modulus less than 3GPa.

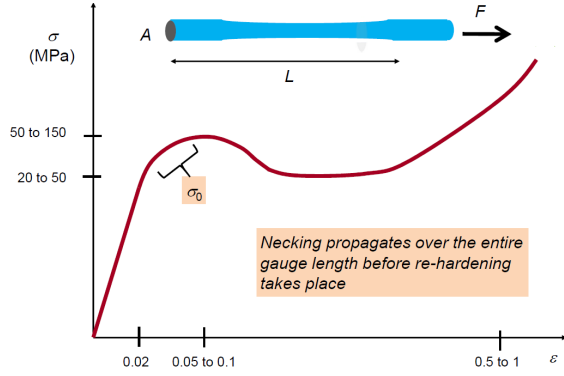


Figure 2.14 Mechanical response under uniaxial tension of a typical (sufficiently ductile) polymer material [71].

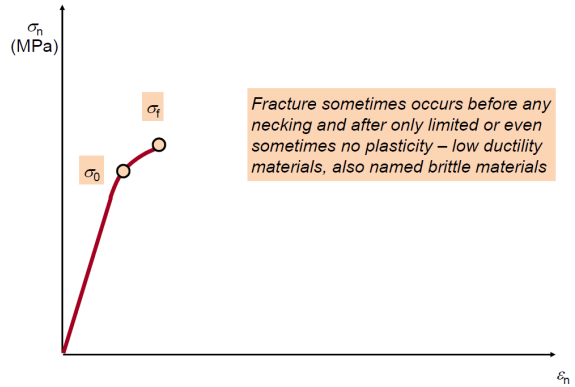


Figure 2.15 Mechanical response under uniaxial tension of some not ductile polymer material [71].

In plastic deformation, a phenomenon called necking takes place, which corresponds to the thinning of the sample during its elongation (Figure 4.5 in appendix). This explains the large deformation without real increase in stress.

Under traction, what gives its strength to the material is first the inter-molecular bonds such as Van Der Waals and hydrogen-bonds. Then with further deformation, the chains entanglements of the network contribution is added and also plays a role to counteract deformation (Figure 2.16).

The tensile test took place at room temperature and the deformation rate was 1mm/min. Tensile tests were performed on samples to characterize their mechanical properties.

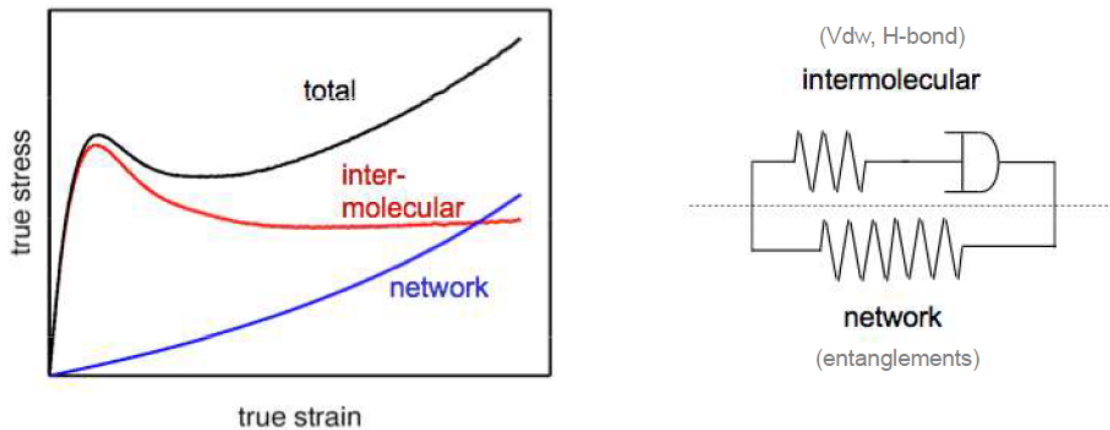


Figure 2.16 Stress decomposition proposed by Haward and Thackray [71].

2.5.5 Scanning electron microscopy (SEM)

SEM reveals details with a magnification that cannot be reached with an optical microscope. The analysis is done by sending an electron beam with an energy between 100 and 30,000 electron volts on a sample. As the beam generated by the electron gun is too wide to have precise images directly, lenses allow to refocus the electrons and have a target of less than 10 nm diameters [72]. The electrons contact the specimen to a depth of 1 micron and the beam is then scanned to form a point-by-point image (Figure 2.17).

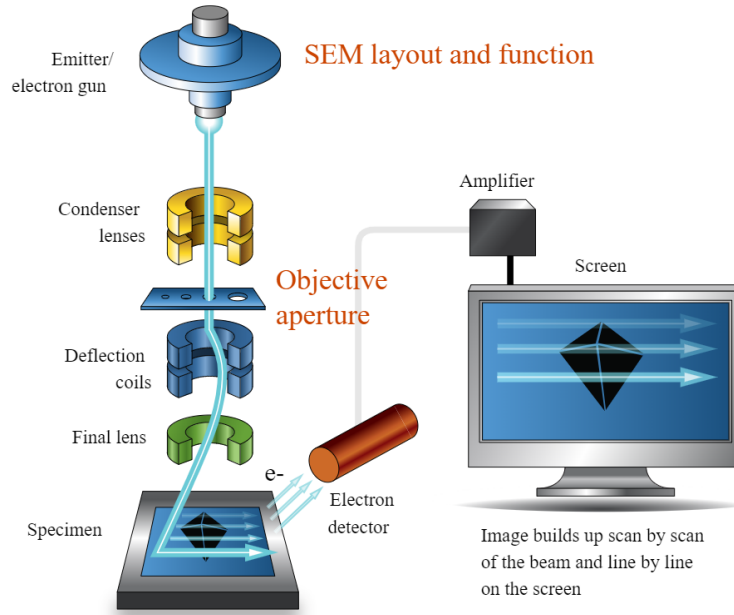


Figure 2.17 SEM structure [73].

Electrons are emitted from the specimen under analysis and a detector will pick up these signals and emit the image through a computer. For the production of the image, secondary and backscattered electrons are used. Figure 2.18 shows the different layers of penetration of the beam in the specimen and the signals emitted. This technique allows to observe the fracture crack opening of the composite material or fibers external surface, for instance.

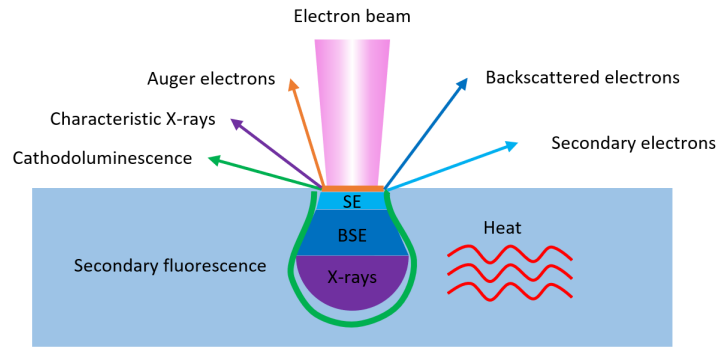


Figure 2.18 Electron beam hits a sample; it interacts with the atoms in that sample. Reproduced from [73].

2.5.6 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is a technique that measures the weight of a sample as a function of time and temperature. The machine is composed of a very precise micro balance in an oven that undergoes a temperature program. The temperature program can vary, it can be dynamic or stay constant or it could be a combination of these with different speeds of temperature variation [74]. Figure 2.19 shows a detailed scheme of the TGA.

The TGA used is a *TGA/SDTA851* from *mettler toledo*. The sample is under an inert gas such as nitrogen to avoid oxidation reactions that lead to the combustion of organic materials. This allows not to alter the mass of the sample and to have a good measure of the thermal stability. The laboratory machine operates under a nitrogen flow of 50ml/min.

An analysis of the thermal stability of the fibers was done with a constant temperature at 180°C for 1h. In addition, the thermal properties of the fibers and the composite were studied under heating from 30 to 600°C at 10°C/min while measuring the weight loss.

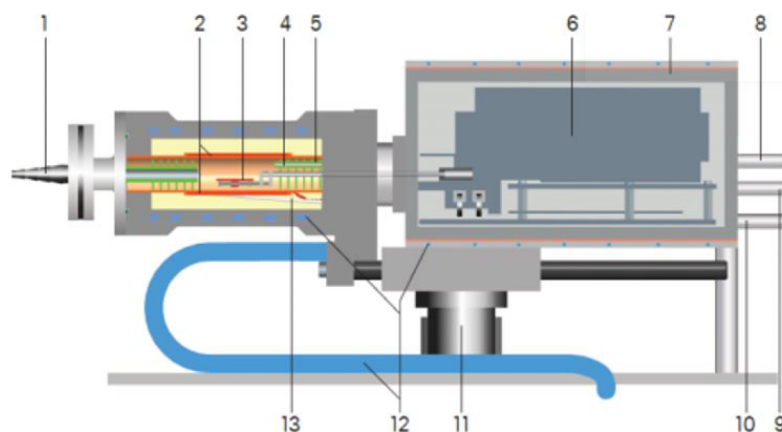


Figure 2.19 Schematic principle of a TGA. Gas outlet (1); Furnace heater (2); Sample support (3); Reactive gas capillary (4); Baffles (5); Parallel-guided ultramicro balance (6); Thermostated balance chamber (7); Protective gas inlet (8); Reactive gas inlet (9); Purge gas inlet (10); Motor for opening sample chamber (11); Cooling circuit (12); Furnace temperature sensor (13). [68]



Figure 2.20 TGA/SDTA854e supplied by Mettler Toledo. Device used for laboratory characterisation.

Chapter 3

Results and discussion

This chapter presents the results from the different characterisation techniques described in the previous chapter. Analyses were performed on the treated and untreated fibers to study the thermal stability and the morphology. The acid treatment was studied for several concentrations. Moreover, the chemically modified PET was analysed with the different parameters studied, starting with the influence of TGDDM epoxy content and reaction time for chain extension. Then, the influence of the fibers reinforcement content and the acid treated fibers in the PET matrix. And finally, the influence of annealing temperatures on the crystallinity of the composite. The results obtained with the characterisation techniques are compared and discussed.

3.1 Influence of fiber treatments

Banana fibers (BF) were treated with sodium hydroxide (NaOH) and succinic anhydride (SA). The treatments are done in order to enhance the thermal stability and the compatibility with the polymer matrix. This permits to avoid fiber burning in the matrix during the composite production. The influence of these treatment on the BF properties are discussed in the section.

3.1.1 Alkaline treatment

BF were treated with a solution of 0.5wt.% (0.25N) NaOH to increase their thermal stability. This treatment removes wax layers and surface impurities responsible for thermal instability [48]. Fibers are characterised thermally with a TGA analysis and the surface morphology with a SEM observation.

3.1.1.1 Thermal characterisation

Figure 3.1 shows the thermograms of TGA curves and DTG curves. DTG stands for derivative thermogravimetry analysis and these curves are obtained by derivation the TGA curves. The DTG curves allows to determine the temperatures at which thermal degradation is the quickest. And the mechanisms of degradation can be deduced from these curves. Table 3.1 shows the results of for the thermal analysis. Temperatures

at which the degradation rate are the highest are noted T_{peak} . Some material have several peaks for different substances degrading at different temperatures in the material. TGA were performed on BF untreated and after the NaOH treatment.

A small degradation can be observed below 100°C corresponding to the moisture loss. This degradation is the fastest at T_{peak1} . The second peak T_{peak2} correspond to the degradation of the lignocellulosic compounds of the fiber. Table 3.1 shows the results of the specific temperatures of the treated and untreated BF. It is observed that the alkaline treatment enhance the thermal stability of BF. The degradation temperature is shifted from 345 to 367 °C. This is consistent with the literature. Joseph et al.[75] studied the effect of alkaline treatment on thermal stability and degradation of banana fibers. The treatment leads to higher thermal properties indicating lower weight loss and shifting of degradation peaks to higher temperature.

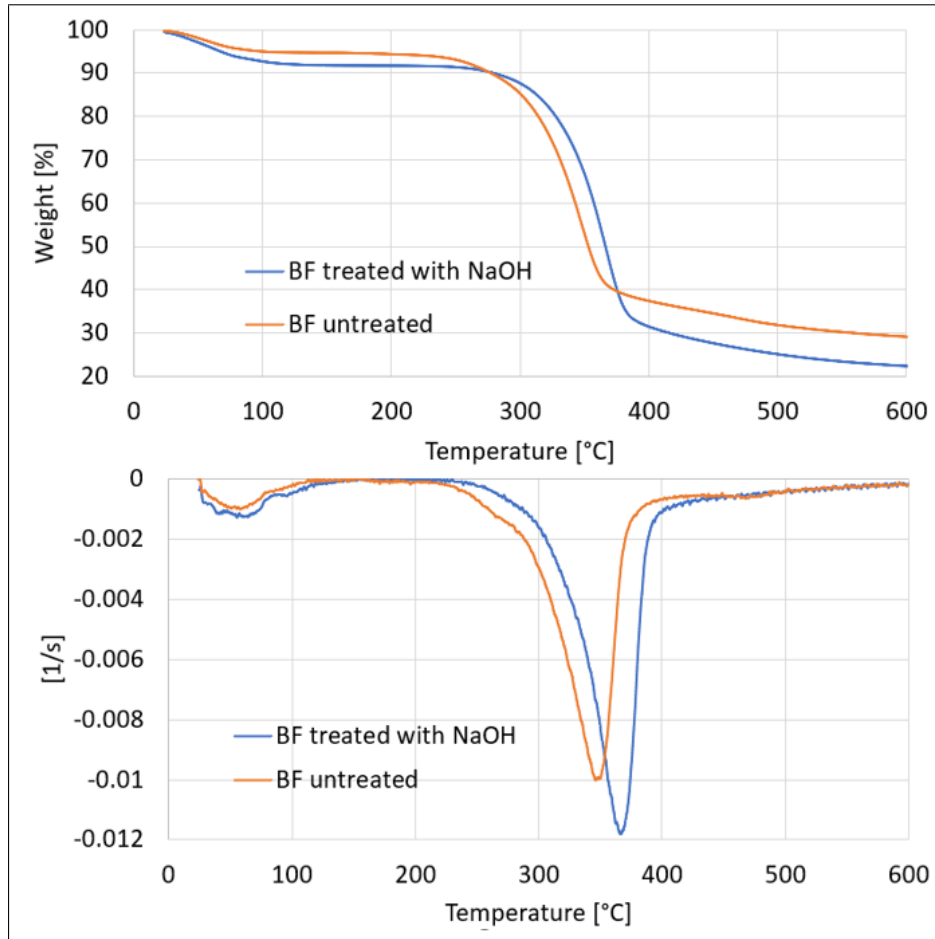


Figure 3.1 TGA and DTG curves of banana fibers untreated and treated with NaOH.

Table 3.1 TGA results of BF untreated and treated with NaOH.

	T_{peak1} [°C]	T_{peak2} [°C]
BF untreated	58	345
BF 5 % NaOH treatment	61	367

3.1.1.2 Morphology

SEM images of untreated and treated banana fibers are shown on Figure 3.2. These images reveal that the alkaline treatment renders the fibers cleaner. As we can see on Figure 3.2 (1) and (2), the BF surface is covered by little scrapings. These are mainly removed as is can be seen on Figure 3.2 (3) and (4) where the BF are well shaped part of the fiber is kept.

On the left of Figure 3.2 (3), the top of a BF is shown where the microfibrils are well linked together and aligned. Contrary to image (5), which shows the end of a fiber where the microfibrils separate and are not held together. What holds the microfibrils together tends to be removed by the alkaline treatment. If the separation of microfibrils is not desired, the alkaline treatment time of BF should not be too long.

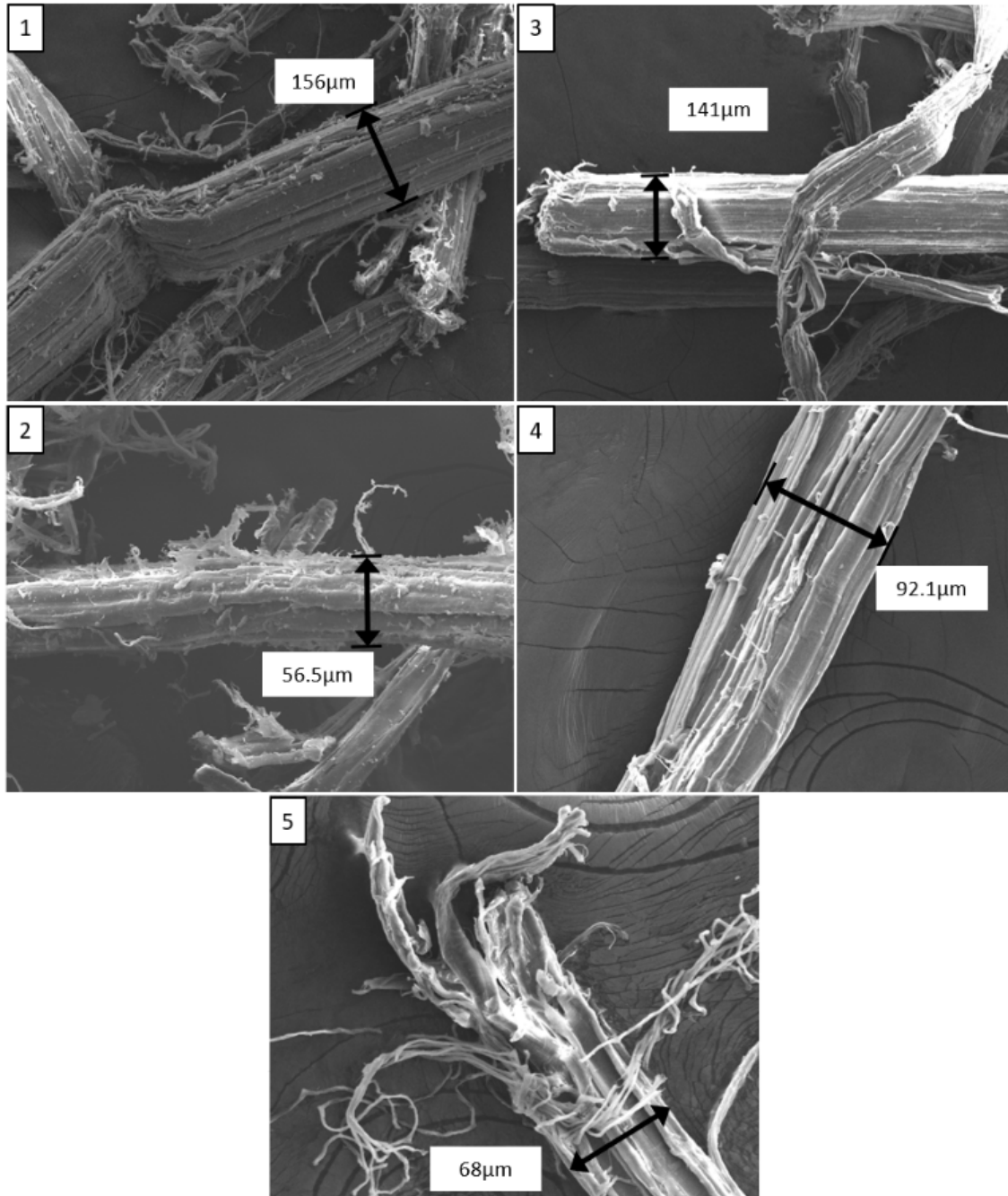


Figure 3.2 SEM images of untreated (1) & (2), and treated (3), (4) & (5) banana fibers.

3.1.2 Acid treatment

BF were further treated with acid in order to increase the cohesion between the CoPS3 matrix and the fibers. Thermal and morphological characterisation of the fibers are presented hereunder.

3.1.2.1 Thermal characterisation

TGA and DTG curves are illustrated in Figure 3.3. Table 3.2 gives the results of the TGA.

We observe two main degradation temperatures: the first one correspond to a degradation of the acid residues on the fiber and the second correspond to the fiber degradation. The succinic acid residues degradation is well represented because the BF have not been washed after the treatment in order to keep the acid groups on the fiber. Caires et al. [76] studied the thermal stability of succinic acid and observed a mass loss in a single step between 165 and 250°C.

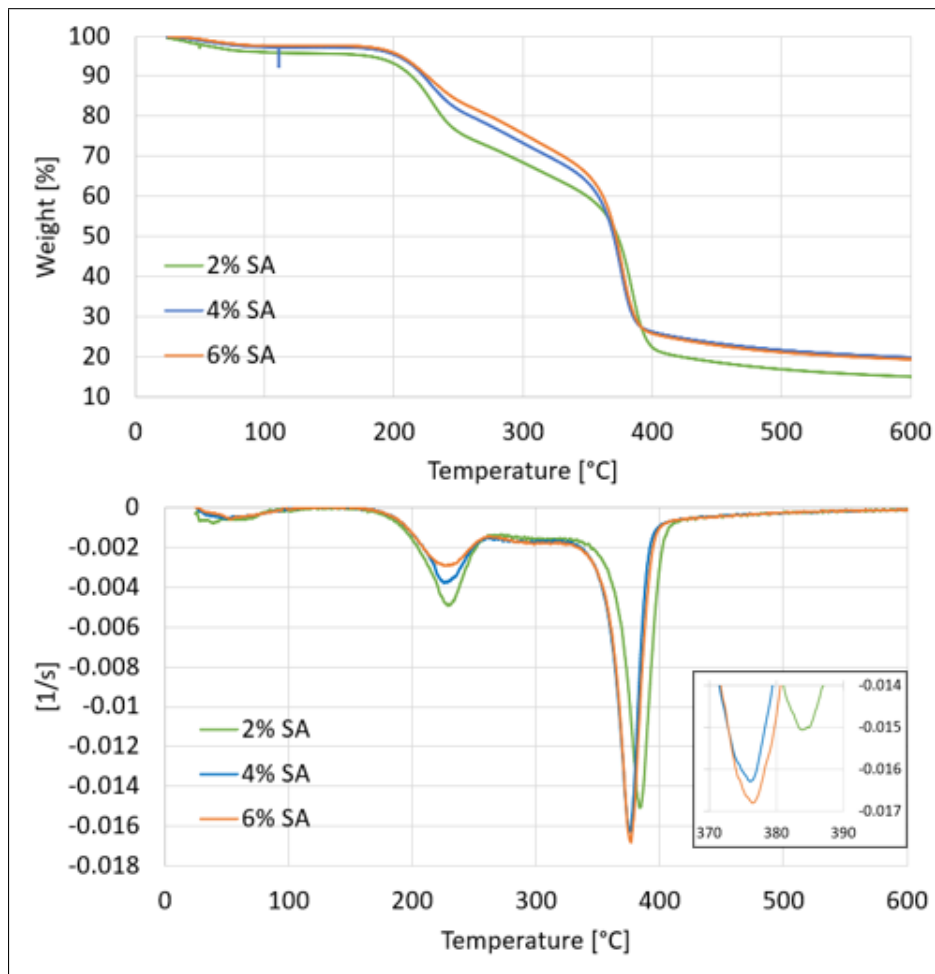


Figure 3.3 TGA and DTG curves of BF with different acid treatments.

Table 3.2 TGA results of BF with different acid treatments.

	T_{peak1} [°C]	T_{peak2} [°C]
BF 2 % SA treatment	228	384
BF 4 % SA treatment	226	376
BF 6 % SA treatment	227	376

3.1.2.2 Morphology

BF were observed by SEM for the different acid treatments. The SEM images are illustrated on Figure 3.4. It is observed that the fibers are cleaner without the acid treatment. With an increase in the percentage of acid in the solution, the treated fibers see their surface more cluttered by succinic acid residues (Figure 3.4 (3), (4)). Figure 3.5 shows the treated fiber after washing (1) and without washing (2). It can be clearly seen that the residues on the surface of the fibers have been removed with washing.

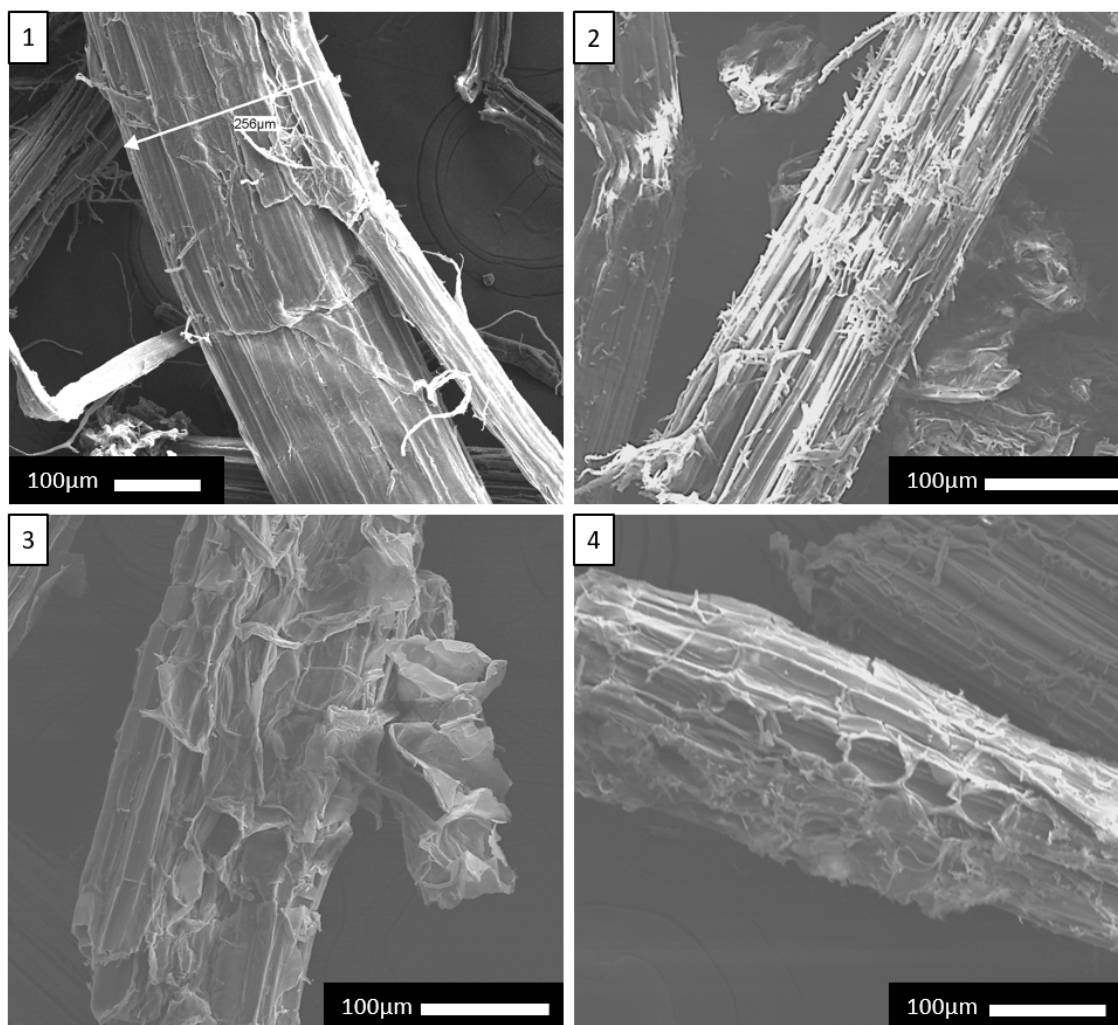


Figure 3.4 SEM images of acid treated BF. (1) 0%, (2) 2%, (3) 4% and (4) 6%wt. of SA for the treatment solution.

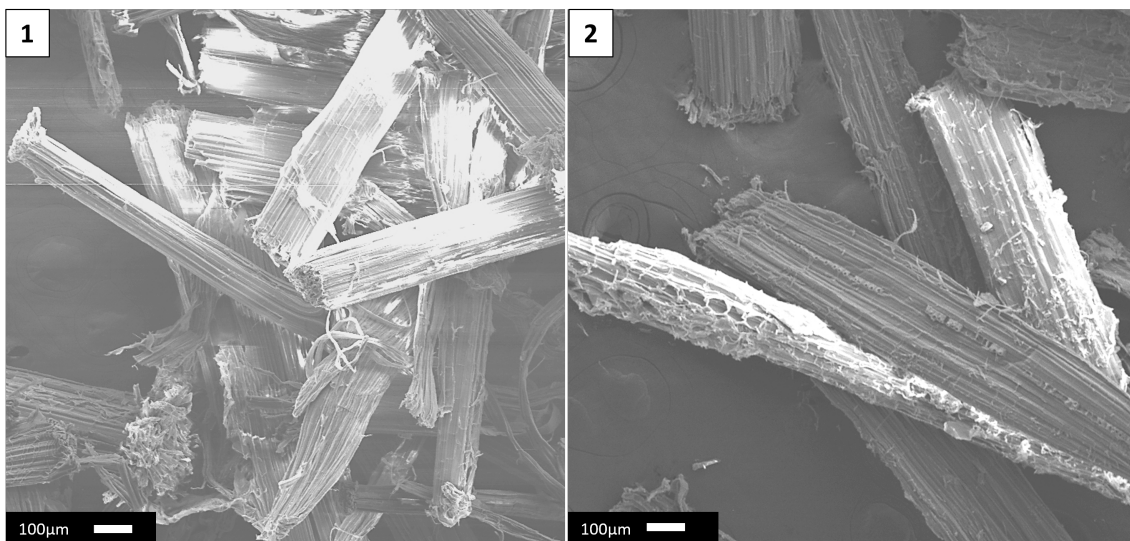


Figure 3.5 SEM images of acid treated BF with 6% SA. (1) washed after treatment, (2) unwashed

3.2 Chemical modification of PET

Before the extrusion of PET/banana fiber composite, the PET thermoplastic is modified chemically and each steps are analysed by DSC and viscosity measurements. It permits to follow how the properties are evolving. Then, TGDDM as chain extender is added and the proportion and the time of reaction has been studied, analysing each sample obtained.

3.2.1 Depolymerisation, repolymerisation and SSP

The depolymerisation, repolymerisation and SSP steps were characterized to observe the evolution of thermal properties and molar masses of the thermoplastic. Repolymerisation with 1,3-propanediol (1,3-PD) and succinic anhydride (SA) provides a co-polyester saturated, CoPS1. This one then undergoes a SSP and CoPS2 is obtained.

3.2.1.1 Determination of molar mass

The viscosity analyses were done on samples for the steps of depolymerisation, repolymerisation and SSP in order to determine the molar masses using the Mark-Houwink equation:

$$[\mu] = 1.91 \cdot 10^{-4} \bar{M}_w^{0.734} \quad (3.1)$$

The results are represented in Table 3.3. The viscosity analysis show that, during depolymerisation reaction of PET, intrinsic viscosity is reduced from 0.53 to 0.12 dL/g (corresponding of M_w from 50 000 to 6500 g/mol). Repolymerisation step contribute to increase the viscosity until 0.18 dL/g. This increase is realised with the incorporation of linear chain extender obtained by coupling 1,3-PD with SA. SSP reaction gives the polymer a viscosity around 0.27 corresponding to 19 600 g/mol.

This low molar mass justifies the addition of a chain extender such as TGDDM in order to have good mechanical properties.

Table 3.3 Results from the analysis of viscosities.

	$[\mu]$ [dL/g]	M_w [g/mol]
Virgin PET <i>lighter C88</i>	0.53	49 700
Depolymerized PET (GPET)	0.12	6 500
Repolymerized PET (CoPS1)	0.18	11 300
Modified PET after SSP (CoPS2)	0.27	19 600

3.2.1.2 Thermal characterisation

A sample of each different step of the depolymerisation has been analysed by DSC. It allows to observe the glass transition temperature, the melting temperature and the crystallisation temperature as well as the degree of crystallization.

The DSC thermogram of second heating at 10°C/min until 180°C is presented on Figure 3.6 for the different steps of the PET modification. Table 3.4 gives the specific temperatures values and the degree of crystallinity. The temperature of cold crystallisation is noted T_c .

The first step was extrusion of PET lighter C88, industrial grade to get PET more amorphous and have the same properties than waste bottles. Secondly, PET was chemically modified by depolymerisation with 1,3-PD. In this step, glycolysed PET (GPET) have a higher degree of crystallinity (26,4%) than extruded PET. Reduction of molecular weight in this condition reduce also the melting temperature as it can be seen Table 3.4. The next step is repolymerisation with the chain extender of 1,3-PD and SA to increase the molecular weight. The result shows a decrease of crystallinity after incorporation of the chain extender. Crystalline phase is modified by incorporation of the new chain. This reduced the kinetic of crystallisation. Finally, it is important to notice that the glass transition temperature is also decreased at a temperature of 45°C. This low glass transition temperature leads to a limitation in terms of temperature of use for potential applications of the material. The copolyester saturated obtained after SSP (CoPS2) is thus very amorphous.

For PET lighter extruded and GPET, a double peak at melting is observed. This means that there are two phases with two different melting points. Moreover, the extruded PET was quenched for amorphization, however a high degree of crystallinity is observed, similar to PET lighter C88. This is due to the thermal program preceding the second heating. In the first heating and cooling, the polymer crystallised. No chemical modification took place. It is logical to observe a similar degree of crystallinity to the initial PET at the second heating.

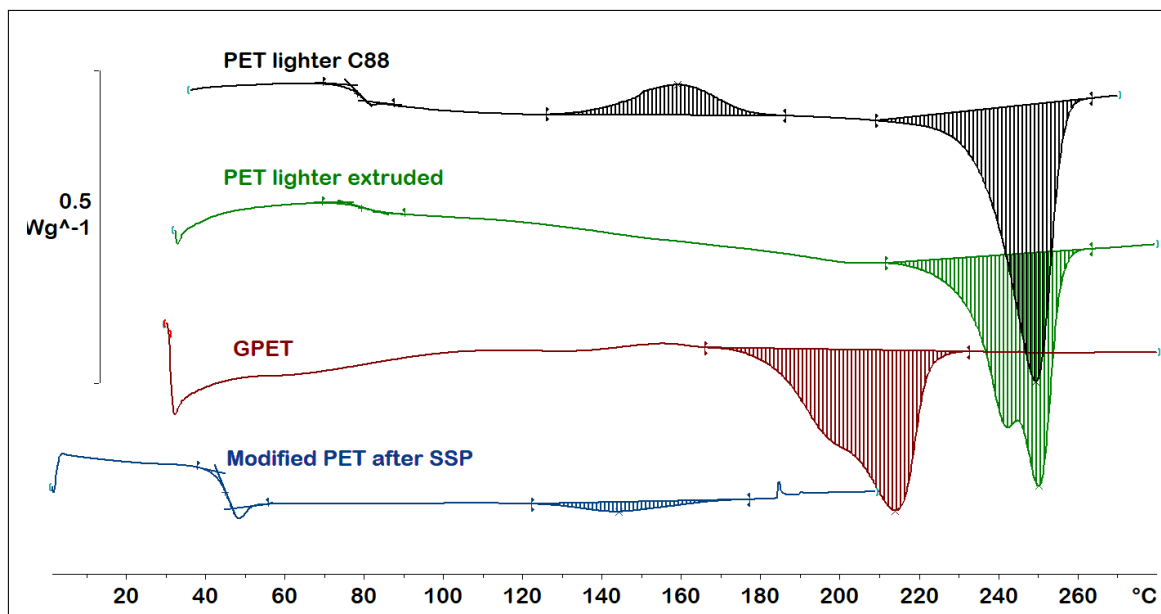


Figure 3.6 Normalized DSC second heating curves of PET during the different process stages. PET lighter C88 is the industrial PET before processing. GPET is the PET after glycolysis and CoPS1 is the co-polyester saturated after SSP.

Table 3.4 Results from the analysis of the DSC curves.

	T_g [°C]	T_c [°C]	ΔH_c [J/g]	T_m [°C]	ΔH_m [J/g]	χ_c [%]
Virgin PET <i>lighter C88</i>	78.2	159.1	7.3	249.4	38.5	22.3
Extruded PET	79.3	-	-	250.2	36.0	25.7
Depolymerized PET (GPET)	-	-	-	213.9	37	26.4
Modified PET after SSP (CoPS2)	45.0	-	-	144.2	2.3	1.6

3.2.2 Influence of TGDDM content as chain extender

TGDDM was used as chain extender for the increase of the global molar mass of the co-polyester saturated obtained after SSP (CoPS2). The polyester obtained after addition of TGDDM is the CoPS3. TGDDM epoxy resin has four functional epoxy groups. This crosslinker could thus very rapidly react with multiple polymer end chains and form a thermoset polymer. For this reason, small quantities equivalent to 0.5, 1 and 2% were used. TGDDM has been added to the thermoplastic when dissolved in dichloromethane to increase dispersion in the CoPS2, followed by dichloromethane evaporation. Afterwards, the mixture was extruded in DSM extruder at 170°C for 10 minutes.

3.2.2.1 Determination of molar mass

Table 3.5 shows the intrinsic viscosities and the corresponding molar masses. The difference between the molar masses for different contents of TGDDM is not very marked especially when the standard deviation is taken into account. However, it is observed that the molar masses have been increase from the CoPS2. M_w is around 26-27 kg/mol for the CoPS3, whereas it was it was around 20 kg/mol for CoPS2.

There are several possibilities for the chain extender reaction. It can react with end-groups of the co-polyester small chains to form branched structures as it has been observed by Raffa et al. [25]. Branched structures does not significantly contribute to the viscosity while increasing the molecular weight. Moreover, the epoxy groups can react with water and form two hydroxyl groups. These hydroxyl groups may cause polymer degradation reacting by transesterification with the chains. Finally, another possibility is the curing reaction of TGDDM with the other molecules of TGDDM. It can crosslink, having the epoxy groups reacting with each other.

Table 3.5 Results from the analysis of viscosities. Average results $\pm$ standard deviation.

TGDDM content [%]	$[\mu]$ [dL/g]	M_w [g/mol]
0.5	0.34 ± 0.01	$27\ 200 \pm 100$
1	0.33 ± 0.02	$25\ 900 \pm 600$
2	0.35 ± 0.03	$27\ 400 \pm 1100$

3.2.2.2 Thermal characterisation

The Figure 3.7 is a thermogram with the curves obtained by DSC for the second heating. The figure is followed by Table 3.6 where specific temperature as well as the degree of crystallinity are given.

It is observed that glass transition and melting temperatures are almost unchanged for different amount of TGDDM. But, the enthalpy of melting increases with the amount of TGDDM. This means that due to TGDDM, the crystallinity of the material increases. Shorter polymer chains tend to crystallize more easily. However, at 2% TGDDM, the molar mass is not lower, on the contrary. One assumption that can be made is that the TGDDM reactions lead both to degradative shortening of chains and to formation of branching structures, increasing the molecular weight [25]. The overall obtained structure having a higher degree of crystallinity.

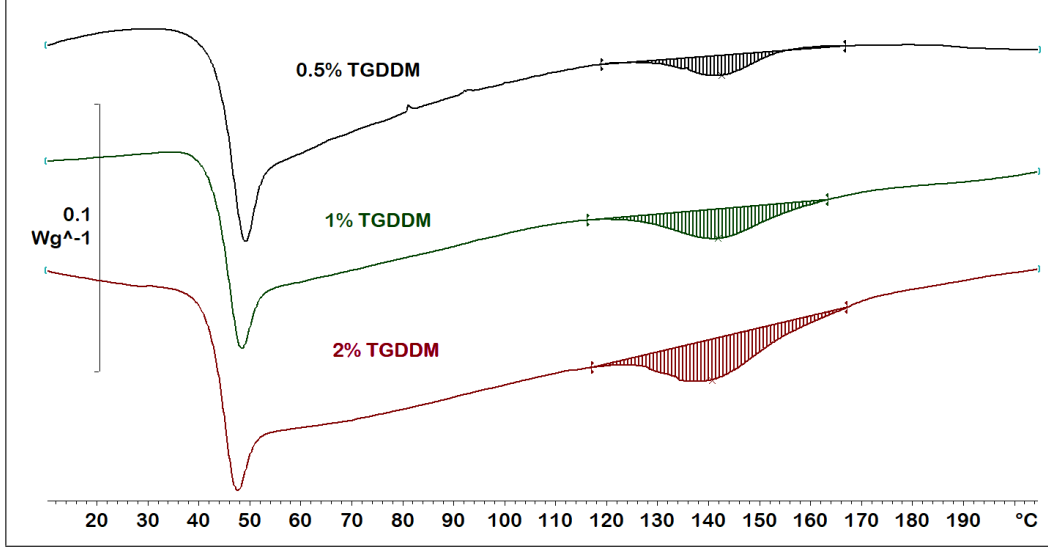


Figure 3.7 Normalized DSC second heating curves for CoPS3 with different content of TGDDM.

Table 3.6 DSC results for CoPS3 with different content of TGDDM.

TGDDM content [%]	T_g [°C]	T_m [°C]	ΔH_m [J/g]	χ_c [%]
0.5	45	142.6	0.6	0.4
1	44.3	141.9	1.4	1.0
2	43.7	140.7	2.1	1.5

3.2.2.3 Thermomechanical characterisation

DMA tests were performed to observe the thermomechanical properties of the CoPS3 with 0.5, 1 and 2 % of TGDDM content. These are shown on Figure 3.8 and results are presented in Table 3.7. The degree of crystallinity, measured by DSC, does not affect the mechanical properties very much as the sample with the highest degree of crystallinity has the lowest module. These are rather correlated with the molar mass which is the highest for a content of 0.5% TGDDM. A decrease in modulus is observed with the addition of TGDDM. This is in agreement with the viscosity analysis where a higher molar mass is observed for a TGDDM content of 0.5%.

The damping coefficient is the ratio between the dissipated energy and the energy stored for each cycled deformation:

$$\tan \delta = \frac{E''}{E'} \quad (3.2)$$

The $\tan \delta_{max}$ gets higher when the amount of TGDDM increase. As $\tan \delta$ represents the ratio of the viscous to elastic response, or in other words, the energy dissipation potential of a material. A higher area under $\tan \delta$ curve means that the material has more energy dissipation potential. With a lower $\tan \delta$ the material acts more elastic.

The assumption that TGDDM did not react with the thermoplastic leads to the

following reasoning. Ten minutes of reaction is probably too short for the TGDDM epoxy groups to react with the end-groups of the polymer. This leads to study the influence of reaction time of TGDDM.

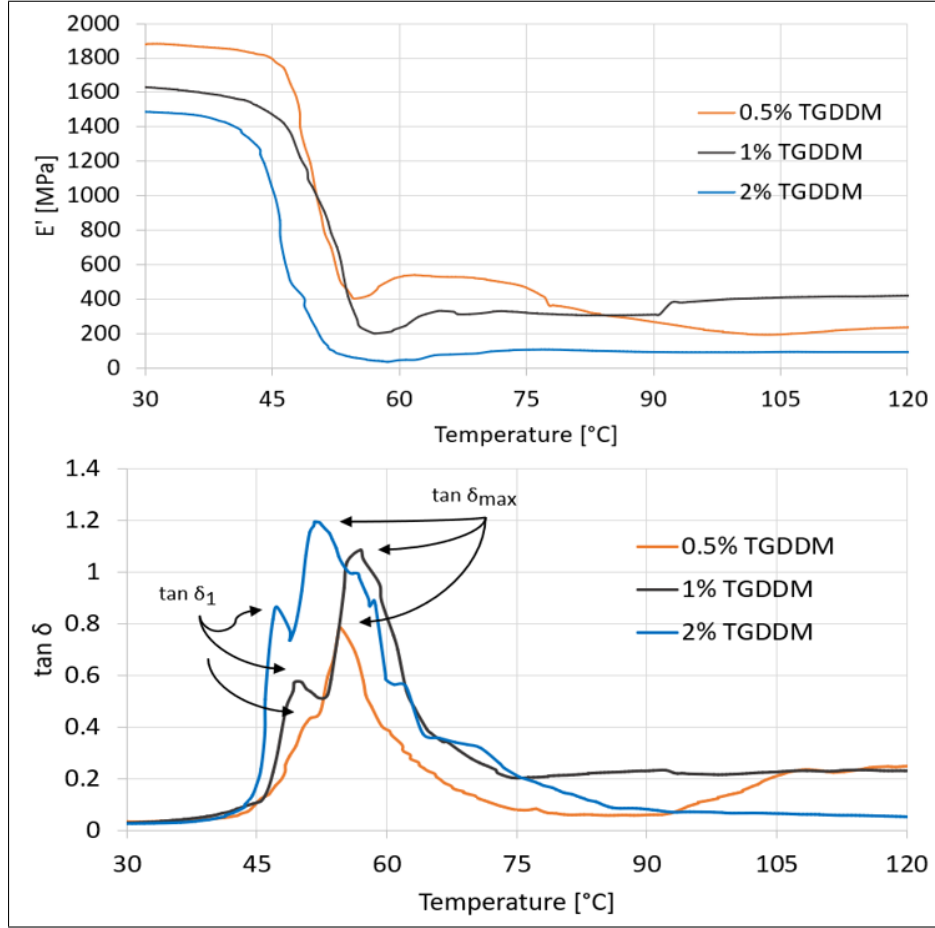


Figure 3.8 DMA curves of CoPS3 for different TGDDM content.

Table 3.7 DMA results of CoPS3 for different TGDDM content.

TGDDM content [%]	$E'_{30^{\circ}C}$ [MPa]	$E'_{110^{\circ}C}$ [MPa]	T_g	$\tan \delta_1$	$\tan \delta_{max}$
0.5	1880	210	54.5	0.42	0.8
1	1630	414	56.8	0.58	1.1
2	1490	90	51.5	0.86	1.2

3.2.3 Influence of time on TGDDM crosslinking reaction

The samples residence time in the DSM extruder was initially set to 10 min. Since the molar mass and the mechanical properties were not improved with the increasing amount of TGDDM. Two additional residence times of 15 and 20 minutes were tested to give more time for the TGDDM epoxy functional groups to react with the end of chains. In this section, an amount of 5wt.% TGDDM is used for the elaboration of CoPS3 with different residence time in the DSM extruder at a temperature of

170°C. The results of TGDDM content showed a slight higher molar mass for the thermoplastic with 2% of TGDDM, however the mechanical properties were not increased. For the following parts of this study, a content of 5% of TGDDM is taken because the properties were quite as good and mainly because TGDDM is not made from a natural source. A lower quantity is therefore justified to go in the direction of an environmentally friendly material.

3.2.3.1 Determination of molar mass

Table 3.8 shows the intrinsic viscosities and the corresponding molar masses. The highest molar mass is for 10 minutes residence time corresponding to a molar mass of 26 000 g/mol. However, the molar mass is lower for 15 minutes and medium for 20 minutes, meaning that residence time is not correlated to the global molar mass. This means that the reaction of the epoxy crosslinker already took place after 10 minutes of residence time. The kinetic reaction of TGDDM is fast.

Table 3.8 Results from the analysis of viscosities. Average results $\pm$ standard deviation.

Residence time [min]	$[\mu]$ [dL/g]	M_w [g/mol]
10	0.33 $\pm$ 0.004	26 000 $\pm$ 60
15	0.31 $\pm$ 0.004	23 900 $\pm$ 60
20	0.32 $\pm$ 0.015	24 900 $\pm$ 400

3.2.3.2 Thermal characterisation

Figure 3.9 gives the DSC curves of the second heating of CoPS3 with different residence time in the DSM extruder. The results are presented in Table 3.9. A slightly higher degree of crystallinity is observed for a residence time of 20 min. But this is not significant. The material is still very amorphous, with less than 1% of crystallinity. Melting temperatures of CoPS3 stays around 141°C (see Table 3.9).

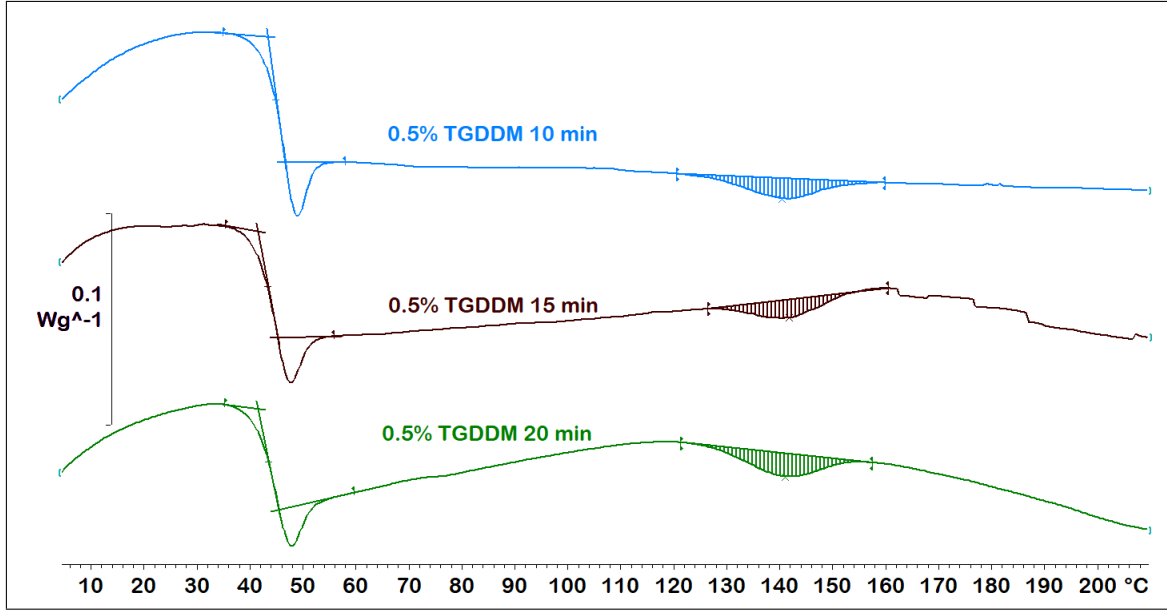


Figure 3.9 Normalized DSC curves second heating of CoPS3 with 0.5% of TGDDM for different residence time in the DSM extruder.

Table 3.9 DSC results for CoPS3 with 0.5% of TGDDM for different residence time in the DSM extruder.

Residence time [min]	T_g [$^{\circ}C$]	T_m [$^{\circ}C$]	ΔH_m [J/g]	χ_c [%]
10	44.8	140.5	0.9	0.7
15	43.3	141.8	0.7	0.5
20	43.5	141.1	1	0.7

3.2.3.3 Thermomechanical characterisation

DMA characterization was done (Figure 3.10) to observe the influence of residence time on the thermomechanical properties. A difference is observed in this case with an increase of modulus when the residence time of CoPS3 in the DSM extruder is longer. As recognized in Table 3.10, the modulus increase goes from 1880 MPa to 2670 MPa.

This increase in mechanical properties is not linked to the degree of crystallinity since the differences in crystallinity are not pronounced, neither to the molecular weight as it is similar for the different residence times.

As explained in section 3.1.2.3, a higher damping coefficient means that the material is more viscous. So for an applied force, the 20 minutes sample will dissipate more energy than the others.

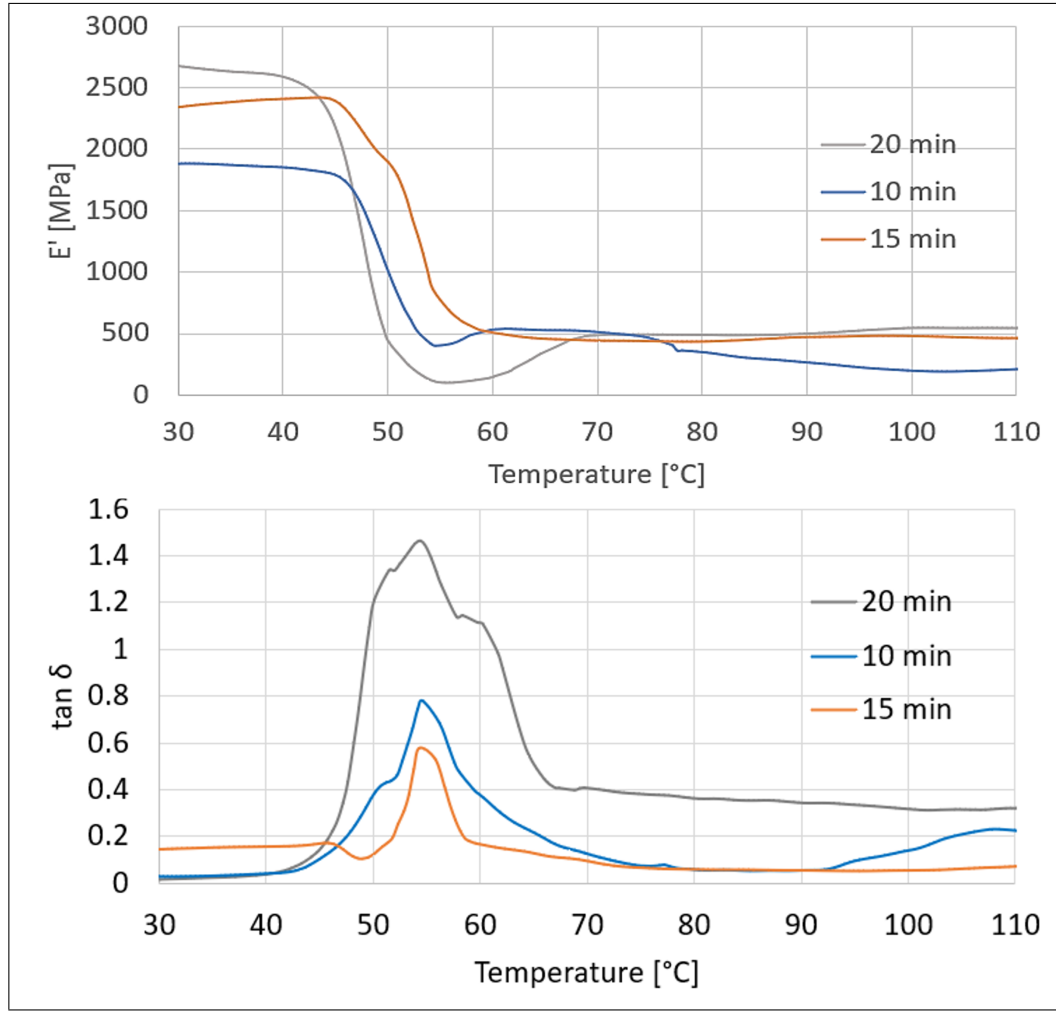


Figure 3.10 DMA curves for different residence times

Table 3.10 Results from the analysis of the DMA curves.

TGDDM content	$E'_{30^{\circ}C}$ [MPa]	$E'_{110^{\circ}C}$ [MPa]	T_g	$\tan \delta_{max}$
10 min	1880	210	54.6	0.8
15 min	2340	465	54.3	0.6
20 min	2670	540	54.4	1.4

3.3 Modified PET/banana fiber composite

The step following the modification of the modified thermoplastic matrix is the incorporation of banana fibers (BF). First, the composite is analyzed with different proportions of alkaline treated BF. The proportion of BF in the composite varies from 0 to 20wt.%. Secondly, the composite is analyzed with BF which are treated with different concentration of SA to modify the interface properties of BF. The BF have been incorporated in the matrix using DSM extruder running for 20 minutes, optimizing the reaction of TGDDM simultaneously.

3.3.1 Influence of BF loading on the composite properties

The alkaline treated BF were incorporated in the CoPS3 matrix to form a composite. Different percentage of fibers were incorporated in the composite. The analysis of the composites were done by thermal, thermomechanical, mechanical and morphological analyses. A composite sample can be observed in the appendix on Figure ??.

3.3.1.1 Thermal characterisation of the composite

Figure 3.11 shows DSC thermograms for different percentage of BF in the composite. The results are presented in Table 3.11. Fibers are known to be nucleating agents [7, 77]. The highest crystallinity is of 0.8% with the sample of 10% BF. However, here the change in crystallinity is not significant unlike what was expected.

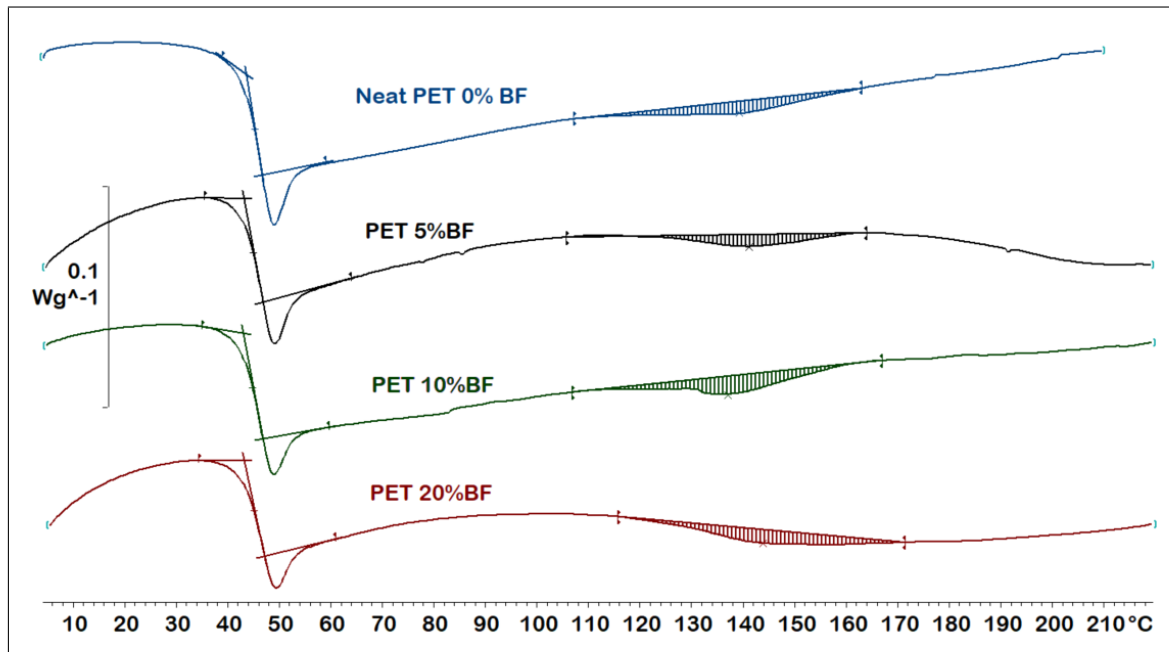


Figure 3.11 Normalized DSC curves second heating of BF/CoPS3 composite for different content of BF.

Table 3.11 Degree of crystallinity for different BF loading at second heating.

BF loading [wt.%]	T_g [°C]	T_m [°C]	ΔH_m [J/g]	χ_c [%]
0	45.2	139.2	0.9	0.6
5	44.9	141.1	0.7	0.5
10	44.8	137.0	1.1	0.8
20	45.1	143.9	1.0	0.7

3.3.1.2 Thermomechanical characterisation

The different samples were analyzed by DMA. The curves are shown in Figure 3.12 and the results are shown in Table 3.12. We can clearly see an increase of the

modulus with the quantity of fibers as expected. Indeed, elementary banana fibers having a higher modulus (29 GPa) than the matrix (2.2 GPa), a composite of the two materials generates a mixture of properties. For a 20% fiber loading sample, the Young's modulus is 4 GPa. BF with a diameter around 200 μm , characteristic of technical fibers, have a lower modulus in the order of 12 GPa [78]. The mechanical properties with the addition of fibers are drastically increased.

The introduction of fibers reduce the $\tan \delta$ peak. This proves the good matrix/fiber adhesion and means that the material is less able to dissipate energy. Similar observation are done by Pothan et al. [79] that studied banana fibers reinforced polyester composite.

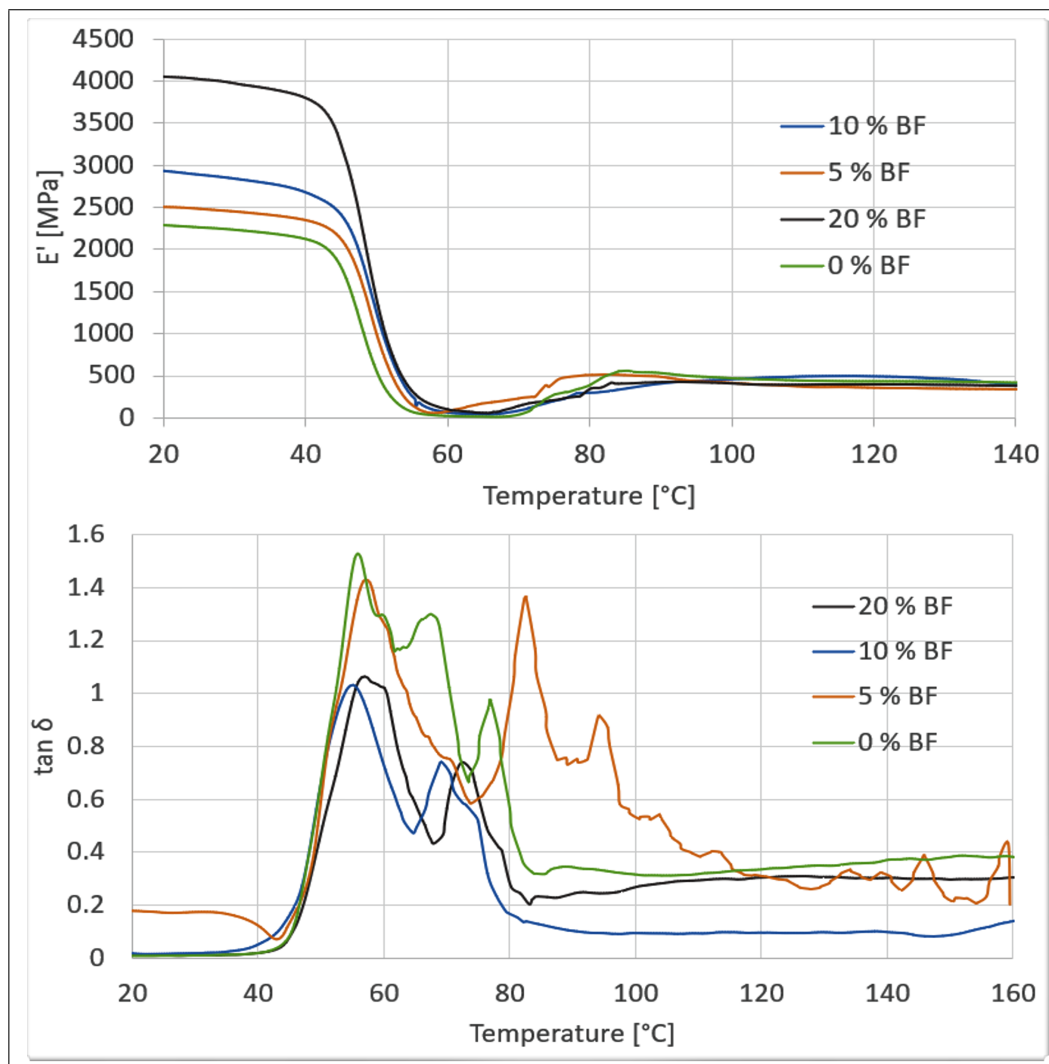


Figure 3.12 DMA curves for different BF loading.

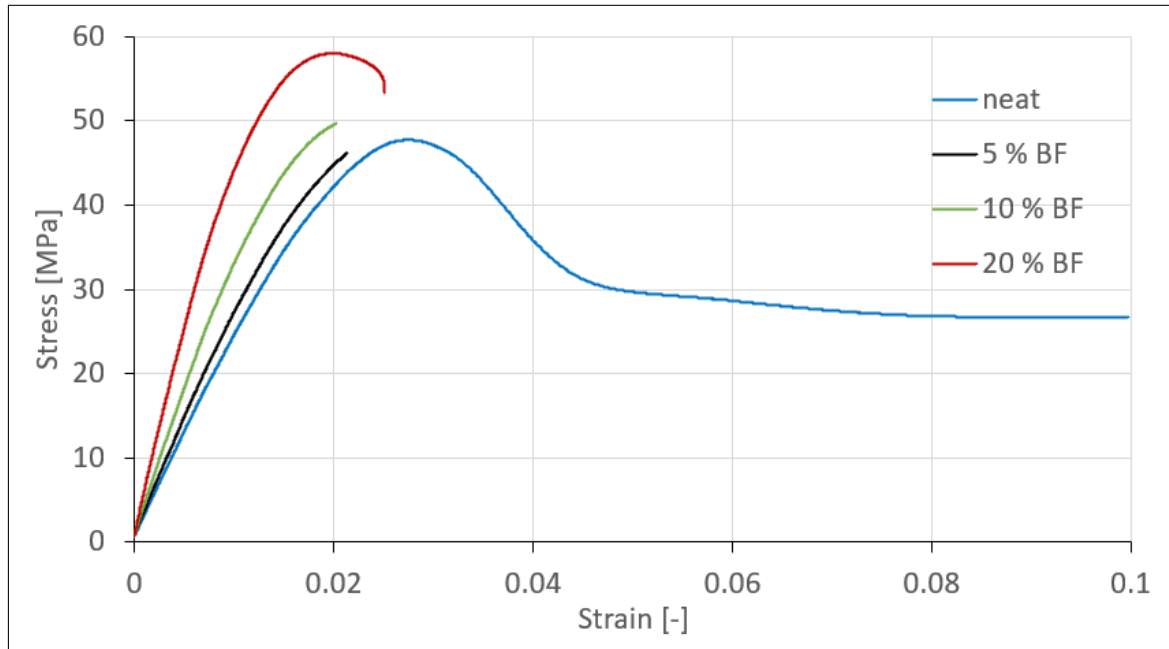
Table 3.12 Results from the analysis of the DMA curves.

BF loading [%]	$E'_{25^{\circ}C}$ [MPa]	$E'_{110^{\circ}C}$ [MPa]	T_g
0	2250	450	55.8
5	2450	400	57.4
10	2850	500	57.2
20	4000	400	57.0

3.3.1.3 Tensile tests

Tensile tests were performed to confirm DMA results. The engineering curves of the tensile tests are shown in Figure 3.13 and the Table 3.13 shows the results obtained.

It is confirmed that the modulus increases with the amount of fibers as observed in DMA. Tensile tests also allows to observe elongation at break and yield strength.

**Figure 3.13** Stress-strain curves of the BF/CoPS3 composite reinforced with different fiber loadings.**Table 3.13** Young's modulus (E), yield stress (σ_y), yeild strain (ε_y) and strain at break (ε_b) of the composite with different concentration of banana fibers content.

BF loading	E [MPa]	σ_y [MPa]	ε_b [%]
Neat	2400 ± 210	42	>110
5%	2700 ± 30	40	2.1
10%	3400 ± 30	42	2.0
20%	4750 ± 120	48	2.5

Without fibers, the material is very ductile. The deformation is higher than 110%. The addition of fibers makes the material brittle. With 5 and 10% of fibers,

the deformation before rupture is minimal. However, for a content of 20% BF, we observe a certain deformation before fracture. This deformation before fracture of the sample could be explained by the fact that the matrix fails slowly while the multiple fibers hold the crack opening for a while before being pulled out of the matrix or fracturing.

Rule of mixture

The upper and lower bounds of the modulus are determined using equations 1.8 in section 1.4.1 *Composite materials*. Figure 3.14 shows the Young's modulus of the composite in between the upper and lower bounds. This model is also called the Voigt and Reuss model. The Young's modulus of the fiber is taken at 20.5 GPa (rough approximation supposed for our fibers) and the one of the matrix at 2.4 GPa.

This graph shows that tensile modulus of our composite follows the Voigt model. Meaning that under loading the two components suffer the same strain [51] and that the orientation of fibers are thus more parallel to the deformation.

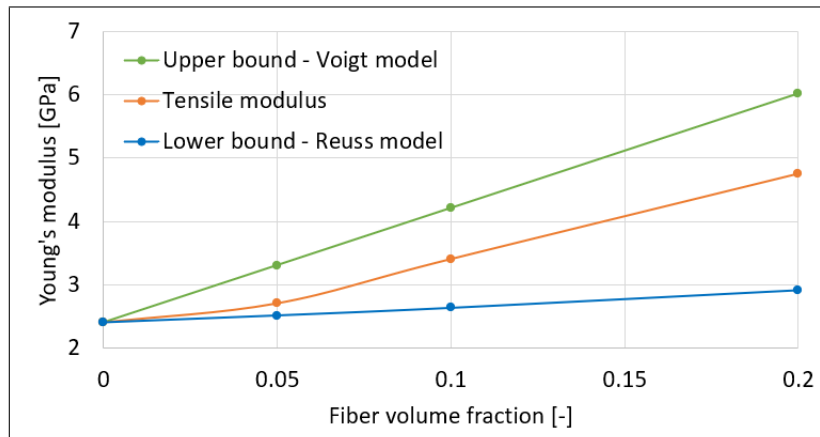


Figure 3.14 Upper and lower bounds on the elastic modulus of the composite with different volume fraction.

3.3.1.4 Thermal characterisation

Figure 3.15 shows the TGA analysis for a composite with 20wt.% BF loading. Degradation can be observed occurring in two mechanism between 350 and 500 °C with T_{peak2} at 450°C, the temperature of the main degradation. Indeed, a weight loss of 5% is observed at 350°C. The first degradation mechanism taking place before 400°C correspond to the fiber degradation. Moreover, there is no moisture loss observed before the main degradation. The composite has a low moisture content and the natural moisture of BF is not released since the BF are trapped in the matrix. With lower BF loadings of 5 and 10wt.%, a slight shift to higher degradation temperatures could be expected since fibers degrades first [68].

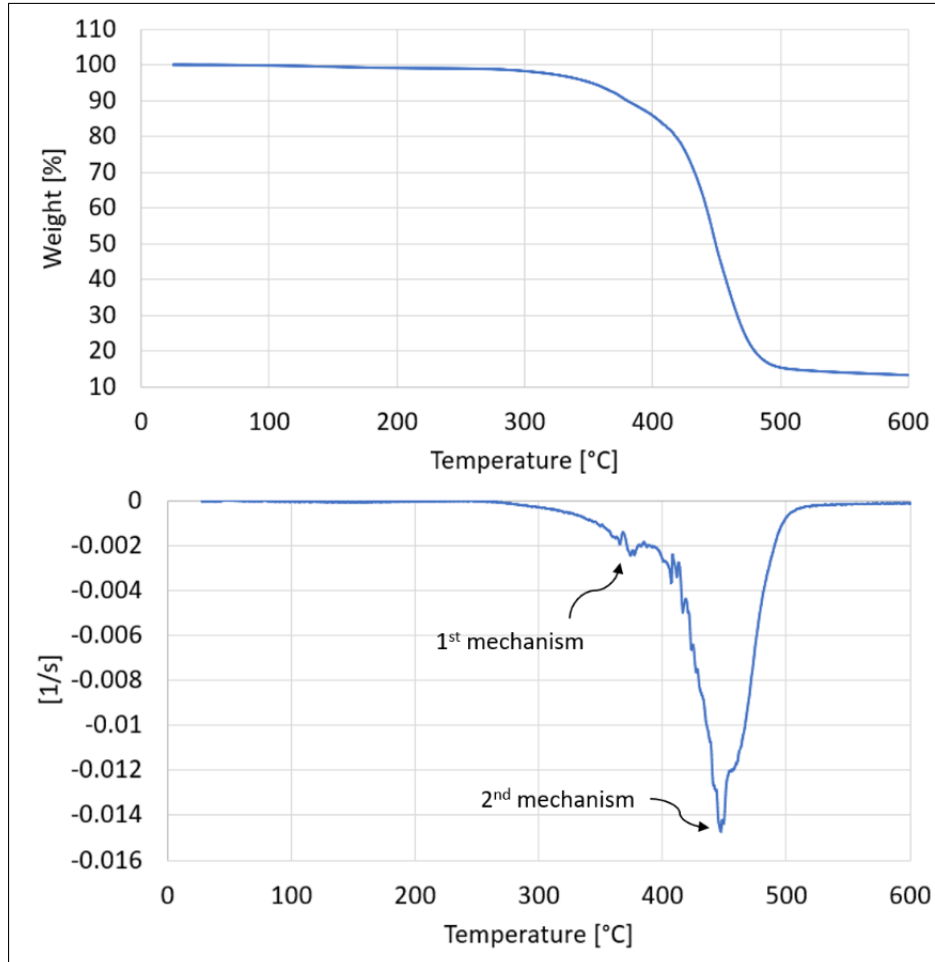


Figure 3.15 TGA and DTG curves of the BF/CoPS3 composite with 20wt.% BF loading.

3.3.1.5 Morphology of the fracture surface

To further study the fracture mechanisms, the failure surface of the samples after tensile test were observed by SEM. Figure 3.16 shows SEM micrographs of the fracture surfaces of the CoPS3/BF composite with (1) 0% of BF, (2) 5wt.% of BF, (3) 10wt.% of BF, (4) 20wt.% of BF. These figures show good dispersion of the fibers in the matrix because they are not all agglomerated to each other.

On Figure 3.16, we can see also undamaged BF (A) that exceeds from the surface of the matrix. And, torn fibers (B) can be also seen. These have a cross-section where the structure of the fiber can be clearly distinguished on Figure 3.17 which is a larger focus of (A) and (B). As we don't see the inside structure of the fiber on the cross-section of the fiber (A), we can conclude that this fiber don't break but slides out of the matrix. This phenomenon only occurs for fibers with a small part exceeding the crack opening face. Fibers with a larger contact surface with the matrix tend to break instead of sliding out. The fiber-matrix interface seems to be strong since globally the fibers are being torn apart instead of sliding out the matrix. This proves a good cohesion.

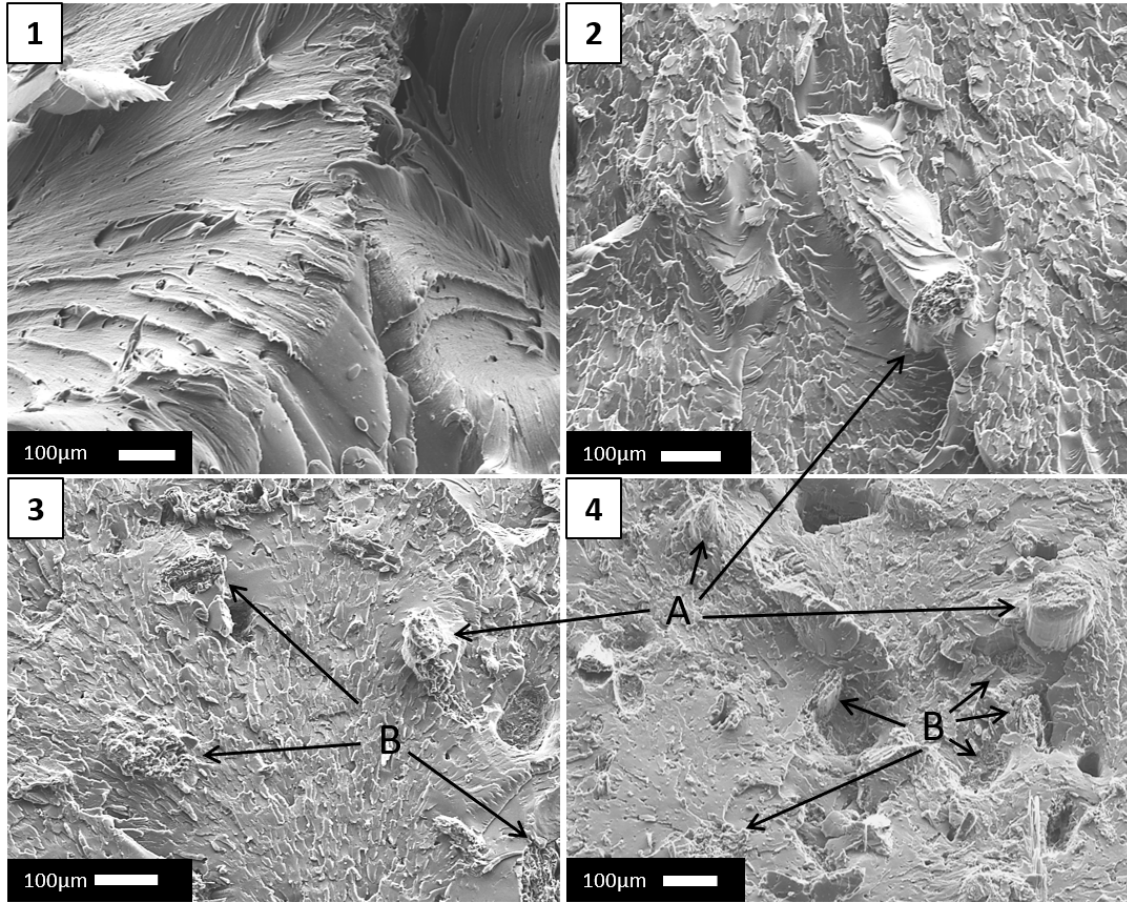


Figure 3.16 SEM micrographs of the fracture surfaces of the CoPS3/BF composite with (1) 0% of BF, (2) 5wt.% of BF, (3) 10wt.% of BF, (4) 20wt.% of BF. The arrows (A) shows undamaged BF and (B) torn BF.

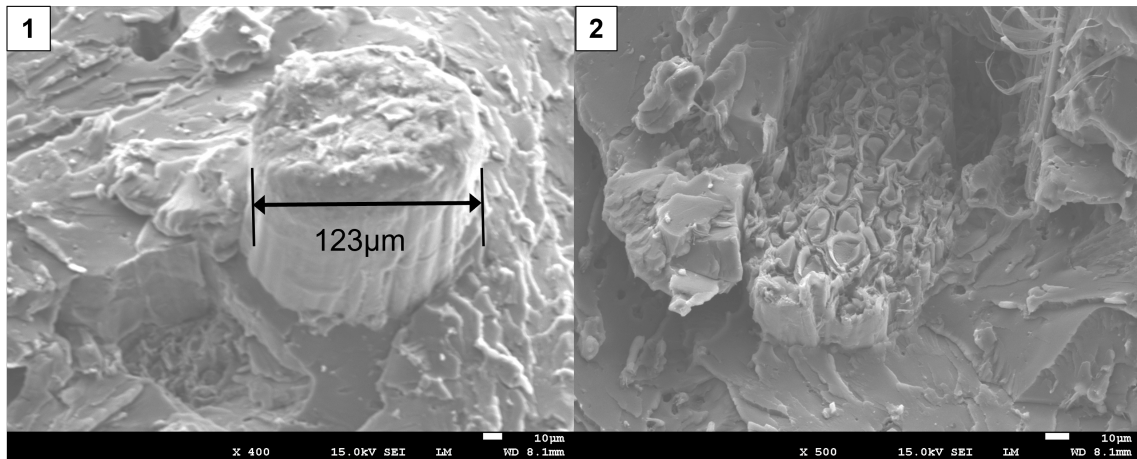


Figure 3.17 SEM of (A) a small part of BF exceeding the matrix and (B) a cross-section of torn BF.

3.3.2 Influence of acid treatment of BF on the composite

The SA treated BF were incorporated in the CoPS3 matrix to form a composite. Fibers have been treated with SA under different concentration. The proportion

of fibers in the matrix was 20wt.%. The analysis of the composites were done by thermomechanical, mechanical and morphological analyses.

3.3.2.1 Thermomechanical characterisation

The samples obtained after extrusion for 20 minutes at 180°C had a brown dark color. Meaning that degradation happened during the extrusion. From the TGA curves above, we can assume that the residue of succinic acid from the BF treatment have burn during the extrusion process.

DMA has been performed on the composite with 20wt.% of BF with different acid treatment concentrations. The curves of the analysis are presented in Figure 3.18 and the results are presented in Table 3.14. Fibers used in this step have not undergone a washing to remove excess of SA on fiber surface.

It can be seen that the modulus of the composite with BF treated with 2% SA is the highest. Meaning that these fibers has the best cohesion with the polymer matrix. The other acid treatments contain more acid residue which could have react with the polymer matrix and decrease the cohesion between the fibers and the matrix.

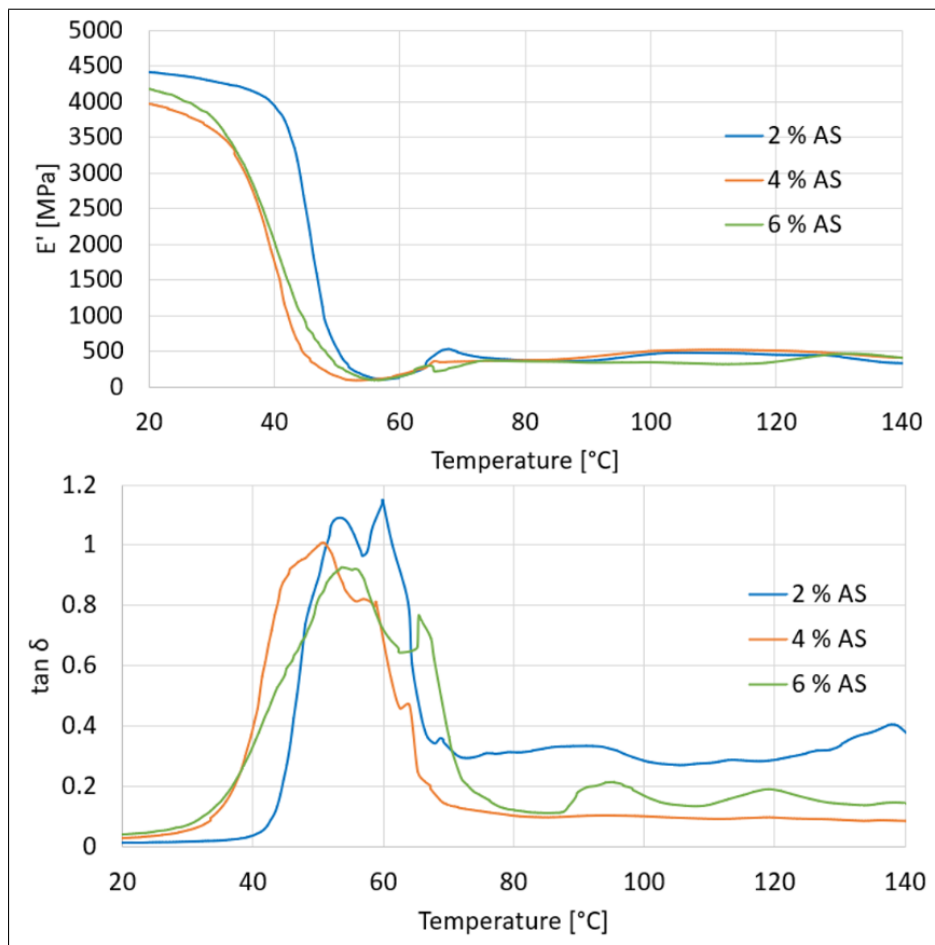


Figure 3.18 DMA curves for different SA content in the treatment of the BF.

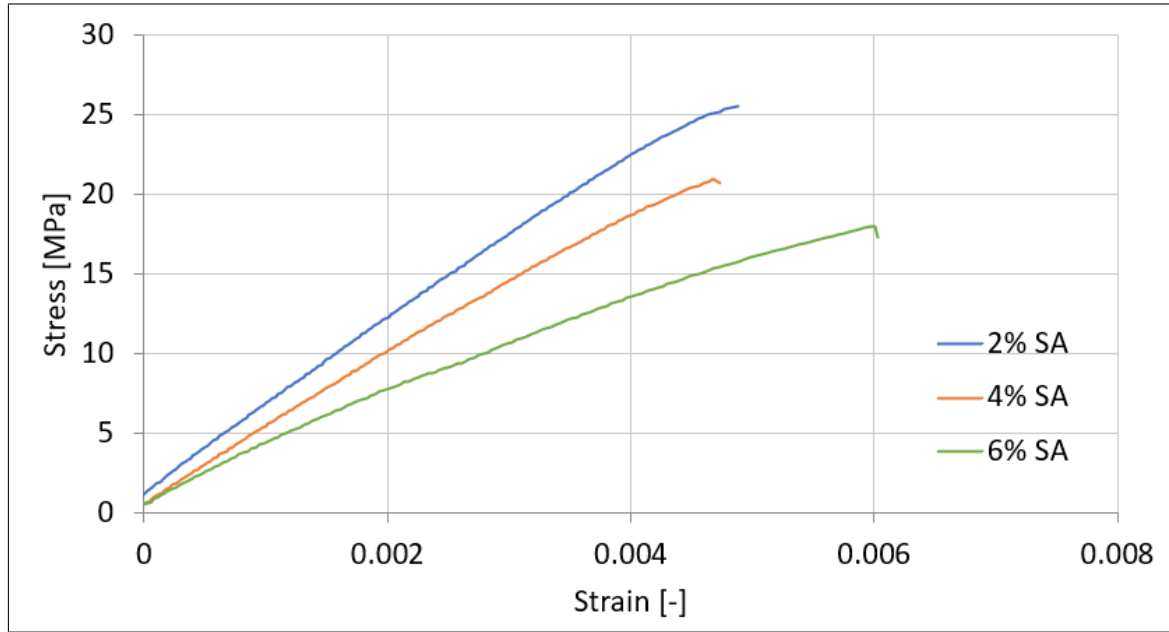
Table 3.14 Results from the analysis of the DMA curves.

SA concentration [%]	$E'_{25^{\circ}C}$ [MPa]	$E'_{30^{\circ}C}$ [MPa]	$E'_{35^{\circ}C}$ [MPa]	$E'_{110^{\circ}C}$ [MPa]	T_g
2	4350	4300	4200	450	53.2
4	3850	3600	3000	500	50.7
6	4050	3750	3100	300	53.6

3.3.2.2 Tensile tests

Tensile tests were performed to confirm DMA results. The engineering curves of the tensile tests are shown in Figure 3.19 and the Table 3.15 shows the results obtained.

A higher modulus is observed for the sample with 2% SA corresponding to 5400 MPa. This Young's modulus is very good compared to the BF without acid treatment composite. However the material is very brittle as the ultimate stress don't exceed 26 MPa. This loss of properties could be attributed to free acid present on fibers which contribute to reduction of molecular weight of CoPS3 by acidification.

**Figure 3.19** Stress-strain curves of the BF/CoPS3 composite reinforced with fiber treated at different SA concentrations.**Table 3.15** Young's modulus (E), ultimate strength (σ_u) and strain at break (ε_b) of the BF/CoPS3 composite reinforced with fiber treated at different SA concentrations.

	E [MPa]	σ_u [MPa]	ε_b [%]
2% SA	5400 ± 160	26	0.45
4% SA	4600 ± 150	21	0.43
6% SA	3300 ± 160	18	0.56

3.3.2.3 Morphology

Figure 3.20 shows the SEM micrographs of fracture surfaces for the composite with acid treated BF. SEM observations of the Figures 3.20 show that fibers are not pulled out (A). Fibers have fractured at the surface. It highlight the good cohesion between the fibers and the matrix.

Figure 3.20 (2 and 3) shows cracks in the matrix (B) on some part. This confirm that increasing the amount of SA could damage the molecular structure of the matrix. The small values for the ultimate stresses obtained for the mechanical characterisation could be explained by the fact that the acid residue was mixed to the matrix during extrusion. It has decreased the mechanical properties of the matrix. Justifying the early fracture.

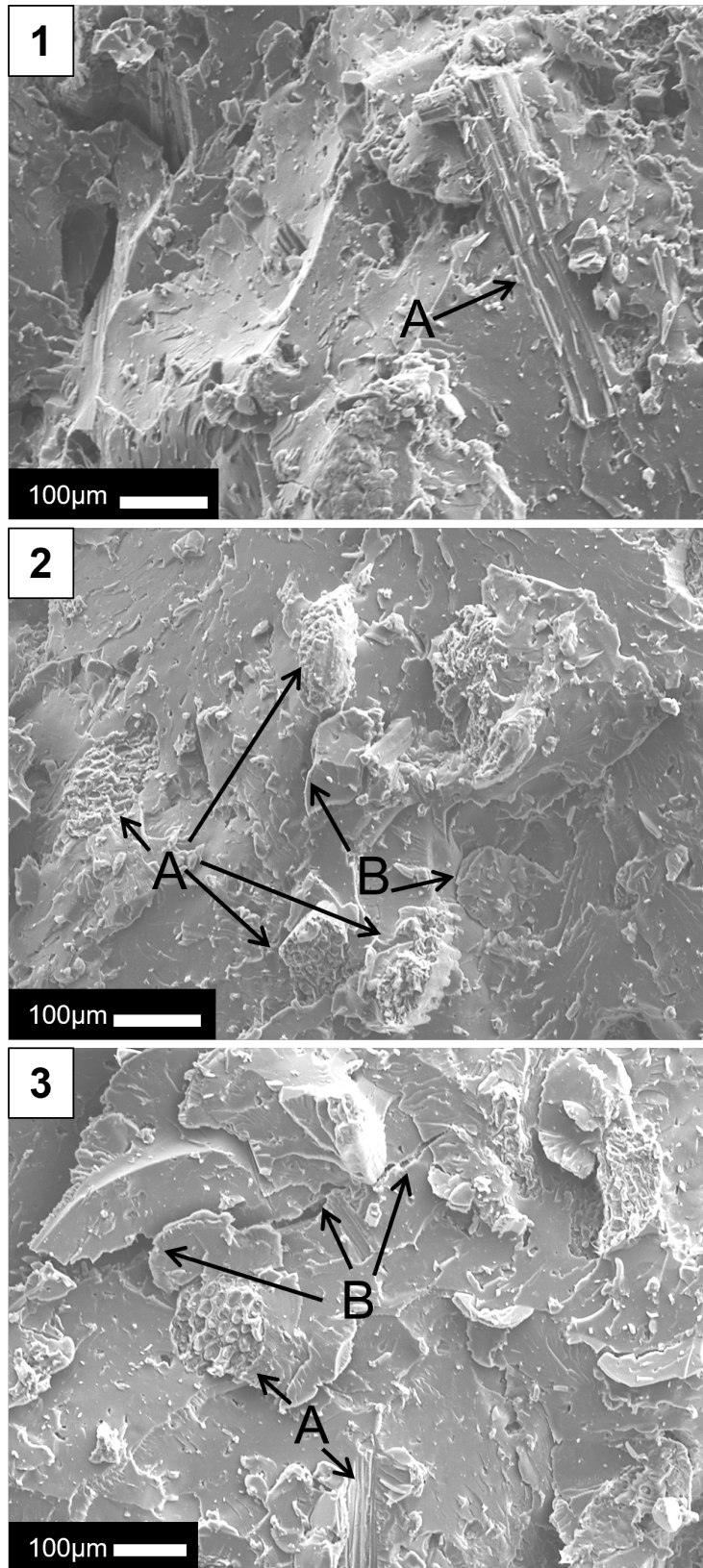


Figure 3.20 SEM micrographs of the fracture surfaces of the CoPS3/BF composite reinforced with fiber treated at different SA concentrations. (1) 2% SA, (2) 4% SA and (3) 6% SA. (A) shows fibers well-integrated or cracked, and (B) shows cracks in the matrix.

3.3.3 Influence of annealing on the composite

As it can be seen for the samples of PET modified, the crystallinity is very low and this induces a low Young's modulus. In order to increase the crystallinity, some samples have been annealed. The annealing behavior has been studied with DSC for a sample of 20wt.% BF composite. This analysis was performed in order to observe the behavior and the crystallinity changes under annealing.

Figure 3.21 shows the method used for the DSC analysis. Figure 3.22 shows the second heating DSC curves after an annealing temperature step ranging from 60 to 110 °C for 20 minutes. We can effectively see in Table 3.16 that the degree of crystallinity increases with the increasing temperature annealing. This means that the modulus of the composite might be further increased by annealing.

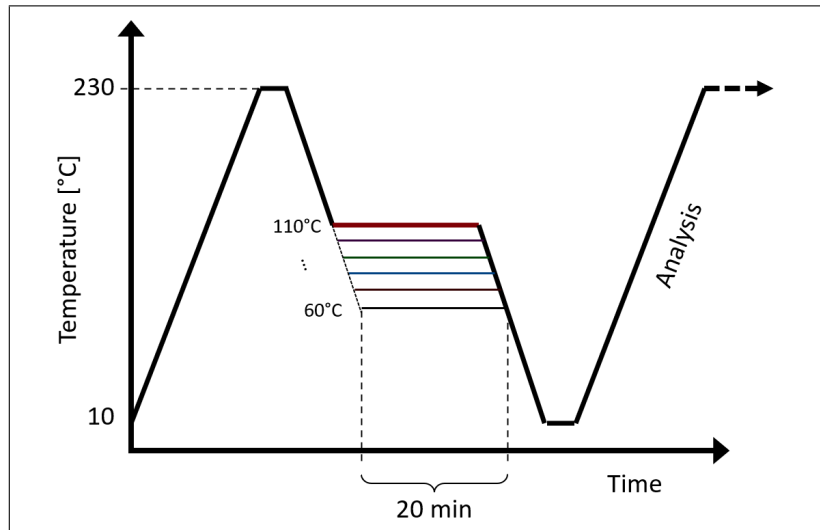


Figure 3.21 DSC method to study the influence of annealing temperatures.

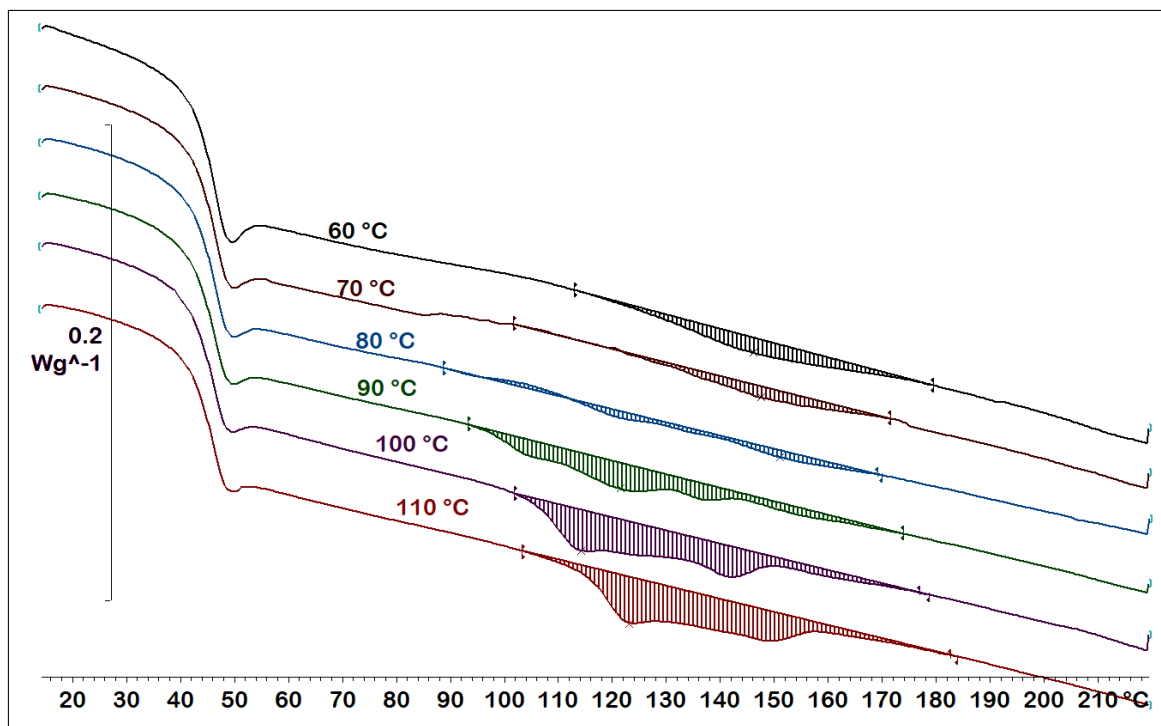


Figure 3.22 DSC curves of heating segments after annealing at different temperatures.

Table 3.16 DSC results : degree of crystallinity for different BF loading at second heating.

Annealing temperature	T_g [$^{\circ}\text{C}$]	ΔH_m [J/g]	χ_c [%]
60 $^{\circ}\text{C}$	49.6	1.2	0.86
70 $^{\circ}\text{C}$	49.9	0.7	0.50
80 $^{\circ}\text{C}$	49.7	0.52	0.37
90 $^{\circ}\text{C}$	49.9	2.28	1.63
100 $^{\circ}\text{C}$	49.6	3.42	2.44
110 $^{\circ}\text{C}$	49.5	3.61	2.58

3.4 Ecological aspect : material selection

After the elaboration of the results, we have a clearer idea of the characteristics of our composite material. To compare it with existing materials, we will assign it an application for which we believe it will be competitive. Let's assume that existing thermoplastic composites tend to be light and rigid. These find applications in the field of sports equipment or in automobile. We therefore take as a starting point, the example of a light, stiff beam for which minimizing the environmental impact during production is sought. It is easy to imagine our object in a cylindrical beam form part of an object such as a crutch, a chair leg, a bicycle frame, etc.

In order to choose the ideal material, we will follow Ashby's approach [51] summarised on Figure 3.23. We start with a translation of the designs according to constraints and objective. The main function will clearly define what the object must do. The constraints are the non negligible conditions that the material must have to accept the function. Then the main objective is set. It says what we want to maximize or minimize. In our case, the material has been studied to have the smallest possible environmental impact by taking recycled and natural elements. The fossil-fuel energy consumed in making one kilogram of material is called its *embodied energy* (H_p). Some of the energy is stored in the created material and can be reused, in one sense or another, at the end of life. The embodied energy lies generally in the range of 25 to 250 MJ/kg, though a few are much higher. The energy to recycle a material is sometimes much less than that required for its first production, typical values lie in the range 10 to 100 MJ/kg. We will therefore take the minimization of the embodied energy as objective for our material selection. The translation of design requirements is the first step and is shown in Table 3.17.

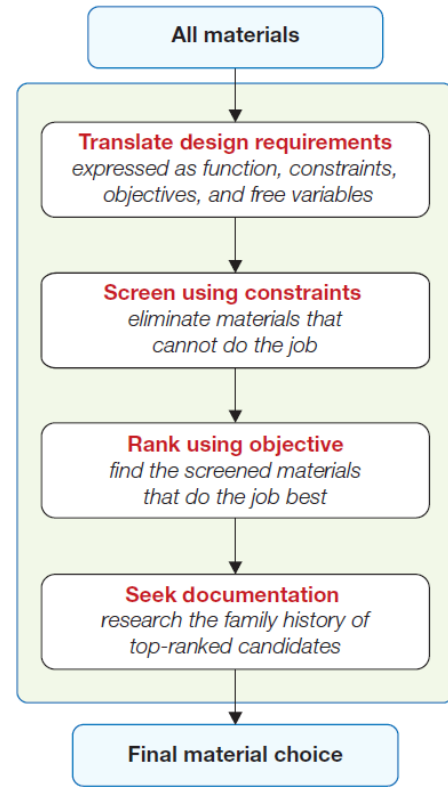


Figure 3.23 The strategy for materials selection. The four main steps—translation, screening, ranking, and documentation—are shown here [51].

Table 3.17 Design requirements for a light, stiff beam, minimizing the environmental impact.

Function	Beam
Constraints	Length L is specified (geometric constraint) Section shape circular (geometric constraint) Beam must support bending load F without deflecting too much, meaning that bending stiffness S is specified as S^* (functional constraint)
Objective	Minimize the embodied energy at production H_p
Free variables	Cross-section area A Choice of material

The embodied energy of the material is expressed : H_p [MJ/kg]. The objective function for the material embodied energy is

$$H_{pm} = mH_p \quad (3.3)$$

The mass m of the cylinder can be written as

$$m = \pi r^2 L \rho \quad (3.4)$$

Where r is the radius of the beam and ρ is the density of the material. The bending stiffness S of the beam must be at least S^* :

$$S = \frac{CEI}{L^3} \geq S^* \quad (3.5)$$

Where C is a constant depending on the bending mode and E is the Young's modulus. The second moment I for a cylindrical shape is

$$I = \frac{\pi}{4} r^4 \quad (3.6)$$

Then,

$$S^* = \frac{CE\pi}{4L^3} \left(\frac{H_{pm}}{\pi L \rho H_p} \right)^2 \quad (3.7)$$

It gives finally

$$H_{pm} = 2\pi L^2 \left(\frac{S^* L}{C\pi} \right)^{1/2} \left(\frac{\rho H_p}{E^{1/2}} \right) \quad (3.8)$$

The quantities of S^* , L and C are all specified or constant. The best materials for a light, stiff and environmentally friendly beam are those with the lowest values of index M where

$$M = \frac{\rho H_p}{E^{1/2}} \quad (3.9)$$

or with the highest values of M^{-1} .

The axes of the selection chart are thus the Young's modulus versus the embodied energy per cubic meter. Figure 3.24 shows the chart with all the existing materials. The material that interest us most are in the upper left part of the chart. Here we can see stone or concrete that are very well placed in terms of Young's modulus and embodied energy per cubic meter. But these materials don't respect some constraints that we imposed. This brings us to the next steps of Ashby's approach : screening, ranking and documentation.

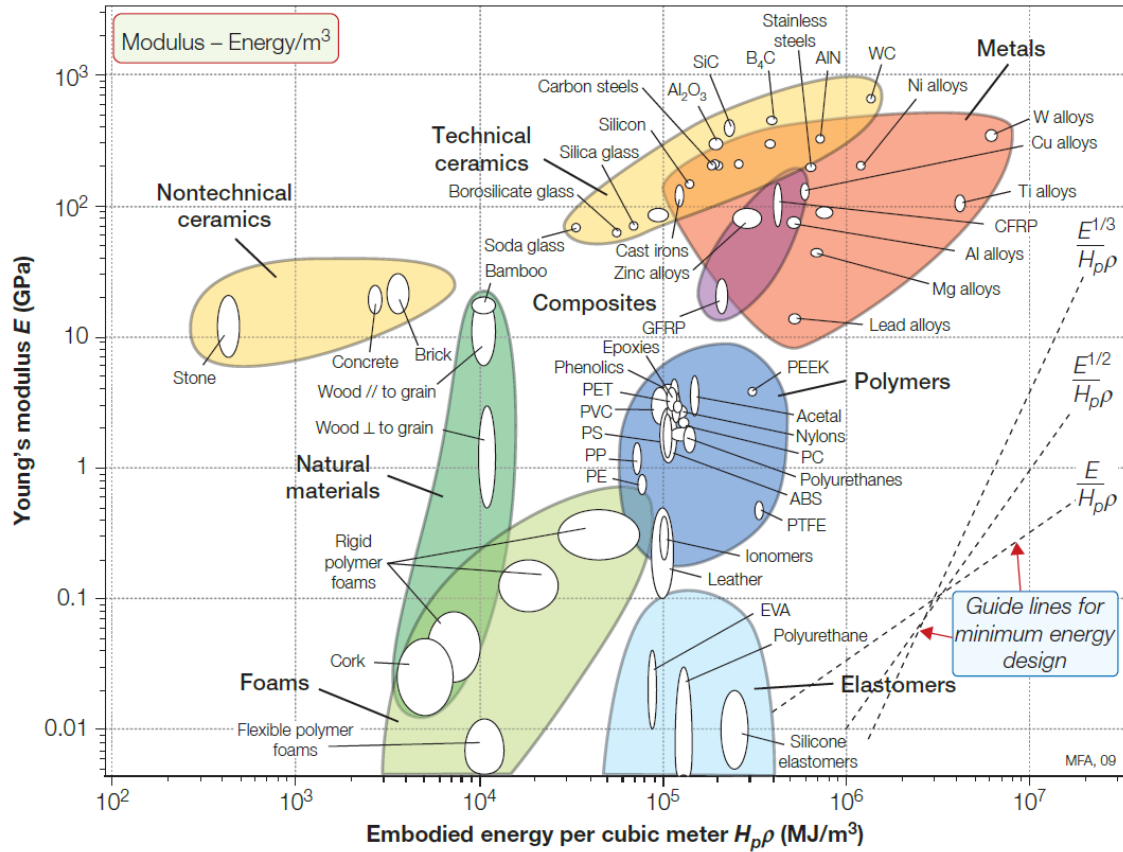


Figure 3.24 A selection chart for stiffness with minimum production energy [51].

Further limits were imposed to keep only sensitive materials in the chart. With a minimum yield strength of 30 MPa and a minimum fracture toughness of 2 MPa.m^{1/2}. The selection chart after screening is shown on Figure 3.25. The dash line M is for the performance index. We can see that woods and biological materials are have the best critters.

Banana fiber composite from recycled PET was added to the chart. It can be seen by the yellow dot. The different data used to place this material in the chart is given in Table 3.18. The values of embodied energies were available on EduPack [80].

Table 3.18 Banana fiber composite embodied energies, densities and Young's modulus.

y-axis	$E_{composite}$	[GPa]	4.7
	ρ_{BF}	[g/cm ³]	1.3
	ρ_{PET}	[g/cm ³]	1.3
	$\rho_{composite}$	[g/cm ³]	1.3
	H_{p-BF}	[MJ/kg]	2
	H_{p-RPET}	[MJ/kg]	27.5
	$H_{p-composite}$	[MJ/kg]	22.4
x-axis	$H_{p-composite} \cdot \rho_{composite}$	[MJ/m ³]	$29.12 \cdot 10^3$

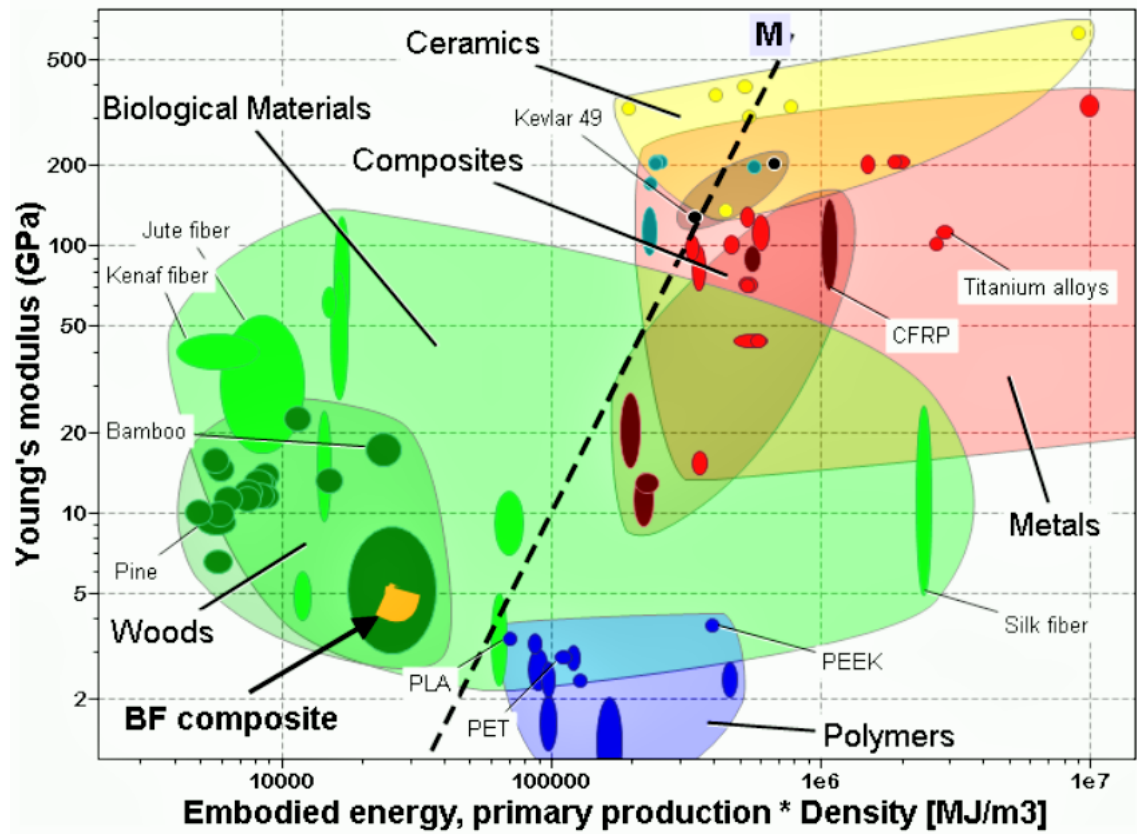


Figure 3.25 Selection chart for stiffness with minimum production energy after screening.

Finally, we can conclude from this study of material selection that our composite is well placed compared to other composites and is found among natural type elements such as wood. Some types of wood such as bamboo or pine are better suited for the application we have defined as an example above. However, there are still materials that cannot fulfill the task of the beam, such as jute or kenaf fibers that cannot be shaped in a beam form. Concrete and stone had an optimal position in the chart but were unfortunately eliminated when imposing toughness and yield stress conditions. To go deeper, there may have an application for which the BF composite stands in better position than all the other materials.

Chapter 4

Conclusion and Perspectives

The design of an environmentally friendly composite was based on recycled PET and banana fibers. PET modification simulated the starting point with recycled PET. It was further modified to lower the melting point and avoid degradation of banana fibers during processing. First, PET was depolymerised by glycolysis using 1,3-PD to reduce the molecular weight. This was followed by a repolymerisation with a chain extender made of 1,3-PD and SA which allowed to reduce the melting temperature and crystallinity while increasing the molar mass or the intrinsic viscosity. A solid state polymerisation (SSP) step was then applied to further increase the molar mass.

Next to this, influence of tetraglycidyl 4,4 diaminodiphenyl methane epoxy (TGDDM) as crosslinker was studied in the modification of the co-polyester saturated (CoPS3). The results show that the addition of TGDDM slightly increases the molar mass and the intrinsic viscosity. However, a higher concentration of TGDDM does not further increase the molar mass as expected. It may rather react with small chains to make a branching structure or react with water molecules and gender degradation by transesterification. Chain extension compensate the degradation caused and the overall molar mass is increased from 19 to 27 kg/mol. It is observed that TGDDM increases the crystalline fraction of CoPS3 and the composite.

Moreover, the influence of reaction time of TGDDM in the DSM extruder shows that it is not correlated to the molar mass. After 10 minutes in the extruder, TGDDM has already reacted with the matrix, proving that the reaction kinetics of TGDDM is high.

Banana fibers (BF) were treated with caustic soda (NaOH) and succinic anhydride (SA). The influence of these treatments on BF and on the behavior of the composite were studied. Alkaline treatment of the fiber increases the thermal stability by 20°C compared to untreated fiber. The composite was loaded with 5, 10 and 20wt.% alkaline treated BF. This percentage increases the mechanical properties such as young's modulus and yield stress. As soon as the fiber is added, the material becomes brittle where it was very ductile without fibers. Indeed, CoPS3 neat has a strain at break exceeding 110%. The highest Young's modulus is observed for 20wt.% BF, and has a value of 4.75 GPa, and this sample has also the highest yield stress equal to 48 MPa. The law of mixtures also teaches us that in our case the deformation is well distributed between the fibers and the matrix, which leads to be closer to Voigt's upper model than to Reuss model. Thermal stability of

the composite reaches temperatures of 300°C for the 20wt.% BF composite and is expected to be higher for lower fiber content.

Acid treatment of fibers was done in different concentrations of SA corresponding to 2, 4 and 6wt.%. The post acid-treated fibers must be cleaned to avoid residues on the fiber surface. These acid residues react with the CoPS3 matrix and completely degrade the mechanical properties, making the matrix brittle. Indeed, for a composite of 20wt.% BF, the highest yield stress is 26 MPa.

Finally, the influence of temperature ranging 60 to 110°C on annealing was studied on the 20wt.% alkaline treated BF composite. It shows that the degree of crystallisation increases from temperatures of 90°C and is the highest for 110°C. This proves that the crystallin fraction can be increased by 20 minutes annealing and improve mechanical properties.

The techniques used for the characterisation are the Ubbelohde viscometer to determine the molar weights, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) for thermal characterization, tensile tests for the mechanical analysis, dynamic mechanical analysis (DMA) for thermomechanical characterization, and at last, scanning electron microscopy (SEM) for morphologic characterization.

Finally, these results allowed us to place the material in a chart and compare it to other materials. The comparison is done to judge if the material could be useful or not. The case of a light, stiff beam was chosen as an example. The objective was minimizing the energy in production and our composite was in the area of the best materials. In the same area were natural elements and woods such as bamboo and pine.

To go further in this research, several prospects could be interesting to study.

- The addition of TGDDM as a chain extender did not initially work as expected. The study of the different proportions of extender added to the polymer was done before studying the reaction conditions of TGDDM with the thermoplastic chain ends. FTIR characterisation on the samples should have been done to ensure the reaction of TGDDM.
- The acid treated fibers should be washed after the treatment with SA. In these conditions, the composite with these acid treated fibers could have had better mechanical properties than the one with alkaline treated fibers. Moreover, the acid treatment of the fibers can replace the alkaline treatment directly, instead of further treating the alkaline treated fibers. This is even more environmentally friendly.
- A good evolution of the mechanical properties is observed with the increase of BF loading. Therefore, the loading content of BF could have been studied in higher concentrations of fibers. A study shows that the optimum properties are reached for a percentage of 40 [79].

- The influence of annealing temperature was done up to 110°C without going beyond. However, the results show an increase in crystallinity. It could be interesting to study the effect of annealing at temperatures in the range of 110 to 140°C and to study the influence of other annealing time. The parameters influencing the crystallinity in annealing are the nucleation temperature T_{Nu} and time t_{Nu} , the growing temperature T_{grow} and time t_{grow} .

Appendix

1. Illustration of the laboratories experiments



Figure 4.1 Banana fibers in the collecting part of the crushing machine.



Figure 4.2 Alkaline treatment of BF setup.



Figure 4.3 Depolymerisation setup with a condensation setup to keep the volatile reactant in the nitrogen gas and a system of water condensation mixture.



Figure 4.4 Repolymerisation setup under a flux of nitrogen gas and a system of water condensation mixture beside.

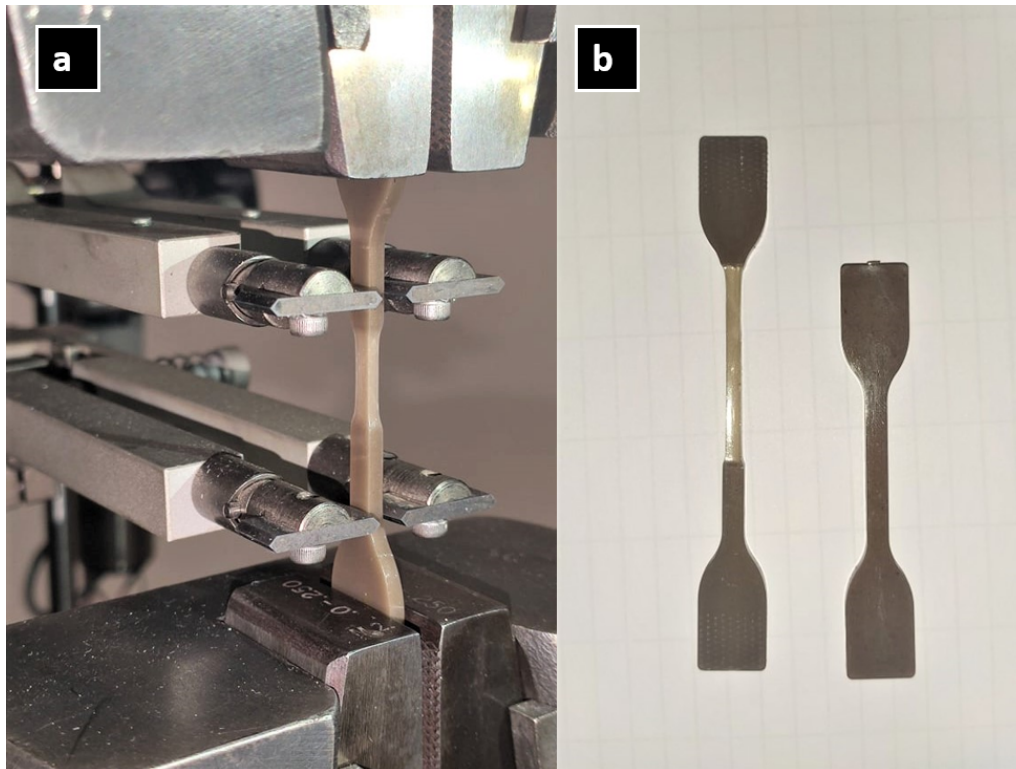


Figure 4.5 Necking phenomenon of a modified PET sample without fibers : (a) specimen during the tensile test, (b) comparative of a specimen tested and untested where the necking phenomenon is clearly visible.



Figure 4.6 Composite sample of CoPS/BF 80/20wt.%. BF alkaline treated.

2. Additional results

TGA were also performed on treated fibers at 180 °C for 50 minutes. Figure 4.7 shows the curves obtained for BF with different treatment. At this temperature, the degradation is only observed for the BF after acid treatment. This degradation is due to the residue of acid because the fibers have not been washed.

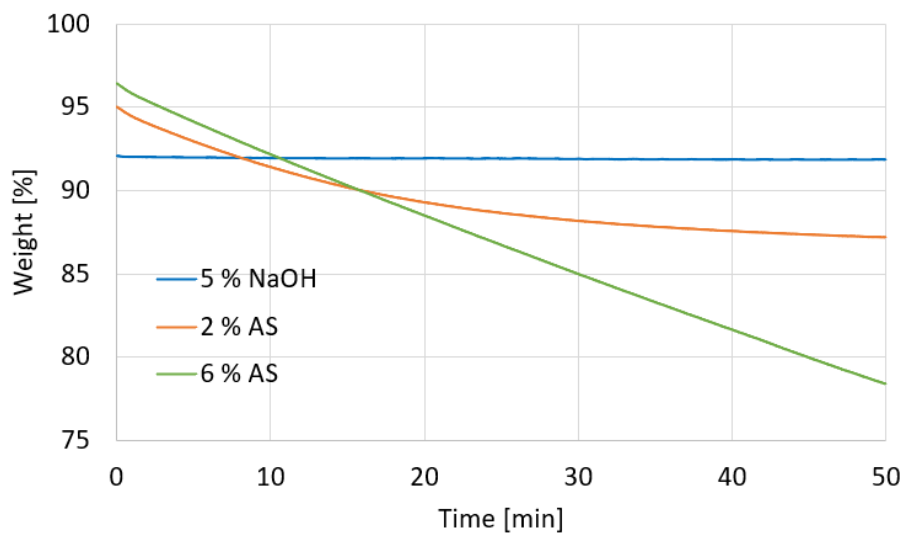


Figure 4.7 TGA curves of BF after alkaline treatment and different acid treatment concentration (during an isothermal segment at 180° for 50 min).

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