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**PROGRAMA DE PÓS-GRADUAÇÃO EM CIÊNCIA E  
ENGENHARIA DE MATERIAIS**

**Doctoral thesis**

**Modification of kapok fibers by cold plasma surface treatment for  
the production of composites of recycled polyethylene**

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Co-advisor: Prof. Dr. Edson Noriyuki Ito

October 2018  
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the production of composites of recycled polyethylene**

Thesis submitted to the Graduate Program in Materials Science and Engineering at UFRN as part of the requirements for the doctoral degree in Materials Science and Engineering.

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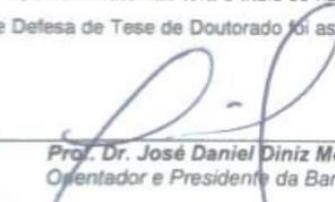
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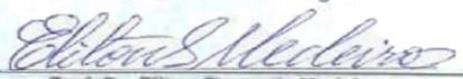
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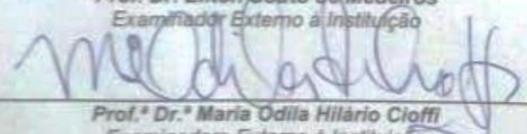
Aos vinte e quatro dias do mês de outubro de dois mil e dezoito, às treze horas, na sala 115 do Setor de Aula IV da Universidade Federal do Rio Grande do Norte (UFRN), realizou-se a Defesa de Tese de Doutorado intitulada "Modification of kapok fibers by cold plasma surface treatment for the production of composites of recycled polyethylene", do Doutorando Murilo José Pereira de Macedo, do Programa de Pós-Graduação em Ciência e Engenharia de Materiais (PPGCEM), tendo como Orientador o Prof. Dr. José Daniel Diniz Melo. A Banca Examinadora foi composta por: José Daniel Diniz Melo (Orientador e Presidente da Banca) - UFRN; Edson Noriyuki Ito (Coorientador) – UFRN; Thercio Henrique de Carvalho Costa (Examinador Externo ao Programa) – UFRN; Eliton Souto de Medeiros (Examinador Externo à Instituição) – UFPB, cuja participação se deu de forma virtual (skype); e Maria Odila Hilário Cioffi (Examinadora Externa à Instituição) – UNESP. Inicialmente, o Orientador expôs aos presentes o roteiro formal da Defesa de Tese de Doutorado e, em seguida, deu início aos trabalhos da Banca, passando a palavra ao candidato para que desse início a apresentação de seu trabalho, marcando o tempo médio de cinquenta minutos para a devida explanação. Concluída a exposição do candidato, o Presidente passou a palavra aos Examinadores, que deram início ao exame oral. Terminada a arguição oral, solicitou aos presentes e ao Doutorando que se retirassem do recinto para que a Banca proferisse o julgamento. Posteriormente, solicitou o retorno do candidato e, em seguida, foi comunicado que o aluno Murilo José Pereira de Macedo foi Aprovado na Defesa de Tese de Doutorado de acordo com as normas vigentes na UFRN. A versão final do trabalho deverá ser submetida, via SIGAA, para fins de homologação, no prazo de 30 dias, contendo as modificações sugeridas pela Banca Examinadora. Conforme o artigo 46 da Resolução nº 197/2013 - CONSEPE, o candidato não terá o título se não cumprir as exigências acima. Nada mais tendo sido tratado, a Ata da Sessão Pública de Defesa de Tese de Doutorado foi assinada pelos membros da Banca Examinadora e pelo candidato ao título.

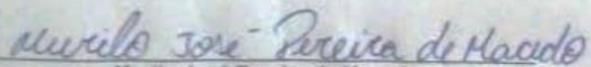
  
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## Dedication

Every battle cannot be won unless you receive true and continuous support.

*I dedicate this work to my family,*  
who gave me unfailing support over this battle!

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## Epigraph

*“Persistence is the shortest path to success”*

Charles Chaplin

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## SYMBOLS AND ABBREVIATIONS

$\Delta H_f$	.....	Enthalpy of sample
$\Delta H_f^C$	.....	Enthalpy of full crystalline material
-p	.....	Plasma treated
a.u.	.....	Arbitrary unit
AFR	.....	Africa Region
ASTM	.....	American Society for Testing and Materials
D <sup>2</sup> TG	.....	Second differential thermogravimetric
DP	.....	Degree of polymerization
DSC	.....	Differential Scanning Calorimetry
DTG	.....	Differential thermogravimetric
Ea	.....	Activation Energy
EAP	.....	East Asia and Pacific Region
ECA	.....	Europe and Central Asia Region
EVA	.....	Ethylene-vinyl acetate
FEGSEM	.....	Field emission gun scanning electron microscope
FTIR	.....	Fourier-transform infrared
F-W-O	.....	Flynn-Wall-Ozawa
HDPE	.....	High-density polyethylene
KPK	.....	Kapok fibers
LACR	.....	Latin America and the Caribbean Region
LDPE	.....	Low-density polyethylene
LLDPE	.....	Linear Low-density polyethylene
MDK	.....	Maddock extrusion element
MENA	.....	Middle East and North Africa Region
MSW	.....	Municipal Solid Waste
OECD	.....	Organization for Economic Co-operation and Development
PE	.....	Polyethylene
PE-g-MA	.....	Polyethylene-grafted-maleic anhydride
PEr	.....	Recycled Polyethylene
PP	.....	Polypropylene
SAR	.....	South Africa Region

SD.....	Standard deviation
SEBS.....	Styrene-ethylene/butylenes-styrene triblock copolymer
SEBS-g-MA .....	SEBS grafted with maleic anhydride
SEM.....	Scanning electron microscope
TGA.....	Thermogravimetric Analysis
T <sub>ONSET</sub> .....	Beginning of thermal degradation
UHMWPE .....	Ultra-high molecular weight polyethylene
ULDPE .....	Ultralow density polyethylene
WPC .....	Wood plastic composites
Wt.....	weight
Wt% .....	percentage weight
WU .....	Water uptake
WWII.....	World War II
X(%).....	Crystallinity

## ABSTRACT

The worldwide production of plastic products has increased significantly over the last decades and their disposal has become an important environmental concern. Recycling provides great opportunities for waste reduction and lower environmental impact. As a recycling alternative, there has been growing interest on addition of biomass residues to polymers to produce composite materials for technological applications. In this study, composites from recycled polyethylene waste and kapok fibers were prepared. Cold plasma treatment was used to improve fiber/matrix adhesion. The effects of plasma treatment on fiber morphology were evaluated using Field-emission gun scanning electron microscopy (FEGSEM) and on chemical structure of the fibers were evaluated by Fourier-transform infrared (FTIR) spectroscopy. Changes in water uptake (WU), mechanical properties and thermal decomposition kinetics behavior of kapok fibers were studied. Results suggest an increase in water absorption after plasma treatment. Composites using untreated and treated fibers were manufactured and characterized. Dynamic mechanical thermal analysis (DMTA) of composites made using plasma treated fibers indicated an increase in storage moduli as well as an increase in glass transition as compared to the pure polymer. Thermogravimetric Analysis (TGA) indicated that the addition of plasma treated fiber produced changes in thermal degradation as compared to the pure polymer due to matrix/fiber interaction. Differential Scanning Calorimetry (DSC) analysis suggested that plasma treatment also produced changes in degree of crystallinity of the fibers. The thermal parameters results also indicated an improvement in thermal insulating characteristic of the composites with the increase in fiber content. Field-emission gun scanning electron microscopy (FEG-SEM) images of composites fracture surface suggest that fiber/matrix adhesion was improved for composites made using plasma treated fibers. Thus, cold plasma is demonstrated as a viable alternative to treat cellulosic fibers and improve fiber/matrix interface of polymer-based composites.

**Keywords:** cold plasma treatment; composites; interface; kapok fibers; plant fibers; recycling.

## RESUMO

A produção mundial de plásticos aumentou significativamente ao longo das últimas décadas e o descarte destes materiais tornou-se uma preocupação ambiental. A reciclagem é uma das ferramentas para a redução do lixo, assim como para a redução dos impactos ambientais. Uma das maneiras de reciclar e obter materiais para aplicações tecnológicas é o uso de recursos da biomassa para obtenção de compósitos. Nesta pesquisa foram preparados compósitos de polietileno reciclado com fibras de kapok (*Ceiba pentandra L.*). Tratamento de plasma a frio foi usado como agente de compatibilização da fibra para a matriz polimérica. Os efeitos do tratamento de plasma na morfologia das fibras foram avaliados por microscopia eletrônica de varredura com emissão de campo (FEGSEM); na estrutura química das fibras foi avaliado por meio de espectroscopia na região do infravermelho com transformada de Fourier (FTIR). Mudanças na propriedade de absorção de líquidos (água e óleo), propriedades mecânicas e o comportamento da cinética de decomposição térmica foram estudados. Os resultados indicam um aumento no padrão de absorção de líquidos após tratamento por plasma. Compósitos usando fibras não-tratadas e tratadas foram produzidos e caracterizados. As propriedades dinâmico-mecânicas indicaram um aumento no módulo de armazenamento assim como um aumento na transição vítrea em relação ao polímero puro. A análise termogravimétrica (TG) apontou que a adição de fibras tratadas resultou em mudanças na degradação térmica quando comparada ao polímero puro. Além disso, a análise por calorimetria exploratória diferencial (DSC) sugeriu que o tratamento por plasma também promoveu mudanças no grau de cristalinidade das fibras. Além disso, parâmetros térmicos também mostraram aumento na característica de isolamento térmico à medida que o teor de fibras aumentou. Imagens de microscopia eletrônica de varredura com emissão de campo da superfície de fratura dos compósitos sugeriu que a adesão matriz/fibra foi melhorada para os compósitos compatibilizados. Assim, plasma a frio é mostrado como uma alternativa viável ao tratamento de fibras celulósicas a para o melhoramento da adesão interfacial entre matriz e reforço de compósitos poliméricos.

**Palavras-Chave:** plasma a frio; compósitos; interface; fibras de kapok; fibras vegetais; reciclagem.

## 1 INTRODUCTION

Plastic and composites based on polymeric matrices have replaced traditional materials, such as metals and wood, in many applications. These “commodities”, as they are referred to in the industry, include polyethylene (PE), polypropylene (PP), polystyrene (PS) and poly vinyl chloride (PVC). Inarguably, these four together have completely dominated packaging practices, from the flexible film of bags to rigid containers. Although there are many advantages of using these materials, their non-biodegradability causes various types of environmental imbalance, such as changes in the equilibrium of oceans and animal feeding patterns (1) when simply discarded into the environment after use.

A study published in 2012, as part of the Urban Development Series produced by the World Bank’s Urban Development and Local Government Unit of the Sustainable Development Network, discusses the consequences of current practices involving solid waste management (2). When not properly disposed, solid waste contributes to air pollution, flooding, and enormous impacts on public health such as respiratory disorders, diarrhea and many vector-borne diseases. Currently, cities around the world generate about 1.3 billion tons of solid waste every year and, by 2025, this number is expected to increase to 2.2 billion tons per year, as presented in the Table 1.1. Estimates have indicated that, in Europe, plastic wastes represent 15-25% of the total municipal waste (3).

**Table 1.1** Municipal Solid Waste (MSW) generation by world regions (2)

Summary by Region								
Region*	Numbers of countries included	2012			Projections for 2025			
		Total urban population (millions)	Urban MSW generation		Projected population			
			Per capita (kg/capita/day)	Total (tons/day)	Total (millions)	Urban (millions)	Per capita (kg/capita/day)	Total (tons/day)
AFR	42	261	0.65	169,120	1,153	518	0.85	441,840
EAP	17	777	0.95	738,959	2,124	1,230	1.52	1,865,380
ECA	19	227	1.12	254,389	339	240	1.48	354,811
LACR	33	400	1.09	437,545	682	466	1.56	728,392
MENA	16	162	1.07	173,545	379	257	1.43	369,320
OECD	27	729	2.15	1,566,286	1,032	842	2.07	1,742,417
SAR	7	426	0.45	192,411	1,939	734	0.77	567,545
<b>TOTAL</b>	<b>161</b>	<b>2982</b>	<b>1.19</b>	<b>3,532,255</b>	<b>7,648</b>	<b>4,287</b>	<b>1.42</b>	<b>6,069,705</b>

\* Symbols definition

AFR ..... Africa Region  
 EAP..... East Asia and Pacific Region  
 ECA ..... Europe and Central Asia Region  
 LACR ..... Latin America and the Caribbean Region  
 MENA ..... Middle East and North Africa Region  
 OECD ..... Organization for Economic Co-operation and Development  
 SAR ..... South Africa Region

Based on this situation, strategies for improving the use of resources must be on the forefront of the agenda for researchers and companies in the coming years. Likewise, academic

and industrial researchers must rise to this challenge in order to find a balance between the use of these materials and their disposal and/or recycling. They must also identify new renewable materials to help create lines of biodegradable products based on natural sources. Along this line, findings from research regarding properties and characteristics of given materials, may be used for indicating suitable applications for each material. Currently, scientific research has provided ways to determine the molecular structure of polymers, as well as development of several kinds of polymers, synthesized from organic molecules – synthetic polymers. Along with other developments, studies that improved polymer technology have changed the scenario, especially post WWII, when synthetic polymers became increasingly important as polymerization control made it possible to change and improve several characteristics in the products. This has encouraged industrial producers to use these materials rather than others from natural sources. Metal and wooden parts have been replaced by plastics in various industrial applications, due to the low cost and relevant properties of these synthetic materials (4). Finally, industrial producers have recognized the benefits of recycling these materials.

Studies have reported many incentives for using recycled plastics, including ecological sustainability, consumer demand, recycled-content legislation and cost effectiveness. Along with these, new recycling technologies have shown to improve the original properties of the products while putting them back into use. Currently, problems associated with recycling have been solved by using automated sorting and the implementation of quality standards in plastic recycling. A previous study (5) reported three essential elements of plastic recycling: “(i) a stable supply source which involves reliable collection and sortation; (ii) an economical, proven and environmentally sound recycling process; and (iii) end-use applications for the recycled polymer which yield economic market values and capture consumer confidence.”

Moreover, attempts at mixing these polymers with natural-based products– such as vegetable fibers – have proven to be worthwhile in obtaining green composites. A recent work has reported the use of kapok husk as filler, creating composites with recycled polypropylene (PP), indicating several possibilities for developing this important set of composites, based on natural resources (6). Creating composite materials from recycled polymers and cellulose-based fibers has long been on the industrial agenda given environmental necessities and cost effectiveness. The use of kapok (*Ceiba pentandra L.*) as a cellulose source for developing composites has gained attention as cellulose-based materials present many desirable characteristics, such as low cost, lightweight, non-toxicity and biodegradability (7; 8). Kapok fibers are distinct among other fibers regarding hydrophobicity and oil uptake capacity, making

it and other kapok-based materials a favorable choice for products concerned with properties linked to absorbance (9).

Composite materials developed from recycled polymers and plant fibers have been in the forefront of research and largely reported on given that this process involves both recycling and natural resources – two issues that address the catastrophic state of plastic waste management, as previously mentioned. The aims of many of the current studies have been to reduce the use of virgin plastic and develop more and lower cost recycling processes for used plastics (10). Thus, these strategies for improving the use of materials and new ways to reuse/recycle must be evaluated and fine-tuned by researchers around the world, especially for polymeric materials as their use has skyrocketed in the last decades. In short, both the development of new technologies and the optimization of current ones are important issues for researchers to consider.

Another current problem in developing composites reinforced with natural products, such as plant fibers, is the processing temperature. This includes the processes of extrusion and injection molding, given that these processes require heating at high temperatures – many times higher than the safe temperature – for lignocellulosic components, because fibers are subjected to thermal degradation when manipulated at elevated temperatures. Thus, understanding the thermal behavior of natural fibers becomes necessary prior to manufacturing composites. With this sense, this study was developed in three steps: the first was a study of thermal behavior of kapok fibers, followed by composite processing using both treated and untreated kapok fibers and, finally, an evaluation of composite characteristics with the addition of plasma-treated fibers.

The properties of many polymers and composites are desirable in various categories of application, however, the extended length of time it takes for these materials to break down turn them into serious environmental problems. Therefore, the development of strategies and technologies for reducing the post-consumption lifetime of these material is the main priority of this study. Clearly, then, recycling technologies together with the recovery of biomass resources are socially relevant fields to be developed and the focus of this paper.

In the first study developed in this work, kapok fiber samples were modified under cold plasma and their thermal degradation properties were evaluated. Thermal decomposition kinetics analyses were carried out in order to determine the activation energy of the main fiber contents, such as cellulose, hemicellulose and lignin.

Subsequently, composites based on plasma modified kapok fibers as filler/reinforcement for polyethylene were fabricated and the effect of plasma treatment on the fiber/polymer interface was evaluated.

Finally, in order to understand the effect of the addition of plasma treated kapok fibers on the recycled polyethylene, the amount of fiber added to the matrix was observed. Changes in mechanical, morphological and thermal properties were evaluated. In addition, correlations between molten behavior of composites and dynamic mechanical analyses were developed.

## 2 OBJECTIVES AND THESIS STRUCTURE

### 2.1. Objective

The objective of this research was to study the mechanical and thermal properties of a composites based on recycled polyethylene and kapok fibers. Plasma treatment was carried out on kapok fibers and its effects on fiber properties and fiber–matrix compatibility were also studied.

The main contributions of this work include providing a better understanding of:

- a. The effect of plasma treatment on the chemical, morphological and thermal properties of kapok fibers (1<sup>st</sup> article);
- b. The effect of plasma treatment on the polymer/fiber interface of PEr/kapok composites (2<sup>nd</sup> article);
- c. The effect of the addition of plasma treated fibers on the mechanical and thermal properties of recycled PE (3<sup>rd</sup> article).

### 2.2. Thesis structure

The overall object of this research involves recycled polyethylene and kapok fibers (biomass residue). Three interconnected studies were carried out as separate articles, constituting three of the chapters of this thesis. This thesis is divided into seven chapters. Chapter one presents a general introduction about the topic in question. Chapter two outlines the main objectives and contributions of this work. Chapters three and four present the theoretical framework for these studies a thorough literature review about polymers, recycling, vegetable fibers, composite materials, coupling processes for composites and mathematical models for thermal studies, as well as recent reports regarding this approach. Articles detailing specific studies on the overall research comprise chapters five, six and seven, which are described as follows:

In chapter five, the first article, entitled “*Surface modification of kapok fibers by cold plasma treatment*”, aims to determine the thermal behavior of fibers before and after plasma treatment. This analysis was performed in order to understand changes in characteristics when fibers are subjected to high temperatures, as in composites processing. Activation energy ( $E_a$ ) of samples was evaluated before and after plasma for a better understanding of the kinetic

parameters. This analysis has largely been used to determine the purity of cellulose. The results are displayed in thermal decomposition behavior and using mathematical models for obtaining  $E_a$ . In addition, changes in morphology, chemical bonds and absorption properties were also analyzed. Chapter six presents the second article, entitled “Effect of cold plasma treatment on recycled polyethylene/kapok composites interface adhesion”. The aim of this work was to evaluate the influence of plasma treatment in kapok fibers on the fiber/matrix adhesion enhancement. In this study, composites were prepared using both treated and untreated fibers to assess the influence of plasma treatment in composites’ performance. The results are displayed in dynamic mechanical, thermal and morphological analyses.

Lastly, the third article, entitled “*Composites from recycled polyethylene and plasma treated kapok fibers*” is presented in Chapter seven. This study was carried out aiming to evaluate the effect of fiber content on the thermal and mechanical properties of composites. The results are obtained are based on thermal changes as well as mechanical behaviors. In addition, correlations between molten behaviors with dynamic mechanical analyses are presented.

Finally, a partial summary of this study is presented, followed by a general conclusion, future perspectives and a list of references.

### 3 BACKGROUND

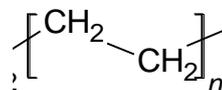
Several materials have been developed over the years with the objective of improving the quality of human life. Some of these materials include polymers, which is an important class of material due to its vast range of application. The first type of polymers was nature-based, such as cotton, starch, leather, proteins and wool, which are easily found in nature and have been used throughout many centuries. A second type, synthetic polymers, was first reported in the literature at the beginning of the twentieth century. The science of polymers arose out of the necessity of scientists to fully understand new materials they had been using for a some time, such as Bakelite and Nylon – the most important ones during that period. The characteristic of the most important materials was given to them because they could spring up possibilities of new materials. Nevertheless, the current problem is the association between chemical structures and physical properties, which has not been completely elucidated by scientists and researchers yet. In addition, polymers are usually shown as long-chain molecules (macromolecules) due to their huge molecular weight. In many studies, authors may refer to polymers as resins, which was the term used before the chemical structure of chains had been properly understood. **Structural groups**, also called **repeat units** are repeated along the chain, forming large molecules. The term **monomer** is related to this single repeated group, which, after several reactions together, becomes a macromolecule and subsequently, a long-chain polymer (11).

Once polymers are manufactured from several parts of a small chemical group, all their inner characteristics are due to the behavior of small molecules. Then, the molecular weight obtained acts as a main characteristic to connect to the polymer properties. In both large and small molecules, it has been shown in the basic literature that at room temperature components showing up to four carbons are gases that boil at about 36°C. In a particular analysis, it is very difficult for some macromolecule to exhibit equal distribution regarding molecular weight. The polymerization process involves several sequential reactions, which take place as a result of many features. Due to this, researchers prefer working out molecular weight averages. For example, compositions of usual alkanes can be analyzed, averaging 20-25 carbon atoms, which are crystalline at room temperature. These components are normally labeled as waxes. Furthermore, chains showing up to 50 carbon atoms in the material are far from being considered polymeric structures (4).

### 3.1 Polyethylene

Polyolefins represent the largest plastics constituent in the world. Approximately 60% of the global necessity is related to these materials. Use of these samples is largely linked to high-density polyethylene in commercial bottles as well as low-density polyethylene (LDPE) in thin films, based on intrinsic characteristics of each type. Polyethylene is a polyolefin known as the smallest repeat unit from all polymers, due to this small chain with only two main carbons, which are from the ethylene group. It is known as a commodity plastic, however, due to its changeability, these polymers are favored in advanced applications if good projects and executions are performed. It is easily processed, it has excellent chemical resistance and it is not expensive. There are many kinds based on primary structure, as defined throughout this section (5; 12).

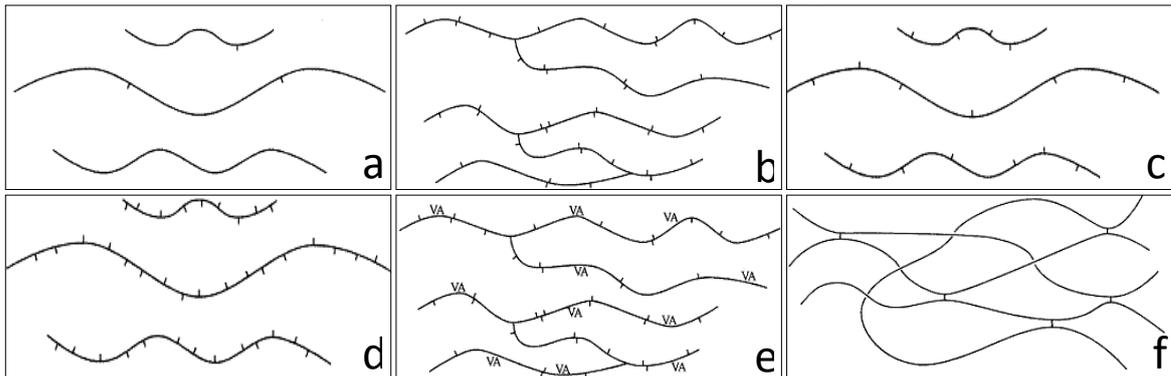
The polyethylene (PE) molecule, in its normal structure, can be shown as a lengthy, backbone-like structure with a great number of covalently linked carbon atoms, which, in turn, are individually connected to hydrogen atoms, and methyl groups are seen at the ends of the chain, as shown in Figure 3.1.



**Figure 3.1** Basic structure of the polyethylene

Resins from PE are conventionally represented throughout the formula  $\text{C}_{2n}\text{H}_{4n+2}$ , in which  $n$  represents the amount of ethylene monomers polymerized to get the polymeric chain. In other words, this characteristic is the degree of polymerization (DP) as well. Usually the DP for obtaining PE is about 250,000 or more, with a molecular weight ranging from 1400 to 3,500,000. It is accepted as convention that low molecular weight PEs, also named oligomers, showing DP from 8 to 100 are not actually polymers, but waxy solids without the properties and features of plastic. Furthermore, if this DP is less than 8, the material obtained might be gases or volatile liquids. Polyethylene is a term that comprises a group formed by several types of structures. Actually, there are many kinds of PE, however, all of them show essentially the same backbone-like structure of covalently linked carbon atoms linked to hydrogen atoms, as previously mentioned. The main differences are related to branches because there are many types, from alkyl to functional groups, such as acid or ester. Based on solid state, both branches

and some less important defects are limiting factors to the crystallinity index. A sample of chains with a small number of defects usually has a greater degree of crystallinity. The literature shows that the increasing concentration of branches in a chain causes a virtual decrease in the density of the solid material. The more branches in a chain, the more empty spaces between chains, which causes an increase in the volume of material, resulting in a decrease in density (13), as shown in the Figure 3.2.



**Figure 3.2** Main classes of Polyethylene-based polymers: (a) HDPE; (b) LDPE; (c) LLDPE; (d) ULDPE; (e) EVA and (f) Ionomers (13)

Each PE type exhibits several different characteristics related to the number of branches along chains, such as density, and mechanical and chemical properties. Based on the theory, PE should exhibit a long chain with no connected branches. However, it is not common to find a “perfect chain” like in the theory. Nonetheless, there are particularities among them that allow us to classify each one as polyethylene (13).

Analyzing all of the PE structures displayed, the one closest to theoretical PE is (a) HDPE, due to its linearity and lack of branches, as well as the lack of many defects throughout the main chains. Its characteristic organization gives this polymer an elevated degree of crystallinity, as well as high density. Some applications need changing before using, and then small groups such as alkenes are copolymerized aiming to reduce this crystallinity level. Commercial resins from HDPE are found with densities between 0.94 and 0.97 g/cm<sup>3</sup> (13).

Unlike the HDPE, PE can be found as low-density structures, called Low Density Polyethylene (LDPE). The main difference between them is linked to the amount of branches in main chains, moving chains away from each other. Having a large number of branches, the crystallization process is virtually blocked, because chain conformation depends on its own movement, which is drastically reduced by branches. These branches in the main chains are based on both ethyl and butyl groups, connected together in the chain. Behavior of chain reactions can change for each situation because several mechanisms are observed and they are

largely linked to pressure, temperature, besides the availability of reactive structures, which allow them to react in diverse ways. As previously mentioned, PE types with a large number of branches reduces crystallization and density tends to diminish compared to other types of PE, showing values between 0.90 and 0.94 g/cm<sup>3</sup> (13).

Researchers and industries have applied PE-based material in many situations and under different processing conditions. To obtain materials with the characteristics needed for these applications, a new specific sort of PE has been developed, which counts on an extremely low density, ranging from 0.86 to 0.90 g/cm<sup>3</sup>, called ultralow density polyethylene (ULDPE). This new material presents this value because during its processing, the reaction has been controlled to induce a high concentration of short-chain branches. It is common to find branches in small distances and with a huge number, hindering the crystallization process, which makes this PE a non-crystalline type material.

PE-based polymers are extremely easy to find in many applications, from research laboratories to specialized industries. In addition, it is possible to synthesize copolymers in order to create very different structures rather than just one kind of polymer. Two of the most relevant of these copolymers are ethylene-vinyl ester copolymers and Ionomers. An important example of the first is the ethylene-vinyl acetate (EVA), which is widely used in diverse applications. This PE has an important characteristic due to the polar groups inside its chemical structure. Branches formed by acetate groups act as a crystallization control, giving these materials the possibility of being either similar to LDPE or elastomeric. Although Ionomers are copolymers as well, they are produced using metal salts from acrylic acids after the neutralization process, to be linked to ethylene resulting in copolymerization. The reason for putting salts in polymeric chains is related to its ability to crystallize, nevertheless, in this case, the density of ionomers appears as the highest in comparison with the aforementioned PE, since elements such as oxygen and metals show an elevated atomic weight, raising the density of this group.

### **3.2 Vegetable fibers**

Ideas to develop products from renewable sources are connected with environmental concerns such as global warming and the misuse of energy, problems that researchers around the world have endeavored to study over the last years. With this in mind, interest in finding and using green materials has increased substantially, this is especially true for natural fibers, since it is a type of renewable material, also available in high quantity and good quality, and

offers suitable mechanical properties. Another reason to discover new sources for using plant fibers instead of synthetics is the environmental cost of manufacturing synthetics, such as glass and Kevlar fibers. Vegetable fibers exhibit different contents of cellulose, hemicellulose and lignin, besides other less important compounds. Although fibers contain many compounds, the main constituent is cellulose, which is lined up forming bundles that are usually linked with other constituents such as lignin, pectin and hemicelluloses (14-17).

Natural fibers are usually defined as “natural composite structures” in which cellulose microfibrils are the reinforcement and, on the other hand, lignin and hemicellulose are the matrix. They can also be considered as naturally occurring composites consisting mainly of cellulose. Each component can be ranked under its main characteristics, as hemicellulose, which is responsible for biological and thermal degradation. On the other hand, both lignin and hemicellulose are responsible for flame degradation properties.

Cellulose was shown as a natural polymer consisting of D-anhydroglucose ( $C_6H_{11}O_5$ ) repeating units joined by 1,4-b-D-glycosidic linkages at C1 and C4 position and showed a degree of polymerization (DP) of nearly 10,000. There are several types of cellulose, nevertheless, the crystal nature of naturally occurring cellulose is known as cellulose I – a monoclinic sphenoid. Cellulose is also moderately chemically resistant, with oxidizing and alkali agents. In contrast, it is readily hydrolyzed by acid under an aqueous solution. Both cellulose and hemicellulose are polysaccharides, nevertheless, the difference observed between them is that cellulose displays a semi-crystalline structure and it is responsible for the hydrophilic characteristic of natural fibers due to the existing hydroxyl groups. On the other hand, hemicellulose shows an amorphous polysaccharide, which has a lower molecular weight compared to cellulose. Due to this characteristic, hemicellulose is partially soluble in water and hygroscopic with the presence of hydroxyl and acetyl groups. Inside the structure, the hemicellulose molecules are normally hydrogen bonded to cellulose and act as a cementing matrix, forming the cellulose–hemicellulose network, which is the main structural component of the fiber cell. Several properties related to cellulose fibers are broadly connected to the nature and age of the plant, as well as with the applied method to extract it from the plant. Finally, as a renewable resource that requires little energy in manufacturing processes, cellulose does not impact negatively on the environment (18-22).

Natural polymers like cellulose are moderately stable. Cellulose-based fibers usually present favorable features such as flexibility and elasticity, based on results from tests with synthetic fibers such as glass and carbon fibers. Frone et al. (23) have reported that these observed properties make it possible to keep large aspect-ratio in the manufacturing process.

With regard to their physical and chemical characteristics, these components are insoluble in almost any kind of solvent. The mechanical properties of plant fibers are widely connected to crystallinity index (CI), which measures the quantity of cellulose inside fiber samples. Fibers with either raised crystallinity or elevated cellulose content show better mechanical properties when compared with similar samples with low crystallinity. Sisal fibers have been reported at about 67% cellulose content and modulus of elasticity of 530 MPa. In contrast, coir fiber shows 43% cellulose content and modulus of 106 MPa (24).

Lignin is another important constituent of natural fiber, being totally amorphous and hydrophobic in nature, along with being a complex hydrocarbon polymer with both aliphatic and aromatic constituents. The lignin content of the bast fibers was shown to influence several characteristics such as its structure, its properties and morphology. Several studies have been carried out over the last years in order to determine structure units of lignin, but the greatest challenge is linked to the impossibility of isolating lignin from fiber in its native state. Some results showed structural units of lignin molecule as 4-hydroxy-3-methoxy phenyl-propane derived (14; 25-28).

In addition, natural fibers such as hemp, jute, coconut, carnauba and sisal fibers, have shown good results in the literature when used to produce biodegradable composites. Numerous studies show that natural fibers prove to be a low-cost, accessible, environmentally friendly alternative to synthetic fibers in composites manufacturing, as products developed using these fibers present good strength per weight of material (29-34).

### **3.3 Kapok fibers**

The Kapok tree (*Ceiba pentandra*), originally cultivated in the East Indies, is a large tree whose fruits contain seed fibers similar to cotton, which have been used for upholstery and lifebelts, due to their water-resistant characteristics. These fibers have different morphological characteristics in comparison to similar fibers, such as cotton, namely its hollow lumen, composed of a thin, tube-like, wall. Consequently, kapok fiber samples exhibit low apparent density. The fibers surrounding the seeds present a circular cross-section area. These fibers fill the inner part of the kapok fruit. These silky and hollow fibers can easily be obtained from the ceiba tree fruit through its opening, as shown in Figure 3.3. Kapok (*Ceiba pentandra L.*) is a cellulosic fiber with a high degree of hollowness (80–90%), considered the largest among natural fibers, it is moisture-resistant, buoyant, resilient and soft. Kapok fibers have many

unique properties that are relatively new to the textile industry and with great potential for studying. Biologically these fibers develop seed protection (35).

Previous studies show, in detail, both the physical and chemical characteristics of kapok fibers. Researchers have found an average external diameter of  $16.5 \pm 2.4 \mu\text{m}$ , internal diameter of  $14.5 \pm 2.4 \mu\text{m}$ , and length of  $25 \pm 5 \text{ mm}$ . Its specific material density is  $1.31 \text{ g/cm}^3$ . These fibers usually show 64% cellulose, 13% lignin and 23% pentosan. Another, more specific study showed that, in addition to the cellulose and lignin contents, the fibers contain 8.6% water, 1.4% to 3.5% ashes, 4.7% to 9.7% water-soluble substances, 2.3 to 2.5% xylan and 0.8% waxes. Another characteristic found is high hydrophobicity, due to a large amount of wax along the fibers (36-40).



**Figure 3.3** Kapok tree pod and details

### 3.4 Composite materials

With advances in materials and the need for specific properties, composite materials arose as a solution due to the wide range possible for mixing components in order to obtain the desired properties. This range of combinations has made fiber reinforced composites more attractive to industry than unreinforced materials. Thus, continual discoveries of natural (and renewable) components has prompted an infinite number of applications and characteristics that can be obtained through the development of composites (41; 42).

It is well known in the literature that mixing properties of both lignocellulosic materials and thermoplastics generated many applications. Lignocellulosic composites using polyolefins as matrix have received greater attention over the last decades, from the scientific community to big industries. Based on studies and observations, it was discovered that nature provides several types of materials, such as natural fibers, which show to be extremely useful in reinforcement composites. It should be noted that some natural and biological structures

occurring in nature are natural composites. Examples of these components are wood (in natural form), bamboo, bone and teeth (42; 43).

Among all of the different types of polymers, thermoplastic has a characteristic of reprocessing after the use and discard, which enables developing thermoplastic composites with enclosing organic material provided from renewable sources. The combination of these two materials has proffered several benefits, from environmental gains to physical and mechanical properties, as well as cost effectiveness and recyclability, which foster new applications. This approach has become even more relevant as a result of the current efforts in the area of environmental and sustainable development. Consequently, composites made of lignocellulosic fibers together with thermoplastic polymers, such as PE, have established their place in current and further developments. Thus, the production of lignocellulosic materials has increased and, as a result, advances have been made in studies aiming to describe the actual behavior and properties of these materials (43-45).

Various authors have reported that composites are the most important class of material as they are used both in advanced applications, such as the aerospace industry, as well as in common products, like electronic packaging, inner parts of automobiles, trains, aircraft, etc. Composite materials are also found in oil exploration and processing and are frequently found in biomedical fields, due to property as biocompatibility (29; 41; 46).

### **3.5 Wood Plastic Composites**

Adopting the composite approach – mixing different materials to improve them and achieve synergism in their properties – there are other composite classifications based on the amount of filler and/or reinforcement applied. Incorporating these components opens up new possibilities and applications. Wood plastic composites (WPC) offer a viable alternative to using common polymers, which are not easily biodegradable. Similar to other common composites, WPCs show matrix and reinforcement (filler) in its inner structure, however, in order to obtain better final characteristics, a coupling process followed by adequate processing (e.g., internal mixer, extrusion and injection molding) are essential. The actual advantages of using WPCs instead of other common composites are largely linked to the possibility of application, replacing both traditional polymers and wood derivatives. Indeed, increased attention is being paid to materials that do not damage the environment when discarded or materials that are easily recycled. Thus, researches for developing WPCs, especially from recycled polymers and connected to wood (cellulose) derivatives, are on the rise (47-49).

Furthermore, fire properties and moisture uptake have become more relevant in evaluating materials in the past few years due to increasingly specific applications, in which the control of flame reduction and biodegradability is essential. Thus, industries around the world have demonstrated interest in developing reliable flame-retardant materials. On the other hand, the ability to absorb water must also be calculated prior to application because biodegradation agents are carried by water from outside to inside, thus affecting the final product if not previously controlled (1; 50).

Interests in developing WPC have increased in the last year both in academic and technological areas due to the new possibilities for application and reduction in the amount of polymer in the composition. The goal for WPC is to increase the amount of cellulose-based materials, promoting the use of natural and renewable material rather than merely synthetic or those with a low level of reinforcement. WPCs can be obtained through several processes, such as injection or compression molding, and is performed by mixing plant fibers with polymer matrixes, similar to classical composites, or by adding wood fiber as filler in a polymer followed by high pressure and temperature for molding. Notably, WPCs alone are not ready for every application, and in some cases, aggregates need to be modified to achieve the desired properties by products such as blowing agents, coupling agents, colorants and fire retardants. Thus, the final properties are entirely linked to several factors, such as volume fraction and aspect ratio, dispersion level, mixing time and processing temperature and fiber-polymer interface bonding (51; 52).

### **3.6 Polymer recycling**

Concerns associated with discarding materials after use increases yearly due to the urgent need to reduce the amount of plastic waste sent to landfills. The accumulation of recyclable materials in many places has aggravated already very serious environmental problems, adding the possibility of causing diseases. In the natural degradation process polymers can emit toxic components, such as aromatic compounds, into the natural environment. Moreover, landfill capacities have drastically decreased and the consumption, in contrast, has exponentially increased. Therefore, saturating landfills as a final solution for managing the discarding of plastic materials is not an ideal choice. Subsequently, facing this dilemma, over the years, attempts to find a better solution/destination has come to the attention of the industrial sector and researchers. They have started developing technologies aimed at reducing the usage of these synthetic polymers, stimulating the reprocessing of these materials

instead of long-term storing measures in landfills. It has been reported that high density polyethylene (HDPE), low density polyethylene (LDPE) and mix of LDPE with linear low-density polyethylene (LDPE/LLDPE), polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS) and polyvinyl chloride (PVC) are the main polymeric constituents in Municipal Solid Waste (MSW). This observation leads to the necessity for increasing methods for recycling to obtain materials with improved properties, and reduce the environmental impact when discarding, as well as the use of virgin samples through reutilizing the polymeric materials after first usage, as reported in a recent study (53; 54).

However, managing polymeric material presents particular challenges. Researchers must address the fact that polymers are rarely additive-free. These additives are usually fillers, pigments, antioxidants and flame-retardants, which complicate the recycling process if the presence of foreign components is not analyzed prior to recycling. Additionally, if processing factors such as flow indices and thermal stabilities are different from one another then final properties would not be reliable (5).

Nonetheless, attempts to improve recycling technologies have increased in last decades due to the amount of discarded materials and the increase in the amount of new materials being released into the environment by human consumption. A study carried out with recycled PET/HDPE composites presents an overview about one possible solution for recycling polymers originating from urban waste (55). The study gathered information reported by several authors.

Mechanical recycling is the first point cited by the authors, which is basically separation and recovery of suitable materials for other usage, with no further changes. Another solution is known as energy recovery, in which polymers are incinerated and hydrocarbon polymers are used as replacement for fossil fuels, then, under pyrolysis or hydrogenation to low molecular weight hydrocarbons for using as fuel and/or polymer feedstock for other processing. Moreover, there is also biological recycling, which is considered more advantageous against biodegradation, which is dependent on polymer and many environmental properties. However, the high cost together with the difficulties in running these experiments, hinder the execution of this process, which is why it is rarely performed. Subsequently, thermal-mechanical recycling was suggested as a viable alternative. To perform this technique, first the samples are mechanically granulated and then extruded for further molding (final shape and characteristics). Initially, this process is easy and to render good results, however, a cost analysis has demonstrated there are disadvantages in using recycled instead of virgin polymers (55-58).

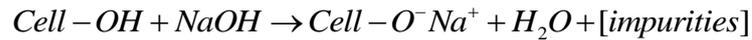
The authors analyzed that to be profitable for industries, the amount of energy to produce the virgin material added to the energy needed for its disposal must be up to the energy to recover used materials and energy during its reprocessing. Unfortunately, this balance does not show good economic results in most cases. From this perspective, recycling is not seen as advantageous. However, environmental benefits are not included in this balance. The actual gains could be achieved by reducing landfills, as well as reducing irrevocable damage to sea-life and the world's oceans, which is commonly caused by unrecycled waste (55-58). Degradation while reprocessing is also a problem regarding recycled polymers, as cited in a previous study about methods for characterizing recycled polymers (57).

### **3.7 Fiber and polymer modification**

There are many advantages in using fibers for composites reinforcement. Nevertheless, the best results would not be achieved unless a strong adhesion between fibers and synthetic matrices occurs. Although fibers normally show desirable properties, they might have characteristics such as incompatibility between them and the polymeric matrix. The main problem is that the performance and stability of composite materials based on fibers is deeply dependent on a good interfacial fiber-matrix bonding. Without any treatment to change polymer-fibers interface, it would be difficult to get a good interface between hydrophilic cellulose fiber and hydrophobic resins because of their natural incompatibility. Furthermore, cellulose fibers can agglomerate, thus reducing the fiber-matrix interface area. It is also reported that waxes on fiber surfaces worsens fiber-resin bonding, thereby creating low wettability (59; 60).

Usually, cellulose fibers are hydrophilic while polymer matrices are hydrophobic. Several treatments can be applied to fibers to modify their structure and improve their properties. Studies have shown that chemical treatments can modify fiber surfaces, with alkaline, acetylation, permanganate and peroxide treatments, among others. Treatments that increase the surface roughness and increases the amount of cellulose exposed on the fiber surface, in a process known as mercerization (alkaline treatment with sodium hydroxide NaOH), is one of the most common processes due to the increase in the number of possible reaction sites. There are other treatments available to apply along with mercerization, such as acetylation. This treatment has been extensively applied to samples of wood cellulose in order to improve both the stabilization of cell walls and dimensional stability (59-62).

Some authors have successfully employed the alkaline treatment with sodium hydroxide to change natural fibers. Actually, this process works removing some oils and waxy substances from external surfaces of the fiber cell wall, thus promoting cellulose fibrils with rough surface that are then susceptible for chemical reactions. This alkaline treatment has been the most used chemical treatment for this surface cleaning process, along with changing the structure of native cellulose I to cellulose II. Chemically this reaction is presented as follows (24; 63; 64).



The mercerization process is conceived of in distinct ways throughout the literature. Some authors have used the definition of mercerization as “a process in which cellulose has been treated under alkali metal hydroxide (solution) of enough strength to convert all cellulose I to cellulose II, also called sodacellulose” (65). However, these authors also reported that residual cellulose I can be found after conversion even if optimum process conditions were maintained. Other authors have indicated that the mercerization process applied with no tension entirely converts cellulose I to II (66; 67). In applying tension to material, it is possible to keep an organized distribution of crystallites, however, it is not possible to achieve total conversion.

Researchers in recent years have found important results about changing cellulose structures, such as mercerization of cotton fibers, which change the native form of cellulose from type I to type II, as previously mentioned, modifying parallel structures to anti-parallel structures. The main advantage is that cellulose II has some inter-sheet hydrogen bonding (68). In addition, other authors found that alkaline treatment could improve interfacial adhesion strength with natural rubber and starch/ethylene vinyl alcohol (EVOH) copolymer resin while changing the thermal behavior of fibers for high values (32).

### **3.8 Plasma treatment**

There are many other treatments that can be performed in natural fibers, which are not chemical methods such as those previously mentioned, including plasma treatment, which is a physical method, acting as an alternative due to its environmental characteristic. Usually plasma treatments for surface modification are grouped in low radio frequency, high radio frequency, and direct current discharge. These treatments have been successful in producing surface modification such as cleaning, etching, deposition and polymerization. Previous studies have shown advantages in using plasma over chemical treatments, such as lower operating costs and shorter treatment times (69-71).

Textile industries have undergone many changes under plasma treatment due to the simplification of the process, with lower costs and time-savings, in addition to being a feasible alternative to a chemical process. It is common knowledge in the field that plasma treatment has been used to modify both fibers and polymers, through changes achieved by plasma gases. However, this process involves only the surface layer and does not change the bulk properties. Nevertheless, the actual changes depend on factors such as chemistry of plasma gases and operating conditions, such as the process time, electric current and working distance. These factors combined induce material chemical alterations from surface activation by the creation of carboxyl and/or hydroxyl groups and physical changes, such as wettability (72-77).

Plasma technique presents environmental advantages as it does not rely on chemical reagents, which makes it eco-friendlier. Furthermore, the changes in the material due to plasma treatment happens only in a thin surface layer, many times a few nanometers deep, which does not modify the inner properties of the treated material (78-80).

Plasma processes can be applied at high or low temperatures. For polymers and plant fibers, it has been shown that cold plasma offers advantages. Cold plasma treatment is capable of improving matrix/fiber adhesion, while bulk properties remain unchanged. Plasma processing occurs in a system with low pressure and low temperature in a vacuum reactor in which an electrical discharge becomes the gases inside the plasma. Chemical and physical characteristics are evaluated from process data, such as gas pressure and flow rate, vacuum chamber geometry, electrical power, and composition of atmosphere. Good results in plasma treatment can only be achieved after carefully combining data such as treatment time, temperature, voltage, pressure and information about the chemical structure of material being exposed to treatment. Several changes may take place in this treatment, such as the addition of new chemical groups to the surface of the material, due to the recombination of chemical bonds (81; 82).

Plasma has been used as a modifier for polymers and fibers for improving matrix/reinforcement interface. A recent review article has presented fundamental information about plasma modifying characteristics. The authors concluded that plasma treatment may be applied in the modification of several adsorbent materials, such as carbon and silicon materials. They also report plasma as an effective and environmentally-friendly technique to induce or graft functional groups on the sample surface, which may be used to control properties, depending on the gas used in the plasma process. These studies attest to the progress that has been made along these lines. Different approaches have also been studied in an attempt to improve the process and thereby the results (83). Energization methods and processing

parameters such as voltage, current and vacuum characteristics have significant impact on the results obtained. Nevertheless, controlling these parameters throughout the process can be complicated. Thus, this can result in non-uniform treatment, such as in the case of surface modification, in which one part of the samples may receive more grafting than another part.

Plasma treatment may be used for removing surface impurities, for introducing functional surface groups and inducing changes in polymer chains. The influence in topography has also been evaluated, in which plasma acted as a modifier in the nanotopography of a cellulose constituent. Studies based on SEM images and performed on cotton fabrics have suggested that the surface of cellulose fibers became rougher after plasma treatment with a significant number of tiny grooves and cracks. Authors have concluded that plasma etched the surface of cotton fabrics (84-86).

Plasma processing acts as physical modification, but chemical reactions may also occur in treated surfaces. It has been reported that plasma induces an increase in surface roughness of fibers by the sputtering effect, which produces an enlargement of the contact area that, in turn, improves fiber/matrix contact (87; 88). Although chemical and morphological modifications have been reported as heterogeneous – not uniform throughout the entire sample - good final results may be achieved if processing control is performed carefully (71; 89).

### **3.9 Models for thermal studies**

In this study, kinetic models were used in order to study thermal parameters of fibers prior to the fabrication of composites. Thermal parameters have been successfully developed using models based on thermal decomposition. It has been reported that having a reaction proceeding at a rate varying with temperature, the peak position changes with the heating rate if other conditions remain unchanged. This variation in peak position can be used for determination of activation energy ( $E_a$ ) in different orders (90). Many other studies have applied this approach in thermal degradation studies.

The reaction mechanism is the target of many studies due to its importance in understanding chemical reactions as well as how these reactions occur in a given situation. In fact, chemical kinetics is connected to the dynamics of reactions throughout a process (7; 91).

Models that describe thermal behavior and thermal degradation kinetics of lignocellulosic materials usually follow the iso-conversional principle. However, there are results based on the Prout-Tompkins integral solution, in which  $E_a$  is reached as a global average of the degradation process rather than energy values in specific conversion rates (92).

The behavior of lignocellulosic materials during heating follow a pattern in which weight starts dropping slowly as pyrolysis begins and then drops abruptly through a narrow range prior to reaching zero, indicating that the reactant is being consumed. Kinetic parameters of the pyrolysis, as reaction order and activation energy determine the shape of curves. The results of degradation analysis are dependent on testing parameters such as atmosphere, sample mass, sample shape, flow rate, heating rate, in addition to the mathematical model considered. Thus, it is recommended to follow the same conditions for all samples in comparative studies (91; 93; 94).

Equations for kinetic studies are based on Eq. 3.1:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \quad \text{Eq. 3.1}$$

In which  $d\alpha/dt$  expresses the rate of conversion at a constant temperature as a function of the reactant concentration loss and rate constant:  $k$  is the rate constant and  $f(\alpha)$  represents the reaction model, which depends on the actual reaction mechanism. Along with this, conversion rate is usually defined as a relation between weights in different times of the experiment.

$$\alpha = (W_0 - W_t) / (W_0 - W_f) \quad \text{Eq. 3.2}$$

In Eq. 3.2  $W_0$  and  $W_f$  are initial and final weights, respectively, and  $W_t$  represents the weight in a specific time.

The rate constant can be obtained from the Arrhenius equation, as given.

$$k = A \exp(-E_a / RT) \quad \text{Eq. 3.3}$$

Where  $E_a$  is the apparent activation energy (kJ/mol),  $R$  is the gas universal constant (8.314 J/K.mol),  $T$  is the sample temperature (K) and  $A$  is the pre-exponential factor ( $\text{min}^{-1}$ ).

The combination of these 2 equations results in:

$$d\alpha/dt = A \exp(-E_a / RT) f(\alpha) \quad \text{Eq. 3.4}$$

However, for a dynamic TGA process the heating rate shall be included. Thus, another term is defined to represent the variation of temperature in the time process  $\beta = dT/dt$ . Including this term in Eq. 3.4, it becomes:

$$d\alpha/dT = \left( A/\beta \right) \exp(-E_a / RT) f(\alpha) \quad \text{Eq. 3.5}$$

The main equations for calculating kinetic parameters based on TGA analysis are summarized in Table 3.1 (7; 95; 96).

**Table 3.1** Most common kinetic methods

Method	Mathematical expression	Plots (graphic)
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Friedman	$\ln\left(\frac{d\alpha}{dt}\right) = \ln[A f(\alpha)] - \frac{E_a}{RT}$	$\ln\left(\frac{d\alpha}{dt}\right) \text{ vs } \frac{1}{T}$
Kissinger	$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) + \left(\frac{1}{T_p}\right) \cdot \left(-\frac{E_a}{R}\right)$	$\ln\left(\frac{b}{T_p^2}\right) \text{ vs } \frac{1}{T_p}$
Flynn-Wall-Ozawa (F-W-O)	$\log(\beta) = \log\frac{AE_a}{Rg(\alpha)} - 2.315 - 0.4567 \frac{E_a}{RT}$	$\log(b) \text{ vs } \frac{1}{T}$

As seen in Table 3.1, Friedman's equation is more general in comparison to others since some thermal aspects and mathematical corrections regarding the analysis are left out. It is a derivative technique and this iso-conversional method directly leads to  $(-E_a/R)$  for a given  $\alpha$  by plotting  $\ln(d\alpha/dt)$  versus  $1/T$ . The Kissinger's method uses different heating rates in the weight-loss test to obtain distinct thermal degradation patterns. Thus, all temperatures at maximum degradation (DTG peak) are used to determine the activation energy ( $E_a$ ). As shown in Table 3.1, the plot results in activation energy for that point. On the other hand, the F-W-O method refers to an integral method and the relation between activation energy and the universal constant of gases may be determined from the slope of the curve at a specific conversion rate. In this method, various curves are plotted to obtain activation energy at many conversion rates.  $E_a$  values have been used as reliable ways for evaluating the purity of cellulose, which is an important characteristic prior to using these fibers as reinforcement or filler in polymeric matrices (94; 96).

The study of the thermal behavior of vegetable fibers is a very important step to evaluate their potential as reinforcement to polymer composites. Activation Energy, Arrhenius pre-exponential factor and the reaction order are parameters of utmost importance to be determined as computational models normally require these three parameters in order to predict the thermal behavior (97).

## 4 LITERATURE REVIEW

### 4.1 Polyethylene, composites and wood plastic composites based on PE

Polyethylene (PE) has been used in a variety of applications: as the main polymer in polymeric blends, composites, eco-composites, wood plastic composites and fire-resistant composites. PE is the most common polymeric matrix for producing composites or wood plastic composites (WPC) due to its low temperature processing and good processability. Recently, the use of polyethylene with wood or cellulose composites has increased due to the abundance and renewability of cellulose-based materials and the good mechanical properties of polyethylene, drawing the attention of industrialists and academics alike. However, the incompatibility between polymer (hydrophobic) and natural fibers (usually hydrophilic) can lower the performance of the composite obtained, mainly in terms of mechanical behavior. In order to increase performance, researchers have found that chemical and/or physical modifications can be applied in polymers and fibers to improve compatibility (98).

In one study, composites made of HDPE and jute fibers were reported and dynamic mechanical and thermal properties were evaluated. Data showed that the HDPE matrix can be effectively reinforced with jute fibers when the optimal concentration of reinforcement and coupling agents are analyzed (99).

Another study used PE in composites with chitosan, which is a biodegradable polysaccharide. The fluidity of the polymer was reduced when chitosan was added to the molten polymer and the final mechanical properties were improved because they were entirely connected to the processing characteristics. Authors also concluded that these improvements in mechanical behavior make these compositions suitable for biodegradable films for short-term applications (100).

Studies have also assessed the problems with the extrusion process for making composites of PE and natural fibers. To carry out this process, the material is fed into the extruder screw and then pushed through the heated barrel chamber. For PE-based materials the acceptable temperature range is from 190 to 230°C. After extrusion, samples are ready to be molded in an injection molding process, in which polymers are heated in a cylindrical chamber until they achieve flow temperature and then are forced into a cold mold, filling the mold by means of high pressure applied hydraulically with a plunger (101-105).

Researchers have reported on the addition of glass fibers to virgin PE enhances its tensile modulus and tensile strength. According one study, tensile strength of the polymer matrices

was increased when glass fibers were added to LDPE and HDPE (106). Similarly, Young's modulus increased with the addition of this filler. Another study has revealed that screw speed in the extruder process is can affect considerably the final mechanical properties of PE composites (46; 107), once high shear rates modifies the viscoelastic behavior of the polymers.

In other studies, composites of recycled polyethylene and vegetable fibers have been produced and the mechanical properties evaluated. Researchers using sugarcane bagasse as reinforcement for producing composites analyzed several properties, such as mechanical, morphological, thermal and chemical, of the composites obtained. They reported an increase of 22 % on impact property (Izod) when 10 wt.% of sugarcane bagasse was added and concluded that it was possible to modify the interface between the matrix and reinforcement by using coupling agents. They observed that using acetylated as opposed to unmodified fibers prompted the interfacial interaction between fibers and matrix (108). In addition, when the interfacial adhesion is strong, the load is transferred from the matrix to the fiber, thus shifting the necessary energy to rupture.

In another study, researchers evaluated the effects of coupling agents on the final properties of recycled PE with natural fibers (50). According to the data obtained, it was concluded that coupling agents improved compatibility between fibers and recycled PE, thus increasing their mechanical properties. However, thermal properties were only slightly changed due to the presence of these coupling agents.

#### **4.2 Thermal decomposition kinetics**

Understanding thermal behavior of polymers, composites, polymer blends and plant fibers is very important since the process of obtaining final products can involve heating prior to molding, which can lead to preliminary degradation, thus impairing proper use.

There are many methods and models based on the Arrhenius equation in which activation energy ( $E_a$ ) may be evaluated from the relationship between weight loss and temperature increase. In the literature, there are many methods for this calculation. The Friedman method is a prime example, constituting the iso-conversional method, making it possible to obtain  $E_a$  from weight loss as a temperature function. However, there are several other methods that can also be applied, such as Kissinger, Flynn-Wall-Ozawa and others (109-112).

In another study, researchers (113) have demonstrated that TGA analysis can be used as a method to determine the lignocellulosic composition of biomass samples. In this study, the

thermal behavior of major biomass components – cellulose, lignin and hemicellulose – were investigated. The analysis was based on the assumption that the differences in the chemical structure of these components lead to different chemical reactivities. Thus, the thermal degradation of each material was observed independently, making it possible to evaluate the amount of these components without using chemical reagents, which is a much greener alternative method than the others previously mentioned.

In another study aimed at reaching a better understanding of the thermal characteristics of natural fibers, the authors evaluated the thermal behavior in order to obtain  $E_a$  of ten common natural fibers. (94). Similarly, researchers in another study developed the thermal behavior of sisal fiber composites and  $E_a$  was obtained using different methods and compositions. In this study, authors were interested in evaluating the changes that the amount of sisal fibers were likely to cause in composites, as well as identifying changes in energy throughout the process of thermal degradation (91). Ultimately, results from these studies and analyses help other researchers select appropriate material for applications, such as polymer composites.

### **4.3 Coupling agents to improve polymer/fiber interface**

Recently, a broad range of studies show that the use of composites over polymers has gained in popularity due to improvements in interface compatibility between polymers and reinforcements through chemical reactions. These advances could only be achieved using coupling agents. From these studies it is clear that the use of coupling agents to improve the matrix/reinforcement interface has gained attention because of the good results that may be achieved in composite performance (49). Among these studies that investigate the use of coupling agents, several have been carried out, primarily for fiber-reinforced composites and wood plastic composites, which is the focus of the present study.

Coupling agents are usually defined as chemical components that have, in their inner structure, components that form strong links with both polymers and lignocellulosic components. As a result, the properties of the final product, primarily the mechanical ones, are improved. Maleated polyolefins are known as the most frequently applied coupling agents due to their affinity with several plant fibers (lignocellulosic) and polyolefins – the most widely used polymers in the world. In a frequently cited study on wood plastic composites (48), researchers found that chemically lignocellulosic plant fibers and polyolefins have two functional domains. These domains are (i) polyolefin (HDPE or PP, e.g.), which reacts with the matrix and (ii) maleic anhydride, that in turn, reacts strongly with lignocellulosic material in

processing temperatures, generating both hydrogen and ionic bonds. The authors of this study also highlighted preliminary preparations that must be done prior to mixing these components for processing. Due to reactivity, these maleated polyolefins are able to react with water (in air moisture) and then release acids, causing health risks and loss of reactivity due to premature reactivity of the main components. Thus, efficiency in coupling is dependent on how these components remain unchanged regarding previous reactions (48; 87; 88). Authors reported the use of maleated polyolefins from 1 to 5 wt.%. However, for wood plastic composites (WPC), this coupling agent is the most expensive component, being responsible for up to 20% of the total cost in the formulation (50; 88; 114).

In another study (115), researchers observed the influence of LDPE-g-MA as a coupling agent in an LDPE/wood flour composite and concluded that both tensile strength and impact strength had increased considerably with the addition of a coupling agent in the processing stage.

The influence of three different coupling agents in HDPE/natural fiber composites was analyzed elsewhere (50). Improvements in mechanical properties with the use of a coupling agent was found using PE-g-MA. According to the results, the use of this coupling agent was found to enhance the mechanical properties of HDPE/wood fiber for bagasse and pine, and improved the behavior of recycled HDPE/pine composites. An increase of almost 50% in tensile strength was reached when the composite had addition of 1.8% of PE-g-MA.

In addition to tensile strength, the impact strength of composites is another property that could be enhanced by using a coupling agent in composite processing. A study was developed by other researchers (116) to analyze the influence of PE-g-MA in HDPE/wood composites. Researchers found that the impact strength was 60% higher in the composite processed with the coupling agent than those composites performed without one. From this and other studies, it becomes evident that reactions for producing composites using maleic anhydride as grafting for polyethylene-based materials may strongly improve the final properties of composites.

Polyethylene-grafted-maleic anhydride (PE-g-MA) is frequently used for PE-based composites and WPC, since maleic anhydride shows good compatibility with cellulose, creating an interface between PE and cellulose fibers. Another popular coupling agent is polyaminoamide-epichlorohydrin resin (PAE), and several studies have been carried out using coupling agents aiming to improve PE/wood composites. One such study (117) aimed at obtaining HDPE/wood flour composites found that the mechanical properties may improve significantly by polymer modification prior to performing a composite using PE-g-MA.

In addition, another study (118) also using HDPE and wood flour composites, evaluated the effect of a coupling agent on the flexural properties of HDPE/wood composites. Researchers concluded that previous treatment with coupling agents improved the modulus of rupture by about 33% and modulus of elasticity by 40% when compared to composites with no coupling agents. In this study, stearic acid was applied together with PAE resin to achieve better results (118; 119).

Similarly, another study found that mechanical properties of HDPE/wood composites had higher levels of improvements using PE-g-MA as a coupling agent (120). Researchers found that the addition of 50 wt.% wood fibers resulted in optimal tensile and flexural strength which was possible throughout the use of lubricants and coupling process. This improvement was attributed to a good dispersion of wood components in the HDPE matrix, generating homogeneity over the evaluated samples. In the same study, water absorption was also evaluated and researchers concluded that increasing the content of wood parts increases absorbability. Another important result was the comparison between virgin and recycled polymers, in which composites with recycled polymers showed lower water absorption values.

Styrene-ethylene/buthylene-styrene triblock copolymer grafted with maleic anhydride (SEBS-g-MA) is another important agent applied as a compatibilizer. A study using this component was performed aiming to evaluate the mechanical properties of PE/wood flour composites, in which the addition of 4 wt.% of this coupling agent improved mechanical properties, such as tensile and impact strength (121).

#### **4.4 Applications of kapok**

Kapok fibers, technically a natural, low cost and hydrophobic-oleophilic material, have great potential to be studied and evaluated in several applications, from oil-water separation, due to its oleophilic property, to reinforcements in polymer-based materials, reducing density and providing biodegradability. Throughout the years, kapok fibers have been used to fill pillows and mattresses, quilts and even soft toys, due to their low density and softness, and more traditionally for horticultural bedding, upholstery and heat insulation. In the literature these fibers are known to have a high degree of oiliness associated with low strength. They are also short, light and show low cohesive force in the spinning process, which initially made them less interesting for economic purposes (9; 36; 122).

Nevertheless, after preliminary studies, new uses for these fibers have been found. Among those, an important application was for oil absorbance, since its cotton-like fiber is

oleophilic. Thus, kapok fibers rose in status as a viable resource as it is inexpensive and a natural feedstock for fibrous deep-bed filtration processes. Initially, only synthetic fibers, such as polypropylene, polyester and polyamide, had been used for this application. However, synthetic materials traditionally cause environmental problems due to their non-biodegradability. Thus, the search for new materials resulted in an increase in the use of natural-based and biodegradable materials as a replacement of synthetic (122).

Several studies have used natural fibers as oil/water separation while aiming to investigate their application potential in an effort to identify the working mechanism and to improve their performance and usage. Early in the 1990s, authors applied horticultural peat as bedding material, aiming to discover the activity of the fibrous filter bed in oil/water separation processes (123). Furthermore, authors showed that the oil/water separation could be optimized using low temperature, low flow and deep bed material and large oil drop after using cotton as bed material to recover oil from oily water (124). It was concluded from that study that the stable oil-in-water emulsions with oil droplet less than 10  $\mu\text{m}$  normally did not actually blend or combine in a peat bed. Another important result about oil removal was reported, in which several types of fibers – including kapok – were applied (125). They found that more than 70% of oil mass removal could be reached when they used hydrophobic bed materials. From that result, it has become known that the water-repellent waxy surface features of kapok and other hydrophobic bed materials improve oil removal.

In addition to water-oil separations, kapok fibers have been used as reinforcement along with cotton, to produce fabrics for using in polyester composites. In that study, they observed a great potential of this cotton-kapok fabric in industries, forming a new class of materials. An increase in flexural strength and modulus was observed when fiber volume fraction increased. This feature indicates the possibility of its use in composite designs for applications involving bending rather than tensile mode (126).

Another study proposed blending different yarns – kapok fibers together with cotton – and analyzed their features. This study evaluated different processes aiming at discovering the most efficient spinning technology for kapok fibers. They obtained several new characteristics and properties depending on performed processing, which lent support to spread out usage of kapok fibers in many unfinished products (37).

Kapok fibers were also applied in polyester-based hybrid composites, as reported elsewhere (127), in which different ratios were considered. Authors found improvements in properties when compared with composites without kapok fibers. In that study, hybrid composites were developed based on kapok/glass fabric in a polyester matrix. Hardness and

tensile properties were analyzed. The ratio kapok/glass fabric 1:3 showed higher tensile strength and the researchers attributed this to the higher compatibility and good dispersion, leading to a better stress transfer in the composites produced. Notably, once both kapok and glass fibers are axially-oriented, stress transferred from one fiber to another throughout the matrix may be spread out with no failure of the composite, providing an increase in the composite strength. Increasing 9 vol.% of kapok fiber increased the tensile modulus by nearly 20% in the polyester matrix. In comparison to glass fabric, kapok fabric has shown a similar trend (126; 127).

Other hybrid composites using both kapok and jute fibers as reinforcements have been produced in another study and important results were found regarding the mechanical behavior and adhesion between matrix and reinforcement. Water absorption was also analyzed for this material. Lower absorption was desirable and reached by adding either kapok or jute fibers. However, the jute-based composite showed lower values of water absorption compared to kapok-based composites (128).

Recently, researchers have begun using kapok husks in place of kapok fibers. Kapok husks can offer new characteristics to composites, such as improved tensile modulus, however decreased tensile strength and elongation at break, if no treatment on the kapok surface is done prior to mixing. This has been confirmed in a study in which recycled polypropylene was used as the matrix with kapok husks acting as reinforcement (6). After modifying kapok husks with stearic acid, the tensile strength, tensile modulus, crystallinity, and thermal stability of the composites were improved.

Microtubes from kapok fibers have also been developed for using as supports in nanoparticle carrier systems. Researchers have obtained a composite made from kapok-polyacrylonitrile (PAN), which performed as a tube to work as a carrier. The assumed reaction for this study was based on the understanding of the hydrophobic characteristic of natural kapok fibers. Researchers presumed that if the fibers were dispersed in a cetyltrimethylammonium bromide (CTAB) aqueous solution, then CTAB would be adsorbed on the fiber surface. Afterward, acrylonitrile (AN) would be adsorbed as well, due to the electrostatic interaction between CTAB and AN, triggering polymerization. Researchers found that in situ prepared PAN on the kapok surface, a thin layer of polymer coating could be performed. In this study, they developed a new method to modify natural plant fibers that might be useful in developing low-cost, high-efficiency catalyst carriers in micro scale systems (129-131).

In studies of wood biodegradation, kapok fibers are also being applied as a substrate for culturing wood-degrading bacteria. In this study, authors also began using kapok fibers due to their hollow structure, making it possible to examine them microscopically without previous

sectioning. Moreover, erosion bacteria, which degrade the outer surface of the fibers, were found to be easily approachable by oligonucleotide probes. These results point to the possibility for further use, in either fluorescence in situ hybridization techniques (FISH) or scanning electron microscopy in situ hybridization (SEMISH), as reported elsewhere (132; 133).

Studies investigating chemical and surface modification in kapok fibers were also performed – addressing modifications from chemical changes to advanced treatments as plasma modification. In a report for textile industries, researchers analyzed dyeing kapok fibers and observed that after plasma treatment, under strict control, water absorption of the fibers was improved as well as dyeing properties, since these are closely related to the ability to absorb water (134). The maximum water absorption level was found to be 4.5 mm for plate spacing and for processing time 90s. Researchers also analyzed mechanical behavior and concluded that after treatment, the breaking strength of the kapok fiber did not change.

Kapok fibers have successfully been applied in water/oil separation, working as an effective bed material for this process. A study reported elsewhere evaluated ways to reduce pollution caused by oil and oil derivatives in water using a filter made of kapok – an inexpensive, natural and renewable component (122). A mixture of diesel/water and hydraulic oil/water was applied and findings showed that the filtration efficiency reached 100 and 99.4%, respectively. The viscosity of each oil influences process efficiency, as observed through the stages of the experiment. This study also highlights the recovery property of kapok fibers, since, after use, the “wet fibers” may be reused again, reducing the cost of treatment.

Even though kapok fibers may be reused in oil/water separation, the oil absorption capacity decreases in further applications, according to a report (135). In this study, the authors observed a reduction of almost 30% in its oil sorption. The large and hollow lumen also helps for this characteristic, as oil can be trapped inside the fiber. Researchers highlighted the importance of environmental characteristics, since these fibers are inexpensive compared to other materials, such as Polypropylene and cotton. Researchers observed that kapok can be retrieved from discarded bedding, upholstery lifeboats and other traditional use items, in order to use as an oil sorbent. After use, the biodegradable samples can be discarded safely into nature, causing no damage to the environment.

A super hydrophobic material based on kapok fibers was performed in another study and the sol-gel method was used to achieve this characteristic. Findings indicated many advantages in using this material to replace the organic oil sorbent, thereby facilitating the large-scale application on water surfaces (136).

Other studies have used kapok fibers in polymerization aiming to improve the oil sorption capacity. Several factors have been found to improve the polymerization reaction. In one study the content of kapok fibers was observed as being 8 wt.% for maximum polymerization. In this study, polybutylmethacrylate (PBMA) was used and kapok husk for developing the composites. Kapok husk was used both to help reactivity and to act as filler. Finally, researchers concluded the composites obtained would be well applied in cases of oil removal. (137).

A relevant study in composite manufacturing, showed that the use of kapok fibers was a viable alternative to other reinforcements (126). In this study, kapok fibers were used together with cotton to work as a reinforcement in polyester-based composites. Morphological, thermal and mechanical properties were evaluated and the researchers observed an increase in flexural strength and modulus with the increase in fiber volume fraction, indicating new possibilities for using these hybrid reinforcements. However, the presence of free water in cellulose cavities as well as water bonded by amorphous regions exhibited negative effects on the mechanical properties. Nonetheless, improvements can be reached if adequate treatments are performed.

In another study, hybrid composites were performed using kapok and glass fibers for reinforcement in a polyester matrix. Researchers analyzed the mechanical behavior of this composite and concluded that hybrid composites showed higher tensile and hardness properties in comparison to the matrix. However, these properties were lower in comparison to a glass fabric-reinforced composite. It was also found that alkali treatment has a significant influence on these mechanical properties (127).

Microtubes for application in gold nanoparticle carriers were developed and kapok fibers were used for developing a composite together with polyacrylonitrile (PAN). These core-shell composite microtubes were successfully developed for working as low-cost and high-efficiency catalyst carriers, given that this composite showed high catalytic activity (130).

Due to their hollowness, microtubes can be developed using kapok fibers. Furthermore, a study demonstrated that the support of kapok fibers improved biological activities, since wood-degrading bacteria was favorably obtained from kapok after chemical modifications (133). In this study, the aim was to investigate if kapok fibers could be used as a substitute for culturing wood-degrading bacteria. Researchers concluded that these fibers are a suitable wood substitute and may be used as a substrate for wood-degrading bacteria growth. Another study also reported kapok as a new, natural fine template for microtube preparation (39). In this study, authors applied kapok fibers based on the benefits provided by homogeneity of the kapok fibers. Throughout the entire process, the high length/diameter ratio was obtained for different

materials. Researchers concluded that using these fibers was successful in the large-scale production of microtubes, where the kapok fiber was used as a template. The final appearance was fairly uniform, since the kapok fiber surfaces are visually smooth. The researchers also commented on the resulting properties of the microtubes, which can be modified based in the conditioning process. Notably, this was the first study in which kapok fibers were used for this purpose, attesting to the forward thinking of these researchers who were also concerned about the use of environmentally friendly and low-cost materials for reactions.

Green composites and eco-composites have also been developed using kapok components. Recent studies have applied kapok husk for developing green composites using polypropylene (PP) as the matrix (6). The same group of researchers who carried out these studies has also published results regarding kapok husks, together with linear low-density polyethylene (LLDPE), in which coupling agents were evaluated with regard to the mechanical behavior of the eco-composites obtained (138). The first study aimed at developing a green composite based on recycled PP and kapok husk for the further production of injection-molded furniture. Kapok husks were previously modified with stearic acid in order to improve adhesion, thereby improving the final mechanical properties. The second study was performed aiming to create eco-friendly packaging, also using kapok husks and LLDPE as the matrix. The effect of coupling agents was evaluated in several properties of the final composites. Ultimately, researchers observed that increasing the kapok husk content caused a decrease in tensile strength and elongation at break, but increased the tensile modulus of the composites. The influence of kapok husks on water uptake was also analyzed and researchers concluded that the hydroxyl group from the kapok was responsible for this decrease in mechanical properties. Poor thermal properties were observed for the samples. However, an increase in these properties could be verified after the incorporation of polyethylene-grafted acrylic acid, which acted as a coupling agent.

#### **4.5 Water uptake in composites**

Several microorganisms need a moisture rich environment to survive, due to the need for water in reproduction and growth. Based on this observation, biodegradation characteristics are connected to water absorption of each material. In several studies, researchers have reported that the water absorption capacity, as well as degradability are the most important properties for biodegradable materials suitable to the environment (139).

Along these lines, absorption was evaluated in order to find a way to keep properties unchanged – primarily mechanical properties (140). This occurred because hydrolysis reactions (degradation) cause a decrease in polymer properties, since molecular weight may be drastically reduced. A decrease in mechanical properties when samples were exposed to water was observed.

Wettability was also observed as a fundamental characteristic for biodegradable properties in a previous report (141). Researchers investigated whether the presence of plant sisal fibers in a polycaprolactone/starch blend matrix would improve the degradation process to facilitate the access of water (also microorganisms). Confirming their hypothesis, hydrophilic fibers acted as a channel for the access of microorganisms. Plant fibers worked as a support for the attack of microorganisms in an aqueous medium. According to the study, the presence of water also led to the hydrolysis of the starch, which is the most bio-susceptible component. Thus, water uptake in this composite is fundamental for understanding degradation by microorganisms (141).

Moisture uptake is known to be different with regard to cellulosic components and plastics, due to their specific natures. Therefore, studies have shown which properties should be present to improve absorption – fine pores, hydrogen bond sites in the wood flour, presence of lumens, among others. These factors contributed to WPC improving moisture uptake (142).

#### **4.6 Polymer Degradation**

The degradation of synthetic materials has been analyzed and studied extensively throughout the years due to the need for disposing of these materials correctly and minimizing the negative impacts on the environment. Polyethylene-type materials degrade under different mechanisms: chemical processes, thermal degradation and biodegradation. This last process occurs slowly in natural conditions, due to the inability of microorganisms to break the chemical bonds and further release low molecular weight products (143).

Researchers have analyzed mechanisms of degradation in studies on the biodegradation process of polyethylene (144). Results from these studies regarding PE biodegradation have indicated two different steps for PE: hydro-biodegradation, followed by oxi-biodegradation. This occurs because of components used in the synthesis of biodegradable PE. The presence of a continuous phase of starch was found to lead to an increase in hydrophilicity and, subsequently, microorganisms have many possibilities for attacking and removing this part. Thus, this new hydrophilic PE remains in the degradation process until total consumption is

reached. The second step led to oxidation, caused by a pro-oxidant additive. In this case, photodegradation and chemical degradation occurs naturally.

It has been reported that synthetic polyolefins, such as PE-based material, are inert materials, and that their backbones consist of only long carbon chains, which can hinder or, sometimes, become impracticable with common microorganisms. Nevertheless, studies have been carried out in order to find and understand ways to degrade polymers with natural sources. A previous study (145) has demonstrated that some microorganisms can change polyolefins with low molecular weights into other products, constituting biodegradation.

In another report, the presence of fungi acting as bioremediation for the amount of LDPE in the oceans was analyzed (146). According to the data, researchers concluded that after thirty days of exposure, the sample had lost part of its weight and CO<sub>2</sub> gas was found, indicating degradation of LDPE followed by the release of CO<sub>2</sub>. Other findings showed that, even for hydrophobic material (such as LDPE), a proper microorganism may biodegrade it. The LDPE film acted as a substrate for microorganisms growth, which in turn, developed a biofilm and started reacting to consume the plastic.

Composites with these LDPE-based materials and chitosan were developed and analyzed with respect to properties of biodegradation in another study (147). A mixture of palm oil with chitosan was performed to enhance the biodegradability properties. Researchers concluded that this hybrid filler proved to be a novel way for increasing the biodegradability rate of the LDPE-based composite. The variation in the weight loss for samples after twenty-one days of incubation was analyzed. The data showed that as the chitosan content increased, the weight loss also increased.

#### **4.7 Plasma treatment for surface modification**

Several studies have analyzed and evaluated changes in surfaces after plasma treatment. Physical-chemical properties of polymers, such as wettability, biocompatibility and adhesivity, have been found to undergo changes throughout this process (148-150). In fact, plasma is capable of removing surface impurities, decomposing polymer chains and introducing functional surface groups. Changes in cellulose nanotopography have also been observed (151).

Attempts to change fiber surfaces using plasma have been investigated since the 70s-80s. One study evaluated the effect of plasma treatment on the structure of mulberry silk for textiles. According to the data, researchers reported the effects of plasma nitrogen in the morphological structure, as well as a decrease in the crystallinity index. They connected this

decrease to the bonding brakes in the crystalline region due to a radioactive transfer of energy (152).

Researchers have laid out new procedures for efficiently functionalizing plasma treatment, verified by a growing number of citations in the literature these treatment for *in situ* polymers and surface modification. The importance of plasma treatments can be linked to the fact that plasma species do not transfix more than 1% for the surface, which means nearly 99% of the material preserves itself entirely unmodified throughout treatment (153).

Low frequency plasma treatment was successfully applied in wool fabrics aiming to turn them from hydrophobic into hydrophilic. Researchers found that the breaking strengths of the fabrics were increased up to 26% after plasma treatment (154).

The modification of cellulose fibers using oxygen plasma for developing composites based on PE was performed in a previous study aiming to characterize the interface. Results showed an increase of 200% regarding the interfacial shear strength (IFSS) for composites made with plasma treated fibers. According to the results of an X-ray photo electron spectroscopy (XPS), the presence of hydroperoxide groups was observed, and researches concluded they could be responsible for grafting in matrix chains (155).

Lignocellulosic fibers are consistently used in treatments where they are under plasma treatment, and some studies have shown differences after plasma treatment in jute fibers. The treatment done under oxygen plasma improved interfacial adhesion as well as hydrophobicity in fibers, which is usually desirable in composites manufacturing. On the other hand, not all treated materials improved their mechanical strength. Differences in plasma processes can provide improvements or deteriorations to the material and, due to this, two reactors were used in processing – radio frequency and low frequency – in which jute fibers were put in each one of the treatments using O<sub>2</sub> in order to improve the interface adhesion among the fiber and polyester matrix. Jute fibers were treated with plasma using oxygen (O<sub>2</sub>) under different reactors and under different plasma powers aiming to improve interface polymer/fibers. In this study (156), increases of approximately 72 and 128% of shear strength were observed for jute/polyester composites when they were treated under low frequency and radio frequency plasma, respectively. Researchers concluded that plasma treatment could improve the mechanical properties. Radio frequency plasma was also shown to perform better than low frequency plasma (156; 157).

Similarly, another study has applied plasma in the treatment of jute fibers in order to improve adhesion in composites using HDPE as matrix. Researchers analyzed the influence of the plasma power in the final characteristic of composites, and they found that optimum

conditions for plasma treatment included power at about 60W and an exposure time of 15 minutes (158). Researchers observed fiber behavior in mechanical testing and it was attested that fiber pull out length decreased for samples in which fibers had been treated under plasma. Thus, this change was attributed to plasma treatment, since the effect of oxidation in the fiber renders the surface more hydrophobic. In this study, changes in flexural strength properties were also observed, which might be due to the crosslinking (inter-monomeric bonds) generated in the process. Furthermore, other mechanical properties, such as the tensile and flexural strengths of composites polyester/jute were also improved in both plasma treatments. Exposure time is also a feature to be considered, given that the best interfacial adhesion between jute fiber and polymeric matrix was achieved at a 15 min-exposure.

Methane gas was also used in plasma processing for wood fibers for reinforcement in the LDPE matrix (155). Results of this study demonstrated improvements in compatibility after fiber treatment. Tensile properties were also improved in composites in which methane gas (in plasma) worked as a coupling agent.

Ramie fibers were treated under plasma for the production of fiber composites. The adhesion of fibers in the PP matrix was improved after plasma treatment and, when pre-treatment using ethanol was done, this improvement in adhesion was greater. This achievement could only be reached due to changes in roughness, which increased after plasma exposure (159).

A reduction in hydrophilicity due to plasma treatment was reported in other studies. Researchers attributed this to the migration of the added chemical polar groups throughout the surface layer. However, since this migration process can be difficult to carry out because of the presence of crosslinking, which can produce changes that are reversible after a short period of time (160; 161).

An increase in the wettability of polyester fabrics after plasma treatment was also evaluated and reversibility in the processing within the first 60 days was found, followed by the stabilization in hydrophilicity. However, an increase in hydrophilicity was found at the end of the process (162).

Lastly, considerable information for improving the effect of plasma treatment on both physical and chemical properties of cellulose-based systems was reported (151). According to the data, plasma was found to create new chemical groups on the surface, inducing changes in morphology, and a decrease in the degree of crystallinity of a cellulose sample. Similarly, in another study, (163) plasma treatment for modifying surface properties of both synthetic polymers and textile materials, such as cellulosic-based fibers, was applied.

**5 ARTICLE 1: Surface modification of kapok fibers by cold plasma surface treatment**

## Surface modification of kapok fibers by cold plasma surface treatment

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### Highlights

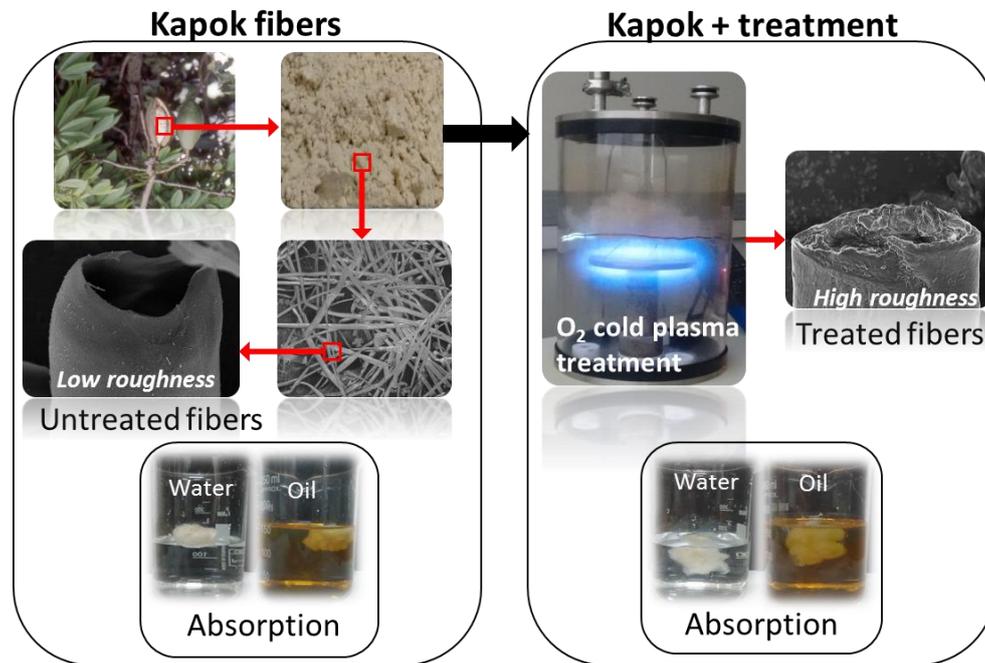
- Cold plasma treatment may be used for surface fiber activation
- Kinetic models show the quality of cellulose from vegetable fibers
- Kapok fibers are oleophilic and plasma enhances this characteristic
- Ability to uptake oil improves after plasma treatment
- Plasma treatment is a feasible approach to improve fiber-matrix adhesion for composites

### Abstract

This work evaluated the effects of cold plasma treatment on kapok fibers (*Ceiba pentandra L.*). Fourier-transform infrared (FTIR) spectra showed changes in characteristic absorption bands, indicating modification of the fiber chemical composition. Surface roughness, observed by field-emission gun scanning electron microscope (FEG-SEM) increased with treatment. Furthermore, the water uptake was significantly affected, the ability to uptake oil increased and a mechanism of reaction was suggested. The thermal behavior by thermogravimetric analysis (TGA) was slightly altered showing that fiber surface was activated by the plasma treatment. Cold plasma may prove to be a feasible approach to improve fiber-matrix adhesion for the production of biodegradable polymer composites.

**Keywords:** cold plasma; kapok fibers; kinetic studies; renewable; thermal behavior

## Graphical abstract



## 5.1 Introduction

The use of vegetable fibers as reinforcements for composites has increased due to their availability in nature, low cost, biodegradability and lightweight as compared to synthetic fibers. Cellulosic fibers have good flexibility and elasticity when compared to mineral fibers, such as glass and carbon fibers, allowing them to keep high aspect ratio during manufacturing process (1; 2).

Materials from renewable resources are of increasing interest due to the growing environmental awareness and new environmental regulations. Natural cellulosic fibers typically exhibit different contents of cellulose, hemicellulose, and lignin as main compounds. Cellulose is the main constituent of these fibers, which is lined up forming bundles, which are usually linked with the other constituents (3-6).

Kapok (*Ceiba pentandra L.*) is a cellulosic fiber with a high degree of hollowness (80–90%), considered the largest among natural fibers. These fibers are composed of two major layers with distinct orientations: the outer layer is composed of cellulose microfibrils, which are orientated transversally to the fiber axis, while the internal layer is parallel to fiber axis (7; 8). Another important characteristic of these fibers is the circular cross section (9; 10). Kapok fibers have been used as oil absorbent, especially for application in areas in which oil had been

accidentally spread (11). Tests for oil retention and oil absorption of kapok fibers have been reported elsewhere (12-14). In addition, studies have been carried out aiming to apply kapok fibers in composite manufacturing using recycled polypropylene. An increase tensile modulus with increasing kapok husk content has been reported in the literature in a study of green composites from kapok husk and recycled polypropylene (15). Nevertheless, polymers and fibers normally have poor compatibility due to differences in polarity of each material, which can be improved by surface treatments of fibers (16; 17).

Plasma treatment can be used to modify polymers and natural fibers by changing fiber surface energy. The process causes surface crosslinking and introduces reactive groups (18). In addition, previous works reported that crosslinking at the fiber surface induces strengthening (19; 20). The surface modification by plasma treatment is a result of a sputtering effect at the fiber surface during the plasma bombardment of the material, which produces chemical modifications (3; 20-22). In a previous research, plasma process was shown to produce surface erosion of cotton fibers, thus resulting in weight loss and increase in the fiber carboxyl and carbonyl group contents (23). Nevertheless, different vegetable fibers exhibit distinct mechanisms when subjected to plasma treatment, due to differences in composition and properties (3). Thus, there is an interest in investigating the effects of plasma treatment on kapok fibers.

Chemistry of plasma reactions occurs in non-equilibrium conditions. Every plasma species, such as atoms in excited states, free radicals, metastable particles, electrons and ions can interact both chemically and physically with solid surfaces, starting reactions and changing surface structures (24). X-ray diffraction analyses before and after plasma treatment have indicated no differences in crystallinity, thus confirming that plasma treatment induced decomposition only at the surface of cellulosic materials (25). In addition, plasma has been used to change electrical resistivity of fabrics such as viscose and cotton (26). Morphology studies of cotton fabrics have suggested that the surface of cellulosic fibers become rougher after plasma treatment with a significant amount of grooves and cracks (27-29). Plasma treatment of cellulosic fibers can also improve fiber/polymer adhesion, as reported in a recent study (30).

Liquid sorption properties of vegetable fibers influence their adhesion to a polymer and are key to some manufacturing operations of fabrics, such as dyeing, and finishing. The ability of wood materials to uptake water is improved after plasma treatment, as shown in a previous study (31).

Thermal stability is also an important characteristic of vegetable fibers intended to be used as reinforcement in polymer composites since traditional processing - such as extrusion or

injection - may involve high temperature and fibers may degrade during processing (32; 33). Mathematical models developed by researchers, based on reactions that occur during heating have been used to describe thermal behavior and degradation kinetics of lignocellulosic materials usually following iso-conversional principle (34). However, there are results based on Prout-Tompkins integral solution, in which the activation energy is calculated as a global average of degradation process rather than energy values in specific conversion rates. Common mathematical expressions for calculating kinetics parameters based on TGA analysis are those by Friedman, Kissinger and Flynn-Wall-Ozawa (32; 35; 36). Other methods for estimating lignocellulosic components decomposition have also been reported (37).

It has been reported in the literature that pyrolysis reaction of cellulose and lignin follows first-order kinetics and generate low-density volatile components. However, the prediction of the exact behavior of each component in plant fibers is not simple due to the unlimited possibilities of growth, that make each material unique with respect to their crystal structure and chemical composition (33; 38). The activation energy has been used as a method for evaluating the purity of cellulose, which is an important characteristic for the use of these fibers as reinforcement or filler in polymeric matrices (33; 36). The decomposition reaction of the fibers can be modeled using activation energy data, Arrhenius pre-exponential factor and the reaction model, usually referred to as kinetic triplet (39).

The aim of this work was to evaluate the effect of cold plasma on the chemical, morphological and thermal properties of the kapok seed fibers. The fibers were activated under cold plasma treatment.

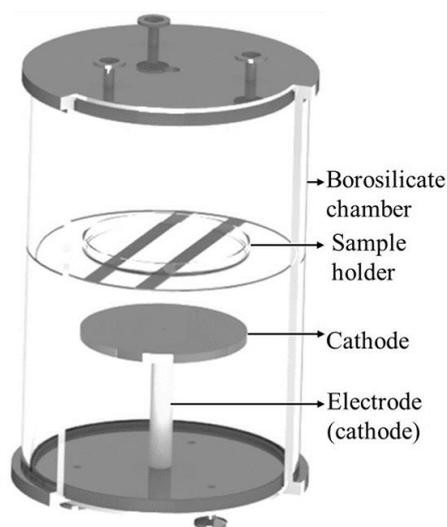
## **5.2 Experimental**

### **5.2.1 Material**

Kapok fibers were obtained from the fruits of the kapok tree, collected in the State of Paraiba, Brazil. Kapok fruit contains husk, fibers and seeds and this research focused on the fibers, only. The fruits were first dried at room temperature. Then, the fibers were obtained by opening up the fruit and isolating it from both seeds and husk, and later dried in an oven at 60°C for 24h. Neither chemical nor washing processes were used. The fibers were kept under vacuum in an oven at 30°C until plasma treatment.

### 5.2.2 Plasma treatment

Plasma treatment was carried out to induce modifications on fiber surface and improve wettability as well as in fiber-polymer interface for further composite preparation. The plasma equipment consisting of a chamber in which coaxial electrodes were used for electrical discharge. Details of plasma equipment used (Figure 5.1) has been reported elsewhere (40). The electric current was controlled over the range of 0.09-0.12A and voltage from 400 to 500 V. The samples' temperature was 72 °C, the flow rate was 10 cm<sup>3</sup>.min<sup>-1</sup> of gas and the work-distance was set to 4.0 cm. The pressure inside the reactor was 1.5 mbar. Oxygen gas was used and exposure times were set to 30, 45 and 60 min, respectively, in order to study the effect of time on the plasma treatment. The chamber was evacuated until 7x10<sup>-3</sup> mbar using a vacuum pump prior to refilling with oxygen gas. Approximately 5g of fibers for each analysis were placed in the sample holder prior to starting the treatment.



**Figure 5.1** Plasma reactor

### 5.2.3 Spectroscopic analysis

Changes in chemical groups of both untreated and plasma treated fibers were observed using Fourier transform infrared (FTIR) spectroscopy in an IRTracer-100 spectrometer. Samples were analyzed in ATR mode and scanned over the frequency range from 4000 to 500 cm<sup>-1</sup> with resolution of 4 cm<sup>-1</sup> and 20 scans per sample. No signal correction process was carried out to avoid loss of data.

#### 5.2.4 Morphological characterization

Morphology of fiber surface before and after plasma treatment was analyzed using a Field-Emission Gun - Scanning Electron Microscope (FEG-SEM) - ZEISS Auriga, operating at 2.0 kV with tungsten filament. Prior to the FEG-SEM analyses, all samples were coated with a thin layer of gold for 60 sec in a Sputter Coater BAL-TEC SCD 005 using argon atmosphere under vacuum, in order to avoid charging sample while scanning.

#### 5.2.5 Absorption testing

Absorption properties of fibers were determined using water (polar molecule) and lubricating oil (nonpolar molecule). Measurements were conducted using fiber samples before and after plasma treatment. For the treated fibers, only those exposed to plasma treatment for 60 min were evaluated since no considerable chemical changes were observed by FTIR for fibers treated for 30 and 45 min. Two Beckers were used: one filled with oil and the other filled with distilled water, both at room temperature. Prior to the absorption measurements, samples were conditioned in an air-circulating oven at 60 °C for 8h. Approximately 1.0 g of fiber was immersed in the liquid (water or oil) for 15 min. The fibers were then removed from the liquid bath and weighed after 25 min. Absorption of oil or water was calculated using Equation 5.1. Five samples for treated and untreated fibers were used for calculating average and standard deviation.

$$\text{Abs}(\%) = \frac{\text{wet weight} - \text{conditioned weight}}{\text{conditioned weight}} \times 100 \quad (5.1)$$

#### 5.2.6 Thermal characterization

Thermogravimetric analyses (TGA) of untreated and treated fibers were carried out in a PerkinElmer STA 6000 apparatus to evaluate the effect of the plasma treatment on the thermal degradation. The samples were scanned over a temperature range of 30 to 600°C under a dynamic flow atmosphere of Nitrogen (99.5% purity) at a flow rate of 50 ml.min<sup>-1</sup>. Four heating rates were used for the thermal decomposition kinetics studies (5, 10, 15 and 20 °C.min<sup>-1</sup>) based on the three described methods.

## 5.3 Results and Discussion

### 5.3.1 Spectroscopic analysis

Plasma treatment was performed to induce changes in chemical bonding and, thus, FTIR spectroscopy analysis was conducted aiming to identify these bonds before and after plasma treatment. The infrared spectra and some characteristic absorption band peaks are shown in Figure 5.2.

Fibers treated for 30 and 45 min remained practically unchanged in comparison to untreated fibers. Thus, these exposure times were insufficient for changing chemical groups of these fibers and no further characterizations of these samples were performed. Nevertheless, the plasma treatment duration of 60 min has changed some chemical bonds, as shown in Figure 5.2.

The spectrum of untreated fibers is typical of lignocellulosic fibers. Cellulose is identified by some chemical groups, such as C-O-C stretching, at 2125 and 1157  $\text{cm}^{-1}$ , while the peak at 3355  $\text{cm}^{-1}$  is related to the stretching of OH group, which represents mainly the hydroxyls of cellulose. Besides, the peak at 1645  $\text{cm}^{-1}$  is related to the O-H deformation, which might be of cellulose and water. The peak at 1373  $\text{cm}^{-1}$  is characteristic of C-H deformation, related to cellulose, lignin and hemicellulose. A peak at 1238  $\text{cm}^{-1}$  is C-O stretching vibration band of hemicellulose and lignin. Furthermore, the peak observed at 1733  $\text{cm}^{-1}$  is attributed to the C=O stretching, characteristic of hemicellulose linkage, that is, it represents the C=O of carbonyl structure. The peaks at 1108 and 1036  $\text{cm}^{-1}$  are also C-O stretching, linked to hemicellulose and lignin. Lignin is identified by C=C bonds, being stretching in 1507  $\text{cm}^{-1}$  and aromatic skeletal vibration in 1458  $\text{cm}^{-1}$ . Thus, the main components of lignocellulosic fibers – cellulose, hemicellulose and lignin – were identified.

Decreasing in peak intensities at 3350  $\text{cm}^{-1}$  was observed in treated fibers. This stretching vibration band is characteristic of bonding of hydroxyl groups of fatty acids, commonly found on the surface of vegetable fibers, especially kapok due to its oleophilic characteristic. The height of this peak was reduced after 60 minutes of treatment, suggesting a reaction with oxygen provided by plasma, while another absorption band at 1645  $\text{cm}^{-1}$ , linked to O-H stretching has disappeared. These changes take place at the most external bonds and they are related to fats. In addition, the peak attributed to the OH groups of cellulose on the fiber surface (1645  $\text{cm}^{-1}$ ) exhibited reduced intensity after plasma treatment. This was associated to a reaction with oxygen while removing fatty acids and waxes during the plasma

treatment. A summary of possible reactions that occur during the plasma treatment is shown in Figure 5.3.

Plasma treatment reduced that intensity, also confirming the modification at the fiber surface. Other authors (15) also attributed these absorption bands to changes in OH groups. The existence of oxygen induces the presence of hydrogen bonds and the reduction of free OH at the fiber surface (9; 10).

An absorption band with peak at  $1597\text{ cm}^{-1}$  was also found. Bands at around  $1600\text{ cm}^{-1}$  are related to instauration (C=C) and they were changed after treatment most likely due to reactions between oxygen coming from plasma and this double bond. These bands were attributed to the presence of lignin, which was also changed due to the treatment. These existent bonds are linked to traces of oils that were partially removed with treatment (41). Another way to confirm this is the increase in peak height around  $1733\text{ cm}^{-1}$ , attributed to carbon and oxygen (42). These bonds at the fiber surface are important because, while in process with a polymeric matrix, carboxyl group (C=O) may react with carbons near to backbone chains and a strong bonding may be obtained, resulting in a strong interface (23).

The absorption band at about  $2847\text{ cm}^{-1}$  for treated fibers has changed in comparison to untreated fibers. This might be attributed to changes in lignin structure  $-\text{CH}_3$ , also observed at about  $2937\text{ cm}^{-1}$  in a previous study, in which two kinds of lignin were analyzed (43). In this work, the peak was found at  $2924\text{ cm}^{-1}$ .

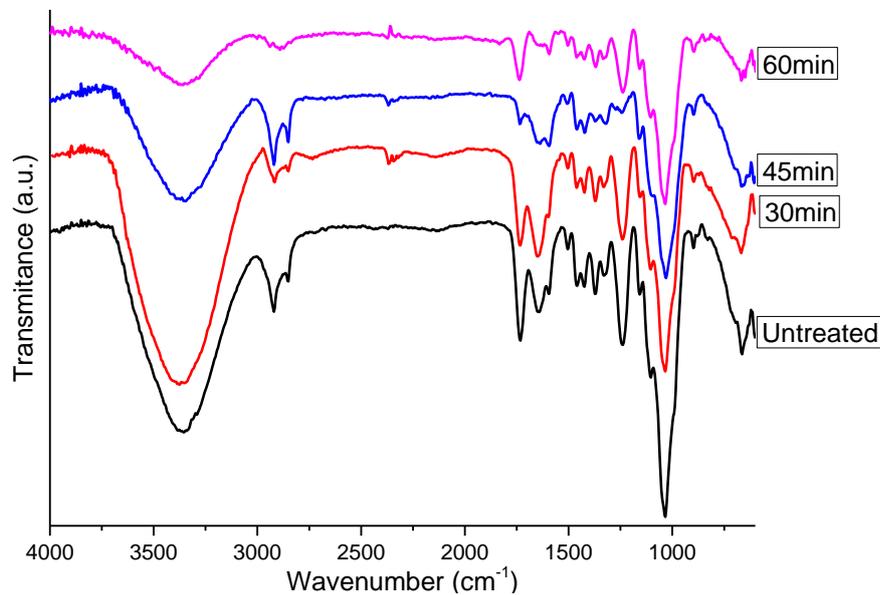
The presence of water was identified by peaks at  $1645\text{ cm}^{-1}$ , which are also associated with  $-\text{OH}$  bonds of cellulose groups. The free hydroxyl groups on the cellulose chains have been associated to sites where the absorption of water occurs (44). An absorption band with peak at  $1421\text{ cm}^{-1}$  characteristic of  $\text{CH}_2$  bonding was observed and linked to both cellulose and lignin. Changes in bands around  $1328\text{ cm}^{-1}$  after plasma treatment were also connected to OH bonding in cellulose groups. The in-plane OH bending absorbance is observed for the untreated fibers. Fibers treated for 60 minutes exhibit a considerably reduction in that peak, as shown in Figure 5.2. This behavior may be related to the plasma action onto the surface cellulose bonds, since inner portions of the samples are not affected by the plasma treatment. Fibers treated for 60 minutes exhibited reduction in heights of peaks around  $660$  and  $595\text{ cm}^{-1}$ , which means reductions in the amount of C-OH bonding. This might be attributed to reactions involving C-OH group and oxygen.

No atmosphere corrections were performed after recording data in order to check hydrophobic/hydrophilic characteristic of samples before and after treatment. Absorption bands with peaks around  $2350\text{ cm}^{-1}$  have been predominantly attributed to moisture in the sample.

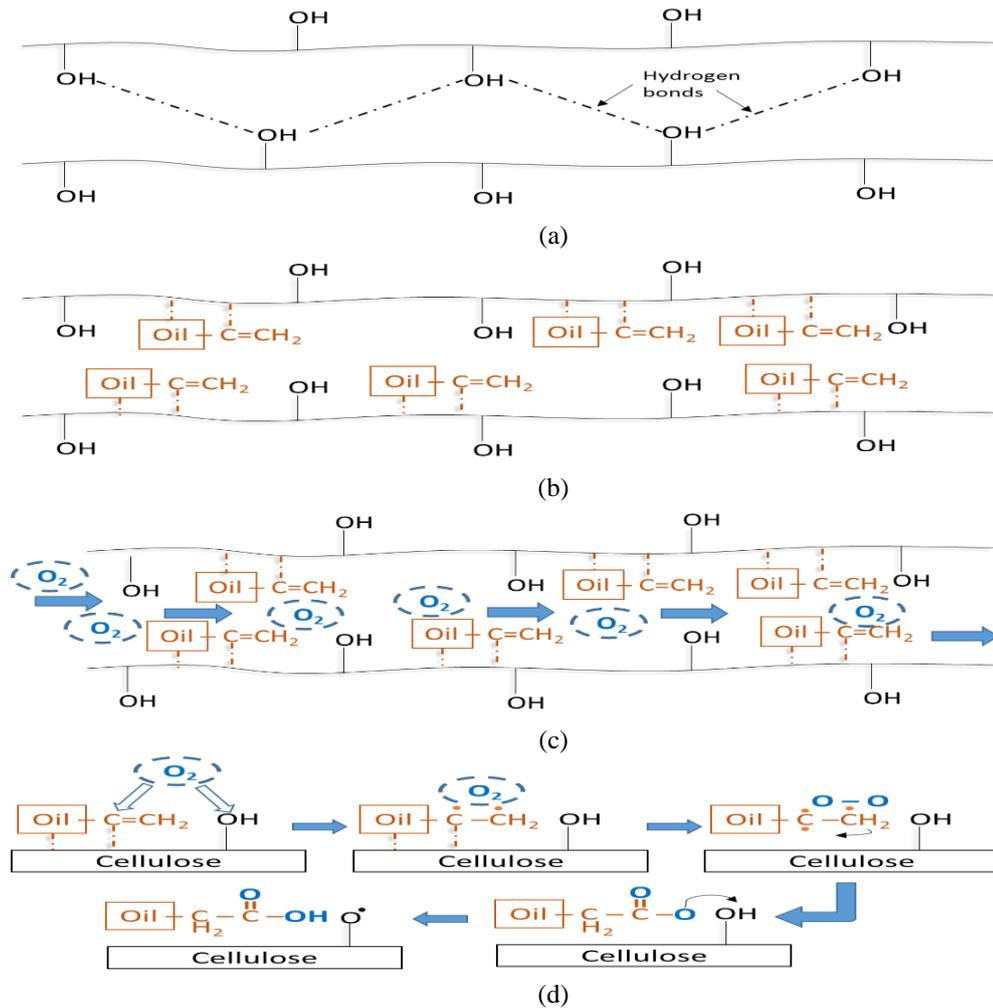
These bands were not observed in the untreated samples. In contrast, the treated samples have this peak, indicating a reduction in pseudo-hydrophobicity as well as increasing in wettability.

The liquid uptake capacity of fibers is related to the contact between the liquid and fiber surface. Plasma treatment removed part of fatty acids and wax from the fiber surface, thus allowing contact between fibers and the surrounding liquid (polar or nonpolar), since the removal of part of this amorphous structure exposes the  $-OH$  which were covered by oils. That is, plasma treatment improved the wettability of fibers. The new absorption peaks after plasma treatment may be related to reactive sites that can improve reactions with polar and nonpolar liquids. Thus, while the hydroxyl groups on the fiber surface increase wettability by water, the remaining oily components renders fibers wettable by oil. Furthermore, the plasma treatment induces surface erosion of fibers opening up channels for liquids to penetrate into surface pores. Therefore, there is a possibility of improvement in wettability by different liquids. This characteristic is relevant for further use of these fibers in composites' manufacturing.

The structure of a typical cellulose fiber and kapok fiber are presented in Figure 5.3a and in Figure 5.3b, respectively. The representation of plasma treatment is summarized in Figure 5.3c and a suggested reaction mechanism that occurs during plasma treatment is presented in Figure 5.3d.



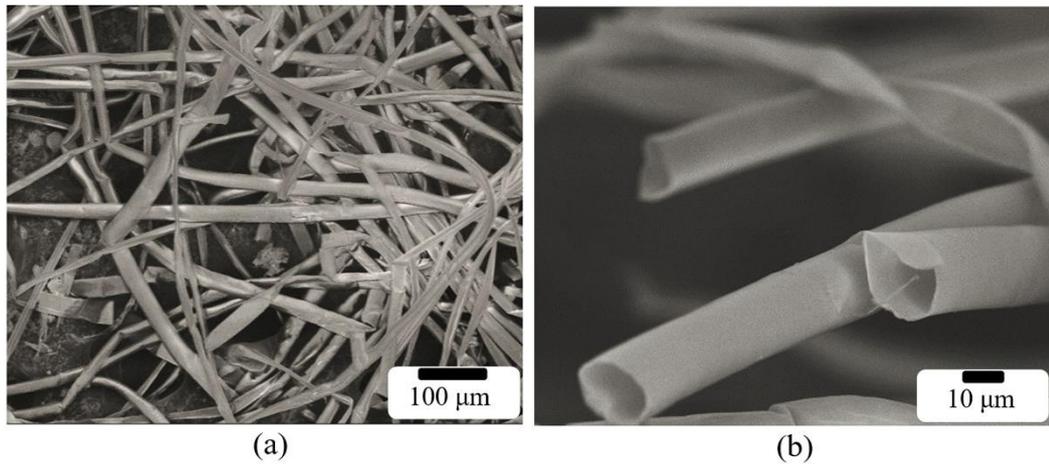
**Figure 5.2** FTIR spectra of untreated and treated kapok fibers



**Figure 5.3** Schematic representations of (a) typical cellulose fiber, (b) kapok fiber, (c) plasma treatment, and (d) suggested mechanism of plasma reaction

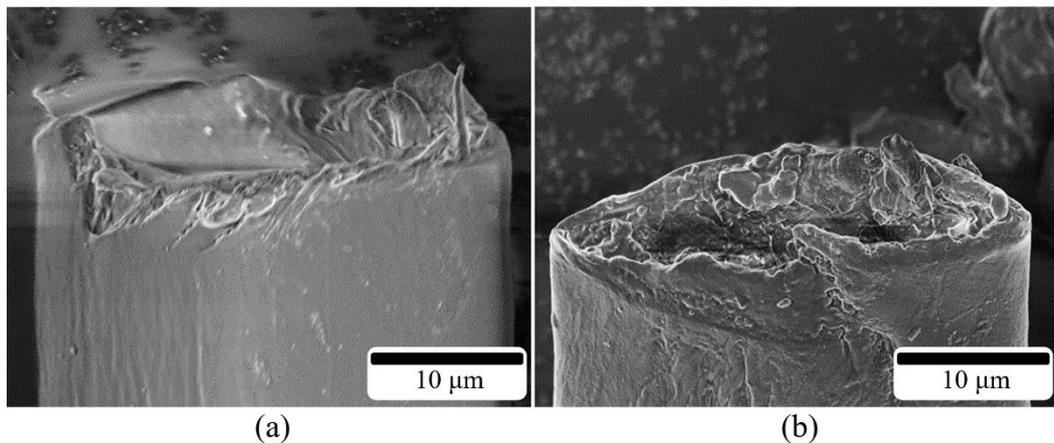
### 5.3.2 Morphological analysis

Differences in morphology of untreated and treated fibers were evaluated using FEG-SEM images. External and internal diameters, wall thickness and surface fiber roughness were parameters observed before and after treatment. The most samples kapok fibers showed external diameter ranging from 12 to 15  $\mu\text{m}$ , on average, and wall thickness of about 1.5  $\mu\text{m}$ . However, samples with diameter from 10 to 27  $\mu\text{m}$  were also observed. Figure 5.3 shows the actual morphology of fibers with the characteristic smooth appearance (Figure 5.4a) and hollowness (Figure 5.4b). The hollowness of 80 to 90% of kapok fibers reported in a previous work (45) can be seen in Figure 5.4.



**Figure 5.4** FEG-SEM images of (a) untreated kapok fiber and (b) details of hollowness

Images before and after treatment (Figure 5.5) were carried out in order to observe any modification on surface roughness produced by the plasma treatment. Figure 5.5a exhibit a fiber before plasma treatment while the plasma treated fiber is shown in Figure 5.5b. According to images in Figure 5.5, the plasma has induced changes on the fiber surface, increasing roughness.



**Figure 5.5** FEG-SEM surface of (a) untreated and (b) plasma treated fibers after 60 min

### 5.3.3 Absorption testing

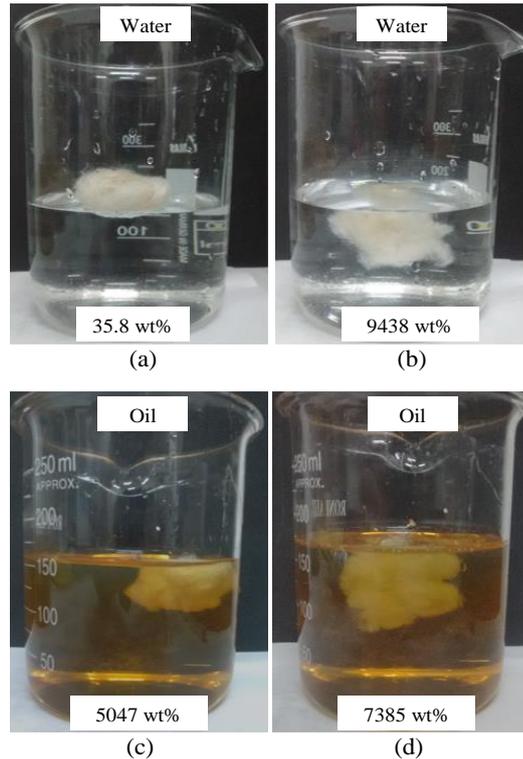
According to measurements, plasma treatment produced a significant effect on water and oil uptake of kapok fibers. Oil absorption was increased from 5047 to 7385 wt.%, and water uptake was increased from 35.8 to 9438 wt.%, as compared to untreated fibers. Cellulose fibers are typically semi-crystalline, with free hydroxyl groups throughout the amorphous portion. These groups attract water molecules forming hydrogen bonds. In addition, the higher level of polar carboxyl and carbonyl groups generated during plasma treatment leads to more polar - and consequently more wettable - fibers, as reported elsewhere (23).

Kapok fibers are naturally oleophilic (13) and the plasma treatment increased the wettability of fibers in nonpolar liquids, such as oil, as a result of surface erosion, which exposes the natural hydrophobic groups on the fiber surface and opens up spaces for liquids to penetrate. A recent study reported that calotropis (*Calotropis procera*) – a fiber similar to kapok – also showed improvement in the oil-absorbing performance (46). This result may be used in further studies of plasma treated fibers using polymeric resins for the production of fiber-reinforced composites. The wettability of the fibers by a polymeric matrix during impregnation is essential for the use of these fibers in composite manufacturing.

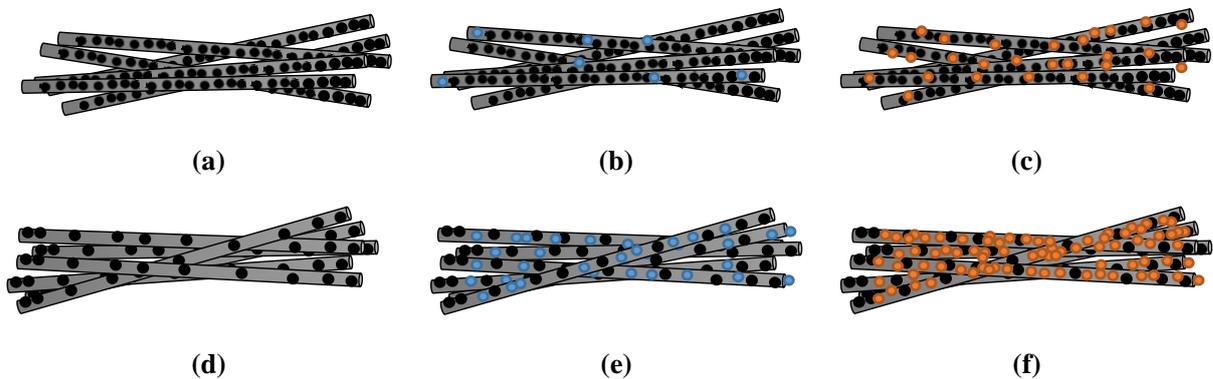
The increment in water uptake may be related to the efficiency of plasma processing for removing oils and waxes from the fiber surface, thus opening up channels for moisture uptake, in addition to changes in surface roughness. In addition, the removal of waxes makes filling of tube-like fiber structure possible. Waxes and fats at the surface of untreated fibers are known to affect wettability. Therefore, plasma treatment has induced reactions and promoted breaking of some fatty acids on the fiber surface, as confirmed by FTIR, thus reducing pseudo-hydrophobicity characteristic.

Changes in relative peaks in FTIR spectra as well as a more irregular surface texture shown in SEM images (Figure 5.5) confirm the plasma modification of the fiber surface. The adsorbed water or oil induced fiber swelling. Figure 5.6a and Figure 5.6b show images of untreated and plasma treated fibers exposed to water, respectively. Figure 5.6c and Figure 5.6d exhibit images of untreated and treated fibers exposed to oil. A conceptual schematic of distribution of natural oil, water and lubricating oil on kapok fibers is presented in Figure 5.7.

Unlike other vegetable fibers, kapok has a combination of two features: it has oil on its surface and its hollowness is considered the largest among natural fibers. Thus, after plasma treatment, the water can access the actual surface, due to the partial removal of oils from the fiber surface. Furthermore, cellulosic fibers are naturally hygroscopic and when oils are removed from the surface, water can penetrate the internal structure of the fibers. The combination of the characteristic smoothness and hollowness of kapok fibers with air entrapped in the fiber lumen hinders water absorption. After plasma treatment, the increase in fiber surface roughness increased and partial oil removal facilitates water filling of the lumen. Besides, plasma treatment occurs at the surface and the inner portions of the fibers remain unaffected. Thus, the lipophilicity of fibers is not reduced after the treatment.



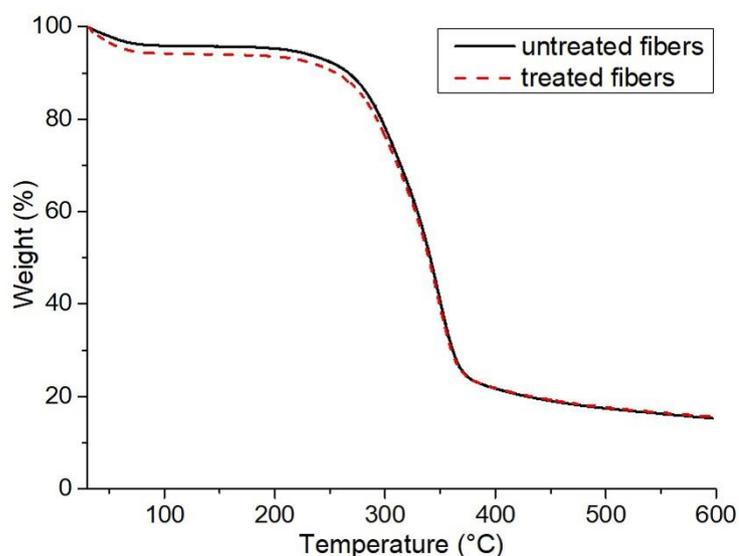
**Figure 5.6** Absorption testing for (a) untreated and (b) treated fibers in water; and (c) untreated and (d) treated fibers in oil



**Figure 5.7** Theoretical distribution of components over kapok surface for untreated fibers (a) dried, (b) in water, (c) in oil, and for treated fibers (d) dried, (e) in water, and (f) in oil

### 5.3.4 Thermal characterization

Thermogravimetric analyses were carried out in both untreated and plasma treated kapok fibers. The main difference between thermogravimetric curves of treated and untreated fibers at  $10^{\circ}\text{C}\cdot\text{min}^{-1}$  was the loss of moisture over the range of 30 to  $100^{\circ}\text{C}$ , which has been attributed to moisture uptake. Plasma treated fibers are more likely to exhibit free oxygen or weak bonds, resulting in changes in polarity and improving wettability to some liquids. Above this temperature range, the thermal behavior was not modified by the plasma treatment, as shown in Figure 5.8.



**Figure 5.8** TGA Thermograms of kapok fibers before and after plasma treatment

Thermal degradation data were also evaluated from TGA thermograms obtained using different heating rates. Results were used for the determination of kinetic parameters and changes in thermal degradation, as a function of heating rate.

The weight-loss curves of untreated fibers exhibited a trend of small increase in  $T_{ONSET}$  (Figure 5.9a) and maximum degradation peak (Figure 5.5b), as the heating rate increased. For treated fibers, other changes in weight-loss curves were observed below the  $T_{ONSET}$ , as the heating rate increased (Figure 5.9c). These changes were attributed to a reaction mechanism, influenced by oxygen provided by the plasma treatment.

New bonds, as observed in FTIR spectra, may affect thermal degradation. Thus, the treated fibers subjected to slower heating rate have decomposed a bit faster than those exposed to higher heating rates. After  $T_{ONSET}$ , the behavior of untreated and treated fibers was similar until final thermal degradation. In addition, the portion affected by plasma was almost entirely consumed below  $T_{ONSET}$ . Free oxygen at the fiber surface may react faster than cellulose. This explains changes in thermal behavior of plasma treated fibers at temperatures below  $T_{ONSET}$ . Free oxygen reacts before reaching this temperature. Thus, the thermal decomposition behavior remains unchanged above  $T_{ONSET}$ , as shown in Figure 5.9d.

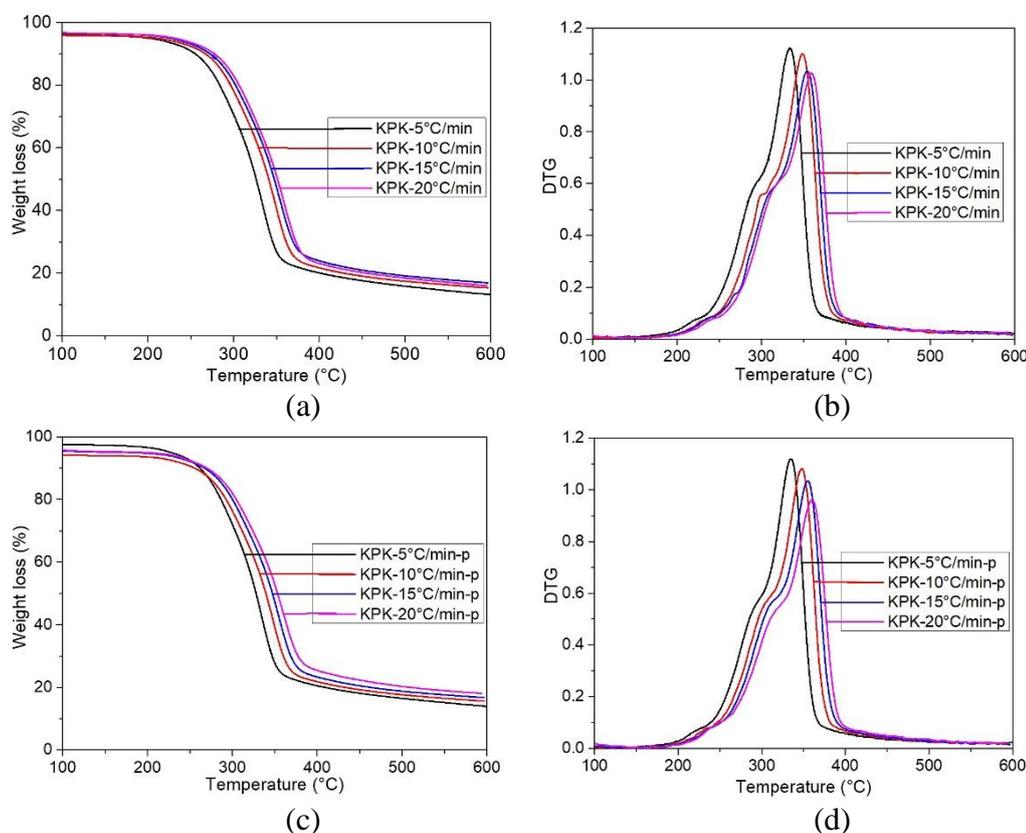
Thermal decomposition behavior of untreated and treated kapok samples was also evaluated using DTG peaks for each heating rate studied. Results are presented in Table 5.1. An increase of about 5% in activation energy ( $E_a$ ) of plasma treated fibers was observed in comparison to untreated fibers. This was attributed to oxygen at the surface of treated fibers, since higher temperatures increases reaction with oxygen, generating residues of incomplete

decomposition reactions. Both CO and CO<sub>2</sub> are obtained. This shifting can be subtle and hard to detect without a specific study of releasing gases by TGA decomposition. Thus, TGA is associated to FTIR for immediate analysis while thermal decomposition occurs.

In general, thermal behavior is not altered significantly by increasing heating rate, but a shift of DTG peaks is observed. The first peak in thermal decomposition is attributed to hemicellulose decomposition. In this work,  $E_a$  of 103 KJ.mol<sup>-1</sup> was obtained. Other cellulose-based fibers show similar values, as reported in the literature (47).

Conversion of cellulose followed a first order reaction and the corresponding reaction energy was 184 KJ.mol<sup>-1</sup>. The maximum percentage of weight loss occurred over the range 330 to 360 °C. Previous studies have reported values ranging from 160 KJ.mol<sup>-1</sup> (Wood-pine) to 183 KJ.mol<sup>-1</sup> (Jute), or Rice straw (197 KJ.mol<sup>-1</sup>) (33; 47; 48).

TGA experiments combined with mathematical models have been applied by many researchers (33; 47; 49) to measure activation energy ( $E_a$ ). A previous study of thermal decomposition kinetics for determining activation energy of the main components of kapok fibers – cellulose, hemicellulose and lignin – the degradation of lignin structures was linked to dehydration, generating products with unsaturated chains and release of water, yielding carbon monoxide, carbon dioxide and methane (50).



**Figure 5.9** Thermal behavior of kapok fibers: (a) TGA for untreated, (b) DTG for untreated, (c) TGA for treated and (d) DTG for treated

Thermal decomposition kinetics pattern for untreated and treated fibers were determined from TGA data. Friedman method was used to evaluate reaction order in various steps of degradation. Friedman method is the simplest model for obtaining thermal and kinetic behavior. The thermal degradation in each step of conversion was evaluated and suggested the presence of different materials with distinct reaction mechanisms.

The actual reaction mechanism is deeply dependent on how fast the components react. For untreated fibers, first-order reactions are observed over 10 - 80% conversion, as shown in Figure 5.10a. On the other hand, plasma treated fibers exhibited first-order reactions in 10% and over 40 - 80% conversion, as shown in Figure 5.10b. The thermal degradation over the range of 20 to 30% of decomposition has changed to second-order reaction at a temperature range of 280 to 315 °C. The reaction observed at 280 °C corresponds to hemicellulose degradation and at 315 °C is related to the degradation of some parts of cellulose and lignin structures. Hence, these changes were attributed to fiber activation, since oxygen provided by plasma has contributed to accelerate reaction. However, as oxygen is consumed, the reaction tends to go back to the original first-order behavior. Even though the reaction was faster for the treated fibers when compared to untreated, this difference is not significant for the bulk decomposition of both since plasma activation affects the fiber surface only, and the bulk properties remain unaltered.

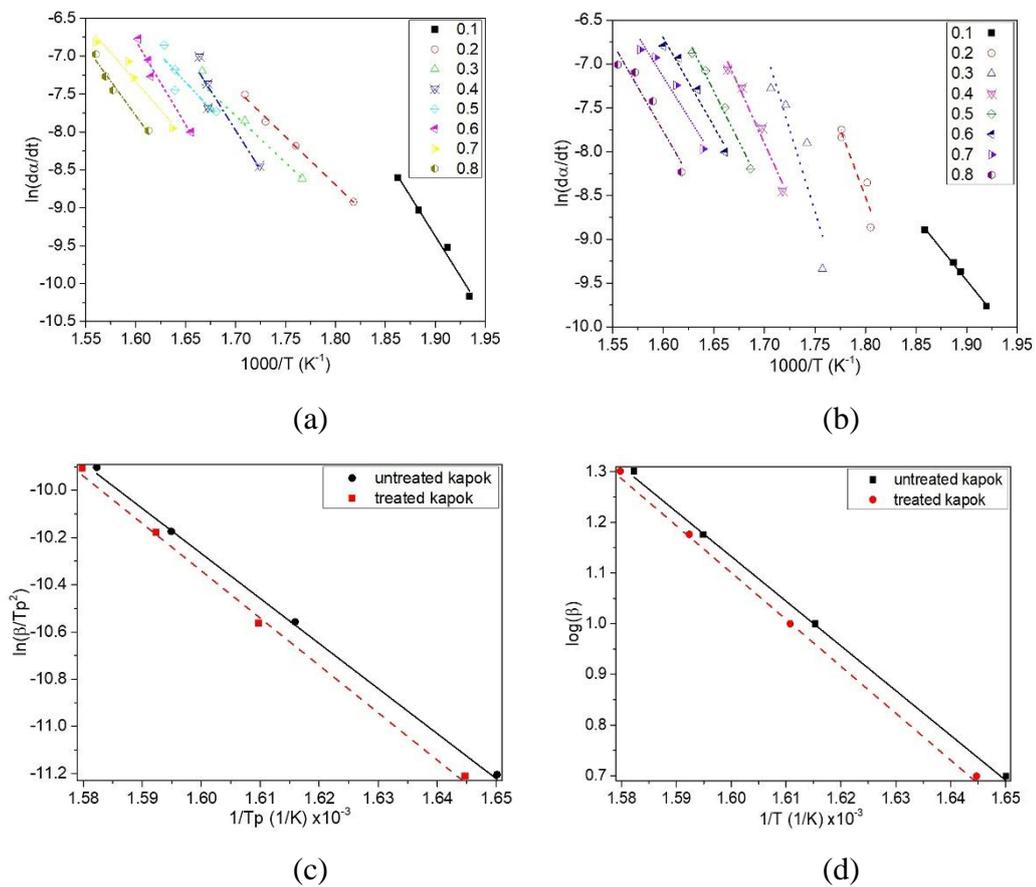
Kissinger and F-W-O methods resulted in similar activation energy ( $E_a$ ). These two models are similar regarding to thermal considerations and were used to determine the actual activation energy for untreated and treated fibers. Thermal properties of untreated and treated kapok fibers are shown in Figure 5.10. For untreated fibers,  $E_a$  values decrease from 10 to 30% of conversion. This behavior is observed over the temperature range of 293 to 327 °C, as presented in Figure 5.10a for untreated fibers and in Figure 5.10b for treated fibers. This temperature range corresponds to hemicellulose degradation.

For plasma treated fibers, an increase in activation energy was observed up to 30% conversion - related to hemicellulose - and followed by a decrease until the reaction was complete. In addition, a significant variation in lignin and cellulose degradation was observed. Exothermic reactions between oxygen and cellulose/lignin components at the fiber surface generated higher  $E_a$  values. Furthermore, for these fibers, the  $E_a$  were shifted when compared to pristine fibers, indicating changes in thermal behavior under plasma surface activation, as shown in Figure 5.10 for Kissinger (Figure 5.10c) and F-W-O methods (Figure 5.10d).

An increase in  $E_a$  means higher energy needed for the degradation reaction. Hence, components with higher  $E_a$  values are more likely to remain safe while processing at high

temperatures. This is an important attribute if the fibers are intended to be added to polymers that are processed at higher temperatures. Difference in peak temperature as well as  $E_a$  values are shown in Table 5.1.

Lower energies in thermal degradation process were related to lignin degradation. These events occurred from 300 to 350 °C temperature range, which is usually reported as being lignin degradation (47). Thermal degradation curves of lignin can be overlapped by those of cellulose and hemicellulose. Thus, due to the similar activation energies for the thermal decomposition of lignin, hemicellulose and cellulose, a reliable model for evaluating energy of each component separately becomes more complex (33). Authors attribute this to the complexity of natural components, such as soil properties, moisture availability and external factors as sunshine exposure.



**Figure 5.10** Kinetic parameters based on Friedman method for (a) untreated and (b) treated kapok fibers, (c) Kissinger method, and (d) F-W-O method

**Table 5.1** Thermal patterns from untreated and treated kapok fibers

Sample		$\beta$ (K/min)	Tp (K)	Activation Energy (KJ.mol <sup>-1</sup> )	
				Method	Value $\pm$ SD
Untreated fibers	1	5	606	Friedman <sup>a)</sup>	142.01 $\pm$ 33
	2	10	620	Kissinger	158.41 $\pm$ 0.38
	3	15	627	F-W-O	160.40 $\pm$ 0.37
	4	20	632		
Plasma treated fibers	5	5	608	Friedman <sup>a)</sup>	198.05 $\pm$ 62
	6	10	622	Kissinger	166.58 $\pm$ 0.37
	7	15	628	F-W-O	168.38 $\pm$ 0.20
	8	20	633		

<sup>a)</sup>The showed values means average from 0.1 to 0.8 of conversion

## 5.4 Conclusion

Plasma treatment was successfully applied for the surface activation of kapok fibers. Changes in relative peaks in FTIR spectra as well as a more irregular surface texture shown in SEM images confirm the plasma modification of fiber surface. The plasma treatment removed oils and wax from the fiber surface improving their wettability. The surface erosion produced by plasma treatment was found to expose the natural hydrophobic groups on the fiber surface while opening up spaces for liquids such as oils to penetrate. The open pores and partial removal of oils and waxes also facilitate water uptake and absorption by the cellulosic fibers. Thus, absorption testing indicated an increase in water and in oil uptake in comparison with untreated fibers. Activation energy data were successfully obtained from thermogravimetric analysis experiments combined with mathematical models. This approach proved successful as an alternative for the determination of the cellulose content. Plasma treatment has the advantage of producing changes at the fiber surface only, increasing the activation energy in comparison to untreated fibers. In summary, plasma treatment proved as a feasible approach for surface activation of kapok fibers, thus improving matrix/filler adhesion.

## Acknowledgements

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**6 ARTICLE 2: Effect of cold plasma treatment on the fiber/polymer interface of kapok/PE composites**

## Effect of cold plasma treatment on recycled polyethylene/kapok composites interface adhesion

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### Highlights

- Cold plasma fiber treatment may be used for the enhancement of fiber/matrix adhesion
- Storage modulus increases when plasma treated fibers are added to polymer
- Plasma is an environmentally friendly process to improve fiber/matrix interface in polymer composites

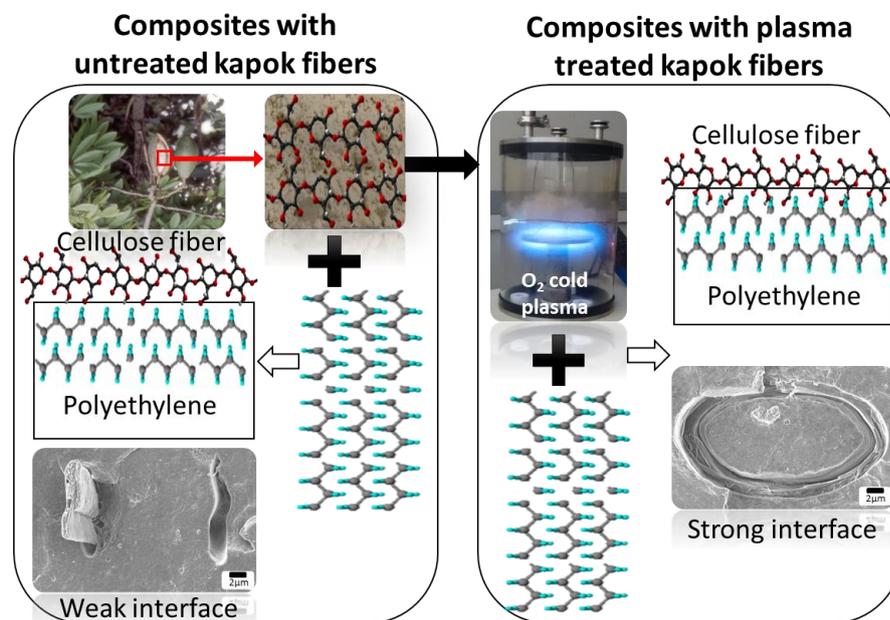
### Abstract

Composites from recycled polyethylene and kapok fibers were prepared using untreated and plasma-treated fibers. Flow properties, mechanical properties and fracture morphology were analyzed in order to evaluate the effects of cold plasma treatment on kapok fibers to improve interfacial bonding between fibers and matrix. Melt flow rate (MFR) measurements indicated a reduction in flow rate of the polymer with the addition of kapok fibers. Storage modulus increased with fiber addition and this effect was more significant when plasma-treated fibers were used.  $\tan\delta$  obtained from viscoelastic characterization also suggested improvements in fiber/matrix interface as a result of plasma treatment. The addition of kapok fibers to polyethylene produced a reduction in onset decomposition temperature determined from thermogravimetry curve. However, the decrease in temperature observed does not limit composite processing. Furthermore, the degree of crystallinity of polyethylene increased with

the addition of untreated fibers and reduced when plasma treated fibers were added. Morphological analysis of failure surface by Field Emission Gun Scanning Electron Microscopy (FEGSEM) suggest that fiber/matrix adhesion was clearly improved when plasma treated fibers were used. Thus, the oxygen cold plasma treatment proved to be an effective non-polluting approach to enhance matrix/fiber adhesion in polyethylene/kapok fiber composites, as opposed to chemical treatments.

**Keywords:** kapok fibers; plasma treatment; polyethylene waste; recycling.

### Graphical abstract



## 6.1 Introduction

Composites are a relevant class of materials due to their specific properties which allow their use in applications ranging from domestic products to advanced applications, such as oil exploration, biomedical products and aerospace industry (1, 2, 3). The growing environmental awareness has led to increasing interest in the use of natural fibers and recycled polymers and their potential to replace synthetic fiber composites at lower cost and with improved sustainability. Thus, vegetable fibers have been largely studied due to their great potential as reinforcement in polymer composites (4, 5).

Polyethylene (PE) is the most common thermoplastic matrix for composites which can be associated to characteristics such as low-temperature processing, good processability and recyclability. The use of polyethylene combined with wood or cellulose has been considered for many technological fields. Cellulose-based materials are abundant and renewable, while polyethylene is recyclable. Elastic modulus and flexural strength of polyethylene can be significantly increased by the addition of natural fillers, as discussed in a previous research on low density polyethylene filled with date palm wood powder (6). Other research focused on how processing affects mechanical properties of extruded flax fiber reinforced polyethylene composites (7).

Although recycled PE/cellulose fiber composites offer great opportunities for sustainable applications, the incompatibility between the hydrophobic polymers and hydrophilic vegetable fibers limit their mechanical properties and thus the number of applications. Hence chemical and/or physical treatments are normally necessary to improve fiber/matrix interface (8), as analyzed in a study in which a composite of recycled polyethylene and sugarcane bagasse was studied (9). Mechanical, morphological, thermal and chemical properties of the composites were evaluated. An increase of 22% in impact strength was reported when 10 wt.% of sugarcane bagasse was added. Authors concluded that interface interaction between matrix and reinforcement was improved considerably by the use of coupling agents. High density polyethylene (HDPE) matrix was also found to be effectively reinforced with cellulosic fibers when optimal concentration of reinforcement and coupling agents are used, as shown in a previous study (10), in which dynamic mechanical and thermal properties of HDPE/jute composites were evaluated.

Physical and chemical treatments have been used to improve the wettability of cellulosic fibers and thus improve interface with polymeric matrices (11, 12, 13, 14). The quality of matrix/fiber interface is one of the most important items for the final characteristic and performance of a composite material, as reported (15). Maleated polyolefins have been used as coupling agents for cellulosic reinforcement due to their affinity with lignocellulosic fibers and polyolefins (16). The maleated components have two functional domains: (i) polyolefin (e.g., HDPE or polypropylene) and (ii) maleic anhydride that reacts with lignocellulosic material at processing temperatures, generating both hydrogen and ionic bonds. The influence of low-density polyethylene-grafted maleic anhydride (LDPE-g-MA) copolymer as coupling agent in a LDPE/wood flour composite has been analyzed over the years, as discussed by other researchers (17). The authors concluded that both tensile strength and impact strength have

increased significantly after the addition of coupling agent in processing. Another work (18) evaluated the mechanical properties of HDPE/wood composites, and high levels of improvements were obtained by using of polyethylene grafted maleic anhydride (PE-g-MA) copolymer as coupling agent. High tensile and flexural strength were achieved for 50 wt.% of wood added to the polymeric matrix. More recently, cashew nut shell liquid was studied as coupling agent to improve mechanical properties of wood flour composites (19). Another recent investigation has reported suitable pre-treatments and functionalization for the modification of the fiber/matrix interface of natural fiber composites, suggesting the current interest in the development of strategies and technologies to modify vegetable fibers and polymer matrices in order to obtain the desired composite properties (20).

Plasma treatment has been studied to improve interface between polymers and cellulosic fibers (13, 21, 22). A recent investigation analyzed improvements in interfacial adhesion of composites by oxygen plasma treatment (23). Another recent study revealed significant improvements in mechanical behavior of polymers after addition of plasma treated fibers (21). It has been reported that the adhesion between ramie fibers and polypropylene matrix was improved after plasma treatment and, when pre-treatment using ethanol was carried out, this improvement in adhesion was more pronounced (24). Another investigation (25) observed increments in shear strength for jute/polyester composites between 72% and 128% after low frequency and radio frequency plasma treatment, respectively. Other study (26) suggested that plasma treatment of jute fibers could improve the mechanical properties of jute fiber reinforced thermoplastic composites.

Kapok (*Ceiba pentandra L.*) is a single-cell natural cellulosic fiber with great potential for the production of polymer-based fiber composites because of its high degree of hollowness (80–90%) – the largest in natural fibers – in addition to other advantageous characteristics such as moisture-resistance, buoyance, resilience, and softness. These unique properties of this circular hollow cross section fiber are very attractive to the textile industry (27).

Dyeing to kapok fibers was analyzed in a previous study and the results indicated that water absorption was improved after plasma treatment, thus improving the dyeing process (28). Authors also found the maximum water absorption level of fibers for the plasma treatment using 4.5 mm of work-distance and exposure time of 90s. It was also observed that mechanical strength of kapok fibers remains unchanged after plasma treatment. In addition, plasma treatment has a characteristic of reversibility by aging. Thus, the phenomenon known as hydrophobic recovery after cold plasma treatment has been described (29). Authors observed

the influence of dipole moment in the process of retarding the effect of hydrophobicity recovery.

The aim of this study was to evaluate the effect of cold plasma treatment to improve matrix/fiber interface in polyethylene/kapok fiber composites.

## **6.2 Experimental**

### **6.2.1 Materials**

Recycled Polyethylene pellets were provided by *Potyplast Reciclagem* (Mossoró/RN-Brazil). This product is a combination of recycled low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) and will be henceforth referred to as simply “recycled PE” (PEr). Kapok fibers were extracted *in natura* from kapok fruits collected in João Pessoa, Brazil. The fruits were dried at room temperature prior to fiber extraction. Then, fibers were isolated from both seeds and husk and later dried in an oven at 60°C for 24h to remove residual moisture. Neither chemical nor washing processes were used. These kapok fibers show an average external diameter of the order of 12 to 15  $\mu\text{m}$ , wall thickness of about  $1.5 \pm 0.4 \mu\text{m}$  and length of  $25 \pm 5 \text{ mm}$

### **6.2.2 Fiber pre-treatment**

Kapok fibers were treated under cold plasma prior to mixing with the polymer. The plasma equipment used consists of a chamber in which coaxial electrodes were used for electrical discharge. Details of this plasma equipment have been reported elsewhere (30). The voltage was controlled over the range of 400-500 V, flow rate of oxygen gas was  $10 \text{ cm}^3 \cdot \text{min}^{-1}$  and the work-distance was set to 4.0 cm. The pressure inside the reactor was 1.5 mbar and exposure time was 60 min.

### **6.2.3 Melt flow rate (MFR)**

Recycled PE was analyzed in an Extrusion Plastometer *CEAST Modular Melt Flow Model 7023* to determine melt flow rate prior to mixing in an extrusion machine. Tests of all samples were carried out according to ASTM D1238, procedure A.

#### 6.2.4 Extrusion and injection molding

Composites were prepared using a single-screw extrusion machine from *AX Plásticos* (Brazil) with 16 mm diameter and L/D ratio of 26 in two steps: mixing and dispersion. The first step consisted of mixing components (fiber and polymer pellets) throughout the barrel with no auxiliary mixing and/or dispersive elements. For the second step a Maddock ® mixer was used for enhancing mixing and dispersion. For both, the temperature profile from the hopper to die was 190/200/200 at a constant screw speed of 40 rpm. Prior to extrusion processing, recycled PE (PEr) pellets and kapok fibers were dried in an air-circulating oven at 60°C for 24 h to remove residual humidity. This process was followed by vacuum oven drying at the same temperature for 8 h. The following compositions were prepared for this study: (1) Recycled polyethylene (PEr); (2) Recycled polyethylene with 10 wt.% of kapok fibers (PEr/KPK10) and (3) Recycled polyethylene with 10 wt.% of plasma treated kapok fibers (PEr/KPK10\_p). Samples of plain polymer and composites were produced by injection molding for the mechanical characterization. These samples were processed in a Haake Minijet II injector after mixing in the extrusion machine, using injection barrel temperature of 215°C and mold temperature of 40°C. The injection pressure was set to 800 bar. Fiber content was limited to 10 wt.% due to processing limitations. Injection of the composites was not properly accomplished at higher fiber contents.

#### 6.2.5 Mechanical and thermo-mechanical characterization

Tensile tests of the composites were carried out in a standard testing machine (EMIC, Brazil) using a load cell of 500 N and following recommendations of ASTM D638-14 standard methods for tensile tests. Specimens type V were manufactured and tested at constant cross-head displacement rate of 10 mm.min<sup>-1</sup>. Tensile strength was determined using five specimens of each composition.

Dynamic mechanical thermal analysis (DMTA) measurements of composites were carried out in a DMA 1 Star System (Mettler Toledo, USA) under three-point bending test mode using test specimens of 30 mm x 10 mm x 1 mm. Measurements were conducted at a constant frequency of 1 Hz and over a temperature range of -140°C to 80°C with heating rate of 10°C.min<sup>-1</sup>.

### 6.2.6 Thermal behavior

Thermogravimetric analyses (TGA) of fibers, polymer and composites were conducted in a PerkinElmer STA 6000 (PerkinElmer) apparatus under Nitrogen atmosphere (99.5% purity) at a flow rate of 50 ml.min<sup>-1</sup>. Samples weighing 6 to 7 mg were placed in an aluminum pan and scanned over a temperature range of 30 to 600°C using a heating rate of 10°C.min<sup>-1</sup>. Nitrogen was used as purge gas prior to each running in order to reduce oxygen concentration at the sample site.

Differential scanning calorimetry (DSC) analyses were carried out to evaluate the influence of plasma treatment on the melting temperature and degree of crystallinity of the composites. The samples were placed in an aluminum hermetic pan and heated from 30 to 200°C, followed by cooling from 200 to 30°C, and then heated again until 200°C. For each running, samples weighing 3 to 4 mg were analyzed under nitrogen atmosphere at a flow rate of 50 mL.min<sup>-1</sup>. The degree of crystallinity  $X_C$  (%) was estimated using the following equation:

$$X_C(\%) = \frac{\Delta H_f}{\Delta H_f^C} \times \frac{1}{W_f} \times 100\% \quad \text{Eq. 6.1}$$

In which  $\Delta H_f$  is the measured enthalpy of the material,  $\Delta H_f^C$  is the enthalpy of the 100% crystalline material (288 J.g<sup>-1</sup>) and  $W_f$  is the weight fraction of matrix in the composite (31).

### 6.2.7 Morphological characterizations

Failure surfaces of composites were analyzed using a Field-Emission Gun – Scanning Electron Microscope (FEG-SEM) – ZEISS Auriga, operating at 3.0 kV with tungsten filament. All samples were first coated with a thin layer of gold for 60s in a Sputter Coater BAL-TEC SCD 005 in argon atmosphere under vacuum.

## 6.3 Results and discussion

### 6.3.1 Composite processing

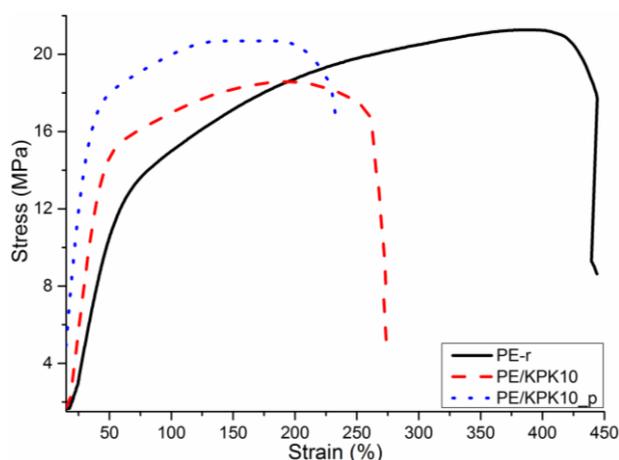
Flow properties were evaluated using MFR data. Flow rate is important for the determination of the proper processing configuration in order improve uniformity of the flow of the polymer in the extrusion process and fiber dispersion. Melt flow rate results are summarized in Table 6.1. As shown in this table, the presence of kapok fibers caused a decrease

in the flow rate of the polymer, that is, an increase in viscosity of the composites. The influence of fibers and/or fillers in compounding by extrusion or injection molding has been reported in the literature as quite dependent on rheological pattern and less dependent on surface modifications (32, 33, 34, 35) that the influence of fibers and/or fillers in compounding by extrusion or injection molding is quite dependent on rheological pattern and less dependent on surface modifications. Nevertheless, results presented suggest that the use of plasma treated kapok fibers improves flow behavior of composites as compared to untreated fibers.

### 6.3.2 Mechanical and thermo-mechanical characterization

Mechanical behavior of the materials produced is presented in Figure 6.1 and the main results are also summarized in Table 6.1. Mechanical tests were conducted to understand the influence of plasma treatment on the final performance of kapok/PE composites. A fiber content of 10 wt.% was considered in this work to understand the influence of plasma treatment of fibers on composite properties. It is known that poor compatibility and weak interface are obtained if untreated natural fibers are added to polymers.

Tensile strength of the recycled polyethylene was not considerably affected by the addition of kapok fibers. However, when kapok fibers were added to polyethylene, the composites exhibited a decrease in ductility in comparison to the pure polymer, which was higher in the case of plasma treated fibers. These results suggest that the plasma treatment improved bonding between fiber and matrix, thus affecting the mechanical performance of composites based on PE and kapok fibers.



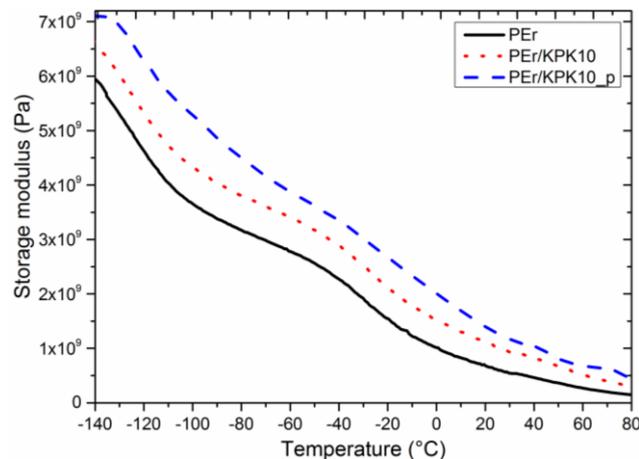
**Figure 6.1** Mechanical behavior of: Recycled polyethylene (PEr); Recycled polyethylene with 10 wt.% of kapok fibers (PEr/KPK10); Recycled polyethylene with 10 wt.% of plasma treated kapok fibers (PEr/KPK10\_p)

Dynamic mechanical properties of the pure polymer and composites were obtained from DMTA. Results of storage modulus ( $E'$ ) over the range of temperature studied are shown in

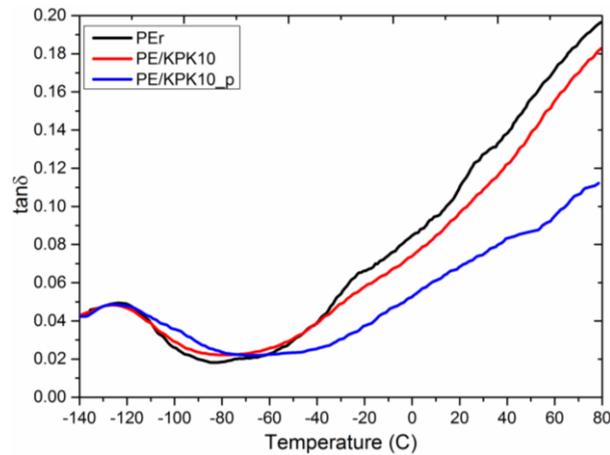
Figure 6.2. The pure polymer and composites showed similar trend for the storage modulus over the entire range of temperature. Based on the results, the  $E'$  values of the pure recycled polyethylene and composites of untreated and plasma treated fibers decrease substantially with increasing temperature. This behavior is due to increased mobility of the polymer chains when higher levels of energy are available.

Improvements in  $E'$  were observed for composites of both untreated and plasma treated fibers, as compared to the pure polymer. However, the increase in  $E'$  was more significant for composites of plasma treated fibers. This has been related to enhancement in fiber/matrix interfacial adhesion. Similar behavior was observed in a previous study of the influence of maleic anhydride polyethylene using both untreated and treated jute fibers with HDPE (10).

Mechanical damping results are exhibited in Figure 6.3. The behavior of recycled polyethylene and its composites of untreated and plasma treated fibers was similar up to  $-60^{\circ}\text{C}$ . Over the temperature range of  $-60$  to  $80^{\circ}\text{C}$ ,  $\tan\delta$  was lower in magnitude for composites of plasma treated fibers, as compared to those made using untreated fibers, suggesting stronger fiber/matrix interface produced by plasma treatment. Previous studies have also reported that strong fiber/matrix adhesion reduces energy dissipation (36; 37). Therefore, the increase in  $E'$  and reduction in  $\tan\delta$  over a range of temperature indicate that plasma treatment of kapok fibers was effective to enhance fiber/matrix interface.



**Figure 6.2** Variation of storage moduli with temperature for: Recycled polyethylene (PEr); Recycled polyethylene with 10 wt.% of kapok fibers (PEr/KPK10); Recycled polyethylene with 10 wt.% of plasma treated kapok fibers (PEr/KPK10\_p)



**Figure 6.3** Variation of  $\tan \delta$  with temperature for: Recycled polyethylene (PEr); Recycled polyethylene with 10 wt.% of kapok fibers (PEr/KPK10); Recycled polyethylene with 10 wt.% of plasma treated kapok fibers (PEr/KPK10\_p)

**Table 6.1** Melt Flow Rate, mechanical and thermo-mechanical properties of PEr/kapok composites

Sample	Melt Flow Rate (g.10 min <sup>-1</sup> )	Tensile strength (MPa)	Storage modulus (GPa) <sup>*1</sup>	Tan $\delta$ <sup>*1</sup>
PEr	9.05±0.15	21.1±1.1	0.606±0.0100	0.12±0.0102
PEr/KPK10	5.81±0.40	18.4±0.8	1.011±0.0154	0.10±0.0260
PEr/KPK10_p	6.15±0.45	20.5±1.2	1.275±0.0076	0.07±0.0100

\*1 values at room temperature

### 6.3.3 Thermal behavior

Thermal behavior of the composites, fibers and pure polymer were evaluated from thermogravimetric analysis and the results are plotted in Figure 6.4. Fibers exhibited thermal degradation at lower temperatures than the pure polymer and composites. The first weight-loss of the kapok fibers was observed from room temperature up to 100°C, which was attributed to loss of water for both untreated and treated kapok fibers. Plasma treated fibers are more likely to exhibit free oxygen or weak bonds, resulting in changes in polarity and improving wettability to some liquids, thus resulting in greater weight loss. Above this temperature range, the thermal behavior was not modified by the plasma treatment.

This behavior was observed by other researchers in a previous study involving coconut fibers (38). Kapok fibers show two steps of degradation, indicated by peaks around 298°C and 347°C. The first step ranges from 200°C to 313°C and is associated with hemicellulose degradation, while the second step ranges from 313°C to 380°C, associated with cellulose degradation. Thermal degradation of lignin occurs between 280°C and 500°C, as previously reported (38-40).

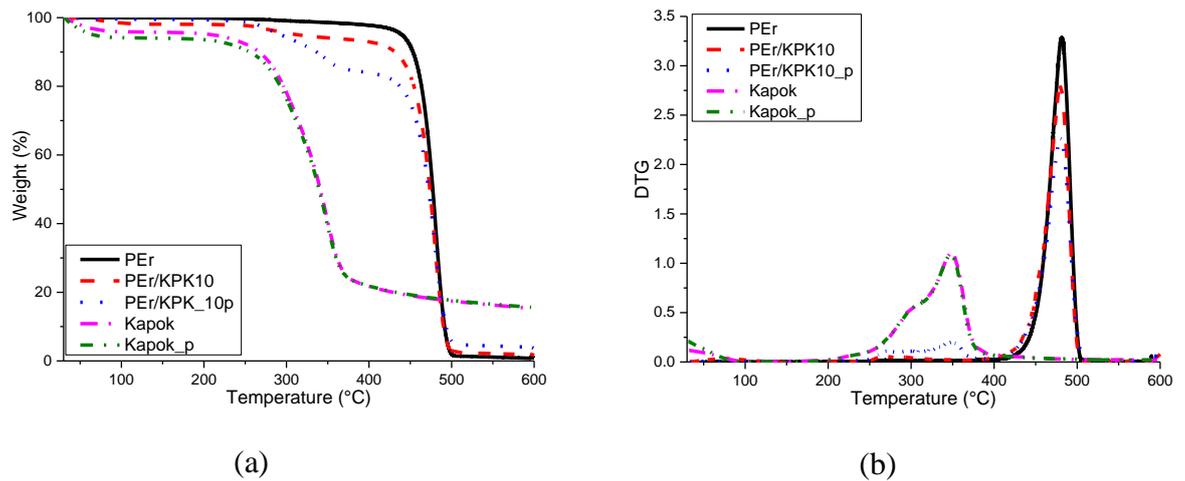
Composites with plasma treated kapok fibers exhibited thermal behavior considerably different, as compared to recycled PE and its composite with untreated fibers, with two well-defined decomposition zones and a thermal event over the range of 250-360°C (Figure 6.4b). This event might be attributed to the increase in available oxygen provided by plasma on the fibers surface. Thus, composites of plasma treated fibers may react faster in comparison to those of untreated fibers. In addition, the difference observed for composites with plasma treated fibers over those with untreated fibers may be related to improved bonding between fiber and matrix, since the thermal degradation of the fibers were not affected considerably by the plasma treatment. A similar effect on thermal stability of composites with plasma treated fibers was also reported in a previous investigation of HDPE with natural fibers (41), in which two stages of degradation were observed.

Onset temperature determined from the thermogravimetry curve changed after addition of untreated fibers and plasma treated fibers in comparison to the pure polymer. The presence of cellulose induced a decrease in this temperature. Thermogravimetric analysis showed that the temperatures in which degradation processes start were about 250°C. Cellulose has many oxidant components in its inner structure and oxygen plasma has also induced oxidant components on fiber surface. However, this lower degradation temperature for the plasma treated fiber composites does not affect composite processing, since the highest temperatures in extrusion and injection machines were 200 and 215°C, respectively.

Decomposition in two steps was observed for composites from TGA data. The first step of degradation was observed over a wide region, with temperatures ranging from 250°C to 360°C, attributed to lignocellulosic components (cellulose, hemicellulose and lignin). This has been reported by other researchers (42; 43). For fiber composites, this process has started at lower temperature due to the releasing of oxygen from cellulose and lignin components. Above 250°C, oxygen would work as oxidizing, turning the thermal degradation even faster. The second step of degradation - from 360°C to 495°C - might be attributed to degradation of recycled polyethylene. Thermal degradation of polymers, in general, involves breaking of bonds in the polymer backbone. For the pure PE samples, the degradation occurs in one step over a narrow region, ranging between 415°C and 495°C.

For both untreated and treated fibers, the weight of the material after the degradation process was about 20 wt.%. This weight represents the incomplete degradation of glycosidic bond functional groups. For composites with plasma treated fibers, the amount of material left after the thermal event was about 2 wt.%, corroborating with the fiber content on the composite (10 wt.%). Thus, this study reveals that plasma treatment was not harmful to the thermal

behavior of composites, since changes occur only in the matrix/fiber interface, thus with little influence on the final characteristics of fibers. Ultimately, plasma treatment offers the advantage of improving mechanical properties while not impairing thermal behavior of fibers. Results of the thermogravimetric analyses are summarized in Table 6.2 showing the influence of fibers as well as plasma treatment on the thermal behavior of the composites.



**Figure 6.4** (a) Thermogravimetry - TG and (b) Derivative Thermogravimetry Curves - DTG curves for: Recycled polyethylene (PEr); Recycled polyethylene with 10 wt.% of kapok fibers (PEr/KPK10); Recycled polyethylene with 10 wt.% of plasma treated kapok fibers (PEr/KPK10\_p); Kapok fibers (Kapok); Plasma treated kapok fibers (Kapok\_p)

**Table 6.2** Thermal data from Kapok fibers, recycled PE and composites

Sample	T <sub>ONSET</sub> (°C)	T <sub>ENDSET</sub> (°C)	Degradation (steps)	T <sub>MAX.DEG/each deg. Peak</sub> (°C)
<b>Kapok</b>	230	370	Two	298/347
<b>Kapok_p</b>	223	370	Two	297/347
<b>PEr</b>	415	495	One	481
<b>PEr/KPK10</b>	254	495	Two	262/480
<b>PEr/KPK10_p</b>	248	495	Three	266/348/479

Thermal curves obtained using differential scanning calorimetry were also used in order to understand the effects of the addition of kapok fibers on the melting temperature of recycled polyethylene matrix as well as the degree of crystallinity of the composites.

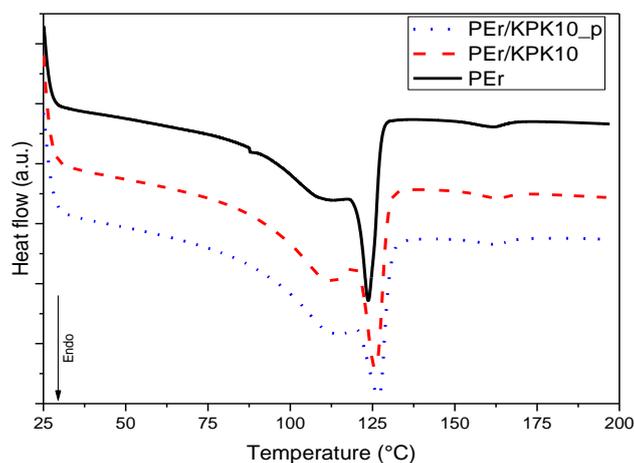
Two melting peaks were determined for the pure polymer at about 113°C and 125°C. Results are presented in Figure 6.5. Previous studies report melting points for LDPE and LLDPE at about 115°C and 123°C, respectively (44; 45). Thus, the two melting peaks determined is an indicative that the recycled polymer used is a blend of LDPE and LLDPE.

The results presented also show that the melting peaks of the composites were shifted to higher temperatures in comparison to the pure polymer. This might be attributed to the presence of dispersed fibers - and therefore new chemical groups such as cellulose - throughout matrix. These results indicated a delay in energy absorption, as observed in the

thermogravimetric analysis, in which the degradation behavior of the composites was affected by the fibers, mainly for samples with plasma treated fibers. An increase of 2°C and 4°C in melting peaks for the composites of untreated and plasma treated fibers, respectively, were observed in comparison with the pure polymer.

The measured enthalpies of fusion and the respective calculated crystallinities for all materials are presented in Table 6.3. Based on this data, it is concluded that the presence of untreated kapok fibers increased the degree of crystallinity of the polymer from 66.7% to 91%. However, when plasma treated fibers were added to the polymer, the effect was the opposite and a decrease in degree of crystallinity was observed. A previous study showed that improvements in interfacial interaction between vegetable fibers and polyolefins reduces the crystallization of the polymer (32). Thus, the reduction in degree of crystallinity of the polymer with plasma treated kapok fibers suggests improvements in fiber-matrix interfacial interaction. Other studies reported degree of crystallinity values from 54 to 67% for PE samples (46; 47).

One of the constituents of the recycled polyethylene waste, the LLDPE, is known to have high elongation at break, due to its chemical structure that allows the polymer chains to get oriented, making the crystallization faster in comparison with other PE of lower chain mobility. As the chains get more oriented, the degree of crystallinity is increased (48).



**Figure 6.5** Melting temperatures for: Recycled polyethylene (PEr); Recycled polyethylene with 10 wt.% of kapok fibers (PEr/KPK10); Recycled polyethylene with 10 wt.% of plasma treated kapok fibers (PEr/KPK10\_p)

**Table 6.3** Enthalpy and crystallinity of recycled PE and PEr/kapok composites

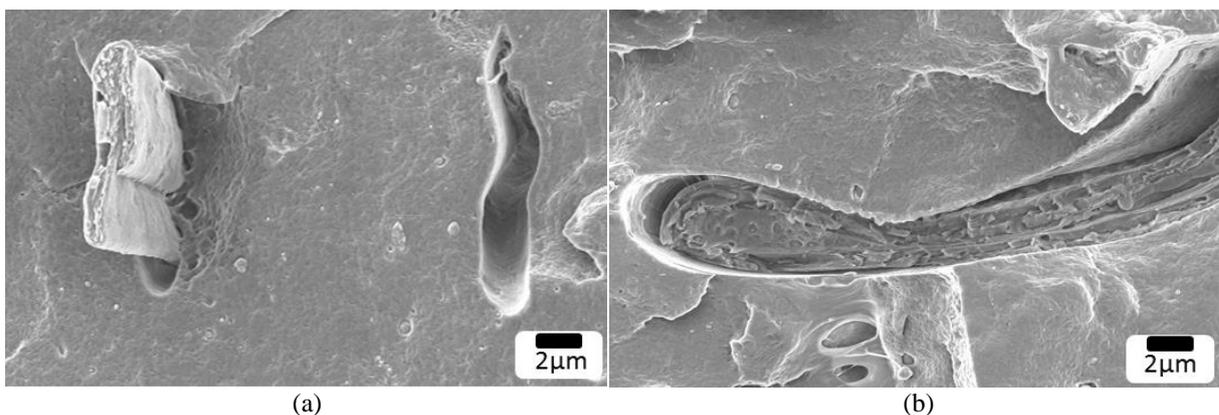
Sample	1 <sup>st</sup> event $\Delta H_m$ (exp)/Temp. (°C)	2 <sup>nd</sup> event $\Delta H_m$ (exp)/Temp (°C)	$\Delta H_m$ (exp) (total)	$W_f$	$X_c$ (exp) (%)
PEr	17.5/113	191.3/123	208.8	1.0	66.7
PEr/KPK10	17.9/113	235.8/125	253.7	0.9	91.0
PEr/KPK10_p	16.2/114	150.5/127	166.7	0.9	58.1

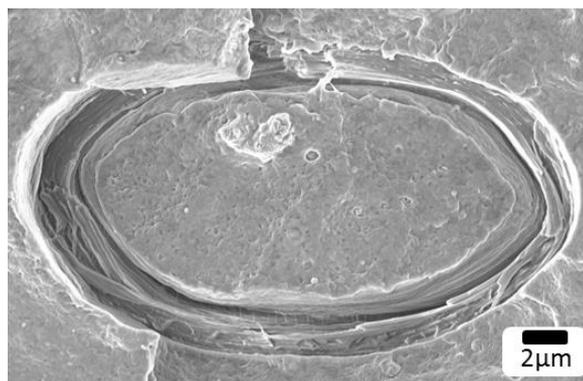
### 6.3.4 Morphological characterization

SEM micrographs of the fractured surfaces of PEr/kapok composites are presented in Figure 6.6. Images of surfaces of composites with untreated fibers show characteristics of poor fiber-matrix adhesion (Figure 6.6a). This leads to low mechanical properties, as reported elsewhere (49). In many areas of the fractured surfaces, untreated kapok fibers were pulled-out from the surface during mechanical testing, as shown in Figure 6.6a. The appearance of the pulled-out fibers remains unchanged, suggesting poor adhesion.

On the contrary, fractographs of fractured surfaces of composites manufactured using plasma treated fibers suggest improvement in fiber-matrix adhesion, with fiber breakage due to the tensile load and no fiber pulled-out, as shown in Figure 6.6b. This improvement in fiber-matrix adhesion is attributed to new bonds formed due to oxygen provided by plasma treatment. For these composites of plasma treated fibers, good wetting of the fibers by the polymer is also observed. In addition, some SEM images suggest that the polymer penetrates the treated hollow fibers, as detailed in Figure 6.6c. Although the percentage of fibers filled with polymer was not determined, this was observed throughout the fractured surface. Thus, composites of plasma treated fibers are stiffer as compared to those of untreated fibers, as confirmed by the results of dynamic mechanical analysis. Thus, improvements in fiber/matrix interface of composites of plasma treated fibers were clearly observed, suggesting that plasma is effective as treatment of natural fibers for the production of polymer-based composites.

Improvements in interface of HDPE/natural fibers with the use of various coupling agents have been reported by previous authors (41). Other reported an improvement in the fiber/matrix interface after plasma treatment, thus producing continuous and regular interfaces (22). In addition, plasma modification of cotton fibers was studied and an increase in carboxyl and carbonyl group contents was found, thus leading to a more wettable fibers (50).





(c)

**Figure 6.6** SEM fractographs of samples: (a) Recycled polyethylene with 10 wt.% of kapok fibers (PEr/KPK10); (b) and (c) Recycled polyethylene with 10 wt.% of plasma treated kapok fibers (PEr/KPK10\_p)

## 6.4 Conclusions

Composites from recycled polyethylene with the addition of untreated and plasma-treated kapok fibers were successfully prepared. Plasma treatment was favorably applied for the surface activation of kapok fibers. Modified fibers were found to enhance the mechanical performance of the composites. This leads to new possibilities for the production of composites of polymers and vegetable fibers, since plasma processing is simple to apply and relatively low cost. It also offers environmental advantages over chemical treatments, e.g. mercerization, which may generate toxic waste, or modifiers (e.g. grafted polymers), which are expensive. In general, mechanical properties of the composites were improved by cold plasma treatment of kapok fibers. Although composites of plasma treated fibers displayed lower thermal stability, processing is not affected, since the typical temperatures in extrusion and injection machines are 200 and 215°C, thus lower than temperatures at which degradation occurs (about 250°C), as determined by thermogravimetric analysis. Morphological analyses of the fractured surfaces suggested good adhesion of the plasma treated fibers with the polymer, which indicates enhancement in interfacial adhesion. In summary, this investigated approach shows that the cold plasma treatment is promising as an environmentally friendly process for the production of composites of vegetable fibers and recycled polymers.

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**7 ARTICLE 3: Composites from recycled polyethylene and plasma treated kapok fibers**

## Composites from recycled polyethylene and plasma treated kapok fibers

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### Highlights

- Recycling followed by compounding is suitable to reduce waste
- Kapok fibers induces reduction in torque while processing in a chamber
- Plasma is an environmentally friendly process to couple fibers and polymers
- Strong adhesion might be obtained using cold plasma as coupling process

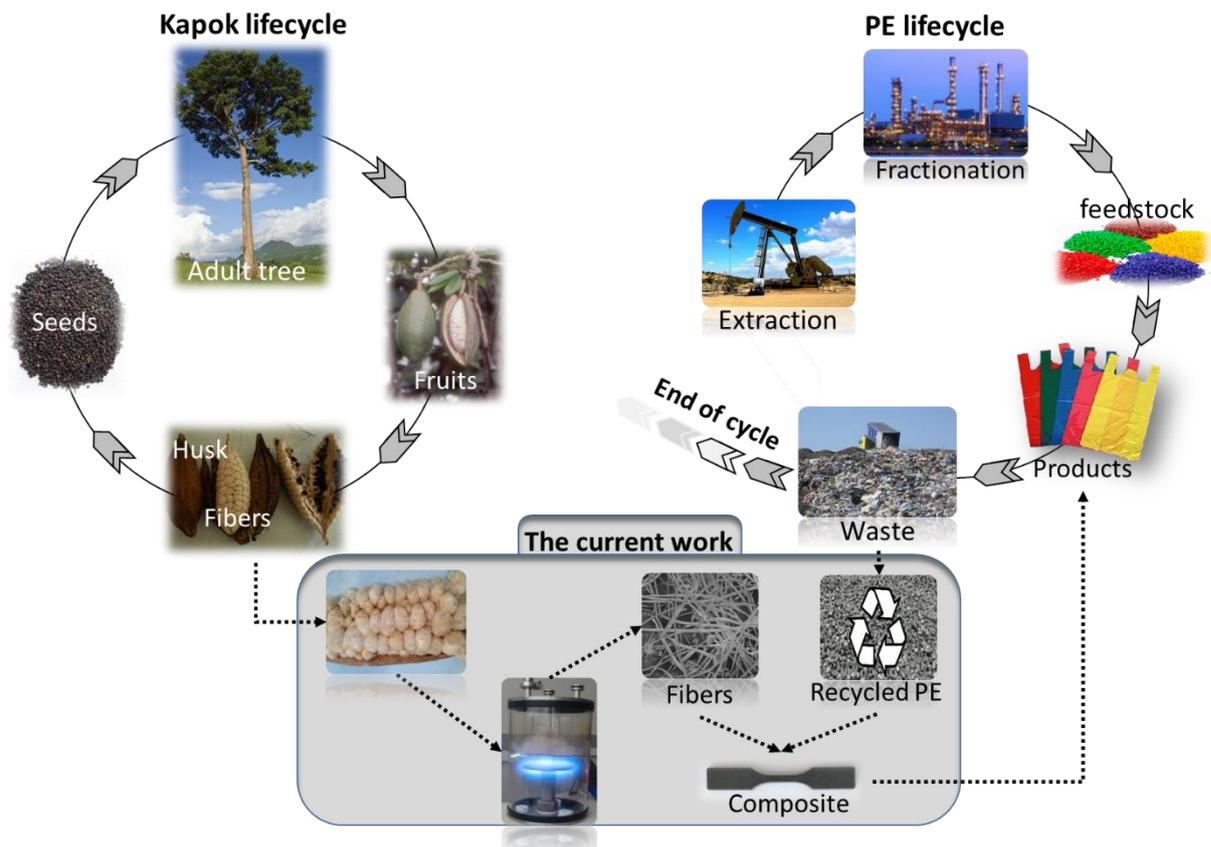
### Abstract

Recycling provides great opportunities for waste reduction and to lower environmental impact. As a recycling alternative, there has been growing interest in adding biomass residues to polymers to produce composite materials for technological applications. In this study, composites from recycled polyethylene and kapok fibers were prepared with fiber contents of 1, 5 and 10 wt.%. Cold plasma treatment was applied to the fiber in order to further improve the fiber/matrix adhesion. Effects of plasma treatment on fiber morphology were evaluated using rheological, thermal, mechanical and morphological analyses. Rheological analysis suggested that kapok fibers promoted a reduction in the steady-state torque during mixing. Differential Scanning Calorimetry (DSC) analysis suggested that as the level of fibers increase, the degree of polymer crystallinity generally decreases. Thermogravimetric Analysis (TGA) indicated that the addition of plasma treated fibers decreases the thermal stability compared to the pure polymer due to the matrix/fiber interaction and lower thermal stability of vegetable fibers. However, the observed decrease in temperature does not limit composite processing. In addition, the thermal conductivity of composites is slightly reduced as the amount of fibers increased. Dynamic mechanical thermal analyses (DMTA) of composites with plasma-treated

fibers indicated an increase in storage moduli, as well as an increase in glass transition temperature as compared to the pure polymer. Field-Emission Gun Scanning Electron Microscopy (FEG-SEM) images of fractured surfaces suggest good fiber/matrix adhesion with fibers remaining vigorously connected to the matrix, which is in accordance with mechanical tests results. Thus, cold plasma is demonstrated as a viable non-polluting alternative to activate cellulose fibers, to improve fiber/matrix interface in polymer composites.

**Keywords:** cold plasma; composites; kapok fibers; polyethylene; recycling

### Graphical abstract



## 7.1 Introduction

Polyethylenes (PE) are the most widely used polymers. Nevertheless, their widespread use increases the waste generated by plastic products. Several applications are used in developing thin films, such as for supermarket bags. The problem is that the lifecycle of these bags is relatively short when compared to the lifetime of the polymer used to manufacture them.

In addition, they remain in nature for many years before starting natural degradation, meaning that recycling these materials is essential (1-3).

The recycling process usually reduces mechanical properties of the material in comparison to virgin raw materials. A suitable proposal to reduce this problem is to manufacture a composite, considering the wide range of reinforcements to obtain the desired properties. This range of combinations has made fiber reinforced composites more attractive to industry than non-reinforced materials. Thus, natural (and renewable) components have prompted an unlimited number of applications and characteristics that may be obtained through the development of composites (4, 5), and several studies have been carried out with the aim of applying vegetable fibers for reinforcement in composite manufacturing (6-8).

The matrix-reinforcement coupling must be properly designed to obtain the desired composite properties. Furthermore, the volume fraction of each constituent phase may influence processing conditions as well as thermal, mechanical and morphological characteristics. Vegetable fibers are typically modified by alkaline treatment (mostly mercerization) to improve compatibility with polymeric matrices (9). Fiber-matrix adhesion might also be improved throughout the grafting process on polymers. For PE-based materials, the most used coupling agent is Maleic anhydride grafted polyethylene (PE-g-MA) and the gains in using PE-g-MA has been reported by other researchers (10, 11). In addition, alternative processes might be carried out to make compatible vegetable fibers with hydrophobic polymers, such as cold plasma treatment. These processes show the advantage of not generating chemical waste, which can be harmful to the environment (12-16).

Thermal properties such as thermal conductivity ( $k$ ), thermal resistivity ( $r$ ), diffusivity ( $D$ ) and volumetric specific heat ( $C$ ) have been largely used to evaluate the influence of fillers and/or reinforcements in composites. Thermal conductivity of general thermoplastic polymers are typically over the range of 0.10 to 0.50 W/m.K (17, 18). For polyethylene samples, values ranging from 0.30 to 0.34 W/m.K have been reported (19). Previous works also reported that crystallinity, chain structure and fiber orientation are responsible for changes in thermal patterns of composites (20).

Various vegetable fibers have been investigated to produce polymer composites with useful properties for many applications. Among those, kapok (*Ceiba pentandra L.*) is a circular cross-section cellulose based fiber with a high degree of hollowness (80–90%), considered the largest among natural fibers (21, 22). This high degree of hollowness makes these fibers very attractive to produce low-density polymer composites. These fibers have been traditionally used in applications including stuffing, upholstery, sound and heat insulation, and life preservers

(23). However, the use of kapok fibers in technological applications is increasing, especially in water/oil separation due to low absorption of water and high ability to uptake oils (24-27). Furthermore, kapok fibers have been used to enhance oil sorption of composites (28). Most recently, these fibers have been used to perform a super-oleophilic material with ZnO needles (29). The use of kapok seeds, husks and fibers to produce composites has been reported by several authors (30-34).

In this work, kapok fibers were treated and activated under cold plasma treatment. The aim of this study was to evaluate the effect of adding plasma treated fibers on the mechanical, thermal and rheological properties of composites using recycled polyethylene as matrix.

## 7.2 Experimental

### 7.2.1 Materials

Recycled polyethylene (PEr) was provided by *Potyplast Reciclagem* (Brazil). Kapok fibers were obtained from kapok tree fruits collected in João Pessoa, Brazil. The fruits were dried at room temperature. Then, fibers were isolated from both seeds and husk, and later dried in an oven at 60°C for 24h. These kapok fibers show an average external diameter in the range of 12 to 15  $\mu\text{m}$ , wall thickness of  $1.5 \pm 0.4 \mu\text{m}$  and length of  $25 \pm 5 \text{ mm}$ .

### 7.2.2 Fiber treatment

Kapok fibers were treated under cold plasma prior to mixing with the polymer. The voltage was controlled over the range of 400-500 V, flow rate of oxygen gas was  $10 \text{ cm}^3 \cdot \text{min}^{-1}$  and the work-distance was set to 4.0 cm. The pressure inside the reactor was 1.5 mbar and exposure time was 60 minutes.

### 7.2.3 Rheological characterization

The rheological behavior of the mixtures was evaluated using a Haake Torque rheometer model Rheocord 90, at rotation speed of 60 rpm, work-temperature of 190°C, and processing time of 10 minutes, for the mixing chamber filled with 60g of material. The following compositions were prepared: (1) Recycled polyethylene (**PEr**); (2) Recycled polyethylene with 1 wt.% of kapok fibers (**PEr/KPK1**), (3) Recycled polyethylene with 5 wt.%

of kapok fibers (**PEr/KPK5**) and (4) Recycled polyethylene with 10 wt.% of kapok fibers (**PEr/KPK10**).

#### 7.2.4 Extrusion and injection molding processing

Pure polymer and composites were mixed under extrusion processing. Materials were prepared using a single screw extruder from *AX Plasticos* with 16 mm barrel diameter and L/D ratio of 26. The temperature profile from the hopper to die was 190/200/200 (°C) at a constant screw speed of 40 rpm. Recycled PE (PEr) pellets and plasma treated fibers were dried in an air-circulating oven at 60°C for 24h to remove residual humidity. This process was followed by vacuum oven drying at the same temperature for 8h prior to extrusion processing. Samples of plain polymer and composites were produced for the mechanical characterization by injection molding. These samples were processed in a Haake Minijet II injector after mixing in the extrusion machine, using injection pressure of 800 bar, barrel temperature of 215°C and mold temperature of 40°C. In addition, specimens for thermal data analysis were molded using a cylindrical hydraulic press by *Arotec* (Model PRE 30Mi). The applied pressure was 250 bar and barrel temperature was set to 175°C. The specimens were heated to barrel temperature, followed by holding for 8 min at this temperature and then cooling down to 40°C. Properties were determined using three specimens of each composition, and three measurements were recorded for each specimen.

#### 7.2.5 Thermal characterization

Differential scanning calorimetry (DSC) analyses were carried out in a DSC Q20 by TA Instruments, under Nitrogen atmosphere (99.5% purity) at a flow rate of 50 ml.min<sup>-1</sup> in order to evaluate the influence of plasma treatment on the melting temperature and degree of crystallinity of the composites with plasma treated fiber. The samples were placed in a Tzero aluminum hermetic pan and heated from 30°C to 200°C, followed by cooling from 200°C to 30°C, and then heated again until 200°C. For each running, samples weighing 3 to 4 mg were analyzed under nitrogen atmosphere at a flow rate of 50 mL.min<sup>-1</sup>. The degree of crystallinity  $X_C$  (%) was estimated using the following equation:

$$X_C(\%) = \frac{\Delta H_f}{\Delta H_f^c} \times \frac{1}{w_f} \times 100\% \quad \text{Eq. 1}$$

In which  $\Delta H_f$  is the measured enthalpy of the material,  $\Delta H_f^C$  is the enthalpy of the 100% crystalline material (288 J.g<sup>-1</sup>) and  $W_f$  is the weight fraction of matrix in the composite (35).

Thermogravimetric analyses (TGA) of fibers, polymer and composites were conducted in a PerkinElmer STA 6000 apparatus under Nitrogen atmosphere (99.5% purity) at a flow rate of 50 ml.min<sup>-1</sup>. Samples weighing 6 to 7 mg were placed in an aluminum pan and scanned over a temperature range of 30°C to 600°C using a heating rate of 10°C.min<sup>-1</sup>. Nitrogen was used as purge gas prior to each running in order to reduce oxygen concentration at the sample site.

Thermal parameters measurements of the pure polymer and composites were carried out in a KD-2 Pro Thermal Properties Analyzer (Decagon Devices, USA) using a dual need SH-1 sensor sizing 3 cm long, 1.3 mm diameter and 6 mm spacing from each other, in accordance to ASTM D5334 standard methods for thermal characteristics of solid materials. Thermal results were determined using three specimens of each composition and three scans were performed for each specimen.

#### 7.2.6 Thermo-mechanical characterization

Dynamic mechanical thermal analysis (DMTA) measurements of composites were carried out using a DMA 1 Star System (Mettler Toledo) under three-point bending test mode. The specimen dimensions were nominally 30 mm x 10 mm and 1 mm. All measurements were conducted at a frequency of 1 Hz and over a temperature range of -140°C to 80°C, with heating rate of 10°C.min<sup>-1</sup>.

#### 7.2.7 Tensile testing

Mechanical tests were performed in a standard testing machine (model DL 3000 - EMIC) using a load cell of 500N at constant crosshead speed of 10 mm.min<sup>-1</sup>, in accordance to ASTM D638-14 standard methods (Type V) for tensile tests. Tensile strength was determined using five specimens of each composition.

#### 7.2.8 Morphological analysis

Fracture surfaces of the pure polymer and composites were analyzed using a Field-Emission Gun – Scanning Electron Microscope (FEG-SEM) – ZEISS Auriga, operating at 3.0

kV with tungsten filament. All samples were first coated with a thin layer of gold for 60s in a Sputter Coater BAL-TEC SCD 005 in argon atmosphere under vacuum.

### **7.3 Results and Discussion**

#### **7.3.1 Rheological behavior**

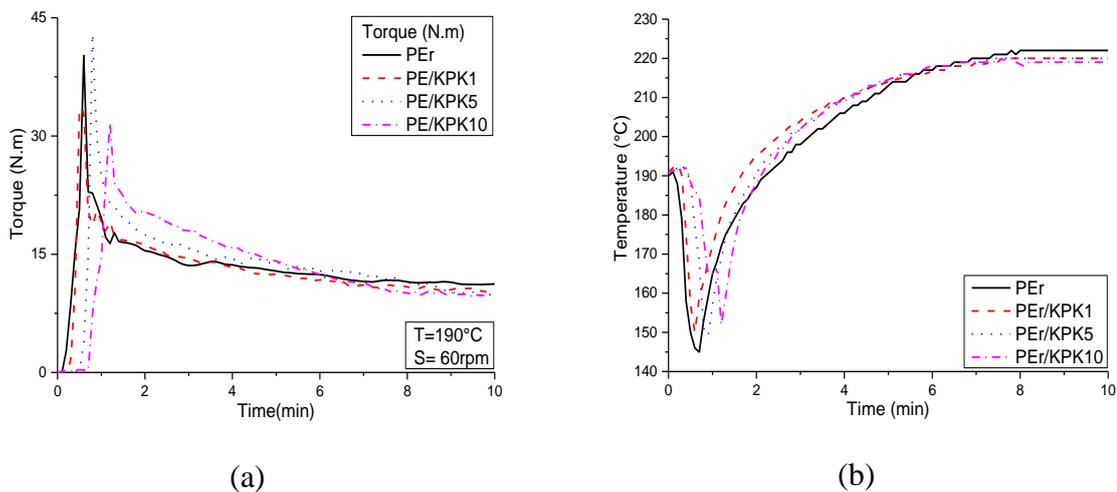
The influence of fiber content on the rheological behavior of the composites was analyzed in a torque rheometer and compared with the measurements using pure polymer. Figure 7.1 exhibits (a) the mixing torque and (b) the temperature as function of processing time. A summary of the main observations is also presented in Table 7.1. At the early stages of processing, the torque reaches a peak as PEr or composites are added to the chamber. Then, the torque tends to decrease as processing-time increases. This behavior is observed because mixing is facilitated as the material is heated. Thus, steady values of both temperature and torque at the end of process may be used as indicators for blending of the compounds.

The torque in steady-state condition is associated to the viscosity of composites in the melted state. It has been reported in the literature that cellulose fibers hinder the mobility of the polymer chain segment while mixing, thus increasing torque (36, 37). Therefore, composites show elevated torques in comparison to a pure polymer. The torque is directly proportional to the amount of fibers for up to 4 minutes of processing, as shown in Figure 7.1 and in Figure 7.2. After that, a tendency to the opposite behavior was observed. This change is attributed to the incorporation of fibers by the polymer, which was enhanced by the cold plasma treatment. Similar improvements in compatibility induced by plasma has been reported elsewhere (37). Kapok fibers are known to be very soft and to exhibit high level of hollowness, in addition to containing oils on their surface. Thus, after being incorporated into the matrix, these oils worked as plasticizing agents, exhibiting a particular behavior when compared to traditional non-oily fibers reported previous works (38, 39).

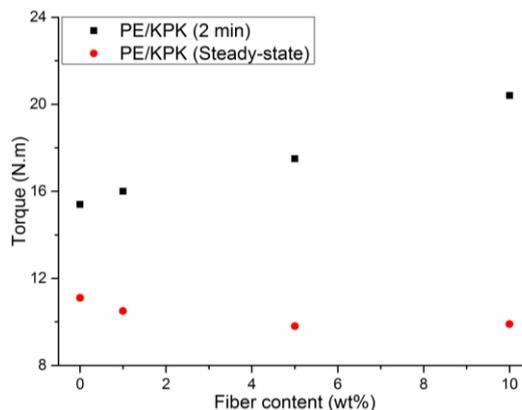
Thus, two opposite behaviors were observed for the composites regarding torque values during mixing. The pattern of higher torque for composites with higher fiber content was observed up to 4 minutes of processing, with a decreasing torque as the processing time increases, while a steady-state torque was reached close to end of processing with lower mixing torque for the composites of higher fiber content. These data are summarized in Figure 7.2. A transition region was observed from 4 to 6 minutes of processing on average, thus representing the beginning of stabilization.

During mixing, the measured temperature and torque profiles for the pure polymer and composites show two main stages. The first stage is observed when PEr or composites were added to the chamber. The melting process is endothermic, producing a rapid decrease in temperature from 190 to 145°C for the pure polymer and to 150°C on average for the composites. After samples were entirely melted, the torque decreased until reaching stabilization torque, which is the second processing stage. This achievement was obtained close to 10 minutes of processing. Due to friction between matrix and fibers under continuous mixing, the temperature of samples continued to increase up to stabilizing at about 220°C for the pure polymer and composites.

The thermal stability of the plasma-treated kapok fibers must be observed to prevent thermal degradation due to the high temperatures in the mixing chamber (Figure 7.1b). Vegetable fibers are susceptible to thermal degradation when exposed to high temperatures. Improvements in mechanical behavior due to the addition of fibers can be achieved unless degradation occurs during mixing.



**Figure 7.1:** Mixing (a) torque and (b) temperature for pure polymer and composites at 190°C and 60 rpm



**Figure 7.2:** In-process and steady-state torque vs kapok fibers content

**Table 7.1:** Rheological results for the pure polymer and composites

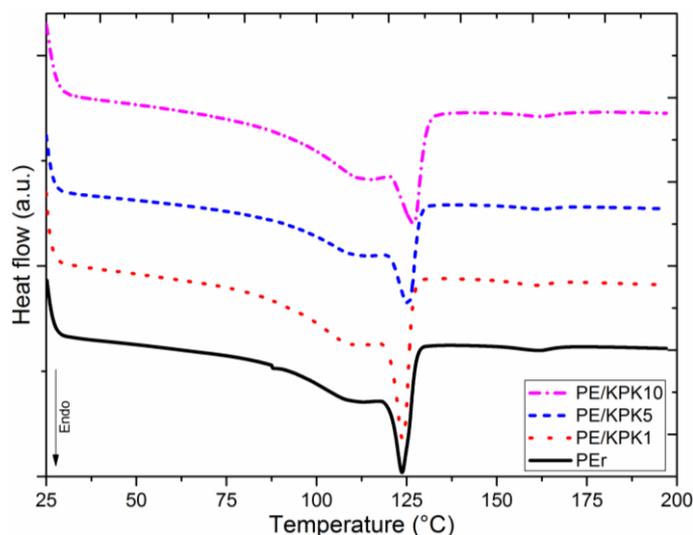
Sample	Torque (N.m)			
	Max.	t=2min	t=5min	t=10min*
PEr	40.1	15.4	12.8	11.1
PEr/KPK1	33.5	16.0	12.5	10.5
PEr/KPK5	42.9	17.5	13.9	9.8
PEr/KPK10	31.7	20.4	14.2	9.9

\* time at the end of processing

### 7.3.2 Thermal characterization

DSC thermograms for the pure polymer and for the composites are displayed in Figure 7.3. Details of crystallinity are given in Table 2. The effect of kapok fibers content on the melting temperature of recycled polyethylene was analyzed. The melting point of low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) has been reported as being about 115°C and 123°C, respectively (40, 41). Thus, there is an indication that the recycled polymer used in this investigation is a blend of LDPE and LLDPE. In addition, LLDPE shows high elongation-at-break values because of its chemical structure in which the chains are well oriented (42); thus, a high degree of crystallinity may be achieved for these materials. The addition of plasma-treated fibers promoted a slight increase in the melting temperature of the composites as compared to the pure polymer (Table 7.2). PE has limitations in some applications due to its relatively low melting point, as reported elsewhere (43). Thus, the addition of plasma-treated kapok fibers allows for enhancing the melting properties of the polymer matrix.

In general, the melting (peak) temperatures of the composites were higher in comparison to the pure polymer as a result of dispersed fibers throughout the polymer matrix. Displacements from 1°C to 4°C in melting (peak) temperatures in comparison with the pure polymer were observed for composites with 1, 5 and 10 wt.% of fibers, suggesting good fiber dispersion. In addition, enthalpies of composite fusion and crystallinity results (Table 7.2) indicated that the addition of fibers to the polymer reduced the crystallinity degree, which also indicates good adhesion of the fiber-matrix interfacial interaction. Reduction in the crystallinity degree of composites with vegetable fibers was also observed in a previous study (44).



**Figure 7.3:** DSC thermal curves of recycled PE and PEr/KPK composites

Thermogravimetric analyses for PEr exhibited a gradual weight loss as the temperature increased, showing single degradation, which started at 415°C and was almost totally consumed until 496°C. The observed residue at that point was of 1.48%, as shown in Figure 7.4a and detailed in Table 7.2. The onset temperature determined from thermogravimetry curve was not considerably changed for composites with 1 wt.% of fibers. However, the onset temperature reduced for composites with 5 wt.% and 10 wt.% of fibers in comparison to the pure polymer. It is important to note that the presence of cellulose induced this decrease. In other words, as the amount of fibers increases, the onset temperature decreases (Figure 7.4a).

The main difference between thermogravimetric curves of the pure polymer in comparison with the composites starts from 238°C, which is attributed to fiber degradation. For composites with 10 wt.% of fibers, the first degradation step took place over the range of 248-409°C. It has been reported elsewhere that this zone is the degradation of hemicellulose, as well as the disintegration of crystalline regions (45, 46). In addition, as the amount of fibers increased, the release of oxygen from cellulose and lignin component also increased, thus starting the degradation process earlier. The second step of degradation occurred from 409°C up to 496°C, which means total polymer and fiber consumption.

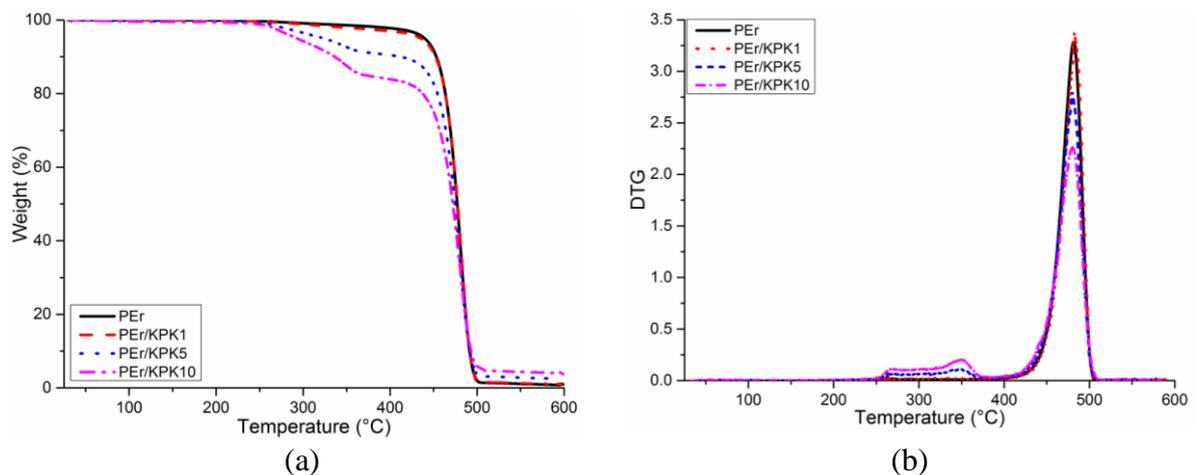
The pure polymer shows single-step degradation, while composites show at least two main degradation steps. From the DTG curves (Figure 7.4b), it was observed that as the fiber content increases, the peaks themselves also become more evident. These two main degradation steps are due to the nature of the composites studied, which are a polymer and a lignocellulosic fiber. Cellulose has many oxidant components in its inner structure and oxygen plasma also induces oxidant components on the fiber surface. However, this lower degradation temperature

for the composites did not affect composite processing, since the highest temperatures in extrusion and injection machines were 200 and 215°C, respectively.

Since the polymers studied exhibit single-step degradation, every additional step that appears in the composites' thermal behavior indicates the influence of fibers on the compounding. This first peak for composites represents total decomposition of hemicellulose and the partial decomposition of lignin (47). This last decomposition is found to occur in a large degradation step from 350 to 500°C (48), together with polymer in this study.

The second main peaks in the DTG curves show similar trends, exhibiting higher values for the pure polymer (415°C) and with slightly lower temperatures for composites, as shown in Table 2. This temperature ranged from 405°C to 409°C for all composite samples. The decompositions of cellulose as well as lignin from kapok fibers occur in these points together with matrix decomposition.

Polymer composites may have their mechanical properties adversely affected by exposure to high temperatures during processing. Nevertheless, the highest temperature observed during processing was 222°C, as compared to 248°C for the onset degradation of composites with 10 wt.% of fibers. Thus, for the composites produced in this study, processing temperature did not impair the mechanical behavior. Adding vegetable fibers was not harmful to the thermal behavior of the composites.



**Figure 7.4:** (a) TGA Thermograms and (b) DTG of the pure polymer and composites

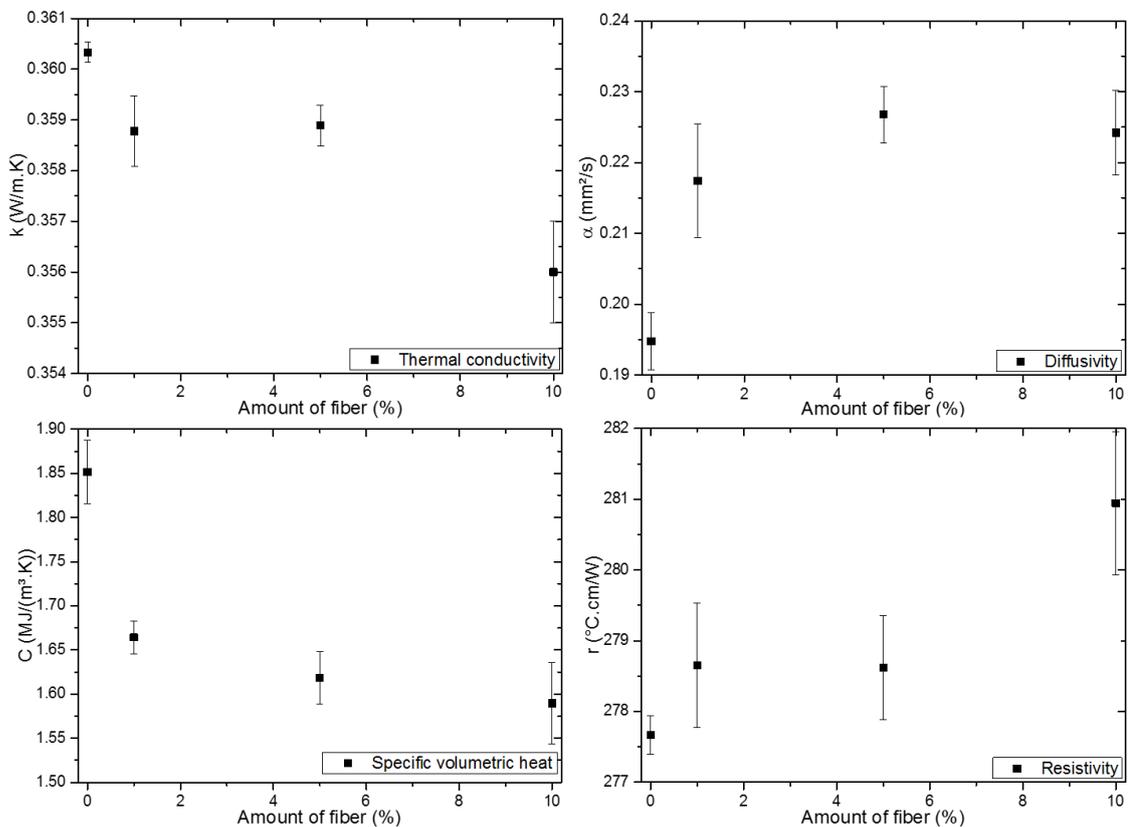
**Table 7.2:** Percent crystallinity and thermal data of pure polymer and PE\_KPK composites

Sample	$\Delta H_m$ (exp) (total)	$X_c$ (exp) (%)	Melting temperature ( $T_m$ ) (°C)	ONSET		Peak at maximum degradation (°C)	
				Temp (°C) <sup>*1</sup>	Wt%	TMD <sup>*2</sup>	Wt%
PEr	208.8	66.7	123	415	97	482	34.8
PEr/KPK1	217.6	76.3	124	262	99	332	97.5
				409	96	482	36.0
PEr/KPK5	176.4	64.5	125	249	99	345	93.1
				408	90	480	35.5
PEr/KPK10	166.7	58.1	127	248	98	350	87.5
				405	84	479	34.1

<sup>\*1</sup>ONSET: Tow-steps of degradation for composites

<sup>\*2</sup>TMD: Temperature at maximum degradation

Thermal parameters of composites were measured to understand the actual influence of fiber content on material properties, since the hollow structure of kapok fibers may change thermal conductivity patterns. Results showed lower thermal conductivity ( $k$ ) and higher thermal resistivity ( $r$ ) for the composites in comparison to the pure polymers. In addition, an increase in diffusivity ( $\alpha$ ) and decrease in volumetric specific heat ( $C$ ) of composites were observed, as fiber content increases. Comparing composites with 1, 5 and 10 wt.% of fibers, it was observed that diffusivity and volumetric specific heat of the composites can be significantly affected even for low fiber contents, e.g., 1 wt.% The measured thermal parameters are presented in Figure 7.5.

**Figure 7.5:** Thermal parameters of the pure polymer and composites

It has been reported that crystallization may increase the intrinsic order of polymer chains, thus resulting in increases in thermal conductivity of polyethylene (18). Accordingly, polyethylene-based composites shall present similar trends. The results obtained in this study show that the crystallinity degree was higher for composites using 1 wt.% of fibers, that is, for this composition, the higher crystallinity degree was expected to produce and increase in  $k$ . Thus, it was observed that the thermal conductivity was the same for composites of 1 wt.% and 5 wt.% of fibers, while for composites with 10 wt.% of fibers, the conductivity decreased due to the high fiber content. The percentage of crystallinity obtained for PEr-KPK10 was 58.1% against 76.3% for PEr-KPK1. A previous study revealed that the size of reinforcement is also connected to the thermal conductivity. The study showed that composites with small size filler (or reinforcement) materials show large interfacial area, causing phonon scattering and hindering their transport, and often have a lower  $k$  (20, 49). Thus, for kapok fibers, the small length combined with the high degree of hollowness provides a large interfacial area per volume with the polymer matrix.

The measured thermal conductivity ( $k$ ) of the polyethylene used in this study was about 0.36 W/(m K). This value is close to those reported in the literature, which are typically in the range of 0.30-0.34 W/(m K) (19). Previous reports have demonstrated that the thermal conductivity of the polymer matrix is determinant for the thermal conductivity of thermoplastic composites (33, 50). Nevertheless, the presence of odd components such as vegetable fibers may affect the crystallization process and, consequently, the thermal conductivity.

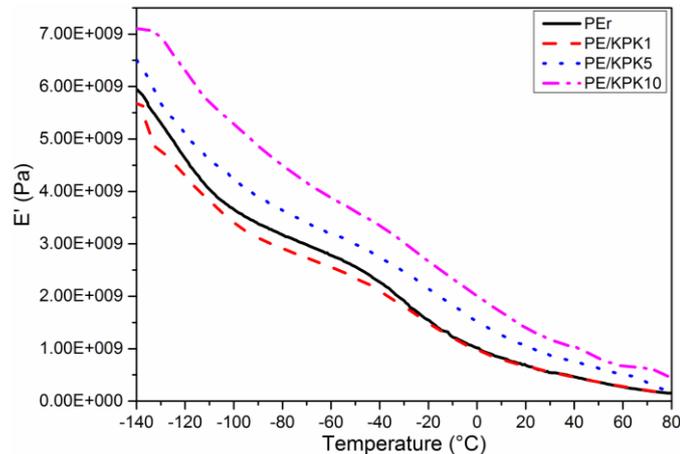
Previous authors have found that thermal conductivity of single polyethylene chains with an extended conformation may be higher than 350 W/(m K) for chain length above 100 nm (51). However, the measured thermal conductivity of polymers almost a thousand times smaller than that of a single polyethylene chain, due to the semi-crystalline characteristic of polymers. The observations evaluated that the heat does not propagate as a wave, as expected in crystalline materials (e.g. metals). Instead, it diffuses slowly in a polymer, which causes disordered vibrations and rotations of all the atoms of the polymers around their equilibrium state (52).

### 7.3.3 Dynamic mechanical thermal analysis

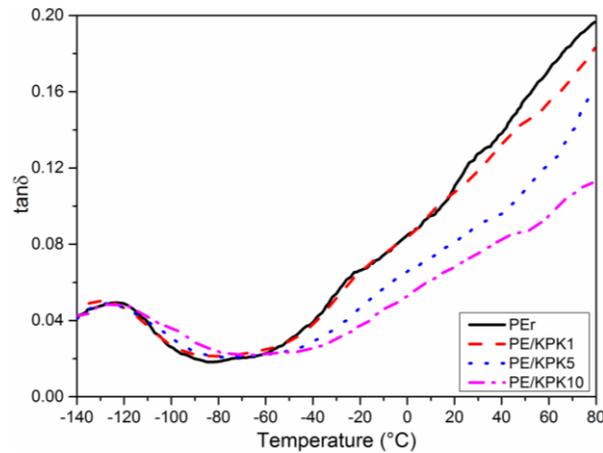
Dynamic mechanical thermal analyses of the pure polymer and composites were performed. Storage modulus ( $E'$ ) of all samples decreased with increasing temperature, as expected (Figure 7.6). The incorporation of fibers into the polymeric matrix produced an

increase in storage modulus, which was more significant for composites using 5 and 10 wt.% of kapok fibers. For the composites with 1 wt.% of fibers, the storage modulus was basically unaffected for the entire temperature range studied.

Relaxation peaks were observed for the pure polymer and composites at about  $-135^{\circ}\text{C}$ , as shown in Figure 7.7. The relaxation commonly observed in polyethylene samples at about  $-120^{\circ}\text{C}$  is linked to the non-crystalline region and has been associated with the glass transition, in accordance with other reports (53). The observed values were  $-135^{\circ}\text{C}$  for the pure polymer and PEr-KPK1,  $-132^{\circ}\text{C}$  for PEr-KPK5, and  $-129^{\circ}\text{C}$  for PEr-KPK10. Thus, the addition of plasma-treated fibers at various contents induced a slight increase in the glass transition temperature of the composites. Based on the data shown in Figure 7.7, the behavior of PEr and composites with 1, 5 and 10 wt.% of fibers was quite similar up to  $-60^{\circ}\text{C}$ . Then, as the temperature and the free volume continue to increase, composites with 1 wt.% of fibers reduces mobility at temperatures above  $20^{\circ}\text{C}$ . On the contrary, composites with 5 and 10 wt.% of fibers started showing reduced mobility from  $-60^{\circ}\text{C}$ . The magnitude of  $\tan \delta$  was the lowest for composites with 10 wt.% of fibers, thus suggesting improvements in mechanical properties. Therefore, the increase in  $E'$  and reduction in  $\tan \delta$  over the temperature range studied indicate that plasma treatment of kapok fibers was effective to enhance the fiber/matrix interface, and as the fiber content increases, improvements in mechanical properties were more significant.



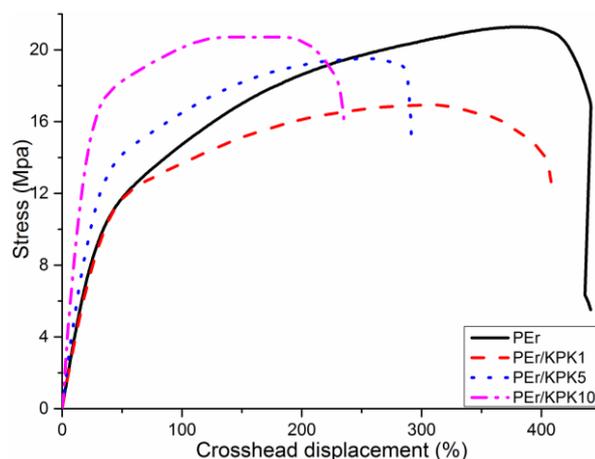
**Figure 7.6:** Storage moduli of the pure PEr and PEr/KPK composites



**Figure 7.7:**  $\tan\delta$  of the PEr and PEr/Kpk composites

### 7.3.4 Tensile Testing

The mechanical behavior of the polymer and composites studied are presented in Figure 7.8. The results are also summarized in Table 7.3. Recycled polyethylene exhibited a ductile mechanical behavior typical for this type of material. The yielding for these samples occurred under maximum loading, which was followed by neck formation. However, this behavior changed as the plasma-treated kapok fibers were added to matrix. The ductility was considerably reduced, and a tendency to semi-brittle behavior was observed as the fiber content increased. In addition, the tensile strength of composites was affected by the addition of fibers, meaning that a reduction in tensile strength was observed for composites with a low amount of fibers. However, as the fiber content increased, the tensile strength also increased. For composites with 10 wt.% of fibers, the tensile strength was essentially the same of that of the pure polymer. Therefore, these results suggest good bonding between fiber and matrix. Ultimately, the plasma treatment of the fibers open up possibilities to control the final properties of composites only by adding different amounts of fibers to the polymer matrix.



**Figure 7.8:** Mechanical behavior of recycled PE and PEr/kapok composites

**Table 7.3:** Thermo-mechanical and mechanical properties of PEr-kapok composites

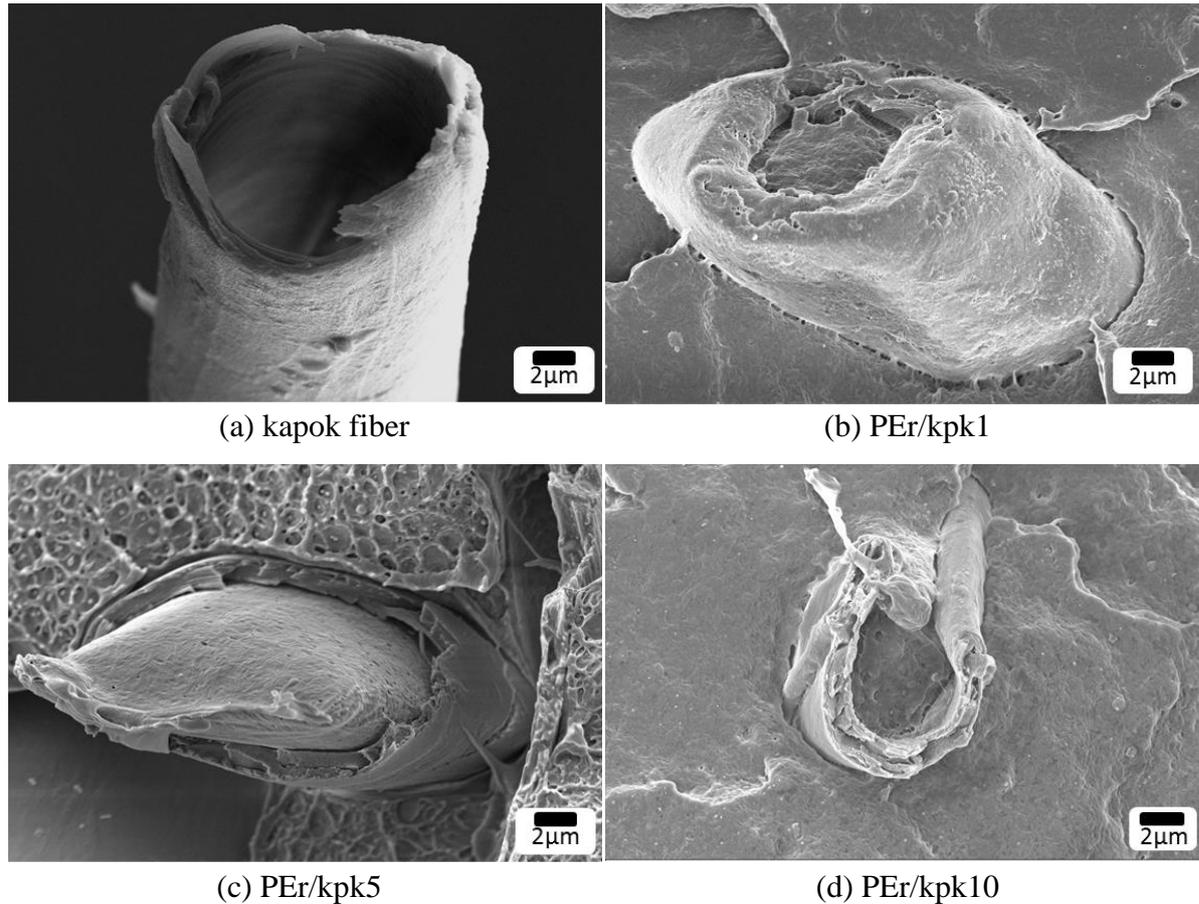
Sample	Storage modulus (GPa)* <sup>1</sup>	Tanδ* <sup>1</sup>	Tensile strength (MPa)
<b>PEr</b>	0.61±0.01	0.12±0.01	21.1±1.1
<b>PEr/KPK1</b>	0.61±0.01	0.11±0.01	16.8±0.8
<b>PEr/KPK5</b>	0.96±0.01	0.08±0.01	19.4±1.1
<b>PEr/KPK10</b>	1.28±0.01	0.07±0.01	20.5±1.2

\*<sup>1</sup> values at room temperature

### 7.3.5 Morphological characterization

FEGSEM of kapok fibers and fractographs of PEr-kapok composites are presented in Figure 7.9. The morphology of the fiber with the characteristic smooth appearance and hollowness (about 80 to 90% of the fiber) is presented in Figure 7.9 (a). The fractographs of the composites fractured under tensile loading indicates strong fiber-matrix adhesion, thus resulting in fiber breakage and no fiber pull-out, independent of fiber content, as presented in Figure 7.9 (b, c and d) for composites with 1, 5 and 10 wt.% of fibers, respectively. New bonds obtained through oxygen plasma treatment resulted in enhanced fiber-matrix adhesion. Thus, good fiber wetting by the polymer was observed for all composites. In addition, the hollow structure of kapok fiber was filled with polymer during processing. This microtube-like morphology develops fiber-polymer interface at the inner and outer surface of the hollow fibers, thereby corroborating the performance observed in the mechanical and thermo-mechanical tests. The fractographs of PEr\_kpk5 (Figure 7.9 (c)) suggest no fiber pull out at the surface fractured under tensile loading.

Improvements in the fiber-matrix interface after plasma treatment has been discussed elsewhere (54). The improvements in fiber-polymer interface are related to the increase in carboxyl and carbonyl groups, thus leading to a more wettable fiber (55). Thus, the addition of these plasma treated fibers results in improved mechanical properties, as observed in the mechanical and thermo-mechanical analyses. Ultimately, the microtube-like structure of kapok enhanced the mechanical properties of the composites analyzed.



**Figure 7.9:** Morphologies of kapok fibers and fractographs of PEr/kapok composites. (a) kapok fiber, (b) PEr/kapok 1 wt.%, (c) PEr/kapok 5 wt.%, (d) PEr/kapok 10 wt.%

## 7.4 Conclusions

In this study, plasma-treated kapok fibers were added to a polymeric matrix to develop a composite using recycled polyethylene and biomass residue. Up to 10 wt.% of kapok fibers were added to the recycled PE. The addition of plasma-treated fibers resulted in lower steady-state torque of composites when compared with the pure polymers in contrast with usual fibers, which is an important result for composite manufacturing. A decrease in onset temperature determined from thermogravimetry was reduced for composites with 5 wt.% and 10 wt.% of fibers in comparison to the pure polymer. However, the onset temperature is above the processing temperature and, therefore, does not impair thermal processing. The results also indicated an improvement in thermal insulating characteristic of the composites with the increase in fiber content. The thermo-mechanical analysis indicated good fiber-matrix compatibility with a reduction in chain mobility at higher temperatures produced by the fibers. Morphological analyses of the fractured surfaces also suggested good fiber-polymer interfacial adhesion. SEM images showed that most fibers kept their microtube-like structure, thus

enabling their filling by the polymers, resulting in good mechanical results as verified by mechanical and thermal mechanical analyses. This study shows the potential of using plasma treatment as an alternative coupling process for recycled polyethylene and vegetable fibers over classical treatments, which typically involve chemical reactions. Ultimately, the investigated approach shows promise as an environmentally friendly process for producing composite materials with different amounts of vegetable fibers.

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## 8 SUMMARY AND GENERAL COMMENTS

These three studies, which were carried out in order to evaluate several properties and characteristics of kapok fibers and composites, allowed a better understanding of the performance of composites manufactured using recycled polyethylene and a biomass residue (kapok fibers). The development of technologies and strategies for using these two materials can be very important, as they can be used to reduce waste, to recycle polyethylene, and as renewable feedstock, such as kapok fibers.

The **first article** of this study was carried out for evaluating thermal properties of kapok fibers before and after plasma treatment for further addition as reinforcement in composites using recycled polyethylene. Thermal properties are important information for processing thermoplastics and composites based on thermoplastic materials, which have to be heated to a certain temperature while processing. Indeed, previous knowledge about thermal degradation is essential to avoid the undesirable degradation of the material. Therefore, this first study contributes to the understanding of this cellulosic material and its properties.

The **second article** has analyzed the differences in composites manufactured with plasma treated fibers against those manufactured with raw fibers regarding mechanical and thermal behaviors. This study evaluated the influence of plasma as a coupling agent in polymer/fiber interface and the consequent improvements in mechanical behavior of the composite.

Ultimately, the **third article** has analyzed the effect of the addition of plasma treated fibers on the final properties of polyethylene matrix composites. In this study, only treated fibers and recycled polyethylene were used. In addition, thermal parameters were observed in order to check the advantages in the use of vegetable fibers regarding to thermal insulation properties.

## 9 CONCLUSIONS

The studies conducted in this research based on cellulose-based kapok fibers and recycled polyethylene have generated results from which it is possible to conclude, that plasma treatment produced modifications on fiber surface which were beneficial to composites processing and final mechanical properties. Improvements in thermal properties of fibers were confirmed by TGA data. Morphological and chemical analyses of the treated fibers also confirmed the effect of plasma treatment. Composites were prepared using recycled PE and plasma treated kapok fibers. Thermal and mechanical properties of the recycled polymer were changed with the addition plasma treatment, creating a new range of applications possible. Hence, the results of this research indicated that plasma treatment of kapok fibers can be used as surface activation, thus improving matrix/filler adhesion when combined with polymers. The effects of plasma as a coupling process and its advantages in comparison to untreated fibers on the final properties of composites were also evaluated. It was concluded from this study that improvements in elastic modulus can be achieved with the addition of plasma treated fibers at 10 wt.%, while the tensile strength is essentially unaffected. Thus, plasma treatment proved effective as fiber modification to improve fiber/matrix adhesion, consequently improving the mechanical properties of polymer-based composites. Ultimately, improving the understanding of cellulose-based fibers and fiber treatments can ultimately support the production of polymer composites for practical applications.

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