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Development and characterization of a new composite material based on polyvinyl chloride and common reed flour

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Abstract

The objective of this work is to develop and characterize a composite material with a polyvinyl chloride matrix and filler of plant origin, common reed flour. The filler is obtained by grinding and sieving. The composites were prepared on a two-roll mixer. Filler contents of up to 30% by weight were added in order to study the effect of this plant powder on the mechanical properties in tensile, water absorption and morphology. The results obtained from the characterizations carried out show that the PVC matrix becomes more rigid but not resistant due to the absence of adhesion between the PVC and the plant filler. PVC which contains plant powder absorbs more water than pure PVC. The dispersion of the filler within the matrix is influenced by the difference in nature between the two phases of the composites.

Keywords: *Biocomposite, plant filler, polymer matrix, PVC, common reed.*

I. Introduction

Polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyvinylchloride (PVC) are thermoplastic materials that have good thermal, mechanical and lightness properties. They are widely used in several applications, particularly in the agricultural, biomedical and food processing/packaging industries.

The waste of these plastic materials has become a big problem for nature and for living beings. Bags and packaging products made of plastics cause a source of environmental pollution due to their stability and its resistance to degradation which can last for years under severe climatic and natural conditions. However, the disposal of solid waste, especially non-biodegradable synthetic polymers, poses serious environmental problems, caused by the emergence of a large number of plastic industries around the world [1].

Various approaches have been undertaken for post-consumer recycling of plastic waste considering the economic and environmental challenge [2,3], but the deterioration of mechanical and physical properties due to peroxidation [4] have limited to a large extent the recycling process

In recent times, the awareness of populations and authorities regarding these environmental problems has strongly encouraged the development of a new concept called "eco" or "organic" which consists of developing materials from resources renewable (from biomass) with the aim of preserving the environment and better managing natural resources. Thus new materials called ecomaterials, biocomposites or eco-designed have emerged [5].

It is with this in mind that the use of renewable resources in plastic materials is becoming more and more common these days, and markets are increasingly geared towards a demand for more environmentally friendly products. To develop and improve them, research is carried out in numerous laboratories internationally. These materials, called eco-materials, bio-composites, wood-polymer composite materials, etc. have taken on importance in various developed and developing societies. The technical advantages of using lignocelulosic materials such as esparto, sisal, cotton, etc. in polymeric materials offers several technical-economic advantages: low cost, low density, high toughness, mechanical strength properties, increased energy recovery and biodegradability [6]. In Algeria several natural fibers are found in abundance. Their harvests and industrialization are a considerable source of income for entire populations. One of the local plant fibers in our region is the common reed. This fiber is interesting from an economic point of view, because of its abundance and availability. Common reed (Phragmites australis (Cav.) Trin. ex Steud.) is growing in several regions of the Netherlands, mostly in nature conservation areas, which are managed by Natuurmonumenten [7]

PVC is commonly used in plastics, pipes, electric wires, window profiles, siding due to its acceptable mechanical properties, fire, moisture & fungus resistant and long lifetime PVC produced from cracking of petroleum or natural gas have a randomly distributed Mw and some degree of viscosity. Additives with PVC can control its physical, thermal, mechanical properties and also improve processability, weathering resistance, colour, cost performance and electrical properties [8].

The general objective of this work is to highlight this plant in the development of a composite material based on PVC and the flour of the latter, then characterize it by physical properties: water absorption, mechanical tensile test and morphological test (optical microscopy).

II. Material and methods

PVC type 3000H is obtained from the calendering company “CALPLAST” in Sétif, Algeria

The added plasticizer is dioctylphthalate (DOP). The industrial grade thermal stabilizer used is a mixture of epoxidized soybean oil (HSE 100S) and NEW STAB 26, and stearic acid as a lubricant. The vegetable filler used is common reed flour (CRF). Common reed flour obtained after sieving having an average particle diameter equal to 180µm.

II.1. Preparation of composites

Films of polyvinyl chloride/common reed flour (PVC/CRF) composites with a thickness of 0.5 mm were prepared using an OFFICINA MECCANICA E FONDERIA RODOLFO COMERIO brand two-roll mixer. The temperature is maintained at 160°C for a mixing time of 15 minutes.

The proportions of the PVC/CRF mixtures used respectively are: 100/0, 90/10, 80/20, 70/30.

II.2. Caracterization

The composite materials prepared were characterized by several techniques, such as the study of tensile properties, the measurement of the water absorption rate, the analysis of the morphology by the optical microscope.

The samples intended for mechanical characterization (tensile test) were cut from the sheets obtained from the two-cylinder mixer, these specimens are tested according to the ASTM D638-72 standard on a Zwick/Roell brand machine with an elongation speed equal to 25mm/min.

Observation of the morphology is carried out on an Optika HC 4*0.1160/0.17 optical microscope.

The water absorption test is carried out as follows:

the samples were dried in an oven at 60°C for 4 hours, then cooled in a desiccator and weighed immediately (m_0).

The samples were then immersed in distilled water at 25°C. Periodic samples every 24 hours were taken, the water on the surface of the sample was absorbed with absorbent paper and the samples were weighed again (m_1). The water absorption rate in (%) was calculated by the following formula:

$$\mathbf{TH} = (\mathbf{m_1} - \mathbf{m_0}) \,/\, \mathbf{m_0} * \mathbf{100} \text{.........}(1)$$

m_0: the mass of the sample before immersion
m_1: the mass of the sample after immersion

III. Results and discussion

III.1. water absorption rate

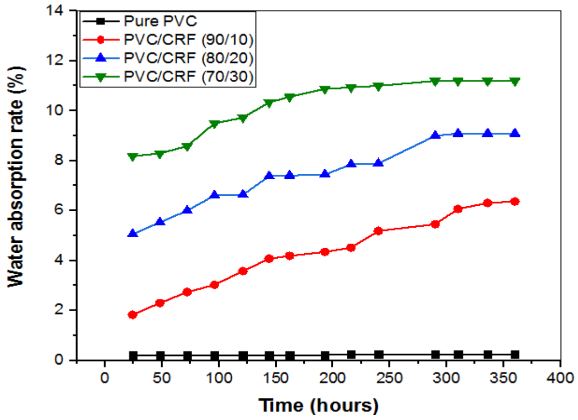

Figure 1: The evolution of the water adsorption rate of PVC/CRF composites as a function of immersion time at different loading rates

Figure 1 represents the variation in the water adsorption rate of PVC/CRF composites as a function of the immersion time in water and the concentration of the filler.

From the figure we can clearly see an increase in the water absorption rate with immersion time and the rate of common reed flour, which is entirely expected, due to the fact that reed flour common is highly rich in hydroxyl groups, the latter form hydrogen bonds with water molecules, so the higher the flour content, the greater the OH concentration and consequently the absorption rate becomes greater. In the case of pure PVC, water absorption is almost zero, this is due to the nature of the polymer which is hydrophobic. The results found in this test are similar to those found in other works [9]

III.2. morphological characterization

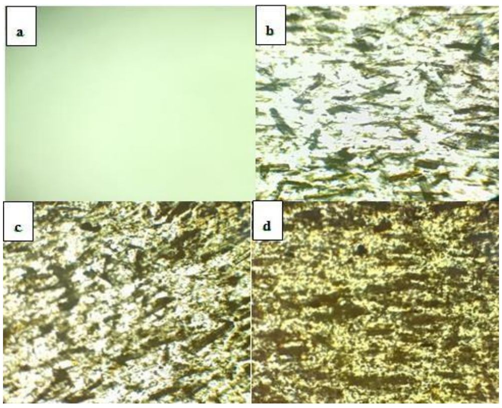

Figure 2 : Photos representing the morphologies of the materials: (a): pure PVC, (b) PVC/CRF (90/10), (c): PVC/CRF (80/20), (d): PVC/CRF (70/30)

Figure 2 represents the morphologies of the PVC/CRF composites as a function of the loading rate. The micrograph of pure PVC (a) presents a single phase, on the other hand those of PVC reinforced by the filler (b, c and d) show the appearance of a second phase corresponding to the particles of the filler dispersed in the matrix. A phenomenon of agglomeration of common reed flour is observed in the images of the formulations containing the filler. This phenomenon was explained by the poor dispersion of the hydrophilic charge in the hydrophobic matrix. Micrographs of the filler-reinforced composites show more agglomerate formation with increasing filler rate.

III.3. Tensile test

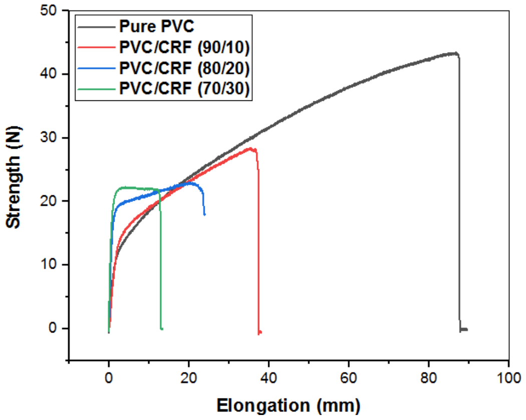

Figure 3 : Curves of variation of strength of PVC/CRF composites as a function of elongation

Figure 3 represents the tensile curves: variation of strength as a function of elongation of PVC/CRF composites at different load rates. From these curves, we calculated parameters such as the modulus of elasticity, the stress at break and the strain at break and we studied the effect of the load rate on these parameters.

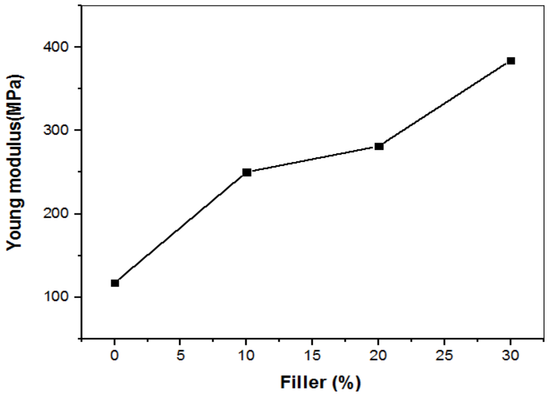

Figure 4 : Variation of the Young modulus of PVC/CRF composites as a function of the loading rate

Figure 4 shows the variation in the Young modulus of PVC/CRF composites as a function of the loading rate. It is observed that the modulus of elasticity increases with the increase in loading rate, this is due to the increase in the rigidity of the matrix: polyvinyl chloride by the addition of rigid plant particles. Common reed flour contains biopolymers which have high crystallinity and therefore rigid behavior. The increase in the rigidity of PVC is also observed in the case of the introduction of wood flour into the PVC [10].

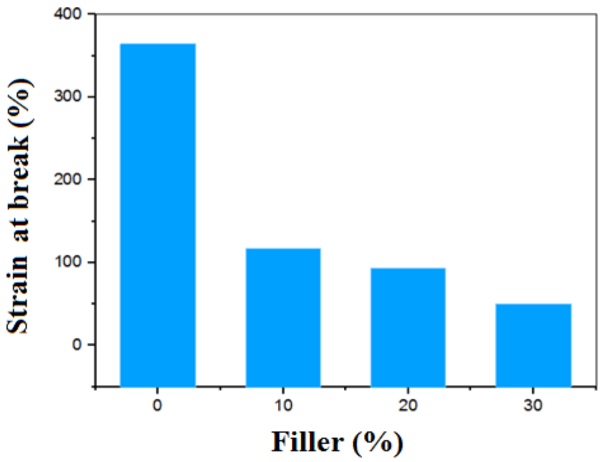

Figure 5 : Variation of the strain at break of PVC/CRF composites as a function of the load rate.

Figure 5 shows the variation in the strain at break of PVC/CRF composites as a function of the load rate. From the figure we observe that the breaking strain of PVC decreases as a function of load rate. This reduction can be explained by the change in the mechanical behavior of the PVC matrix from a flexible behavior to a rigid behavior which resists deformation (less deformation). This is always due to the presence of a rigid plant powder within the matrix and this is confirmed by the values of the modulus of elasticity. The tensile results are similar to those found in a study of composites based on polyvinyl chloride reinforced with palm fibers [11].

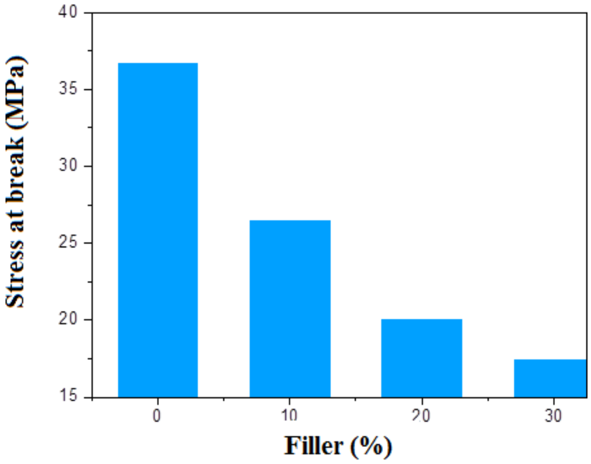

Figure 6 : Variation of the breaking stress of PVC/FRC composites as a function of load rate

Figure 6 shows the variation in the breaking stress of PVC/CRF composites as a function of the loading rate. From the histograms we notice that the results obtained show that this mechanical property tends to decrease depending on the flour content compared to pure PVC.

This reduction is due to the fact that the particles have a hydrophilic character and the PVC is hydrophobic, which leads to water absorption and to the incompatibility that exists between the matrix and the plant filler.

IV. Conclusions

The various tests and analyzes carried out on the prepared materials showed that:

The water absorption rate of the composites increases depending on the charge rate in the PVC matrix, this confirms that the common reed is a hydrophilic plant

The study of the mechanical properties of the composites produced shows that:

The addition of common reed flour changed the mechanical behavior of the plasticized PVC from a flexible material to a rigid material which tends to become fragile with the increase in the loading rate. This result is confirmed by the reduction in deformation.

Examining the morphology of the different composites allowed us to conclude that:

The dispersion of common reed flour in the PVC matrix is affected by the presence of humidity between the particles of the filler (formation of agglomerates) as well as the absence of interfacial adhesion between the two phases, This is confirmed by the reduction in the breaking stress of the composites.

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Green composites: A review of materials and perception

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Abstract

The purpose of manufacturing a composite material is to take advantage of the recognized properties of each component in order to build one that will be better suited to certain applications. A composite is a material that tries to combine the properties of its components (generally a polymer matrix and reinforcement) to improve certain characteristics such as breaking strength, or rigidity, for composites for mechanical uses.

Previously, composite materials were most often thermoplastic or thermosetting matrices reinforced with carbon fibers, glass ... However, in recent years, composite materials reinforced with natural fibers have attracted the attention of researchers because they could be an effective solution to solve the problems of environment, biodegradability and oil depletion. This review paper is mostly an introduction to the description of composite materials with vegetable reinforcements.

Keywords: *Biocomposite, Biodegradables, Biopolymers, Interface treatments, Lignocellulosic biomass,*

I. Introduction

Every second on earth, an area of forest equivalent to 19 tennis courts disappears; the desert increases by 78 m^2 in China, 1600 t of ice melts in Greenland and 720t of CO_2 are emitted from oil into the atmosphere [1]. These figures show that it is crucial to take into account the effects of human activities on the environment. It is in this context that eco-materials are being developed and that the term sustainable development is increasingly mentioned. This notion of sustainable development requires consideration of environmental issues.

Biodegradable polymers (biopolymers), which have been the subject of much research, appear to be an increasingly credible alternative to address environmental concerns. Biopolymers are divided into two classes: agro-polymers, such as starch, proteins, etc., and biopolyesters (PHA, PLA, etc.). However, while bioplastics have seen extensive growth in applications such as disposable packaging films, they still lack the mechanical properties to be used in applications such as those found in the automotive industry [2].

The current obstacles that face the use of PLA are its properties which are still considered too weak for them to be able to definitively replace petroleum-based polymers and which are mainly their resilience, their water resistance as well as the cost. Often considered too high. In order to overcome these shortcomings, it is therefore necessary to seek solutions which make it possible to improve the various properties of these biopolymers, either by incorporating natural reinforcement, thus allowing the development of composites. [3].

These composites are characterized by two main aspects, economic and technical. Composites are materials with high technical performance with interesting physical and mechanical properties for relatively easy manufacturing and implementation. Over the past decade, the vision of industrial development has changed direction by integrating the environmental aspect into the search for innovative materials. The objective of technical performance having been achieved and in view of the question rose today concerning the environment and the impact of the evolution of man on his environment; a new problem arises, namely, can man continue to evolve while being in adequacy with the environment in which he lives? To answer this problem, researchers and industrialists have sought to use plant resources for the production of new materials. Today, agro-materials or bio-sourced materials partly meet this need [4].

For the reinforcement of polymers, plant fibers have important specific mechanical properties (at least for some of them) and many advantages if we are interested in environmental impacts. These are renewable resources, naturally biodegradable, neutral in terms of CO_2 emissions into the atmosphere and requiring little energy to produce.

These fibers can replace glass fibers in many areas or make it possible to reach new markets [5]. Currently, food waste is a major concern for businesses, governments and consumers. One of the largest sources of food waste occurs during industrial processing, where substantial by-products are generated. Fruit processing creates many of these by-products, from undesirables to fruit skins, seeds, and fleshy parts. These by-products make up to 30% of the initial mass of processed fruit. Millions of tons of fruit waste are generated worldwide from spoilage and industrial by-products, so finding alternative uses for fruit waste is essential to increasing their values. This goal can be achieved by transforming fruit waste into reinforcement and integrating it into polymeric materials [6].

Many research works have been carried out to modify and improve the properties of polymers, by adding reinforcements of plant origin to form composites [7].

This present review towards a description of biocomposite materials with vegetable reinforcements, and situate the context of development and use of these products. Knowledge of the structure and chemical composition of each of the constituents is necessary to understand the study of the interactions between the reinforcing fibers and the matrices.

II. Biocomposites

Biocomposite is the general term for composite materials that are entirely or to a large extent produced from biomass: natural fibers are combined with petrochemical or biological polymers to achieve very good, often well-matched, mechanical properties.

Other, bio-composites is the combination of bio-sourced or petro-sourced matrix with natural fibers. The most common types are wood-plastic composites and natural fiber composites [6].

III. Biopolymers matrix

Biodegradable polymers are sustainable polymers synthesized from renewable resources such as biomass instead of the conventional fossil resources such as petroleum oil and natural gas, preferably based on biological and biochemical processes.

They are characterized by the nature of carbon neutral or carbon offset in which the atmospheric CO_2 concentration does not increase even after their incineration [6,7].

III.1. Classification of biodegradable polymers

Biodegradable polymers and biopolymers can be produced from renewable and fossil resources. Briefly, there are 3 main types of materials, which are called bio-polymers: those of natural origin, artificial ones and their composites [8,9].

- Materials of natural origin are those synthesized by living beings: animals, plants and micro-organisms. We find:

The family of polysaccharides (carbohydrates) such as starch, cellulose, lignin, chitin, the family of proteins such as gluten, casein, collagen and gelatin, and the family of lipids; rapeseed, soybean, sunflower oils To this family, we could include carbonaceous elastomers such as natural rubber [10,11].

Polymers of bacterial origin resulting from the fermentation of sugars and starch by bacteria or produced by genetically modified micro-organisms (biotechnology). Depending on the bacteria, various polymers are obtained such as PHA, [10,11].

Biosynthetic polymers, whose monomer from biomass are obtained by fermentation. The polycondensation of these bio-monomers gives polyesters; the best known is poly (lactic) acid PLA [10,11].

A new generation of polymers from renewable resources but this time non-biodegradable; traditional bio-based polymers such as PE, PET, PA, [10,11].

- Biodegradable materials from petroleum resources obtained by industrial synthesis processes. The best known are PBS (poly butylene succinate), PBAT (poly butylene adipate terephthalate), and PCL (poly caprolactone) [10,11].

On the other hand, there are traditional polymers of fossil origin such as PE or PET to which an additive is added which promotes its biodegradability. The end of life of these materials results in a biodegradation of the additives and in a physical (visual) degradation without molecular disintegration of the synthetic elements [10,11].

Table 1: General classification of polymers [10-12].

	Not Bio-sourced	**Bio-sourced**
Biodegradable	**Bio-polyesters** from conventional chemical synthesis: Polycaprolactone PCL, Polyester amide PEA, co-polyester: PBSA, PBAT, etc…	**Agro-polymers** polysaccharides: starch, cellulose; gelatine, casein, gluten… **Bio-polyesters from microorganisms:** PHAs, **Bio-polyesters synthesized from renewable monomers**:

		PLA…
Not Biodegradable	**Traditional polymers** PE, PET, …	**Traditional polymers** from synthase of renewable origin, PE …

IV. Lignocellulosic biomass reinforcement

Lignocellulosic biomass is the most abundantly available form of terrestrial biomass on Earth, with an estimated 181.5 billion tonnes generated annually, among which about 7 billion tonnes are produced from dedicated agricultural, grass and forest land and another 1.2 billion tonnes stem from agricultural residues [13].

Thus, lignocellulosic biomass represents an immense, inexpensive and renewable resource for the production of biofuels, bio-based chemicals and materials. It includes mainly crop residues (cane bagasse, rice straw, rice hulls, corn Stover, corn stalk, wheat straw, barley straw and pulp), organic wastes (waste newsprint, recycled paper, pulp/paper mill sludge), woody biomass (e.g., aspen and poplar, pine and spruce and forestry residues), herbaceous biomass (coastal Bermuda grass, switchgrass, reed canary grass and timothy grass) and organic fraction of municipal solid wastes [30].

Interest in lignocellulosic biomass reinforced polymer composite materials is rapidly increasing both in terms of industrial applications and basic research. Their availability, renewability, inexpensively, biodegradable, low density and as well as satisfactory mechanical properties make them an attractive ecological alternative to glass, carbon and synthetic fibers used for the manufacture of composites [14].

IV.1. Chemical composition of lignocellulosic biomass

Lignocellulosic biomass is composed of three main biopolymers: cellulose, hemicellulose and lignin [15-17].

In a much lower proportion they also contain extractables, proteins and certain inorganic compounds [18].

➢ Cellulose

Cellulose is the most abundantly synthesized biopolymer by the plant kingdom on the planet. This parietal polysaccharide represents 40% of all terrestrial organic matter. Its molecular structure, widely studied, allows its supramolecular organization, based on the formation of hydrogen bonds in large numbers. This supramolecular organization defines crystalline zones and amorphous zones in the assembly, in variable proportions depending on the origin and the treatment imposed on the raw material. It nevertheless makes it possible to consider cellulose as a semi-crystalline biopolymer [19].

Cellulose is made up of a sequence of gluçopyranose cycles with a glycosidic bond of the β 1-4 type. The degree of polymerization (DP) varies according to the plant species. It is for example 10000 for cotton, 9000 for hemp, flax and ramie. However, the glass transition temperature of amorphous cellulose, which would be above 200°C, cannot be assessed with precision because cellulose degrades thermally from 180°C.

The melting temperature of the crystalline zones is not accessible because it is located beyond the degradation temperature [20, 22].

➢ Hemicelluloses

Hemicelluloses are by definition polysaccharides that are soluble in water and can be extracted from the wall of plant cells by alkaline solutions. They are amorphous polysaccharides, with a molecular mass lower than that of cellulose. They are composed of neutral sugars: xylose, arabinose, galactose, glucose, mannose, and uronic acids. In their natural state, they have a degree of polymerization between 200 and 300 and their structure depends on the plant species [23].

➢ Lignin

Lignin is after cellulose the most abundant renewable organic material on the surface of the earth. Lignin is three-dimensional polymers resulting from the radical polymerization of three phenylpropenic alcohols whose structure depends on the plant species: coumaric alcohol, coniferyl alcohol and sinapyl alcohol [24].

IV.2. Advantages of using natural fibers

In general, the use of natural fibers as reinforcements for composite materials is justified for:

- Develop materials and technologies that take into account the impact on the environment. Natural fibers are biodegradable and renewable materials.
- Promote a local resource in industrialized or less industrialized countries. Natural fiber composites open up new outlets for agricultural products.

The choice of fibers coming from a natural environment and presenting interesting mechanical performances is guided by:

- Their origin and function.
- Their availability: a natural fiber is considered available if the volume of fibers present on the market is sufficient to produce industrial parts. Its production is linked to outlets.

- Their often complex composition and structure. Although composite materials are often presented as original and innovative, the natural environment already offers a wide range of them. A multitude of natural materials, some rigid but light, such as walnut shells, and others flexible but resistant, such as wood, owe their mechanical properties to their composite structure [25,26].

V. Surface modification

The hydrophilic nature of natural fibers comes from lignocellulose which contains many polar hydroxyl groups. These fibers are therefore intrinsically incompatible with hydrophobic thermoplastics.

The main limits of use of these fibers, such as Reinforcement in such matrices leads to poor fiber-matrix interfacial adhesion, and the difficulty in mixing is mainly due to the low wettability of the fibers with the matrix which would lead to low interface composites [27, 28-31].

According to the literature, many attempts have been made in modifying the fiber-matrix interfacial characteristic, due to incompatibility between the two phases [28-31]. Among these various methods of modification, chemical treatment is mentioned.

These chemical modifications call upon interface agents. Indeed, the interface plays a preponderant role in the behavior of the composite when it is subjected to constraints. The interface agent ensures reinforcement/matrix compatibility by transmitting the stresses on either side of the interface, without relative displacement. Several essential roles are assigned to the interfaces for a good behavior of the composite:

- Ensure physical continuity from one component to another through all materials, preventing, for example, the formation of porosity.
- Transmit effort. Indeed, the matrix distributes and transmits the forces to the fibers via the interfaces [32].

The most widely used technique is alkaline treatment [33-36]. The alkalization process affects the natural fibers and brings a clear performance with respect to the quality of fiber-matrix adhesion. This treatment increases the fiber/resin contact surface. Some authors advocate that this improvement is due to the elimination of non-cellulose compounds (cuticle layers oils, oils and dirt) from the surface. Thus, it leads to an improvement of the interfacial bond between the fiber and the matrix [37,38]. Alkaline treatment is often practiced to extract residual lignin, hemicellulose, and to remove natural and artificial impurities. It also promotes fibrillation of the bundles [39,40]. The concentration of the alkali, the temperature and the treatment time of the fibers are essential parameters of the treatment process. The optimization of these parameters contributes to the improvement of the mechanical properties of the composite material [41].

Zafar et al. [42] reported jute fiber and poly lactic acid biocomposites obtained by treated as well as in treated NaOH solution using a twin-screw extruder and found different effects of treatment of jute fiber at FTIR and stated the formation of hydrogen bonds. Polarized light optical microscopy pictures clearly intimated there is an improvement in trans crystallinity at the matrix fiber interface. In the scanning electron microscopy the images showed the matrix covered fiber surfaces when composites combined with surface-treated jute fibers. They mentioned that untreated jute fiber in PLA Tensile and modulus strength has been improved.

Jayabal et al. [43] reported the tensile, flexural and impact properties of a woven coir polyester composites when the surface is treated by the alkali solution. He mentioned with the help of scanning electron microscopy (SEM) images that the coir fiber treated with the alkali solution have improved the tensile, flexural and impact properties when compared with the raw and untreated coir fiber.

Siregar et al. [44] have studied the impact of alkali treatment on the mechanical properties of short Pineapple Leaf Fiber (PALF) reinforced High Impact phenyl ethylene (HIPS) composites. Where NaOH is employed as an alkali. The fibers were treated with completely different concentration of NaOH (0%, 2% and 4%) resolution. It was determined that adhesion of fiber/matrix is improved by treating the short PALF fibers with an alkali resolution before production of a composite.

VI. State of the art on composite materials

Natural fiber reinforced composites have received considerable attention in the research community. We can cite as examples the work carried out by certain researchers.

Kimura et al. [45] They examined compression-molded PLA composites reinforced with ramie fibres, using non-twisted commingled yarn made of ramie and PLA fibres as raw material. The best mechanical values, i.e. tensile strength, bending strength and stiffness, were obtained at ramie fiber volume content between 45% and 65%. Large proportions of ramie also increased the notched impact strength considerably.

A study of injection molded flax and man-made Cordenka fiber reinforced PLA was carried out by Bax and Müssig [46] The composites' mechanical qualities improved with a rising fiber mass content of 10 up to 30%. Flax/PLA and Cordenka/PLA composites clearly differed in their impact strength characteristics: While the impact strength of pure PLA could be multiplied by adding Cordenka, the values of flax/PLA composites were inferior to the pure matrix.

David et al [47] determined the mechanical properties of the PLA/jute fiber composites and showed that the tensile strength of composites was significantly higher than that of PLA. But the elongation at break of the composites is still very low as about 2%.

Ngo et al [48] focused on tensile and flexural properties of varied volume fraction of kenaf fiber; Vf (20, 40 and 60%) reinforced polymer composites. It is obtained, when increase in kenaf fiber, the tensile and flexural strength increased which is up to the maximum value and the properties were decreased at Vf of 40%. Further increase of fiber Vf at 60%, deteriorate occurs. The fibres tend to aggregate which weakens the interfacial area and debonding tends to take place between the fibres and matrix that at Vf greater than 50%.

Ochi et al. [49] studied the properties of kenaf fiber /PLA composites fabricated at a molding temperature of 160°C. The result showed that the flexural strength of the kenaf fiber reinforced composites increased linearly up to a fiber content of 50%. The biodegradability of kenaf/PLA composites was examined for four weeks using a garbage processing machine. The results have shown that the weight of composites decreased 38% after four weeks of fabrication.

Hammiche et al. [50] assessed the effects of the Alfa fiber content and the fiber surface treatment on the mechanical properties as well as the degradation of composites based on poly (hydroxybutyrate‐co‐valerate) (PHBV) in an aqueous medium. The idea behind is to develop eco-friendly composites by exploiting the use of natural fibers and PHBV biopolymer. Based on the obtained results, the main findings are summarized below: Morphological changes occurred on the fiber surface after chemical surface treatment.

Improvement of mechanical performance of composites reinforced with lignocellulosic fibers needs strong adhesion. Alkali treatment of alfa surface fibers enhances both of the tensile strength (by 4–16% according the percentage of alfa fibers) and the rigidity (by 7–25%) of PHBV/alfa composites. SEM micrographs highlighted differences in microstructure of untreated and treated composites confirming the enhancement of the quality of the fiber-matrix interface owing fiber surface-treatment. The treated composites were highly biodegradable compared to both neat PHBV and untreated composites. All elaborated composites undergo degradation more pronounced into seawater (compared to distilled water) that is wealthy in microbial populations indicating their environmentally friendly character.

Klaai et al. [51] reported the hydrolytic aging of biocomposites which were composed of Alfa fiber and Polylactic acid (PLA) prepared by extrusion. To improve the fiber/matrix compatibility, the Alfa fiber has been treated with a dispersing agent which is BYK W-980. Spectroscopic (FTIR), thermal and water absorption tests before and after hydrolytic aging of biocomposites have been studied and compared. The results revealed that PLA/Alfa biocomposites in the presence of BYK W-980 are more resistant to hydrolytic aging compared to untreated composites.

Klaai et al. [52] focused on tensile and thermal properties of prickly pear seed fibres as reinforcement in polylactic acid biocomposites.

The results show that the mechanical and the thermal properties of the biocomposites with treated fiber are better than that of neat PLA and the biocomposites with untreated fiber.

VII. Conclusions

This review has provided a concise summary of the major material attributes of green composites; description, Knowledge of the structure and chemical composition of each of the constituents.

Undoubtedly, environment-friendly, fully biodegradable reinforced plastics or ‘green’ composite materials will play a major role in greening the products of the future.

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Optimization and Formulation of Mixed Niosome/Cyclodextrin Encapsulation Process for Béjaia Propolis Extract

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Abstract

This study focuses on the preparation and optimization of a mixed cyclodextrin and niosomal suspension containing propolis extract from the Melbou region. The experimental design was utilized to determine the key parameters influencing encapsulation efficiency and particle size. The extraction yield of propolis was found to be 12.16%. The flavonoid content, specifically quercetin, was quantified using UV-visible analysis.

The optimal niosomal suspension exhibited an encapsulation efficiency of 34.81% and an average particle size of 557.283 nm, compared to 426.80 nm for the placebo. Thermogravimetric analysis (TGA) revealed enhanced thermal stability of the encapsulated extract, with significant improvement compared to the unencapsulated extract. The niosomal formulation delayed the onset of mass loss at 220°C, indicating effective preservation of volatile and bioactive components.

These findings suggest that niosomal encapsulation can enhance the stability and bioavailability of propolis extract, offering promising applications in pharmaceutical and nutraceutical formulations.

Keywords: *Natural product, propolis extract, niosomes, mixte encapsulation, cyclodextrins.*

I. Introduction

For millennia, bee products, particularly propolis, have been used by humans for their numerous beneficial properties such as antimicrobial, anti-inflammatory, antioxidant, and wound healing activities [1]. Propolis is a resinous substance collected by bees from the buds and bark of certain trees and mixed with their salivary secretions [2]. It exhibits a characteristic balsamic odor and a range of colors. Despite its recognized biological properties, the application of propolis is often limited by its poor solubility in aqueous media, reduced bioavailability, and chemical degradation [3].

To overcome these limitations, encapsulation by cyclodextrins [4, 5]or niosomes [6] are a promising strategy. Cyclodextrins (CDs), natural oligosaccharides, can encapsulate hydrophobic molecules, thus enhancing their solubility, stability, and bioavailability. Concurrently, niosomes are nanocarriers capable of loading both hydrophilic and lipophilic substances, making them particularly suitable for drug delivery [7].

Mixed encapsulation, combining the benefits of CDs and niosomes, represents an innovative approach to optimize the delivery of active compounds. This method aims to improve the protection and efficacy of propolis formulations [8, 9].

In fact, Machado et al.(2018) explored the interest of niosomes prepared from Span 80 and Tween 80 enhanced with β-cyclodextrin (β-CD) or modified amphiphilic β-CD (Mod-β-CD) to encapsulate methyl orange (MO) and methyl yellow (MY). This modification improved dye encapsulation efficiency and release rates, especially for MO, without significant changes in vesicle size and morphology [8].

Our study focuses on the optimization and characterization of the mixed niosome/cyclodextrin encapsulation of propolis extract from Bejaia region. To the best of our knowledge, this is the first time this technique has been applied to Algerian propolis. The originality of this work lies in the dual use of CDs and niosomes for shared encapsulation of the propolis extract. This dual encapsulation aims to offer superior protection and enhance the bioavailability of propolis.

II. Material and methods

II.1. Material

II.1.1. Chemicals

Quercetin, aluminum chloride ($AlCl_3$), Span 60 and cholesterol were purchased from Sigma-Aldrich;
Methanol and ethanol (Biochem Chemopharma)
Sodium nitrite ($NaNO_2$) (Biochem Chemopharma)
Sodium hydroxide (NaOH) (Biochem Chemopharma)
PM-βCD were obtained from Orsan (France). All reagents were of analytical grade.

II.1.2. Raw propolis

The raw propolis is collected in the region of Melbou (Bejaïa) Algeria with geographical coordinate: 36°38′23″, 5°21′39″, in the month of March 2024.

II.2. Methods

II.2.1.Propolis extraction

Ethanolic extracts of propolis (EEP) are obtained using an agitation method. The chosen parameters include the amount of propolis (33.33 g), duration (41 minutes), with the volume and temperature of the solvent fixed at 100 ml and 50 °C, respectively [10].

II.2.2. Preparation of niosomal solutions with optimal conditions using experimental design

To determine the optimal conditions for the encapsulation process, a Box-Behnken experimental design were carried out.

The factors were: cyclodextrin concentration (C CD) [3.333-30 mg/ml], Span concentration (C Sp) [20-60 mg/ml], and cholesterol concentration (C Ch) [5-20 mg/ml]. The responses studied were encapsulation efficiency (EE) and the size of the formed niosomes. This method enabled us to optimize the formulation, achieving the best encapsulation conditions for the propolis extract. The experimental matrix is presented in the Table 1.

In this process, two distinct phases were prepared: an aqueous phase containing PM-βCD and the extract diluted in water, and an organic phase composed of cholesterol, Span 60, and ethanol.

II.2.3. Encapsulation efficiency: Quantification of flavonoids (Quercetin)

The quantification of flavonoids. such as quercetin aims to assess the concentration of these compounds in samples. Flavonoids are phytochemical compounds found in many plant-based foods such as fruits, vegetables, wine, and tea. Quercetin in particular is a well studied flavonoid known for its potential antioxidant, anti-inflammatory and other health benefits [11].

This method relies on the use of AlCl3 to form a yellow complex with flavonols and flavones. 400 µl of the extract are mixed with 120 µl of NaNO2 and left to rest for 5 minutes. Then 120 µl of AlCl3 solution are added to the mixture stirred and allowed to react for 6 minutes. After this period 800 µl of NaOH are introduced. The absorbance of the solution is measured at a wavelength of 510 nm. Simultaneously, a calibration curve for quercetin is established at different concentrations. This method allows for the precise quantification of quercetin in various samples providing valuable insights into the flavonoid content and potential health benefits of the analyzed extracts [10].

Table 1: The experimental matrix

Exp No	C CD (mg/ml)	C Sp (mg/ml)	C Ch (mg/ml)
1	3.33	20	12.5
2	30	20	12.5
3	3.33	60	12.5
4	30	60	12.5
5	3.33	40	5
6	30	40	5
7	3.33	40	20
8	30	40	20
9	16.67	20	5
10	16.67	60	5
11	16.67	20	20
12	16.67	60	20
13	16.67	40	12.5
14	16.67	40	12.5
15	16.67	40	12.5

II.2.4. Determination of niosome size

To determine the size of niosome suspensions using an optical microscope, a drop of the suspension is placed on a slide and covered with a coverslip. An ocular micrometer calibrated with an objective micrometer is used to measure the size of the niosomes. The divisions on the ocular micrometer, converted into length units through calibration, allow for the calculation of the niosome size by multiplying by the calibration factor.

II.2.5. Preparation of Optimum niosomal solution and its validation

We identified the optimal niosome manufacturing conditions for the encapsulation system. To validate the experimental design, the optimal formulation was prepared using 3.333 mg/ml of PM-βCD, 20 mg/ml of Span 60 and 20 mg/ml of cholesterol and the responses were evaluated (the blank sample or placebo prepared using the same conditions).

II.2.6. Characterization of optimal mixed niosomal solution

II.2.6.1. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was conducted using a Mettler Toledo thermogravimetric analyzer. Approximately

22 mg of extract. 76.5 mg of niosomal formulation. or 33.5 mg of placebo were analyzed. Measurements were taken from 40°C to 600°C at a heating rate of 20°C/min under inert atmosphere.

III. Results and discussion

III.1. Extraction yield of propolis

The extraction of bioactive compounds from propolis, such as flavonoids and phenolic compounds, was performed using a solvent evaporation method. This procedure produced a viscous brown extract, known as "ethanolic propolis extract". The extraction yield is expressed as a mass percentage, indicating the mass of dry extract obtained relative to the mass of raw propolis. The yield of the ethanolic propolis extract depends not only on the extraction techniques used but also on the chemical composition of the raw propolis itself. The yield of the ethanolic propolis extract from the Melbou region was determined at 12.16%.

III.2. Quantification of flavonoids in propolis extract (Quercetin)

III.2.1. Calibration curve

The results are presented in the form of a quercetin calibration curve (Figure 1).

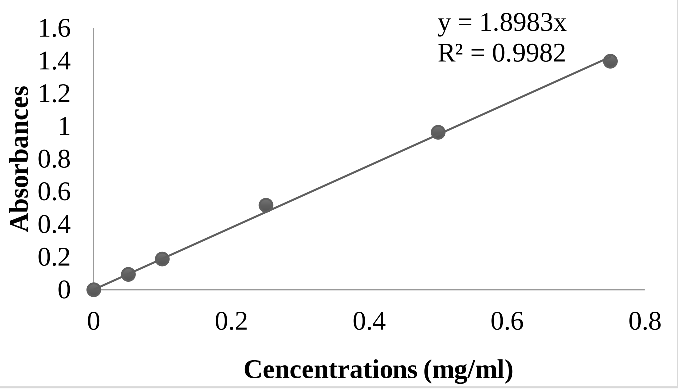

Figure 1: Quercetin calibration curve for flavonoid quantification.

The calibration line passes through the origin, providing a linear equation of the form y=a*x, where y is the absorbance, a is the slope, and x is the quercetin concentration. The equation is:y=1.8983*x and R^2=0.999.

The curve Abs=f(C) demonstrates the proportionality between the absorbance and quercetin concentration. This relationship is supported by the correlation coefficient R^2, which is close to 1 with a value of 0.999, confirming a very strong correlation between the two variables. Using this curve, the concentration of the propolis extract was determined to be 0.1275 mg/ml.

III.3. Determination of experimental design responses

Following the preparation of niosome suspensions (extract-PM-βCD-niosomes) by varying the quantities of Span 60 (C Sp) and cholesterol (C Ch) according to the experimental design, both the encapsulation efficiency (E.E) and particle sizes were determined (Table 2).

The results indicate that Span 60 has a significant impact on particle size, with a notable increase at higher quantities. PM-βCD also appears to influence particle size, although its effect is less pronounced than that of Span 60. Conversely, cholesterol has a relatively minor impact on particle size compared to the other components. The encapsulation efficiency increases with higher amounts of Span 60 and PM-βCD, while cholesterol does not significantly influence the encapsulation efficiency.

The results suggest that the use of Span 60 generally leads to the formation of larger and more stable niosomes due to its long alkyl chain. This enhances the encapsulation efficiency of hydrophobic active substances, such as propolis, due to the hydrophobic properties of Span 60 and the rigidity it imparts to the membrane. In contrast, PM-βCD improves the encapsulation capacity by increasing both stability and solubility. Cholesterol's effect is only apparent when its quantity is increased. Same results were found by Taouzinet et al [12] when studing the encapsulation of vitamin E by liposomes [12].

Mathematical Model

The modeling using the Box-Behnken experimental design allowed us to obtain the following model:

For particle size:

$Size=1390.17+37.4849*CD-140.667*Span-11.0627*CHL-205.051*CD^2+151.424*Span^2-75.5692*CHL^2+7.31327*CD*Span+6.17966*CD*CHL+61.6237*Span*CHL$.

For encapsulation efficiency:

$EE=41.5452+3.66721*CD+2.01403*Span-0.0883176*CHL+2.36712*CD^2+0.619395*Span^2+6.17367*CHL^2-0.544675*CD*Span-2.33982*CD*CHL-2.00022*Span*CHL$.

Statistical Analysis

The statistical parameters for particle size and encapsulation efficiency are summarized in Table 3. These parameters include R^2, Adjusted R^2, Lack of Fit, and Reproducibility. R^2 and Q^2, represent the model's ability to explain and predict the observed results, respectively. When these parameters are close to 1, it indicates that the model can explain the variation in the data and provide accurate predictions, confirming the model's validity.

These parameters demonstrate the reliability and validity of the model in explaining and predicting the particle size and encapsulation efficiency, supporting its use in further optimization studies.

Table 2: Determination of experimental design responses

Exp No	C CD (mg/ml)	C Sp (mg/ml)	C Ch (mg/ml)	Size (nm)	EE (%)
1	3.33	20	12.5	466.2	38.02
2	30	20	12.5	628.43	52.12
3	3.33	60	12.5	947.91	43.65
4	30	60	12.5	1050.56	54.01
5	3.33	40	5	1122.09	50.05
6	30	40	5	1229.34	64.53
7	3.33	40	20	1090.35	55.89
8	30	40	20	1201.75	54.79
9	16.67	20	5	1199.28	46
10	16.67	60	5	1311.45	60.1
11	16.67	20	20	973.33	53.69
12	16.67	60	20	1478.82	55.2
13	16.67	40	12.5	1427.4	43.18
14	16.67	40	12.5	1365.52	40.19
15	16.67	40	12.5	1427.4	40

Table 3: Statistical analysis values.

Parameters	R2	R2 Adj	Q2	Lack of Fit	Reproducibility
Size	0.985	0.959	0.775	0.216	0.984
EE	0.957	0.879	0.656	0.241	0.949

III.4. Propolis extract entrapped in CD/noisome caracterisation

III.4.1. validation of optimal noisomal solution

After preparing the niosomal suspensions according to the parameters defined in the experimental design. The particle size of the optimum reached 557.283 nm and 426.80 nm for placebo; on the other hand, the encapsulation efficiency was 34.81%.

According to our results an increase in particles size was observed in the former, confirming that the extract has been encapsulated into the niosomes vesicles.

III.4.2. Thermogravimetric Analysis (TGA)

The thermogravimetric analysis (TGA) (Figures 2) reveals distinct thermal degradation patterns for the propolis extract and the niosomal encapsulated propolis extract. The unencapsulated propolis extract shows a significant mass loss starting at approximately 50°C. This initial decrease is likely due to the evaporation of volatile compounds present in the propolis extract such as essential oils and alcohols. These compounds are known for their high volatility, which leads to their evaporation at lower temperatures [4]. The degradation process continues steadily up to 400°C, indicating the breakdown of various bioactive compounds within the extract.

In contrast, the TGA profile for the CD/niosomal encapsulated propolis extract demonstrates enhanced thermal stability. The mass loss does not begin until around 220°C, suggesting that the encapsulation effectively prevents the early evaporation of volatile components. This encapsulation effect is crucial as it indicates that the volatile and potentially bioactive compounds of the propolis extract are retained within the cyclodextrin and niosomes, thus enhancing their stability. Beyond 220°C, the degradation pattern of the encapsulated extract mirrors that of the placebo, indicative of the breakdown of the niosomal components such as cholesterol, Span 60, and cyclodextrin, eventually leading to total decomposition at around 400°C.

Comparing these results with existing literature, it is evident that encapsulation via niosomes significantly improves the thermal stability of bioactive compounds. For instance, Ghumman et al. (2023) observed that encapsulating curcumin in niosomes enhanced its thermal stability, preventing significant degradation up to 200°C, similar to our findings with propolis [13]. Similarly, Sun et al. (2018) demonstrated that the encapsulation of essential oils in cyclodextrins, liposomes or niosomes protected the volatile compounds from early evaporation, thereby preserving their bioactivity during thermal processing [14, 15].

These comparisons underscore the effectiveness of niosomal encapsulation in stabilizing thermally sensitive bioactive compounds. The delay in the onset of degradation for the encapsulated propolis extract highlights the potential of niosomes as a robust delivery system for enhancing the stability and efficacy of natural extracts in various applications, including pharmaceuticals and nutraceuticals.

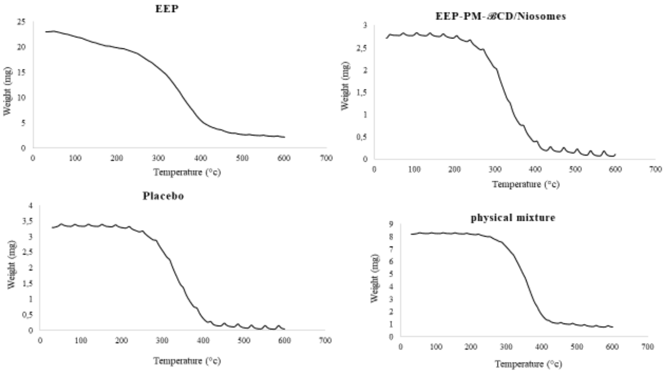

Figure 2: Thermogravimetric graphs of EEP, encapsulated EEP, placebo (blank) and physical mixture respectively.

IV. Conclusions

This study successfully prepared and optimized a CD/niosomal suspension containing propolis extract from the Melbou region (Béjaia).

The optimal CD/niosomal suspension demonstrated significant improvements in thermal stability compared to the unencapsulated extract, as confirmed by thermogravimetric analysis (TGA). The extraction yield of propolis from the Melbou region was determined to be 12.16%.

Using UV-visible analysistotal flavonoid content was determined, specifically quercetin, in the propolis extract. The encapsulation efficiency of the optimal CD/niosomal suspension was calculated to be 34.81%, with an average particle size of 557.283 nm, compared to 426.80 nm for the placebo.The enhanced thermal stability of the encapsulated extract, with a delayed onset of mass loss at 220°C, indicates effective preservation of volatile and bioactive components. These results highlight the potential of CD/niosomal encapsulation to enhance the stability and bioavailability of Algerian propolis extract, promising applications in pharmaceutical and nutraceutical formulations.

Acknowledgment

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Conflict of interest

The authors declare no conflict of interest. financial or otherwise.

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Biopolymer Applications Journal **Nadira BELLILI et al.V 3 ,N°2, 2024, pp.18-22**
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Study of the properties of a hybrid composite thermoplastic matrix/vegetable fillers.

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Abstract

The study carried out in this work aimed to develop and characterize hybrid composites based on polychloride of vinyl reinforced with date stone flour (DSF) and starch with PVC%/DSF%/ starch % percentages: 80/0/0, 80/20/0, 80/15/5, 80/10/10, 80/5/15 and 80/0/20 respectively. We were particularly interested in the problem of matrix-filler interfacial adhesion due to different characters of the constituent deferens. Several techniques have been used to characterize the composites developed, and the impact of hybridization on the mechanical and physical properties elaborate materials were studied. The incompatibility and poor interfacial adhesion between the different constituents leads to the appearance of phenomenon of embrittlement of the prepared materials, and consequently the reduction in stress, elongation at break and a reduction in elasticity of hybrid composites. The physical properties that were inspired by the density measurement state that the fillers used give the composites developed a lightness compared to virgin PVC.

Keywords : *Polyvinyl chloride, Date stone flour, Starch, Hybrid composites.*

I. Introduction

Environmental awareness as well as government legislations around the world have encouraged academic and industrial research to develop environmentally friendly composite materials that are durable and biodegradable [1].

Composite materials reinforced with natural fibers are increasingly sought after in various fields such as the industrial sector, particularly in the field of transport and the automobile industry, which require high-performance lightweight materials, recycling possibilities, the minimum of impact on the environment, and a reduction in the cost of materials [2-7].

In our work we were interested in the exploitation of date stone flour with starch as polyvinyl chloride reinforcements. However, the majority of research work has been devoted to the valorization of these nuclei in the form of: activated carbon, supplement in livestock feed, in traditional medicine and for its antimicrobial and antiviral properties, preparation of citric acid and proteins.

Algeria produces nearly 1,100,000 tonnes of dates/year, more than 10% of production is soft dates and the average weight of date stones ranges between 10% and 15% of the weight of dates. These stones are rejected and are considered a by-product of the date industry, they are poorly exploited and represent a loss of biomass deposits [8].

Among the plastic materials most used for the preparation of these composites, polyvinyl chloride (PVC). The latter is one of the most produced plastic materials. Its global production is 35 million tonnes per year. It is used in various sectors and is in third position in production after polyethylene and polypropylene [9,10].

One of the interesting solutions to meet this dual requirement is the hybridization technique [11]. The usage of hybrid polymer composites is increasing day-to-day because of their outstanding properties [12].Hybridization is the fact of using two or more types of reinforcements within the same composite. The term hybrid is defined in several ways in the scientific literature. Some the term hybrid is necessarily associated with a synergy between the reinforcements, which allows an additional improvement in the properties of the composite compared to a simple mixture. The behavior of hybrids can be seen as a weighted sum of the properties of the individual components and presenting a favorable balance between the advantages and disadvantages inherent in these components. Therefore, a balance between cost performance and sustainability. The main objective of this work is the development of PVC/ date stone flour (DSF)/Starch hybrid composites and the study of the effect of hybridization on the mechanical, physical, morphological and rheological properties of the materials developed.

II. Material and methods

PVC (Type 3000H) manufactured by CIRES (USA) (from the plastic calendering company "CALPLAST" in Sétif, Algeria) was used to prepare the formulations. The added plasticizer was dioctylphthalate (DOP). The industrial-grade heat stabilizer used was a mixture of epoxidized soybean oil (HSE 100S) and NEW STAB 26, with stearic acid as the lubricant. The natural fillers used are date stone flour (DSF) and starch. The starch used is cornstarch, which is bought directly from the shop.

To prepare the DSF, the collected nuclei underwent several pre-processing steps: Pulp- stone separation, the stone are then washed in hot water to remove traces of pulp and all kinds of impurities, followed by drying in the open air and grinding. The diameter of the selected flour particles is less than 63µm.

The PVC resin and the various additives are, mixed in a beaker using a spatula until the mixture becomes homogeneous. Sheets of 0.4 mm in thickness of F0, (formulation based on PVC and these additives), F20A (formulation based on 80% PVC, these additives and 20% starch), F20DSF (formulation based on 80% PVC, these additives and 20% DSF), F10A10DSF (formulation based on 80% PVC, these additives, 10% starch and 10% DSF), F5A15DSF (formulation based on 80% PVC, these additives, 5% starch and 15% FND) and F15A5ND (formulation based on 80% PVC, these additives, 15% starch and 5% DSF), were prepared using a calendar. The temperature along the twin cylinder mixer is maintained at 160°C for a residence time of 15 min. The sheets are, and then cut into the appropriate shape for characterization.

The properties of the PVC/DSF/Starch composites developed are then determined by the tensile test, the Water absorbing test and by measuring the density.

III. Results and discussion

A. Mechanical properties of PVC%/DSF%/ starch % composites determined by the tensile test

Figure 1 represents the variation in the stress at break and the maximum stress of the composites F0, F20DSF, F10A/10DSF and F20A.

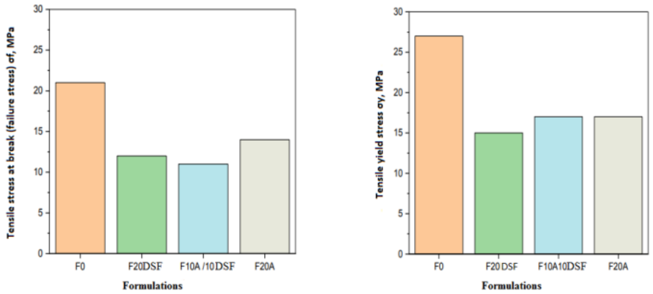

Figure 1. The variation in the stress at break and the maximum stress of the composites

The presence of particles of the fillers used with a hydrophilic nature in the hydrophobic PVC matrix reduces the tensile strength of the composites developed due to the incompatibility and poor interfacial adhesion between the different constituents. The reduction in breaking stress is estimated at 48, 43 and 34% for F10A10DSF, F20DSF and F20A respectively. The estimate of the reduction in the maximum stress of the reinforced composites compared to the virgin matrix is of the order of 44, 37, and 37% for the F20DSF, F10A10DSF and F20A composites respectively. The sharp decrease recorded is consistent with composites reinforced with date stone flour because it is more hydrophilic than starch. This is confirmed by the water absorption test.

Indeed, this loss of stress can be explained by the tendency of the filler particles to group together, forming agglomerates and resulting in poor dispersion, which induces heterogeneities and non uniform stress transfer within the matrix. This result is in agreement with several research studies. Islam et al. [13], recorded a decrease in breaking stress from 27.5 MPa for virgin PP to 25 MPa for composites filled with 25% coconut fiber. Djidjelli et al. [14], recorded a decrease in tensile strength of approximately 63% for PVC loaded with 30% sisal fibers compared to virgin PVC.

The variation in the elongation of the composites F0, F20DSF, F10A/10DSF and F20A is, shown in Figure 2.

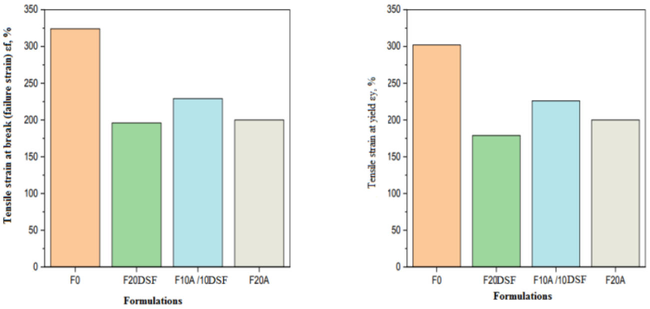

Figure 2. Evolution of the elongation of the developed composites

From Figure 2, we observe a significant drop in the elongation at break of filled composites compared to virgin PVC. This result is explained on the one hand, by the hydrophilic nature of the DSF and FA which absorb more humidity and causes swelling in the polymer matrix, on the other hand due to the volume occupied by the particles of the fillers, the Inter-chain interactions and the mobility of polymer chains are reduced, creating defects in the system and therefore material embrittlement. The phenomenon is more proven by composites reinforced with DSF particles.

S. Kormin et al [15], explained the decrease in elongation of LDPE/starch composites with increasing loading rate by the generation of internal deformation forces and a poor matrix-starch interface.

Figure 3 represents the evolution of Young’s modulus of the prepared composites.

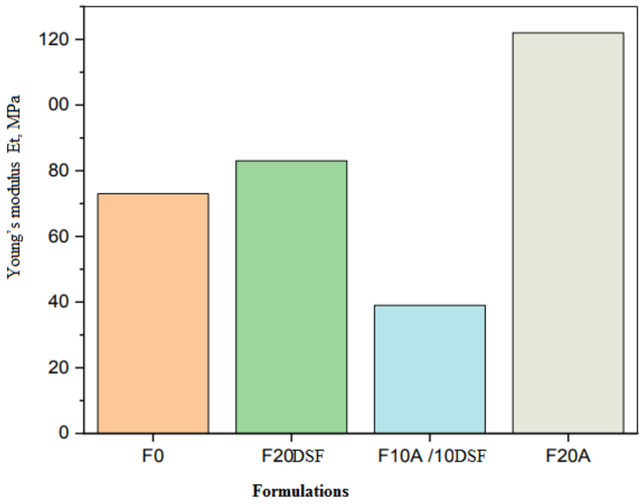

Figure 3. Evolution of Young's modulus of the prepared composites

From Figure 3, we can see that the incorporation of DSF and FA into the PVC matrix increases the rigidity of the material and reduces their elasticity. We also see that the Young modulus is significantly reduced for the hybrid composite.

A. Water absorption test

Water absorption analyzes are carried out to determine the influence of hybridization on the physicochemical properties of the materials produced. The water absorption behavior of the composites is compared to that of PVC resin and the results are reported in the figure 4.

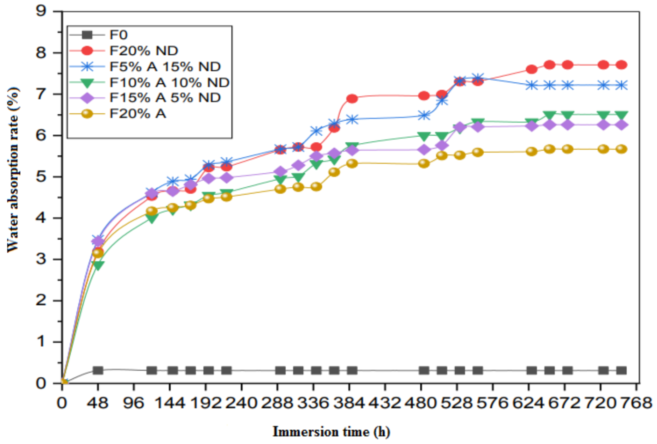

Figure 4. Evolution of the water absorption rate of the different composites developed as a function of immersion time.

The results show that the water absorption of F0 is negligible and does not exceed 0.31% whatever the immersion time due to the hydrophobic nature of this polymer, while the addition of starch or date stone flour with PVC matrix increases the water absorption rate with increasing immersion time in distilled water. This increase is attributed to the increase in the concentration of hydroxyl groups which have a strong affinity with water. This can be explained by the presence of hydroxyl groups in the two fillers used (a major constituent of corn flour and in the kernels of date) S. Sahi et al. [16], A. Hamma et al. [17]. These groups form hydrogen bonds with the water molecules absorbed by these hydrophilic reinforcements. Plus the concentration of OH group in composites is higher, the greater the water absorption rate. We can also attribute this phenomenon to poor filler/matrix interfacial adhesion leading to an increase in microvoids. The results of this test allowed us to reveal the hydrophilic nature of the fillers used and that date stone flour is more hydrophilic compared to starch. Indeed, the F20DSF composites absorbed a higher quantity of water than the F20A composites. This is also confirmed by the increase in the quantity of water absorbed by increasing the rate of date stone flour in the hybrid composites, in fact, the hybrid composites F10A10DSF, F5A15DSF and F15A5DSF) reached their water saturations of 6.51%, 7.22% and 6.26% respectively. From these results, we can say that the rate of water absorption depends on the time and the nature of the charge incorporated in the PVC matrix. These results are in agreement with the results observed by ESPERT.A et al. [18] who found that the hydrophilic nature of plant fillers is responsible for water absorption.

B. The density

The low density of lignocellulosic materials is one of the major advantages of their use as fillers in thermoplastic-based composites. Know the value density of date stone flour and starch makes it possible to predict the mass of a material reinforced by these loads. The results of the density test of the different composites developed F0, F20DSF, F5A15DSF, F10A/10DSF, F15A5DSF and F20A are shown in Figure 5.

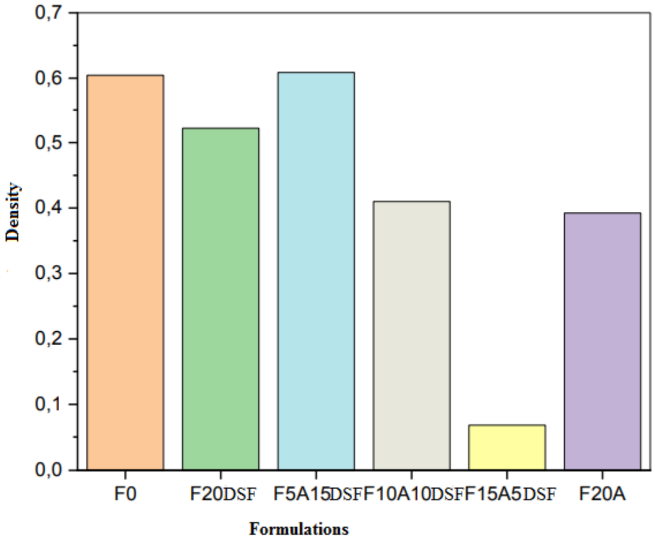

Figure 5. Evolution of the density of the different composites produced as a function of type and filler rate.

In this regard, the incorporation of date stone flour and starch flour into the polyvinyl chloride leads to low density composites compared to PVC virgin. The higher the starch content, the lower the density of the hybrid composites. The highest density value corresponds to the composite loaded with date stone flour. This is attributed to the highly hydrophilic nature of DSF compared to starch and the presence of micro voids in composites due to interfacial incompatibility charge/matrix. These empty microphones will subsequently be, filled with air, increasing the density of its materials Masri T. et al. [19].

A. Conclusions

The study carried out in this work aims to develop composites based on polyvinyl chloride reinforced by hybridization of two fillers: date stone flour and flour of starch with different loading rates ranging from 5 to 20%. The impact of hybridization on the mechanical and physical properties of the materials produced was, studied. The incompatibility and poor interfacial adhesion between the different constituents' leads to a reduction in the stress of hybrid composites compared to the virgin matrix. The lowest value is, recorded for composites reinforced with starch flour. The phenomenon of embrittlement of the prepared materials induced by the creation of defects in the system, produced by the volume occupied by the particles of the fillers used, leads to the reduction in the elongation at break of hybrid composites. This phenomenon is more obvious for the F 20DSF composite. A reduction in elasticity of the composites induced by the rigid nature of the fillers incorporated in the PVC matrix was observed and manifested by the increase of Young's modulus. This reduction is more significant for hybrid composites.

The increase in the quantity of water absorbed by increasing the rate of date stone flour in the hybrid composites confirms the more hydrophilic character of date stone flour compared to starch. The density of composites is significantly lower than that of virgin PVC, which affirms that the fillers used give the composites produced lightness, or composites filled with starch are the lightest materials.

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Biopolymer Applications Journal **e-ISSN: 2800-1729** **Lisa Klaai et al. Vol.3 N° 2, 2024, pp 23-27**

A Review of Composite Materials

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Abstract

Unlike conventional materials, composites have become an optimal option for a range of modern, industrial, clinical, and sports applications. This is combined with their noteworthy physical, thermal, electrical, and mechanical properties; the key concepts of composites are its physical properties, mechanical properties, tooling, design, inspection and repair. Military vehicles, such as airplanes, helicopters, and rockets, placed a premium on high-strength, light-weight materials. This review article attempts to give an overall outline of composite materials.

Keywords: *Classification of composites, Composite materials, Matrices, Processes, Reinforcements,*

I. Introduction

In recent years, the use of composite materials has seen considerable growth in industry, especially in the fields of civil engineering, mechanics, aeronautics, aerospace, etc [1].

Composite materials are materials that combine two materials that are different in both their shape and their mechanical properties in order to increase their performance by taking advantage of each of these materials. In general, they have remarkable qualities which are based on the mechanical properties of a fiber (carbon, boron, or organic aramid) which has exceptional tensile strength and rigidity (greater than that of the best steels).

These fibers are embedded in a matrix (metallic or organic) whose complex role is to bind the fibers, keep them aligned, and transmit the loads applied to them [2]. In reality the two constituents of composite materials which are the matrix and the reinforcement combine to give a heterogeneous material often anisotropy, where the properties will be different from one direction to another.

Composite materials with an organic matrix and glass or carbon fiber are finding more and more applications in the production of structural parts of various dimensions in numerous industrial sectors such as civil engineering and biomechanics, aeronautics, automobile manufacturing, shipbuilding. These sectors have turned to this alternative given the elongation of their structure with mechanical properties equal to or superior to those of metal parts. The long-term behavior of these types of materials is a very important area in their lifetime and operation [3].

In this review we clearly present a bibliographic summary on composite materials, this summary contains definitions and the different constituents of composite materials and some areas of application.

II. What is a composite material?

A composite material can be defined as the assembly of several materials of different natures. Composites are most often made up of a matrix in which we disperse reinforcements (fibers) in a controlled or uncontrolled manner. The matrix maintains the reinforcements and ensures load transfers, while the reinforcements mainly provide their high mechanical characteristics (modules and elastic limits, mechanical resistance, etc.) [5].

The purpose of this association is to obtain a material whose specific properties are superior to those of the components taken separately. The concept of composite material, by the choice of the constituents and their respective proportions, as well as by the choice of the shape, dimensions and arrangement of the reinforcements, therefore makes it possible to design a material having the specific characteristics sought [6].

II.1. Classification of composites

Today there are a large number of composite materials that can be classified either according to the shape of the components or according to the nature of the components [5].

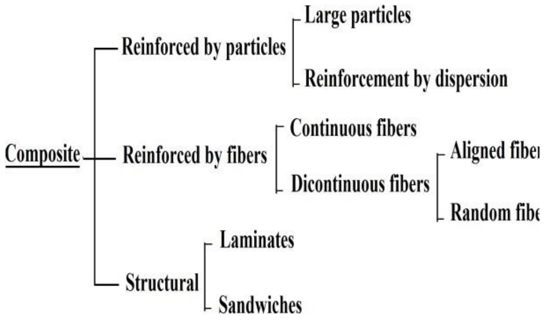

Figure1: Schematic classification of different types of composites.

II.1.1. According to geometry

a. Particle composites

A composite material is a particle composite when the reinforcement is in particle form.

A particle, as opposed to fibers, does not have a preferred dimension. Particles are generally used to improve certain properties of materials or matrices, such as rigidity, temperature resistance, abrasion resistance, reduction in shrinkage, etc.

In many cases, particles are simply used as fillers to reduce the cost of the material, without reducing its characteristics [7,8].

b. Fiber composites

A composite material is a fiber composite if the reinforcement is in the form of fibers. The fibers used are either in the form of continuous fibers or in the form of discontinuous fibers: staple fibers, short fibers. The arrangement of the fibers and their orientation make it possible to modulate the mechanical properties of the composite materials on demand. [7,8].

c. Structural composites

The manufacture of reinforcement can be done with fibers dispersed randomly or oriented in one or more directions. Axes of reinforcement can be defined by the crossing of threads (weaving). 3D structures have also been developed to improve the reinforcement of the material and provide a solution to delamination problems [7,8].

II.1.1. According to nature of the constituents

a. Organic matrix composites (OMC)

Organic Matrix Composites are, as their name suggests, composites whose matrix is mainly made up of polymer resin. This organic matrix can be either thermosetting, meaning it hardens when heated, or thermoplastic, meaning it can be softened and reformed by heat [9,10].

b. Metal matrix composite (MMC)

A metal matrix composite (MMC) is a material bringing together two elements: a metal matrix, for example aluminum, magnesium, zinc[9,10].

c. Ceramic Matrix Composite (CMC)

A Ceramic Matrix Composite (CMC) is a ceramic matrix in which ceramic fibers are incorporated. This unique combination of materials has revolutionized the aerospace industry, making components more resistant to extreme conditions and lighter compared to previous technologies [9,10].

II.2. Main constituents of a composite material

Among the main constituents of a composite material, we find:

II.2.1. Matrix

In a large number of cases, the matrix constituting the composite material is a polymer resin. Polymer matrix composites (PMC) exist in large numbers and each has a particular field of use [11]. PMCs are characterized by high matrix/filler interfacial adhesion and performance far superior to that of virgin polymers. For example, they have high stiffness, high strength along the alignment direction of fillers and good abrasion resistance. These good properties can only be achieved thanks to the role played by the polymer matrix in connecting the fibers together and allowing the transfer of stresses between them. PMCs are extensively used in a wide range of high-tech engineering products, e.g. in transportation (aircraft, boats, warship), marine structures and sports goods (rackets, rowing eights, fishing rods), and many others.. The classification of the types of matrices commonly encountered is given in Figure 2.

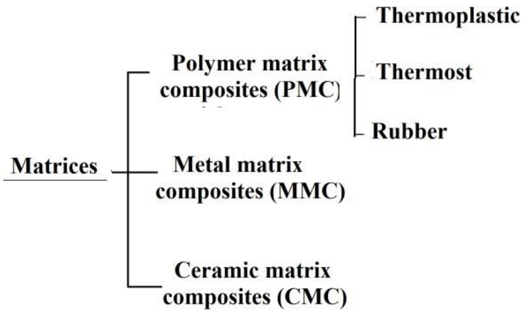

Figure 2: Classification of matrix

a. Thermoplastics

Thermoplastics are polymer chains linked together by weak bonds, they are in solid form (granules, plates, etc.) which are shaped by softening them by heating, then solidifying them by cooling.

They represent 80% of plastic materials consumed, the most common are; poly (vinyl chloride) which is used in the manufacture of pipes, poly (vinyl acetate) which is found in glues and adhesives, polyethylene which is used to make toys, bottles or bags from supermarkets, polypropylene for food boxes or floor coverings, polystyrene which is used in the composition of food containers, etc.

Their recyclability and thermo-reversibility constitute one of the great advantages which are becoming more and more important nowadays [12].

b. Thermosets

Thermosets are polymers that can only be shaped once but have high mechanical and thermomechanical properties compared to thermoplastics. They are in viscous liquid form and are shaped by triggering a chemical polymerization reaction by adding a hardener, which results in solidification.

The best known are unsaturated polyesters (vinyl ester, allelic derivatives, condensed polyesters, etc.), epoxy resins, condensation resins (phenolic, aminoplasts, etc.) They offer many important fundamental advantages over thermoplastics such as fatigue and impact resistance, longevity and corrosion resistance [12].

c. Elastomers

Elastomers are extremely flexible and elastic polymer materials, widely used in many industries for their unique properties. Their name derives from their main characteristics: elasticity and reversible deformation. These materials are essential in the manufacturing of products ranging from tires to pharmaceuticals to sports equipment [12].

d. Metal resins

Metal matrix composites are materials that combine the hardness of metals and the rigidity of ceramics. This type of resin is used as a binder in applications requiring a material with good specific properties and good temperature resistance. At present, these applications remain few in number and are limited to high-tech sectors because of the cost of implementation and the complexity of impregnation [12].

e. Ceramic resins

Ceramic matrices are composed of one or more metals combined with an element, the most common of which is oxygen, such as AL_2O_3 (Alumina), SiO_2 (Silica), MgO. (Magnesia).

Much less widespread than their organic matrix counterparts due to high cost, CMCs are intended for applications at very high temperatures. They are mainly used in the space industry and military aeronautics, as well as for the design of high-end components such as brake discs or pads.

Ceramics have many advantages for such applications: they can withstand very high temperatures, are lighter than many metals, and have good chemical stability. Unfortunately, their great fragility strongly limits their range of use [12].

II.2.2. Reinforcement

Often in the form of fibres, the purpose of reinforcements in composite materials is essentially to increase their mechanical properties (rigidity, breaking strength, hardness, etc.) and to improve physical properties, such as behavior in fire and abrasion, temperature resistance or electrical properties. The characteristics sought in the reinforcements are low density, compatibility with the matrices and ease of implementation [13,14].

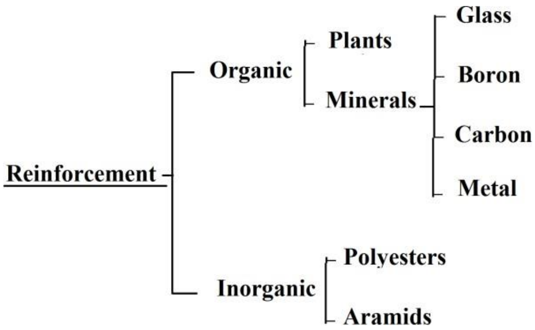

Figure 3: Types of reinforcement

a. Aramid fibers

Aromatic polyamides which contain aromatic groups more than 85% are called aramids, the known aramid fibers are Kevlar. They have high tensile mechanical properties like carbons but their compressive strength is low. The poor mechanical strength in compression is generally attributed to poor adhesion of the fibers to the matrix in the composite material.

To remedy this, fiber enzymes can be used. The use of hybrid fiber composites also allows remedying the weaknesses of aramid fiber composites [15]. Hybrid reinforcements such as glass – Kevlar or carbon – Kevlar are widely used in the leisure sector (skiing, tennis rackets, etc.).

b. Ceramic fibers

Ceramic-type composite materials are often made up of ceramic reinforcements and matrix. The fibers are produced by chemical vapour deposition on a support wire. These fibers have applications where the temperature is very high between 500°C and 2000°C. These materials are used in particular in the hot parts of aircraft engines [12].

c. Carbon fibers

Carbon fibers are thin filaments made of elemental carbon with structures that change from those of amorphous carbon to those of crystalline graphite. These fibers are made from a base polymer called a precursor; the chemical and physical properties of the final carbon fibers strongly depend on the qualities of the precursor [12].

d. Glass fibers

Glass fibers have an excellent performance-price ratio which places them by far at the forefront of reinforcements currently used in the construction of composite structures. The latter have a low tensile modulus, but an interesting tensile strength [15]. They are made of silicates and considered anisotropic materials.

e. Other types of fibers

This part brings together all the fibers that remain, generally these fibers are used for specific applications (special papers, for good electrical conductivity). They have relatively low elastic moduli compared to the other fibers already mentioned. The fibers concerned are:

- Fibers of plant origin (cellulose, flax, hemp, etc.);
- Fibers of mineral origin (asbestos, silica);
- synthetic Fibers (tergal, nylon, etc.) from polyesters, polypropylene or polyethylene;

II.2.3. Fillers and Additives

The fillers, generally in the form of fragmentary elements, powders or liquids, are incorporated into the resin to reinforce the mechanical properties. They can be mineral, organic (vegetable or synthetic) or metallic, and are generally used in the same way as in "traditional" plastics. Non reinforcing fillers can be also used to reduce the cost of dies. Additives, such as coloring or mold release agents, are widely used when designing structures made of composite materials [12].

III. Processes for implementation composite materials

The aim of this paragraph is not to detail the different techniques for developing composite materials but to present them in their entirety and to specify in which cases they are used. There are several methods for developing and formatting composites which can be grouped into categories [16]:

- By extrusion; widely used with thermoplastics;
- By impregnation; often used with fabrics and threads;
- By deposit; for sandwich composites.

These techniques are often followed by molding which defines the shapes of the material. Molding can be done in several ways:

- By compression; (cold or hot, by resin injection): this is a method used for composites with a high reinforcement rate to obtain parts with deep and delicate shapes.
- Under pressure; (contact, simultaneous injection): this is the simplest method allowing parts to be obtained in large series and at low prices. The reinforcement rate is however limited.
- Vacuum, for small and medium series parts
- Continuous: the parts obtained are flat or corrugated; sandwich composites are often prepared using this technique.
- By pultrusion: which usually occurs after impregnation of the fibers (yarns, laminates, fabrics), the profiles obtained are rectilinear or curved with constant section. This technique produces materials with fairly high mechanical characteristics.
- By centrifugation: technique reserved for cylindrical shapes (tubes, pipes).
- By filament winding: (circumferential, helical) allowing the design of advanced cylindrical and spherical parts. The proportion of fibers in the composite is quite high, which gives high mechanical characteristics. On the other hand, this method is very expensive [16].

IV. Conclusions

Composite materials are advanced designing materials. Composite materials are becoming an alternative to conventional materials and are used in various applications. This review article provided a general overview of composite materials constituents.

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Study of the effect of MAPP rate on the morphology and thermal properties of PP/r-PET blends

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Abstract

The morphological and thermal study of the blends based on polypropylene (PP) and poly (ethylene terephthalate) recycled (r-PET) without and with a compatibilizer MAPP. PP/r-PET /MAPP Melt blending, the effect of blend composition of (r-PET) and MAPP was followed by morphological and thermal studies. The results obtained were discussed compared to the base polymer. In the absence of the compatibilizing agent (MAPP), PP/r-PET blends at different concentrations of r-PET exhibit clear phase separation with poor dispersion of r-PET in the PP matrix. The addition of MAPP in the blends PP/r-PET leads to a reduction of the particle size of the dispersed phase (r-PET) in the PP matrix, as well as improved interfacial conditions.

Keywords : *Polypropylene, poly(ethylene terephthalate) recycled, compatibilizer, blend, thermal proprieties*

I. Introduction

A recent concept (which is increasingly taken into account in our daily lives) is the concept of sustainable development, which depends in part on the reduction of waste and/or its management. This involves their treatment with a view to their recovery or recycling. A large part of the waste is made up of plastic materials used in convenience products, household appliances, construction, transport, etc. Unfortunately, plastic materials, in general, have a major drawback which is their resistance to biodegradation. One of the possible solutions to reduce or eliminate them is recycling. This can be mechanical or chemical. Mechanical recycling consists of reusing waste for the manufacture of a finished or semi-finished material. However, this type of recycling generally results in a decrease in the properties of the polymer. Among these plastics, poly(ethylene terephthalate) (PET) is considered one of the most important technical polymers. PET is mainly used for the manufacture of films, fibers and containers (bottles). PET has very good characteristics for its use in packaging: high transparency in blown containers, good mechanical properties for a minimum thickness, dimensional stability during handling (even at high temperatures), relatively low cost (price per container) and low permeability to gases such as CO_2 [1]. For all these reasons, PET is increasingly used as a packaging material. Its widespread use generates large quantities of waste that require the implementation of recycling techniques.

PET recycling is not easy because of its degradation during reprocessing, caused by temperature, moisture and contaminants. The degradation leads to the decrease of molecular weight and loss of properties [2]. One way to improve the properties of recycled polymers is to blend them with unmodified polymers (polyolefins) with good properties. Polypropylene (PP) is widely used in this case [3], because of its good properties (lightness, transparency, high mechanical strength, electrical insulation, inertness to chemical aggression and use at high temperatures) [4]. It has been reported that blends of polyolefins (especially polyethylene (PE) and PP) and PET can display good mechanical and permeability characteristics. However, PET and polyolefins have very different chemical structures, making them immiscible with each other. The major drawback resulting from this incompatibility is that the resulting blends exhibit poor mechanical properties. The most frequently used means to partially overcome this performance deficit is compatibilizing, which consists of creating chemical affinities between the constituents of the blend in order to reduce interfacial tensions, improve adhesion between the phases and stabilize the morphology [5]. Some of these studies have focused on techniques to improve the compatibility between the two polymers [6, 7]. Maleic anhydride-grafted PP (MAPP) can be used as a compatibilizing agent in PP/PET-r blends [8-10]. It has been reported that the use of MAPP in PP/PET-r blends can improve the dispersion and adhesion between the two components [8]. It has also been indicated that the use of MAPP as a compatibilizing agent can improve the strength and stiffness of PP/PET-r polymer blends [9].

II. Material and methods

PP 500P polypropylene with a melt flow index of 3.00 g/10min was provided by SABIC Basic Industries Corporation (Saudi Arabia). Poly(ethylene-terephthalate) (r-PET), or waste r-PET, was recovered from waste mineral water bottles. The size of r-PET pieces ranged from 2 to 5 mm. Maleic anhydridegrafted-polypropylene (MAPP) with a melt flow index of 2.63g/10 min was provided by Arkema (Insa de Lyon, France).

II.1. Blend preparation

Several formulations based on a PP/PET-r mixture were prepared with and without compatibilizing agent MAPP according to the compositions indicated in Table PET-r flakes were dried at 120 °C for 24 h to remove any trace of water that may cause hydrolytic degradation of the material during use.

The PP/r-PET blend (matrix) was extruded at the melting temperature of PET at 265°C and 120 rpm for 2 min using a laboratory scale co-rotating twin-screw mini extruder (15mL Micro compounder, DSM Xplore, University A. Mira of Bejaia, Algeria). The compounds were subsequently injection molded using a laboratory scale injection-molding machine (12mL Micro injection Molder, DSM Xplore, University A. Mira of Bejaia, Algeria) at 180°C barrel temperature, 90°C mold temperature, and 10 bars injection and holding pressure. Samples were molded for mechanical and physical characterization.

Table 1: Composition of PP/PET-r blend formulations.

The blends	PP(unite)	r-PET	MAPP
PP/PET-r$_{10}$	90	10	0
PP/r-PET$_{10}$/2,5%MAPP	87,5	10	2,5
PP/r-PET$_{10}$/5% MAPP	85	10	5
PP/r-PET$_{10}$/10%MAPP	80	10	10
PP/PET-r$_{20}$	80	20	0
PP/r-PET$_{20}$/2,5%MAPP	77,5	20	2,5
PP/r-PET$_{20}$/5% MAPP	75	20	5
PP/r-PET$_{20}$/10%MAPP	70	20	10
PP/PET-r$_{30}$	70	30	0
PP/r-PET$_{30}$/2,5%MAPP	67,5	30	2,5
PP/r-PET$_{30}$/5% MAPP	65	30	5
PP/r-PET$_{30}$/10%MAPP	60	30	10

II.2. Characterizations

Sample morphology was performed on Hitachi S- 3500N Variable Pressure Scanning Electron Microscope (Hitachi High Technologies Canada) with an accelerating voltage of 20.0 kV. Specimens were freeze-fractured in liquid nitrogen and then coated with a thin layer of carbon for characterization.

In thermogravimetric analysis (TGA), the mass of a sample, maintained in controlled atmosphere, is recorded as a function of the temperature (rise, fall orisothermal) or time. Saved thermograms provide informationmainly on the physical phenomena of vaporization, sublimation or desorption, but also on decomposition or oxidation reactions, particularly in the case of polymers.

In this study we used a TGA Q500 type device from TA instruments. He is composed of a sample boat driven by a high precision microbalance. The basket is introduced into an oven allowing the sample to be subjected to a ramp in temperature from 20 to 600 °C with a speed of 10 °C/ min, under a flow of inert gas (N_2).

X-ray diffraction is a non-destructive analysis method generally used to determine the mineralogical composition of a sample. The spectra of the X-ray diffraction analysis were recorded using a “PANalytical Expert-Pro” type apparatus equipped with a copper anticathode tube and a monochromator using a Kα1 line of wavelength λKα1=1.5405 Aº. For crystallinity measurements, the diffracted intensity as a function of the angle 2θ between 5 and 45° is measured in reflection.

III. Results and discussion

III.1. Morphology of Blends

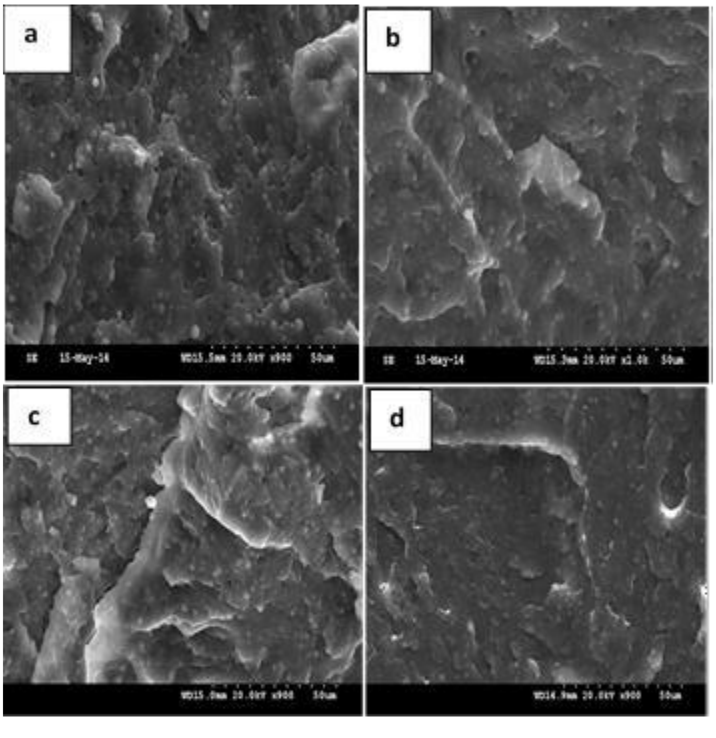

Figure 1: SEM micrograph of PP / r-PET 80/20 blend (a), PP / r-PET / 2.5% MAPP (b), PP/r-PET/ 5% MAP(c) P, PP/r-PET /10% MAPP (d).

Analysis of the surface morphology of the three samples, shows the presence of a homogeneous surface characterized by a reduction in the size of the particles of r-PET embedded in the PP matrix in comparison with the non-compatible PP/r-PET mixture micrograph (Figure 1.a). This reduction in the size of the dispersed phase is significant with the increase in the content of MAPP. The morphology change is the result of interfacial interactions between the r-PET particles and the PP matrix. The addition of 10% MAPP significantly reduces the size of r-PET particles: the PET-r particle size is changed from 2,88 µm for the non-compatible PP/r-PET20 mixture to 2,02 µm, 1,75 and 0,77 µm for PP/r-PET 20 /2,5% MAPP mixtures, PP/r-PET/5% MAPP and PP/r-PET/10% MAPP, respectively. In addition, the PET-r particles appear to be "included" in the PP matrix, this can be explained by the chemical bonds created between PET-r and MAPP, thus forming anchor points between phases, and on the other hand, the absence of voids as well as the homogeneity of the structure, which suggests the existence of a certain cohesion between the matrix and the dispersed phase.

III.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed under inert atmosphere for all blends to study the thermal degradation of these samples.

The TGA and DTG thermograms are presented in Figures 2, 3 and 4. The temperatures corresponding to the decomposition steps (5, 10 and 50%) and the temperatures corresponding to the maximum degradation rate are essential to evaluate the thermal stability of a polymer (Table 2).

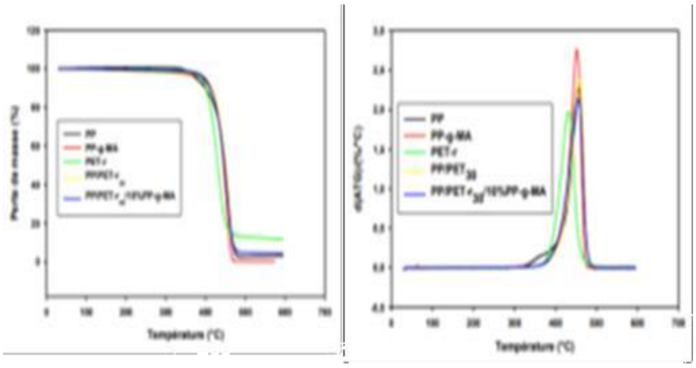

Figure 2: ATG/DTG thermograms of PP, PET-r, MAPP and PP/PET-r 10 blends in the presence of 10% MAPP.

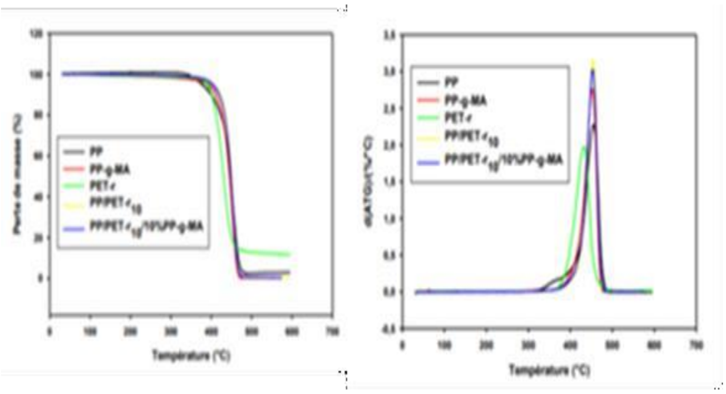

Figure 3: ATG/DTG thermograms of PP, PET-r, MAPP and PP/PET-r 20 blends in the presence of 10% MAPP.

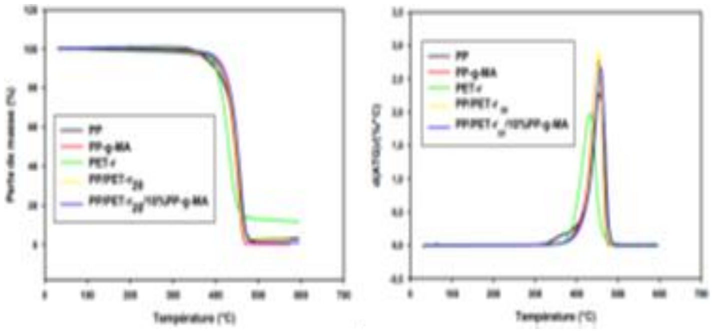

Figure 4: ATG/DTG thermograms of PP, PET-r, MAPP and PP/PET-r 30 blends in the presence of 10% MAPP.

Table 2: Results of thermal properties determined by ATG.

Formulations	Tdégradation 5% (°C)	Tdégradation 10% (°C)	Tdégradation 50% (°C)	T at Vmax (°C)	Résidue at 600°C (%)
PP	377,68	399,75	447,99	452,36	3,02
PP/rPET10	405,47	422,38	448,28	452,48	0,48
PP/rPET10C	403,17	419,66	448,75	453,20	0,35
PP/rPET-20	402,55	418,00	449,87	454,36	2,49
PP/rPET-20C	402,93	418,42	451,92	457,61	1,075
PP/rPETr 30	400,09	416,00	447,60	456,18	4,50
PP/rPET-30C	397,52	412,10	450,84	457,61	4,36
r-PET	389,46	400,71	430,87	433,29	11,60
PP-g-MA	391,91	410,97	445,36	525,52	0,17

The ATG thermograms show that PET-r undergoes a single-step mass loss in the temperature range 370-465 °C. The maximum of the DTG thermogram, which corresponds to the temperature at which the maximum mass loss rate is recorded, gives a value of 433 °C (Table 2), which is due to the thermal degradation of the PET-r chain [11]. The residual mass at 600 °C is 11.6% (Table 2).

Polypropylene also degrades in a single step in the region 346-482°C. The temperature corresponding to the maximum rate of degradation of PP is 454°C.

Binary PP/PET-r blends (PP/PET-r10, PP/PET-r20, PP/PET-r30) in the absence of PP-g MA as well as ternary blends (PP/PET-r10/10%PP-g-MA, PP/PET-r20/10% MAPP and PP/PET-r30/10%PP-g-MA) compatibilized with 10% MAPP show the same thermal behavior. According to Table 2, the temperature values corresponding to the maximum degradation rates of binary mixtures (in the absence of MAPP) are lower than those corresponding to ternary mixtures (in the presence of MAPP), which implies a faster degradation of the latter. This part allows us to conclude that the presence of MAPP in binary mixtures has an influence on the thermal stability of the corresponding mixtures [12,13].

III.4. X-ray diffraction (XRD) analysis

The changes that can occur in the microstructure of PP/r-PET blends after addition of the polypropylene-maleic anhydride graft copolymer (MAPP) were monitored by X-ray diffraction (WAXD). Figures 5, 6 and 7 show the diffractograms of the PP/PET-r10, PP/PET-r20 and PP/PET-r30 blends in the presence of the compatibilizing agent MAPP

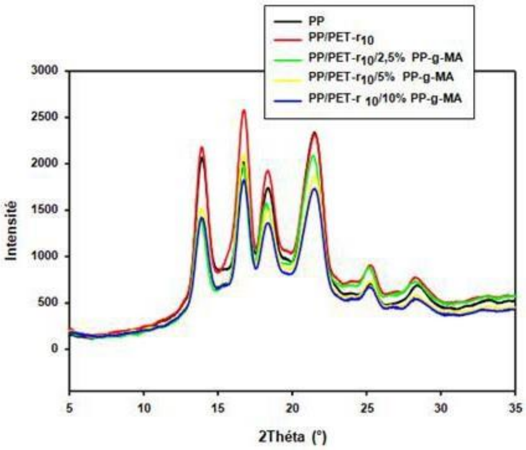

Figure 5: X-ray diffraction of PP/PET-r10 blends at different PP-g-MA rates.

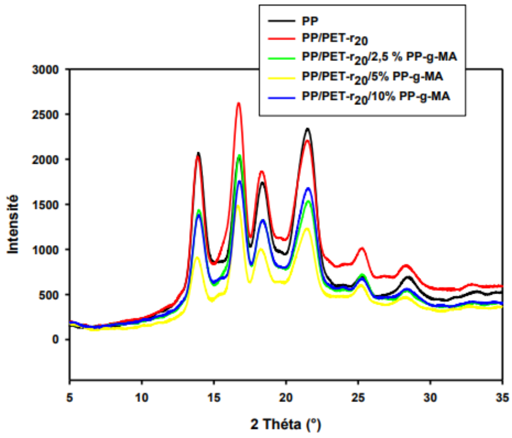

Figure 6: X-ray diffraction of PP/PET-r 20 blends at different MAPP rates.

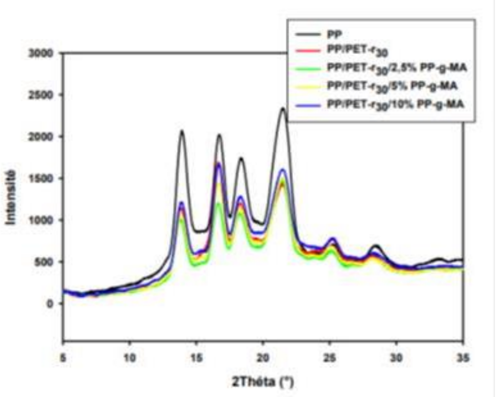

Figure 7: X-ray diffraction of PP/PET-r30 blends at different MAPP rates.

The diffractogram profiles of PP/PET-r blends at different PET-r contents (10, 20 and 30%) containing the polypropylene-maleic anhydride graft copolymer are similar to those of the non-compatibilized blends. However, it can be noted that with the increase in the compatibilizer content, the peaks tend to shift slightly towards lower diffraction angles. This shift may be due to the interactions between PP and PET-r with MAPP.

IV. Conclusions

In this study devoted to the study of the optimization of the rate of the MAPP compatibilizing agent, we were particularly interested in the problem of adhesion to the interface of PP/r-PET blends at different rates of MAPP, by varying the rate of 2.5, 5 and 10%. The highlighting of the compatibilizing was examined by the different analysis techniques.
All the results obtained indicate that the addition of MAPP as a compatibilizing agent improves the morphology of PP/r-PETpolymer blends at different MAPP levels. This results in a decrease in the size of the PET-r particles embedded in the PP matrix and an improvement in the interfacial adhesion between the two polymers. The presence of MAPP in the PP/r-PET binary blends has an influence on the thermal stability of the corresponding blends.

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Synthesis And Characterization Of Poly (Glycolic Acid) By Azeotropic Polycondensation

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Abstract

Poly (glycolic acid) synthesis was achieved through azeotropic polycondensation of a Hydroxy acid (glycolic acid), in the presence of a catalyst ($SnCl_2$, $2H_2O$) and an organic solvent, xylene, at a temperature of 170°C for 10 hours under atmospheric pressure. The synthesized product was characterized using several analytical methods: Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and viscometric molecular weight measurement. FTIR analysis confirmed the presence of characteristic absorption bands corresponding to different functional groups of poly (glycolic acid). XRD analysis revealed the presence of a crystalline phase constituting approximately 26%. The molecular weight of the synthesized poly(glycolic acid) was determined to be 9300 g/mol.

Keywords: *poly(glycolic acid), polycondensation, synthesis, biomaterials.*

I. Introduction:

In recent years, there has been growing interest in biodegradable synthetic polymers. These biomaterials are used in both surgery (prostheses, sutures, etc.) and pharmacology (trapping and controlled release of active ingredients). Polymers, especially poly(lactic acid) and poly(glycolic acid), play a privileged role due to their biodegradable and biocompatible nature [1, 2]. Polyglycolide or poly(glycolic acid) is a biodegradable and thermoplastic polymer, and the simplest linear aliphatic polyester. It is generally synthesized either by condensation from an α-hydroxy acid (glycolic acid) or by ring-opening polymerization from a cyclic dimer. It is hydrophobic and soluble in organic solvents such as dichloromethane, chloroform, and THF. However, it is insoluble in methanol, ethanol, and ether. Currently, polyglycolide and its copolymers like poly(lactic-co-glycolic acid), poly(glycolide-co-caprolactone), and poly(glycolide-co-trimethylene carbonate) are widely known as materials for the synthesis of absorbable sutures and are evaluated in the biomedical field [3, 4]. Our work is dedicated to the synthesis of poly(glycolic acid) through azeotropic polycondensation of glycolic acid. This polymerization reaction is carried out at different reaction times (6h, 8h, 10h, 12h). The resulting products were characterized using various analytical methods such as infrared spectroscopy, X-ray diffraction, and others.

II. Experimental Section

II.1. Synthesis of poly (glycolic acid)

In a 500 ml round-bottom flask equipped with a cooling system and a reflux condenser, glycolic acid is introduced and dehydrated at 100°C for 2 hours. Then, tin chloride $Sn(Cl)_2 \cdot 2H_2O$ was added at a concentration of 0.5% of mass of glycolic acid along with xylene. The mixture was heated to 170°C under atmospheric pressure and inert gas (argon) for varying reaction times (6h, 8h, 10h, 12h). The obtained viscous product is allowed to cool, then methanol is added until precipitation occurs. The product is, then, recovered by filtration and air-dried for one week.

- **Purification:** in order to purify the obtained product, the powder is ground and dissolved in chloroform. Methanol is used for precipitation, followed by air-drying to obtain a white powder.

II.2. Characterization methods

II.2.1. Fourier-Transform Infrared Spectroscopy (FTIR)

The infrared spectra of the obtained product were recorded using KBr pellets and a "SHIMADZU IRTF 8300" Fourier-transform infrared spectrometer.

II.2.2. X-ray Diffraction (XRD)

X-ray diffraction measurements were performed on an "expert prof panalytical" instrument, vertical model, with a wavelength λ = 1.540598 Å. The X-ray source is a ceramic tube with a copper band.

II.2.3. Thermogravimetric Analysis (TGA)

Thermal decomposition temperature determination is carried out using a "SETARAM/TGA92" instrument. The temperature raised from 30 to 450°C under a flow of air at a rate of 10°C/min.

II.2.4. Determination of Viscosimetric Molecular Weight

The determination of viscosimetric molecular weight was performed using a capillary viscometer (Ubbelhode tube). Solutions of different concentrations were prepared for each product in chloroform. Using an Ubbelhode tube with a viscosity constant of 0.00111 in a water bath at 30°C, we have determined the outflow time t_0 for the solvent and t for each solution. We use the Mark-Houwink relation to determine molecular weights according to the following equation:

$$[\eta] = k\,M^{\alpha}$$

In our study, chloroform is the solvent, and the values of the constants k and α are respectively 0,129.10-3, 0,82.

- Degree of polymerization (DPn)

The degree of polymerization refers to the number of monomer units in a polymer chain, characterizing the polymer's size [5].

$$M = M_0 . DP_n$$

M and M_0 : the molecular weights of the polymer and the monomer, respectively.

III. Characterization of poly(glycolic acid)

III.1. Infrared Spectroscopy (IR)

The IR spectrum of poly(glycolic acid) shown in Figure 1 indicates the presence of several functional groups, predominantly between 500-2000 cm^{-1}. The most characteristic band appears at 1750 cm^{-1}, attributed to the stretching vibration mode of carbonyl groups C=O in ester functions present in PGA. Two medium stretching bands between 2900 and 3000 cm^{-1} characterizing the (CH_2) group. Several absorption bands in the region of 1230-1000 cm^{-1} correspond to the vibration of (C-O) groups, and two other bands between 720 and 950 cm^{-1} are attributed to the (C-H) group. These absorption bands characterize the poly(glycolic acid) product [6,7].

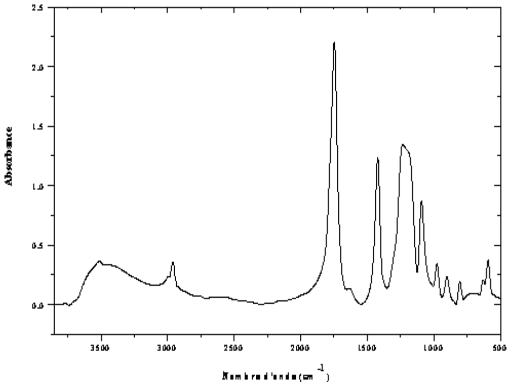

Figure 1: FTIR Spectrum of Poly(glycolic acid)

The entirety of the absorption bands of poly(glycolic acid) and their vibration modes are presented in Table 1.

Table 1: Absorption Bands of PGA and Their Vibration Modes

Frequency (cm^{-1})	Functional Group Attribution	Reference (cm^{-1})
721	δC=O	704
756	δC-H	756
800	νC-C-COO	870
969	νCH_3 + νC-C	964
1090	νs C-O-C	1100
1426	δas CH_3	1452
1750	ν C = O	1740-1790
2960	CH_2	2947-2962

3514	OH	3510

III.2. X-ray Diffraction (XRD)

The X-ray diffraction results for a sample of PGA powder, shown in Figure 2, indicate the presence of a crystalline phase characterized by two crystalline peaks. The most intense peak is located at 2θ = 28.5°, and the less intense one at 2θ = 21.9°. The crystallinity percentage of PGA is determined to be 26%.

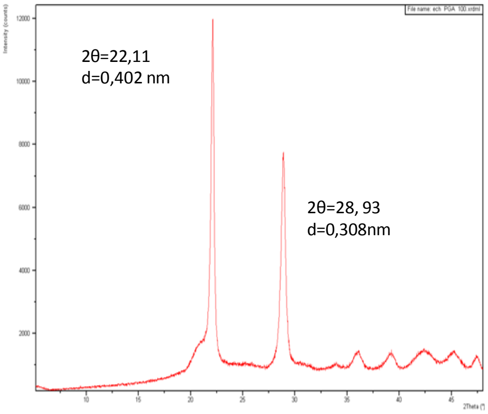

Figure 2: X-ray Diffractogram of Poly(glycolic acid)

III.3. Thermogravimetric Analysis

The thermograms presented in Figures 3 and 4 show that the degradation onset temperature for poly(glycolic acid) is 302.55°C, with a maximum mass loss rate occurring around 302.4°C.

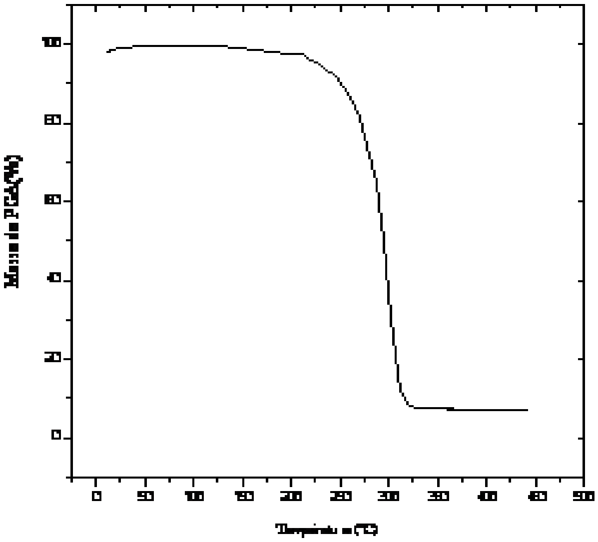

Figure 3: Mass Loss of Poly(glycolic acid) as a Function of Temperature

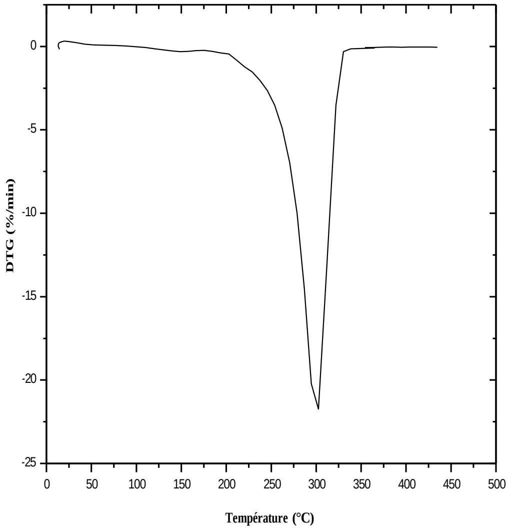

Figure 4: Degradation Rate of Poly(lactic acid) as a Function of Temperature

III.4. Viscosimetric Molecular Weight of Poly(glycolic acid)

The viscosity results of poly(glycolic acid) are presented in Figure 5, showing the curves (ηsp/c) and (Ln η_r /C) as a function of concentration.

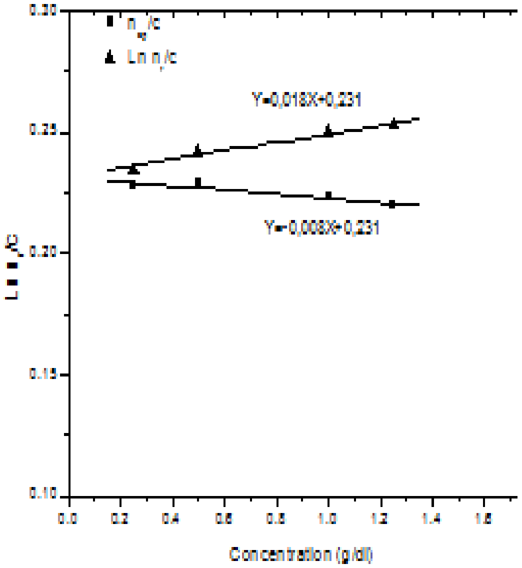

Figure5: Variation of PGA Viscosity as a Function of Concentration

The plot of ηsp/C values against concentration allows for the determination of intrinsic viscosity [η] (y-intercept). Using the Mark-Houwink relationship, the molecular weight can be calculated.

- Intrinsic viscosity [η] = 0.231
- Molecular weight M = 9300 g/mol
- Degree of polymerization DPn = 122

IV. Conclusions

Based on this study, the following conclusions can be drawn:

FTIR analysis showed the presence of all absorption bands corresponding to various functional groups of poly(glycolic acid).

X-ray diffraction confirmed the presence of crystallinity peaks in poly(glycolic acid).

Thermogravimetric analysis (TGA) demonstrated that the synthesized product exhibits thermal stability up to 302°C.

The viscosimetric molecular weight of poly(glycolic acid) is approximately 9300 g/mol.

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