CHARACTERIZATION, MECHANICAL AND THERMAL PROPERTIES OF POLYANILINE (PANI)-EPOXY COMPOSITE USING DIFFERENT TYPES OF NATURAL FIBERS

by

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ABSTRAK

Dalam kajian ini, tiga jenis serat semulajadi iaitu hampas tebu, sekam padi dan sabut kelapa telah dimasukkan ke dalam PANI matriks / epoksi. Semua serat semula jadi telah diselaraskan dengan peratusan yang sama iaitu 5wt%. PANI / epoksi dicampur dalam bekas dan dikacau dengan baik sehingga ia menjadi sebati. Kemudian, semua serat semula jadi telah ditambah ke dalam PANI / epoksi dan dikacau sehingga sebati sebelum dimasukkan ke dalam acuan untuk membiarkan komposit mengeras bagi satu hari. Kesan haba (Analisis Termogravimetri, TGA, Dynamic Mengimbas Calorimetry, DSC), mekanikal (kekuatan tegangan, modulus keanjalan, pemanjangan pada waktu rehat) dan morfologi (Mikroskop Imbasan Elektron, SEM) telah disiasat. Daripada keputusan, didapati bahawa kekuatan tegangan didapati menurun dengan penambahan serat semula jadi. Antara tiga jenis serat semulajadi, serat hampas tebu mempunyai nilai yang paling tinggi kekuatan tegangan. Untuk pemanjangan pada takat putus, ia telah berkata, pemanjangan pada waktu rehat telah menurun dengan penambahan serat semula jadi. Untuk modulus keanjalan, terdapat peningkatan modulus keanjalan dengan tambahan serat semula jadi. Terdapat dua tingkah laku penurunan berat peringkat yang hampir pada masa yang sama pada 200°C dan 350°C untuk ketiga-tiga jenis serat semula jadi. Penambahan serat semula jadi telah mengurangkan peratusan penurunan berat. Ini menunjukkan bahawa penambahan serat semula jadi ke dalam PANI / epoksi telah meningkatkan kestabilan terma. Suhu peralihan kaca (T_g) telah meningkat dengan tambahan serat semula jadi.

Mechanical, Thermal and Morphological Effect of Natural Fiber as Filler for Polyaniline (PANI)-Epoxy Composite

ABSTRACT

In this study, three types of natural fiber that are bagasse, rice husk and coir were incorporated into PANI/Epoxy matrix. All natural fiber was set to the same percentage that is 5wt%. PANI/Epoxy was mixed in a container and stirred well until it become homogenously. Then, all the natural fiber was added into the PANI/Epoxy and stirred it until homogenously before put into the mould to let the composite cure for one day. The effects of thermal (Thermogravimetric Analysis, TGA, Dynamic Scanning Calorimetry, DSC), mechanical (tensile strength, modulus of elasticity, elongation at break) and morphological (Scanning Electron Microscope, SEM) were investigated. From the results, it was found that the tensile strength of the composite found to be decreased with addition of natural fiber. Between three types of natural fiber, bagasse fiber has the highest value of tensile strength. For elongation at break, it has been said that the elongation at break was decreased with the addition of the natural fiber. For the modulus of elasticity, there are increases in modulus of elasticity with addition of natural fiber. There are two stage weight loss behaviors that are almost at the same at 200°C and 350°C for all three types of natural fiber. Addition of natural fiber has reduced the percentage of weight loss. This indicates that addition of natural fiber into PANI/Epoxy has improved the thermal stability. The glass transition temperature (T_g) was increased with the addition of natural fiber.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Increase in demand for eco-friendly materials, increasing depletion rate, and soaring prices of petroleum based plastics and pressing environmental regulations have all triggered a growing interest towards the field of composites (Netravali et al., 2003; Abdul Khalil et al., 2012). Composites materials are formed by combining two or more materials to improve properties of their original components.

In general, polymer composites consist of a polymer resin as the matrix and one or more fillers are added to serve specific objectives or requirements. For example, composites for aerospace and sports applications require high mechanical and thermal properties. Traditionally synthetic fibers such as carbon or glass fibers have been used to reinforce composites and are able to produce such properties. However, with the growing global environmental concerns, their slow biodegradability is a disadvantage. Therefore researchers are finding other viable approaches to enhance or accelerate the biodegradability of polymeric composites. For this reason natural fibers provide good prospective as reinforcements fillers in thermosets, thermoplastics, and elastomers. Some main advantages of using natural fibers in composites are low cost, sustainability, light weight, and being nonabrasive and nonhazardous and more importantly they can accelerate biodegradability of the polymeric composites (Fowler et al., 2006; Kumar et al., 2014).

Natural fibers can be defined as substances produced by animals and plants that can be spun into thread, rope or filament in a next step be matted, bound, woven or knitted. Natural fibers have received great interest as reinforcing material for polymer based matrices because of the environmental issues in combination with their low cost and some intrinsic interesting properties (shape ratio, density, mechanical behavior, high disposability, and renewability) (Kalia et al., 2011). Moreover, they are recyclable and biodegradable. Natural fibers were intensified as they have huge potential to replace some synthetic fibers. Research and development on the use of natural fibers reinforced composites has been in existence as early as 1900s. In 1930s Henry Ford developed soya based matrix reinforced with natural fibers to form a natural fiber composites used for car body panel. Such development was driven by economic reason. Nowadays, the interest in the use of natural fiber reinforced plant based polymer composites is mainly due to the environmental reason.

The increased demand for electricity conductive materials with good mechanical properties has aroused the interest of several research groups for the development of systems consisting of particles of conductive polymer dispersed in insulating polymer matrices. This strategy is very interesting from a technological point of view because the final material is able to combine the electrical conductivity of conductive polymers and good mechanical properties and processability of conventional polymers (Ikkala et al., 1995).

Among the conductive polymers, polyaniline (PANI) has proven one of the most versatile because of the ease of polymerization, good thermal stability and ability to be easily converted in the conductive form from the protonation with strong acids (Chiang et al., 1996). The polyaniline protonated with mineral acids such as

hydrochloric acid and sulfuric acid, is practically insoluble in most organic solvents and is dispersed in a conventional polymer matrix as if it were an inorganic filler, due to the total lack of compatibility. The development of techniques protonation (doping) using functionalized protonic acids (such as dodecylbenzenesulfonic acid, DBSA, and camphorsulfonic acid, CSA) has brought significant progress in this area due to the increase in processability and improved in solubility in conventional solvents (Cao et al., 1992). For example, polyaniline doped with DBSA (Pani.DBSA) has been used to prepare various mixtures, both in the molten state and in solution. Some examples in the literature for polymers blended with conventional melt Pani.DBSA include: polyolefins, polystyrene (Zilberman et al., 1997), SBS, EVA (Bar et al., 2001) and various vulcanized elastomers (Faez et al., 2001; Gazotti et al., 1999).

1.2 Problem Statements

Important considerations when selecting an epoxy resin candidate are the stiffness (elastic modulus) and the yield and ultimate strength and toughness properties. Other factors such as thermal properties, processability, cost, availability, and health concerns are also of a great importance. The epoxy versatile characteristic and its diversity made it suitable for different industrial applications such as laminated circuit board, electronic component encapsulations, surface coatings, potting, fiber reinforcement, and adhesives. However, the pervasive applications in many high performance fields limited the epoxy use. The limitations of epoxy can be overcome by incorporation and modification before their industrial applications. Currently, modified epoxy resins are extensively used in fabrication of

natural fiber-reinforced composites and in making its different industrial products because of their superior mechanical, thermal, and electrical properties.

The interest usage of natural fibers as a filler has grown over the past few years due to the advantages it offers. The use of natural product as filler in the conducting polymer-epoxy solution is a new attraction in the polymer composite technology. However, the polyaniline is intractable, i.e., neither could it be processed in the melt state (as it decomposes at the temperatures below a softening or melting point) nor could it be processed in solution (as it cannot be dissolved in conventional organic solvents except that it is poorly soluble in few strong polar solvents such as *N*-1methylpyrrolidone (NMP), *N*,*N*-dimethylformamide, and dimethyl sulfoxide). Therefore, different solutions that have been offered to improve their bonding and compatibility such as the use of coupling agents and surface treatments via mechanical, physical, and/or chemical modifications. Besides that, a natural fiber is cheaper than compared to synthetic fibers that are non-biodegradable and pollute the environment. It will reduce the cost when using the natural fibers compared to synthetic fibers. Moreover, the proper utilization of natural fibers not only resolves the waste disposal problems but also reduces environmental pollutions.

1.3 Objectives

The aims of this research are:

1. To study the types of natural filler on physical, mechanical and morphology of polyaniline (PANI)-epoxy composite.
2. To determine the compatibility of (PANI)-epoxy as a matrix with different type of natural fiber fillers for finding special characteristic of the composite

1.4 Scope of Study

The scope of this study is to investigate the effect of different type of natural fibers as a filler that are rice husk, sugarcane waste (bagasse) and coconut husk (coir) for polyaniline (PANI)-epoxy composite that involves several mechanical testing and analysis such as tensile, flexural and impact test, scanning electron microscope (SEM), thermo gravimetric analysis (TGA), differential scanning calorimetric (DSC) and Conductivity test. Tensile strength is used to measure the strength of the composite. SEM is an imaging technique that is used to observed the morphology of the composite, TGA is used to measure the thermal properties of the composite and DSC is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature.

CHAPTER 2

LITERATURE REVIEW

2.1 Polyaniline (PANI)

Polyaniline (PANI) as a conducting polymer shows an advantageous connection of small weight, good electrical conductivity, and chemical affinity to the traditional polymer matrix such as epoxy resin, PMMA, PVC and other. PANI is also a cheap material, as it is easy to produce, modify and process. PANI is a very stable conducting polymer with good damping and antistatic properties, resistant to most organic solvents. The conductivity of polyaniline depends on the degree of its oxidation. Conductivity can be improved by choosing an appropriate method and suitable conditions for its synthesis (oxidizing polymerization, electrochemical polymerization, synthesis of the conducting salt PANI-HCl) or by modifying the polymer (doping with sulfonic acid) (Zawadzka et al., 2009).

Polyaniline is one of the interesting conductive polymers. PANI has a high level of ion exchange and good redox properties and electrical conductivity, and excellent environmental stability (Stejskal et al., 2002). It is easy to prepare by the oxidation of aniline monomer in aqueous medium. There are three individual forms that are leucoemeraldine, emeraldine, and pernigraniline based that should be recognized when discussing about the PANI.

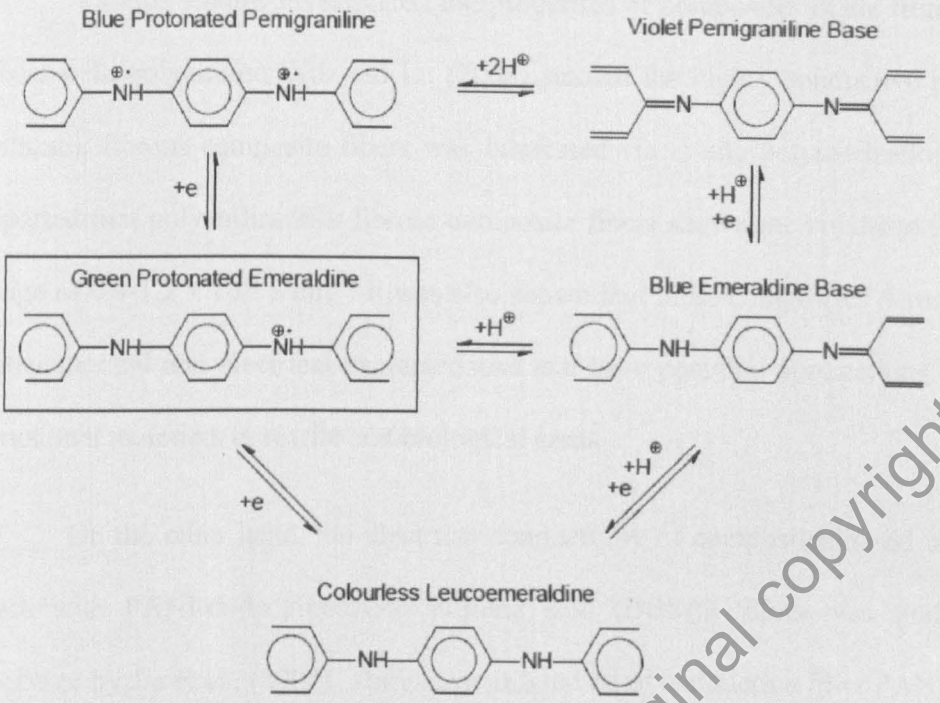

Figure 2.1: Protonated emeraldine obtained after the polymerization of aniline can be oxidized to pernigraniline or reduced to leucoemeraldine. Emeraldine and pernigraniline may be deprotonated to the corresponding bases.

(i) Leucoemeraldine base

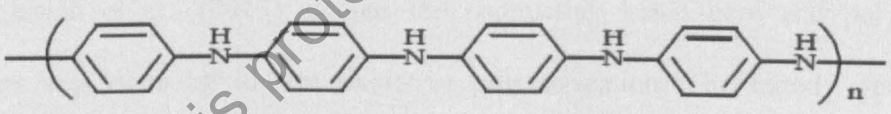

Figure 2.2: Leucoemeraldine base

(ii) Pernigraniline base

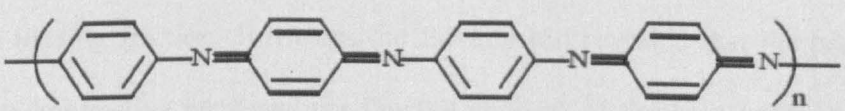

Figure 2.3: Pernigraniline base

(iii) Emeraldine base

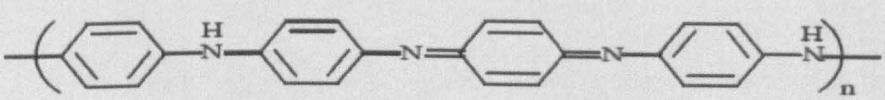

Figure 2.4: Emeraldine base

Various studies investigated the properties of composites made from natural fibers with polyaniline. Xia and Lu (2008) studied the highly conductive polymers with silk fibrous composite fibers was fabricated via in-situ polymerization. It was reported that polyaniline/silk fibroin composite fibers shown the conductivity in the range of 0.9-1.2 x 10^{-2} S cm^{-1}. It was also shown that these composites demonstrated better thermal and electrical characteristics and have potential applications as novel functional materials in textile and biological areas.

On the other hand, the electrical conductivity of composites based on epoxy resin with PANI-dodecylbenzene sulfonic acid (DBSA) fillers was studied and analyzed by Jia et al., (2003). They have utilized all of conductive filler PANI-DBSA in form of powder and paste in matrix polymer bisphenol, hydride hardener and epoxy resin as well as accelerator to form the composite. Results demonstrated that a conductivity of the order 10^{-3} was achieved at high filler content.

Izwan et al., (2013) studied the conducting kenaf core and polyaniline biofibers was done by in situ oxidative polymerization. The latterly developed conducting kenaf core achieved enhancement in conductivity acceptable seven grants compared to the raw kenaf core. Tensile strength of the kenaf core-polyaniline composites was weakened compared to that of epoxy resin/kenaf core composite at the same loading fraction. However, the flexural test revealed that the presence of kenaf core-polyaniline increased the flexural strength of the epoxy resin composite by appropriate 50 wt% loading. SEM of the epoxy resin/kenaf core-polyaniline composite indicated useful adhesion between components.

2.1.1 Application and Properties of Polyaniline

PANI has a good application potential in antistatic and anticorrosion coatings, electrochemical actuators, non-linear optical and light-emitting devices, electrochemical device, electrochemical capacitors, electronic and bioelectronic components, microwave and radar absorbing materials, shielding of electromagnetic interference, rechargeable batteries, and erasable optical information storage, (Kalendova et al., 2008), and others.

There are several properties of PANI that are PANI electrical properties can be reversibly controlled by protonation and charge transfer doping. It is also environmentally stable and inert where stainless steel is corroded. PANI is applicable to electrical, electrochemical, and optical applications and it is currently used in cell phones and calculators, and other LCD technology etc.

2.2 Epoxy as polymer matrix

Various polymers are used as matrix materials for composites. The polymer matrix materials can be divided into two groups that are thermosets and thermoplastics. In these days mainly thermoset polymers are used as high performance composite matrix materials. The thermoset materials such as epoxy, polyester, vinylester and polyimid are changing from liquid to solid phase by an irreversible process, at the end get a crosslinked structured. If this crosslinking process is done they cannot be re-melted, however the temperature change greatly affects their mechanical properties. Their main advantage is that they are in a fluid phase at room temperature and for their processing only low or moderate pressure is required, and they are low cost materials. Unfortunately their recyclement is not fully

solved yet. Polyester and epoxy thermoset matrix materials are used widely in industrial applications.

Epoxy resin contributes strength, durability and chemical resistance to a composite. Epoxy can present better properties as a matrix and such type of composites are nature friendly and cost effective (Jena et al., 2012). As its thermosetting resin, it can cure in room temperature and they are used widely in natural fiber composite.

Jia, W et al., (2003) reported that electrical conductivity of composites were based on epoxy resin with PANI-DBSA fillers. Due to their vast applications electrically conductive thermosetting composite materials containing metallic filers are widely used now a day. The composite material used was conductive filler PANI-DBSA in form of powder and paste in matrix polymer bisphenol, an epoxy resin, anhydride hardener and an accelerator. The variation of electrical resistivity which is the inverse of electrical conductivity was plotted with content of PANI powder. With 40% wt. /wt. of filler content electrical conductivity of the order of 10^{-8} ohm-cm was observed which gradually increases or the resistivity gradually decreases as the wt. % of filler material increases. At higher filler content conductivity of the order 10^{-3} was also achievable in the experiment. Interestingly, the usages of this type of composites are widely used due to their vast applications electrically conductive thermosetting composite with metallic fillers.

2.3 PANI/Epoxy system

Polyaniline (PANI) is one of the most intensively studied intrinsically conducting polymers because of its high polymerization yield, good environmental stability, tunable conductivity, and relatively low cost, and has received considerable attention over recent years as a promising conducting polymer for many electronic applications, such as sensors and actuators, electromagnetic interference shielding (Wang et al., 2005) , electrostatic discharging, to mention just a few. However, the polymer is intractable, i.e., neither could it be processed in the melt state (as it decomposes at the temperatures below a softening or melting point) nor could it be processed in solution (as it cannot be dissolved in conventional organic solvents except that it is poorly soluble in few strong polar solvents such as *N*-methylpyrrolidone (NMP), *N*,*N*-dimethylformamide, and dimethyl sulfoxide). Therefore, practical applications have remained limited. Although the significant efforts directed in improving the processability of the polymer, such as the structural modification of PANI by ring or N-substitution, in situ polymerization of aniline with conventional polymers (Gangopadhyay et al., 2001; Dhawan et al., 2002) or inorganic materials (Xia et al., 2002), graft polymerization of aniline on other materials (Li et al., 2002), and so on, preparation of PANI composites or blends, in the form of adhesives, coatings, films, and so on, are considered one of the most promising ways in that both the electrical properties of the PANI guest and the mechanical properties of the insulating host matrix is combined in the composites or blends (Anand et al., 1998), especially from the technological and industrial points of view.

Solution blends also have been extensively studied, primarily with the use of polyaniline doped with camphor sulfonic acid in the PMMA matrix, due to the high solubility of both in m-cresol (Anand et al., 1998; Heeger, 1993; Cao et al., 1993). In addition to these two techniques, another method that has received attention is the emulsion polymerization of aniline in the presence of the insulating polymer (Oh et al., 1997; Ruckenstein et al., 1995).

The epoxy resin is a thermoset polymer matrix cured as widely used in the preparation of composite materials, mainly due to their excellent properties such as thermal stability, solvent resistance, good adhesion, among others. These properties are directly related to the choice of the agent and the curing cycle. Most composites epoxy resin mentioned in the literature, seeks to improve the fracture toughness of the resin, by raising its critical stress intensity factor (KIC). The addition of tenacificantes or flexibilizing agents, which may be liquid elastomers, or functionalized thermoplastic polymers, constitute the most classical way to improve the fracture properties of the epoxy resin (Barcia et al., 2000; Bagheri et al., 1999).

Epoxy resins are one of the most important high performance polymers in many application fields, ranging from the surface coatings, electrical/electronic components, high performance composites, and adhesives to high-tech applications (Ellis 1994; Hamerton et al., 2002). The first conductive PANI/epoxy composite was prepared by Kathirgamanathan (1993) by mechanical mixing of toluenesulfonic acid (TSA)-doped PANI with epoxy resin and then cured with *cis*-1,2,3,4-tetrahydrophthalic anhydride. Latterly, the similar procedure was adopted by Jia et al. (2004) in preparing conductive PANI/epoxy composites with

dodecylbenzenesulfonic acid (DBSA) doped PANI. The other approach in preparing conductive PANI/epoxy composite was mixing solution of conductive PANI with solution of epoxy resin and then cured. For example, both the camphorsulfonic acid (Peltola et al., 1995) and DBSA-doped PANI (Tsotra et al., 2002) were used in preparing the conductive composites. In addition, Yang et al., (2004) reported a third approach, in which the solution of the nonconductive emeraldine base form of PANI was mixed with epoxy resin and cured, and the cured composite was then doped by dipping in a TSA solution.

The study mixtures containing polymer dispersed conductor in a thermosetting matrix, such as epoxy resin has the advantage possible development of materials having conductive properties, which can be applied in coatings able to dissipate loads electrostatic nature, anticorrosive coatings, conductive adhesives, among other applications (Cassignol et al., 1999). Some studies in the literature, use physical blend of polypyrrole and epoxy resin (Fournier et al., 1997). Coating polyaniline-based epoxy resin with anti-corrosive properties, it has also been developed from mixing in solution involving the camphorsulfonic acid doped polyaniline and epoxy resin (Talo et al., 1997).

2.4 Natural Fiber as Filler

Due to growing social, economic and ecological awareness along with government emphasis on the environmental impact and sustainability, the proper utilization of natural resources and wastes are strongly encouraged (Al-Oqla et al., 2014). Consequently, the natural fiber composites (NFCs) have become valuable

choice for various industrial applications. In NFCs, natural fibers are used as fillers or reinforcing materials for polymer matrices (Thakur et al., 2012; Sapuan et al., 2013). NFCs are attractive from environmental point of view which enabled them to be used as an alternative to the traditional carbon/glass polymer composites (Faruk et al., 2012). They are used in various applications including packaging, furniture, automotive industries, disposable accessories, building, and insulation materials (Thakur et al., 2014). In addition, these NFCs show several advantages and superior characteristics over traditional composites due to the low cost and densities along with acceptable specific strengths and moduli (Alves et al., 2010) which offer the opportunity to produce light weight products. Futhermore, NFCs are also used in producing recyclable and bio-degradable products (Mir et al., 2010).

On top of that natural fibers have many advantages over glasses such as reduced tool wear in machining, reduced dermal and respiratory irritation, availability, CO_2 sequestration enhanced energy recovery, (Sarikanat et al., 2010; Kalia et al., 2011; Faruk et al., 2012). In spite of that, natural fibers suffer from certain abundant drawbacks like low durability, poor water resistance, and poor bonding with the matrix.

Natural fibers can be divided based on their origins such as leaf fibers, fruit, seed fibers, and bast fibers as shown in Figure 2.5. Wide range of natural fibers has been used to reinforce the different types of polymer matrices. Such fibers include bamboo, coir, wheat straw, bagasse, curaua, doum fruit, etc. (Jawaid et al., 2011; Majeed et al., 2013). Several factors might affect the finally produced NFC and can determine their mechanical, electrical, biological characteristics.

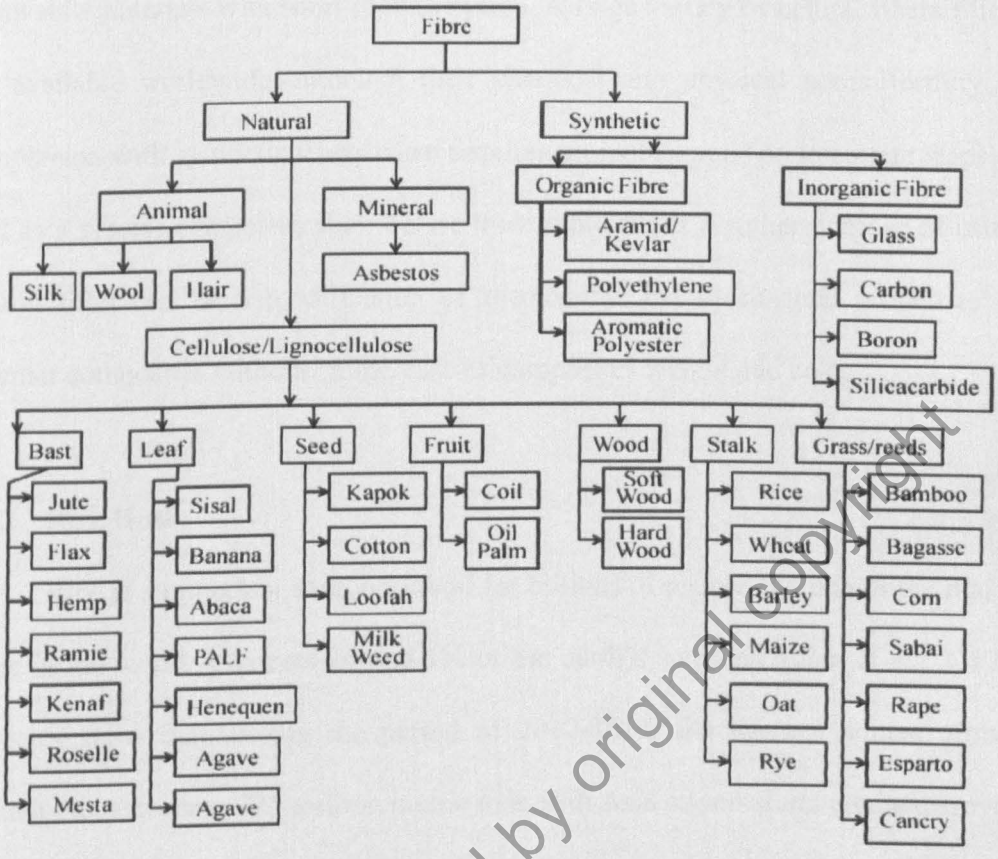

Figure 2.5: Classification of natural fibers (M. Jawaid et al., 2011)

2.4.1 The Usage of Natural Fiber as Filler for PANI/Epoxy System

The use of natural fibers as a reinforcement for various materials was recorded already in ancient Egypt; however, their rediscovery can be dated to the beginning of 20th century. Current special issue is devoted to the role of natural fibers as reinforcements for various biodegradable and non-biodegradable polymer matrices. The application of natural fillers can be seen as an approach to adjust material performance of polymer composites supposing that filler/matrix interactions will be optimized and a hygroscopicity of natural fillers will be hindered. One of the reasons given for using of fibers from oneyearplants can be a quicker and economically favorable production of composites based on environmentally friendly, abundant