

# Chapter 2

## **LITERATURE REVIEW**

## **2. Literature Review**

### **2.1 Cellulose Fibers for Reinforcement**

The idea of using cellulose fibers as reinforcement in composite materials is not a new or recent one. Man had used this idea for a long time, since the beginning of our civilization when grass and straw were used to reinforce mud bricks [14]. In the past, composites, such as coconut fiber/natural rubber latex, was extensively used by the automotive industry [15]. However, during the seventies and eighties, cellulose fibers were gradually substituted by newly developed synthetic fibers because of better performance [15]. Since then, the use of cellulose fibers has been limited to the production of rope, string, clothing, carpets and other decorative products [14]. Over the past few years, there has been a renewed interest in using these fibers as reinforcement materials to some extent in the plastics industry. This resurgence of interest is due to the increasing cost of plastics [17], and also because of the environmental aspects of using renewable and biodegradable materials.

#### *2.1.1 Utilization of cellulose fibers: Opportunities and limitations*

There is a wide variety of cellulose fibers that can be used to reinforce thermoplastics. These include wood fibers, such as steam-exploded fibers, and a variety of agro-based fibers such as stems, stalks, bast, leaves and seed hairs. These fibers are abundantly available throughout the world, particularly in developing countries like India,

and they come from renewable resources [14, 17]. Other large sources are recycling agro fiber-based products such as paper, waste wood, and point source agricultural residues such as rice hulls from a rice processing plant [17].

Cellulose fibers, depending on the part of the plant from which they are taken, can be classified as:

#### 1. Grasses and reeds

These fibers come from the stems of monocotyledonous plants such as bamboo and sugar cane [13, 18]. Both types of fibers can be used to reinforce plastics [14].

#### 2. Leaf fibers

Leaf fibers are fibers that run lengthwise through the leaves of most monocotyledonous plants such as sisal, henequem, abaca and esparto [13, 18]. These fibers, which are also referred to as ‘hard fibers’, are the most commonly employed as reinforcing agents in plastics [14].

#### 3. Bast fibers

These fibers (bundles) come from the inner bark (phloem or bast) of the stems of dicotyledonous plants [13, 18]. Common examples are jute, flax, hemp, and kenaf.

#### 4. Seed and fruit hairs

These are fibers that come from seed-hairs and flosses, which are primarily represented by cotton and coconut [14, 18].

## 5. Wood fibers

These fibers come from the xylem of angiosperm (hardwood) and gymnosperm (softwood) trees. Examples include maple, yellow poplar and spruce.

The potential fibers named above can be separated from the original plant in several ways like retting, scrapping and pulping [18]. Cellulose fibers are generally lignocellulosic consisting of helically wound cellulose microfibrils in an amorphous matrix of lignin and hemicellulose. These fibers consist of several fibrils that run along the length of the fiber. The properties of these fibers are very difficult to measure with a considerable number of fibers (between 500 and 4000) needing to be tested to obtain statistically significant mean values ( $p < 0.05$ ) [18]. These properties are also strongly influenced by many factors, particularly chemical composition and internal fiber structure, which differ between different parts of a plant as well as between different plants [14, 20]. Ray (1953) [21] in his study on the influence of lignin content on the mechanical behavior of jute (Figure 2.1), found a gradual decrease in both the strength and stiffness of the fiber with lignin removal. The extensibility of the fiber was also found to follow the same trend [21]. Similar experiments, which were carried out on sugarcane fiber (Collier *et al.*) [21] provided additional evidence of the significant contribution of lignin to fiber strength. The most efficient cellulose fibers are those with high cellulose content coupled with a low microfibril angle [17, 22], such as jute that has a cellulose content of more than 60 % and a microfibril angle in the range of 7-12° [21] to the fiber axis (Figure 2.2). Data on the chemical composition and microfibrillar angle, as well as their physical properties

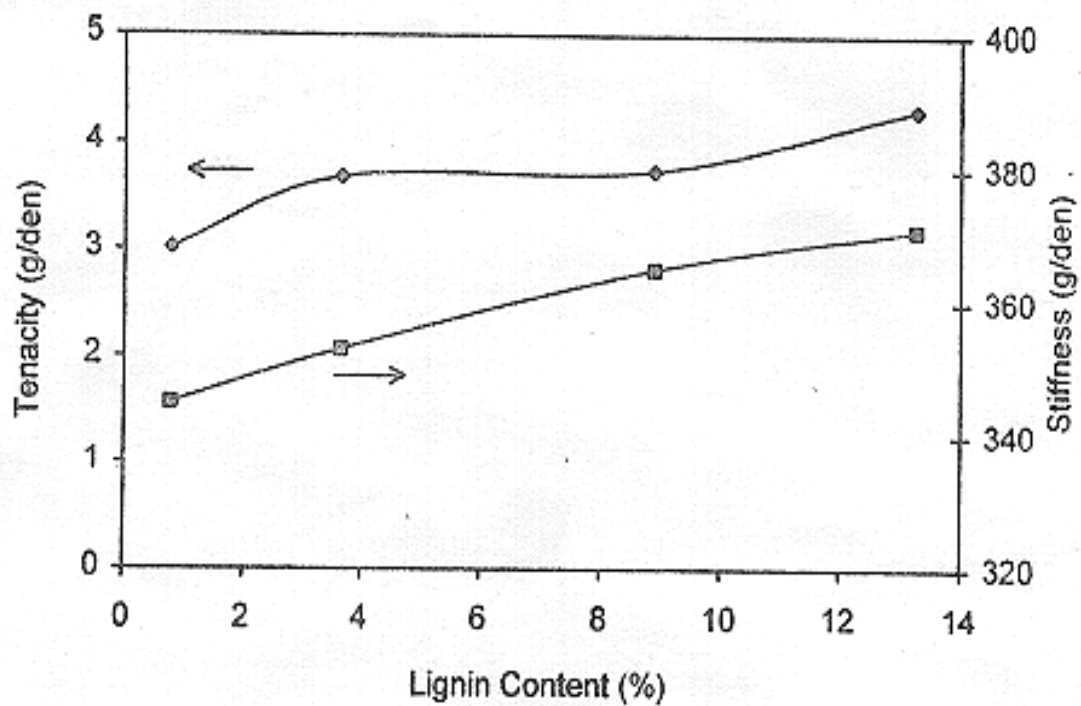


Figure 2.1 Variation in the strength and stiffness of jute fibers with lignin content [21].

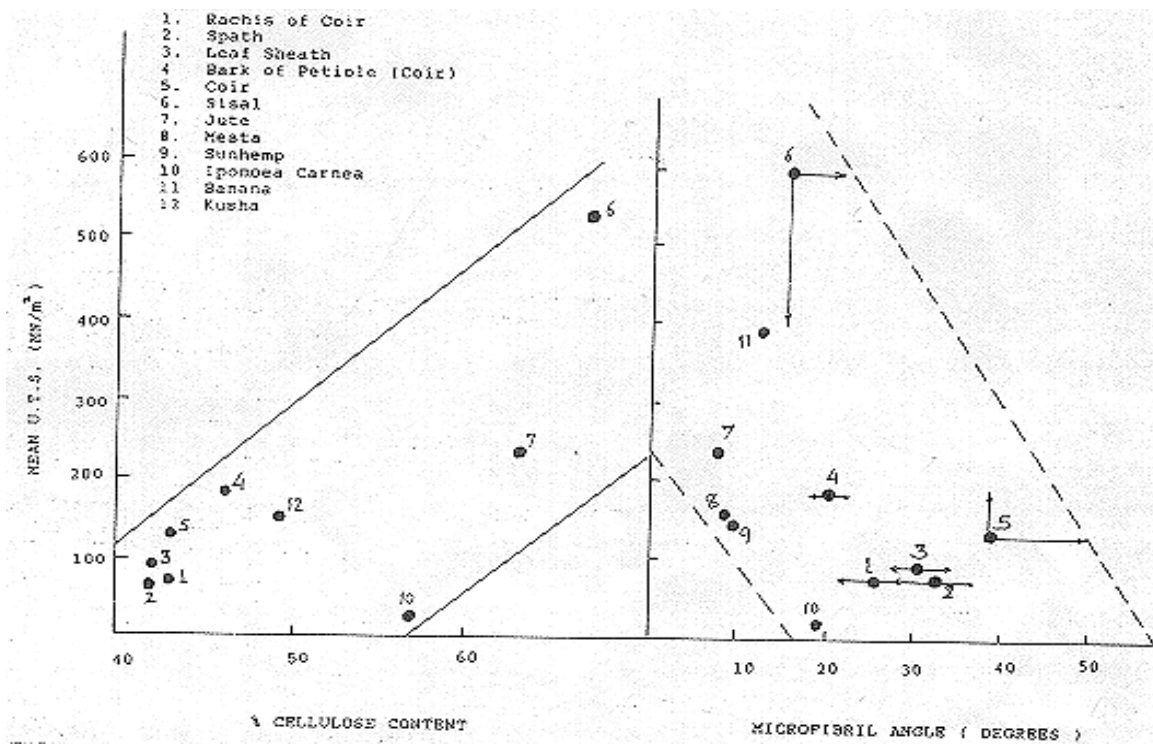


Figure 2.2 Relationship between the strength of cellulose fibers and their cellulose contents and microfibril angles [22].

(Table 2.1), is critical in order to dictate the specific use of a certain fiber, and this has been reported by many investigators in the literature. The data, however, is incomplete and needs to be expanded to include other potential fiber sources. Other factors that may affect the fiber properties are maturity [21], separating process, microscopic and molecular defects such as pits and nodes [21], type of soil and weather conditions under which they were grown [14].

Cellulose fibers present many advantages compared to synthetic fibers which make them attractive as reinforcements in composite materials. They come from an abundant and renewable resources [23, 24] at low cost [13, 23, 24, 25, 26] (Table 2.2), which ensures a continuous fiber supply and a significant material cost saving [8] to the plastics industry. Cellulose fibers, despite their low strength, can lead to composites with high specific properties [24] because of their low densities [13, 25, 26, 28, 29] (Table 2.3).

Unlike brittle fibers, such as glass and carbon fibers, cellulose fibers are flexible and will not fracture when processed over sharp curvatures [17]. This enables the fibers to maintain the desired aspect ratio for good performance (Table 1.1). Their non-abrasive nature permits a high volume fraction of filling [13, 17, 24, 25, 26, 28, 29] during processing, and this results in high mechanical properties without the usual machine wear problems associated with synthetic fibers especially glass and ceramic. Cellulose fibers are also non-toxic [27], easy to handle and present no health problems like glass fibers that can cause skin irritations and respiratory diseases when the fibrous dust is inhaled [16]. They offer a high ability for surface modification [23], are economical, require low amounts of energy for processing [13, 23], and are biodegradable [13, 24, 27]. In terms of socio-economic issues, the use of cellulose fibers as source of raw materials is beneficial

Table 2.1 Mechanical properties of some cellulose fibers [22].

Fiber	Diameter ( $\mu\text{m}$ )	Density ( $\text{g/cm}^3$ )	Moisture content (%)	UTS <sup>1</sup> (MPa)	Modulus (GPa)
Cotton		1.5		500-880	0.05
Jute	200	1.45	12	460-533	2.5-13
Coir	100-450	1.15	10-12	131-175	4-6
Banana	80-250	1.35	10-12	529-754	7.7-20.8
Sisal	50-200	1.45	11	568-640	9.4-15.8
Flax		1.50		1100	100
Kraft fiber		1.54		1000	40
Sunhemp	48	0.673		200-300	2.68
Pineapple	20-80	1.44		413-1627	34.5
Palm leaf	240			98.14	2.22
Mesta	200	1.47		157.38	12.62
Kusha grass	390			150.59	5.69

<sup>1</sup> Ultimate tensile strength



Table 2.2 Annual fiber production / availability of some of the cellulose fibers (tons) [22].

Fiber	India	World	Cost (U.S. \$ / kg)
Coir	160,000	282,000	0.03
Banana	1632	100,296	0.10
Sisal	3000	600,000	0.05
Palmyrah	100	Not known	0.07
Pineapple	Not estimated	Not estimated	0.05
Glass			0.33
Carbon			> 16.00
Stainless steel			> 4.00

Table 2.3 Properties of fibers and conventional bulk materials [8].

Material	Tensile modulus (GPa)	Tensile strength (GPa)	Density (g/cm <sup>3</sup> )	Specific modulus (GPa cm <sup>3</sup> /g)	Specific strength (GPa cm <sup>3</sup> /g)
Aluminum (2024-T4)	73	0.04	2.7	27	0.15
Douglas-fir (12% MC)	12	0.05	0.5	24	0.1
E-glass	72	3.5	2.5	28	1.4
S-glass	85	4.6	2.5	34	1.8
Kevlar-49	130	2.8	1.5	87	1.9
Graphite Thornel 25	186	1.2	1.4	133	0.8
Spruce pulp	60	1.5	0.6	100	2.5

because it generates a economic development opportunity for non-food farm products in rural areas [13]. These mentioned advantages are benefits and not likely to be ignored by the plastics industry for use in the automotive, building, appliance, and other applications [13].

Despite the advantages mentioned above, use of cellulose fibers in thermoplastics has not been extensive. Possible reasons that contribute to unsatisfactory final properties of the composite include: (i) Limited thermal stability [13, 23, 24, 25, 29, 30] at typical melt processing temperatures of about 200°C. This limits the type of thermoplastic that can be used with the fibers [6, 13]. (ii) Poor dispersion characteristics in the non - polar, olefinic thermoplastic melt due to strong hydrogen forces between the fibers [23, 28]. (iii) Limited compatibility with many thermoplastic matrices [23, 28, 29] due to their highly hydrophilic character [26]. This results in poor mechanical properties of the composites produced. (iv) High moisture absorption of the fibers [23] that can affect the dimensional stability of the composite [17, 25] and the interfacial bond strength; and (v) high biodegradability when exposed to the environment. This limits the service life of composites particularly in outdoor applications. There are many reports on the potential use and limitation of cellulose fibers as reinforcement in thermoplastics available in the literature. These studies show that the problems mentioned above are common, independent of the type and origin of the fiber employed [14]. Other factors that may hamper increased use of cellulose fibers in plastics are problems and costs associated with the collection and storage which are not yet mechanized and standardized to produce fibers of high and uniform quality [31].

### 2.1.2 Chemical modification of cellulose fibers

Chemical modification of cellulose fibers is usually applied to correct for deficiencies of the fibers as described in the previous section. Modification may result in improved performance of the composites produced. This can be done through several approaches, including plasma activation and graft polymerization with vinyl monomers, which are very well described in the literature. These, however, will increase the fiber cost.

The primary drawback of using cellulose fibers is their limited thermal stability with noticeable degradation occurring as the melt processing temperature approaches 200°C [30]. This excludes some manufacturing processes and limits the type of thermoplastic that can be used to such low-temperature polymers as polypropylene, polystyrene and polyethylene [13, 17]. Higher processing temperatures that reduce melt viscosity and facilitate good mixing, however, are possible, but only for short periods. If degradation occurs, cellulose fibers can be responsible for the formation of tar-like products and pyrolysis acids that may have various damaging effects both on the processing equipment and the composite properties [32]. One simple method that can be used to overcome this problem involves acetylation. This procedure was first applied by Stamm in 1947 [33]. Rana *et al.* (1997) [34] studied the effect of acetylation on jute fibers at different reaction times and reaction temperatures. The modified fibers were characterized by FTIR, DSC, TGA and SEM studies. The extent of moisture regain and thermal stability was reported. From the study, the authors found that the thermal stability of acetylated jute is higher than that of untreated jute [34].

Another major drawback of using cellulose fibers as reinforcing agent is the high moisture absorption [13] of the fibers due to hydrogen bonding of water molecules to the hydroxyl groups within the fiber cell wall. This leads to a moisture build-up in the fiber cell wall (fiber swelling) and also in the fiber-matrix interface [13, 17]. This is responsible for changes in the dimensions of cellulose-based composites, particularly in the thickness and the linear expansion due to reversible and irreversible swelling of the composites [13, 35]. As a consequence, the fiber-matrix adhesion is weak and the dimensional stability of cellulose-based composites particularly for outdoor applications will be greatly affected. Singh and Jain (1980) [3] investigated the effect of weathering on jute-polyester reinforced composites. Table 2.4 shows properties of these composites before and after exposure to natural weathering for 7 years. They found decreases in composite properties as a result of weathering. Adsorption and desorption of moisture by the composites during the study produced high shrinkage stresses which caused surface crazing and debonding of resin and jute fibers [22]. This led to a reduction in mechanical properties of the composites studied.

Other than dimensional stability, the hygroscopic and hydrophilic nature of cellulose fibers also influences the composites' processability [30]. The tendency of cellulose fibers to absorb moisture causes off-gassing (void formation) during compounding. This results in a molded article with a microstructure having variable porosity and resembling that of a high-density foam [30]. The pores formed will act as stress concentration points which then lead to an early failure of the composite during loading.

Table 2.4 Physical properties of jute fiber and glass fiber reinforced sheet before and after weathering for seven years [22].

Property	Unweathered		Weathered	
	Sheet jute reinforced	Sheet glass fiber reinforced	Sheet jute reinforced	Sheet glass fiber reinforced
Bulk density (kg/cm <sup>3</sup> )	1150	1300	1025	1250
Fiber content (%)	12-15	28-32		30-35
Water adsorption at 25 °C (%)				
a) 24 hours	2.34	1.03	3.23	1.28
b) 3 days	2.88	1.17	4.16	1.69
c) 7 days	3.87	1.27	5.07	1.97
Water adsorption at 100 °C, 1 hours (%)	3.08	1.05	3.90	1.34
Flexural strength (MN/m <sup>2</sup> )				
a) Dry	23.00	107.40	11.60	103.30
b) 24 hours water soaking	32.10	123.20	28.20	99.20
c) 3 days soaking	42.60	135.20	19.60	98.90
d) 7 days soaking	34.00	74.10	19.10	64.90
Tensile strength (MN/m <sup>2</sup> )	24.20	76.00	9-20.6	63.00

The amount of moisture absorption in the cellulose fibers can be dramatically reduced through chemical modification, such as acetylation, of some of the hydroxyl groups present in the fibers [13, 17, 21]. This effect is shown in Table 2.5. Other feasible methods include graft polymerization with vinyl monomers such as acrylonitrile. Ghosh *et al.* (1994) [14] and Samal *et al.* (1994) [14] recently grafted acrylonitrile on jute and pineapple leaf respectively to enhance the fiber properties. The moisture regain was found to decline dramatically as the degree of grafting increased for both systems. As for mechanical properties, these increased with degree of grafting.

The incorporation of cellulose fibers into synthetic polymers is often associated with a lack of fiber dispersion [26] due to the wide differences in polarity and also the strong intermolecular hydrogen bonding between the fibers [33]. This lack of fiber dispersion can result in clumping and agglomeration of cellulose fibers [17] which will act as stress concentration points to initiate cracks during loading. This effect contributes to inferior mechanical properties. This problem can be overcome by pretreatment of the fibers with polymer coating materials. The introduction of polymer coatings on fiber surfaces helps to separate fibers from each other, eliminating the hydrogen bonding that holds them together [14]. This approach also induces bond formation between the fibers and the matrix resulting in improved composite properties. Gatenholm *et al.* (1993) [36] studied the effect of the chemical composition of the interface on the dispersion of cellulose fibers in polystyrene (PS), polypropylene (PP) and low-density polyethylene (LDPE) [24]. Cellulose fibers surface-coated with butyl benzyl phthalate (BBP)-plasticized PVC (also known commercially as Santoweb W), were used

Table 2.5 Equilibrium moisture content (EMC) of various acetylated cellulose materials (65% RH, 27 °C) [37].

Material	Reaction weight gain by acetylation (%)	Acetyl content (%)	EMC (%)
Southern pine	0	1.4	12.0
	6.0	7.0	9.2
	14.8	15.1	6.0
	21.1	20.1	4.3
Aspen	0	3.9	11.1
	7.3	10.1	7.8
	14.2	16.9	5.9
	17.9	19.1	4.8
Bamboo	0	3.2	8.9
	10.8	13.1	5.3
	14.1	16.6	4.4
	17.0	20.2	3.7
Bagasse	0	3.4	8.8
	9.4	14.4	5.3
	12.2	15.3	4.4
	17.6	19.0	3.4
Jute	0	3.0	9.9
	15.6	16.5	4.8



as reinforcements. Based on SEM micrographs, improved fiber dispersion was observed in PS. Another approach involves the use of dispersion aids, such as stearic acid, which facilitate fiber dispersion by decreasing both the size and number of fiber aggregates as a result of significantly reduced fiber to fiber interaction and improved fiber wetting by the polymer matrix. Raj *et al.* (1995) [38] investigated the influence of various processing aids/coupling agents in improving fiber dispersion as well as compatibility between the fiber and the matrix [27]. Stearic acid and mineral oil were used as additives and maleated ethylene as a coupling agent. The results showed that the addition of stearic acid during the compounding greatly improved the fiber dispersion in the polymer matrix compared to untreated fibers as seen in SEM micrographs of fracture surfaces of the corresponding composites. This effect was also reflected in improved mechanical properties of the composites (Table 2.6).

Cellulose fibers are not compatible, i.e., do not wet, with many thermoplastic matrices and this is also due to differences in polarity [26]. Cellulose fibers are hydrophilic while most of the thermoplastics (polyolefins) are hydrophobic. This leads to the presence of voids or porosity [14], and to weak fiber-matrix interfaces and poor overall mechanical properties. There are several possible strategies for improving compatibility between cellulose and thermoplastic matrices, and the most extensively used methods are the use of coupling or compatibilization agents, and surface treatments of the fibers. Coupling agents such as isocyanates and silanes modify the fiber-matrix interface by forming a bridge of chemical bonds between the two components [39]. This results in improved fiber-matrix adhesion, which is reflected in the mechanical properties of the composite produced.

Table 2.6 Tensile properties of HDPE-cellulose fiber composites [38].

Processing aids	Fiber content (%wt.)	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
Control	10	23.7	8.6	1.16
	30	29.8	6.0	1.60
Stearic acid	10	26.6	8.0	1.28
	30	35.2	6.0	1.86
Mineral oil	10	26.5	8.6	1.26
	30	33.8	6.1	1.84
Maleated ethylene	10	25.9	8.2	1.29
	30	36.1	6.0	1.94

Gatenholm *et al.*(1991) [40] studied the nature of adhesion in composites of modified cellulose fibers and polypropylene. Cellulose fibers were surface-modified with polypropylene maleic-anhydride copolymer and characterized by contact angle measurement, ESCA, FTIR, and SEM techniques. Composites reinforced with surface-modified cellulose fibers showed significantly improved mechanical properties compared to composites with untreated cellulose fibers. This was due to improved fiber wetting, dispersion and fiber-matrix adhesion as seen in SEM micrographs. Interfacial interactions involved were covalent and hydrogen bonds that formed across the fiber-matrix interface.

Lignocellulosic materials including cellulose fibers degrade easily when exposed to nature (Table 2.7) [35]. Nature builds lignocellulosic resources from carbon dioxide and water, and it has all the tools to recycle them back to the starting chemicals [34]. Possible ways of degradation include biological, thermal, aqueous, photochemical, chemical, and mechanical means of degradation. In order to produce cellulose fiber-based composites with a long service life, the degradation processes caused by nature need to be retarded [35]. One way of preventing or slowing down the natural degradation process is by modifying the cell wall chemistry of the material which is responsible for many of its properties (Table 2.8) [35, 41]. This can be accomplished by chemical modification such as acetylation [41] using acetic anhydride to produce an acetylated material. The effect of several chemical reaction systems on the biological resistance against attack by termites is shown in Table 2.9.

Table 2.7 Degradation reactions that occur when lignocellulosic resources are exposed to nature [35].

---

<b>Biological Degradation</b>	
Fungi, Bacteria, Insects, Termites	
Enzymatic Reactions	- Oxidation, Hydrolysis, Reduction
Chemical Reactions	- Oxidation, Hydrolysis, Reduction
Mechanical	- Chewing
 <b>Fire Degradation</b>	
Lighting, Sun, Man	
Pyrolysis Reactions	- Dehydration, Hydrolysis, Oxidation
 <b>Water Degradation</b>	
Rain, Sea, Ice, Acid Rain	
Water interactions	- Swelling, Shrinking, Freezing, cracking
 <b>Weather Degradation</b>	
Ultraviolet Radiation, Water, Heat, Wind	
Chemical Reactions	- Oxidation, Reduction, Dehydration, Hydrolysis
 <b>Mechanical Degradation</b>	
Dust, Wind, Hail, Snow, Sand	
Mechanical	- Stress, Cracks, Fracture, Abrasion

---

Table 2.8 Cell wall polymers responsible for the properties of lignocellulosics in the order of importance [35].

<b>Biological Degradation</b>
Hemicellulose
Accessible Cellulose
Non-Crystalline Cellulose
<b>Moisture Sorption</b>
Hemicellulose
Accessible Cellulose
Non-Crystalline Cellulose
Lignin
Crystalline Cellulose
<b>Ultraviolet Degradation</b>
Lignin
Hemicellulose
Accessible Cellulose
Non-Crystalline Cellulose
Crystalline Cellulose
<b>Thermal Degradation</b>
Hemicellulose
Cellulose
Lignin
<b>Strength</b>
Crystalline Cellulose
Matrix (Non-Crystalline Cellulose + Hemicellulose + Lignin)
Lignin

Table 2.9 Weight loss in chemically modified Southern Pine after 2 weeks' exposure to *Reticulitermes flavipes* [35].

Chemical	Weight gain (%) by chemical modification	Wood weight loss (%)
Control	0	31
Propylene oxide	9	21
	17	14
	34	6
Butylene oxide	27	4
	34	6
Acetic	10.4	9
	17.8	6
	21.6	5

## 2.2 Properties of Cellulose Fibers-Thermoplastic Composites

The reinforcement caused by short fibers, including cellulose fibers, in the thermoplastic matrix is governed by the following parameters: i) fiber dispersion, ii) fiber-matrix adhesion, iii) fiber aspect ratio, iv) fiber orientation, and v) fiber volume fraction [5, 6]. Studies to understand the influence of these factors on cellulose-based composites have been carried out and reported in the literature by many investigators such as Gatenholm (1993) [36] and Kokta (1991) [32]. Some of these studies will be briefly described in this section.

### 2.2.1 *Fiber dispersion*

The primary requirement for obtaining a satisfactory performance from short-fiber composites, including cellulose-based composites, is good fiber dispersion in the polymer matrix. Good dispersion implies that the fibers are separated from each other (i.e. there are no clumps and agglomerates), and each fiber is surrounded by the matrix. Insufficient fiber dispersion, on the other hand, results in an inhomogeneous mixture of resin-rich areas and fiber-rich areas. This is undesirable because the resin-rich areas are weak and the fiber-rich areas (i.e., clumps) are susceptible to microcracking. Microcracks contribute to inferior mechanical properties of composites. It is therefore important to ensure homogeneous fiber dispersion in order to achieve maximum strength and performance of the composite materials. There are two major factors that affect the extent of fiber dispersion, fiber-fiber

interaction such as strong hydrogen bonding between the fibers, and fiber length [6]. The same factors also account for the tendency for some fibers, such as cellulose fibers, to agglomerate during mixing. The fiber length used in the preparation of composites is critical. It should not be too long, otherwise the fibers may get entangled with each other [6]. This will cause problems with fiber dispersion. If fibers are too short, the stress transfer area will be too small for the fibers to offer effective reinforcement. According to Derringer (1971) [6], commercially available fibers such as nylon, rayon, and polyester need to be cut into lengths, of approximately 0.4 mm for best dispersion.

As mentioned before, one of the major drawbacks of using cellulose fibers as reinforcement is because of their poor dispersion characteristics in many thermoplastic melts, such as polypropylene and polystyrene, due to their hydrophilic nature. Several methods have been suggested and described in the literature to overcome this problem. Among them are fiber surface modification, use of dispersing agents such as stearic acid, and fiber pre-treatments such as acetylation. Fiber dispersion can also be improved with increased shear force and mixing time [6]. A careful selection of initial fiber lengths, processing aids, processing techniques as well as processing conditions then is necessary in order to produce high performance composites.

Raj and Kokta (1989) [38] investigated the influence of using various dispersing aids (stearic acid and mineral oil) and a coupling agent (maleated ethylene) in cellulose fiber reinforced polypropylene composites. Tensile strength and modulus of the composites studied were found to increase with fiber content when either stearic acid or mineral oil (1% by weight of fiber) were added as processing aids during the compounding. The properties also were found to be affected by the amount of processing



aid used. Maximum increases in the properties were observed when the processing aid was added in 1% concentration (by weight of fiber). A further increase in the amount of processing aid caused the properties to decline dramatically. Stearic acid was found to perform better in improving the fiber dispersion compared to mineral oil.

Good fiber dispersion is generally the ultimate objective of any mixing process [6]. Various mixers are available to mix short fibers in thermoplastics such as extruders, plasticorder, injection molding machines and kneaders. Different mixing techniques, however, do not produce composites with the same degree of fiber dispersion. Woodhams *et al.* (1990) and Myers *et al.* (1992) used a thermokinetic mixer to mix cellulose fibers with thermoplastics and found the technique effective in dispersing the cellulose fibers within thermoplastic matrices [13, 17]. The effectiveness of the technique was then confirmed by Sanadi *et al.* (1994) [13, 17]. Pereira *et al.* (1997) [27] investigated the effect of several processing techniques on the properties of polypropylene composites reinforced with short sisal fibers. The equipment used involved a cold mixer, press, injector, two-roll mill, and twin-screw extruder. The sisal fibers were pretreated with silanes prior to processing to ensure good compatibility with the matrix. From the study, they concluded that processing techniques and routes can greatly influence composite properties. Both were also found to produce a great variation in the dimension and dispersion of the sisal fibers within the composites studied. The best processing method involved a twin-screw extruder.

### 2.2.2 *Fiber-matrix adhesion*

Fiber to matrix adhesion plays a very important role in the reinforcement of composites with short fibers [6]. During loading, loads are not applied directly to the fibers but to the matrix. To have composites with excellent mechanical properties (ultimate strength but toughness), the load must be transferred effectively from the matrix to the fibers. This requires good interaction as well as adhesion between the fibers and the matrix, i.e. strong and efficient fiber-matrix interface. This can be controlled by either surface treatment applied to the fiber or by the use of additives such as coupling agents. Although the mechanism of stress transfer is not clear, it has been postulated that it takes place through shearing at the interface [6]. Many studies have been done on various composite systems either to improve the efficiency of the interface in transferring stress or to understand the mechanism involved.

Cellulose fibers have not been extensively used to reinforce thermoplastics. This is because of several major drawbacks discussed in the previous section. Poor compatibility with and dispersability in hydrophobic thermoplastics leads to poor wetting and interfacial bonding between the fibers and the matrix resulting in composites with poor mechanical properties. These problems, however, can potentially be overcome. The use of coupling agents, polymer coating materials, fiber pre-treatments, and chemical grafts have been reported to improve wetting as well as interfacial bonding between cellulose fibers and thermoplastic matrices. This is due to improved fiber-matrix adhesion as well as fiber dispersion.

Childress and Selke (1993) [42] investigated the effectiveness of several additives in enhancing mechanical properties of wood fiber/high-density polyethylene composites. The additives used were ionomer-modified polyethylene (ION), maleic anhydride modified polypropylene (MAPP), and two low molecular weight polypropylenes (LWMPP1 and LWMPP2) [30]. The effect of these additives on tensile properties, impact strength, creep as well as water sorption, were evaluated at 1,3, and 5 percent additive addition. The mechanical properties of the composites studied increased with increasing additive concentration. The most effective additive was MAPP, followed with ION. LWMPP1 and LWMPP2, however, did not show any promising results.

Thomas *et al.* (1996) [43] reinforced polystyrene with benzoylated sisal fibers. The results revealed better compatibility between treated cellulose fibers and the polystyrene matrix, and this resulted in enhanced tensile properties of the resulting composite. SEM micrographs revealed evidence of improved fiber wetting and fiber-matrix adhesion between the components. These improvements were attributed to the similarity between the phenyl-structure present in both benzoylated sisal fibers and polystyrene, which makes them thermodynamically compatible with each other.

### 2.2.3 Fiber aspect ratio

Fiber aspect ratio, i.e. the length to diameter ratio of a fiber, is a critical parameter in a composite. An expression relating critical fiber aspect ratio ( $l_c / d$ ) to interfacial shear stress ( $\tau_y$ ) has been proposed by Cox [2] on the basis of shear-lag analysis (eq. 2.1) [6].

$$l_c / d = \sigma_{fu} / 2 \tau_y \quad [\text{Eq. 2.1}]$$

where:

$l_c$  = critical fiber length

$d$  = diameter of fiber

$\sigma_{fu}$  = fiber ultimate strength in tension

$\tau_y$  = interfacial shear stress

At control  $\sigma_{fu}$ , the equation reveals an inverse relationship between  $l_c / d$  and  $\tau_y$ , where  $l_c / d$  becomes short (low) as  $\tau_y$ , i.e. interfacial shear stress (transfer) becomes efficient (high). Interfacial shear stress, which influences fiber aspect ratio, can be varied by modifying the fiber-matrix interface by using chemicals such as coating agents.

For each short-fiber composite system, there is a critical fiber aspect ratio that may be defined as the minimum fiber aspect ratio in which the maximum allowable fiber stress

can be achieved for a given load [6]. This parameter is determined not only by fiber and matrix properties, but also by the quality of the fiber/matrix interface [44]. Load is transferred from the fiber to the matrix by shear along the fiber/matrix interface. Figure 2.3 shows how variations in fiber stress and shear stress at the fiber/matrix interface occur along the fiber length [40]. For maximum reinforcement, the fiber aspect ratio of any composite system should be above its critical value. This will ensure maximum stress transfer to the fibers before the composite fails. If the fiber aspect ratio is lower than its critical value, insufficient stress will be transferred and reinforcement by the fibers will be inefficient [6], i.e., the fibers are not loaded to their maximum stress value. By contrast, if the fiber aspect ratio is too high, the fibers may get entangled during mixing causing problems with fiber dispersion [6]. The effect of fiber length on fiber stress, which is commonly used to define critical fiber length, is shown in Figure 2.4 [40]. During processing, fibers, such as glass and carbon fibers, are often broken into smaller fragments [6]. This may potentially make them too short to be useful for reinforcement [6]. However, cellulose fibers are flexible [12], and resistance to fracture during processing can be expected [12]. This enables the fibers to maintain a desirable fiber aspect ratio after processing. Several investigators have suggested that an aspect ratio in the range of 100-200 after processing [6, 12] is essential for high performance short-fiber composites.

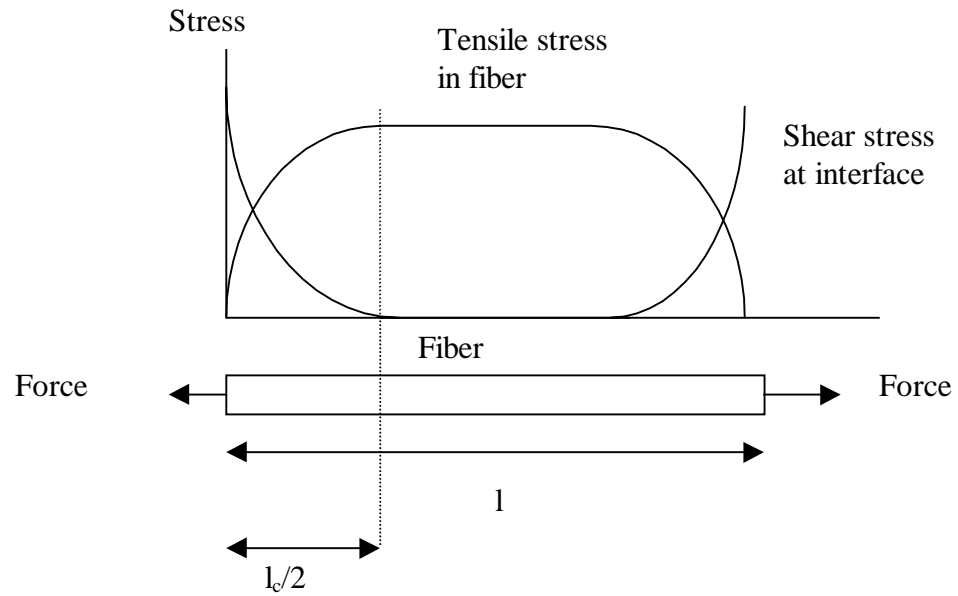


Figure 2.3 Fiber tensile stress and shear stress variation along the length of a fiber embedded in a continuous matrix and subjected to a tensile force in the direction of fiber orientation [Taken from Gatenholm, ref. 40].

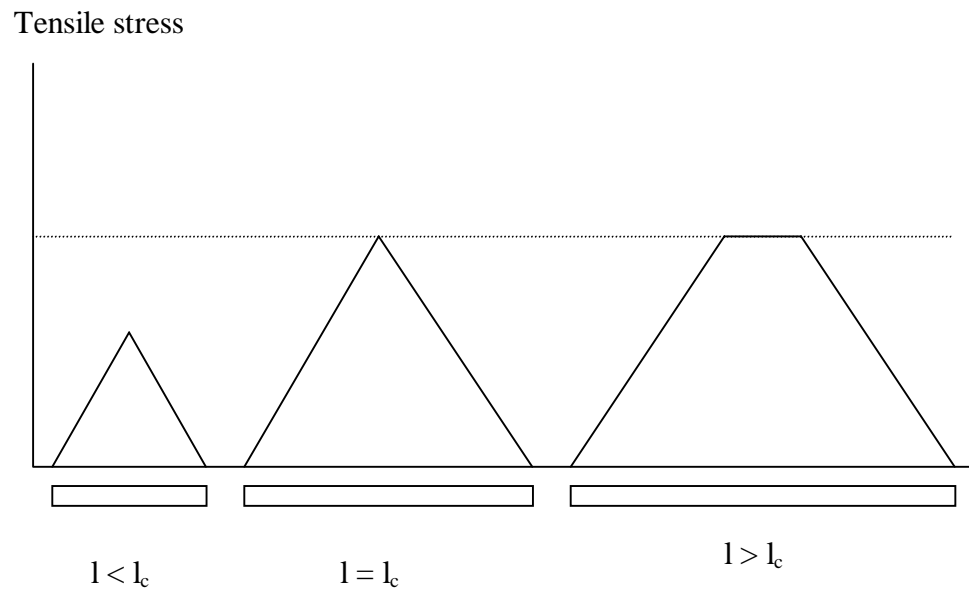


Figure 2.4 Effect of fiber length on fiber tensile stress [Taken from Gatenholm, ref. 40].

#### 2.2.4 Fiber orientation

Fiber orientation is another important parameter that influences the mechanical behavior of short-fiber composites [5, 45]. This is because the fibers in such composites are rarely oriented in a single direction [5], which is necessary for the fibers to offer maximum reinforcement effects. As a result, the degree of reinforcement in a short-fiber composite is found to be strongly dependent on the orientation of each individual fiber with respect to the loading axis [45]. Changes in fiber orientation take place continuously and progressively during the processing of short-fiber composites. The changes are related in a complex way to the geometrical properties of the fibers, the viscoelastic properties of the matrix, and the change in shape of the material which is produced by the processing operation [46]. In these operations, the polymer melt will undergo both elongational or extensional flow and shear flow [2]. The effect of these flow processes on the fiber orientation is illustrated in Figure 2.5.

Thomas *et al.* (1996) reinforced polystyrene with benzoylated sisal fibers [31]. The influence of fiber length, fiber content as well as fiber orientation on the composite produced were evaluated. Randomly oriented composite specimens were prepared by injection molding while the unidirectionally oriented composite specimens were prepared by a combination of injection molding and compression molding. The specimens were then observed under an optical stereomicroscope to confirm fiber orientation. A longitudinally oriented composite (the fibers are oriented parallel to the test direction) was found to show the best mechanical properties. This was followed by randomly and transversely oriented composites ie, the fibers are oriented transverse to the test direction.



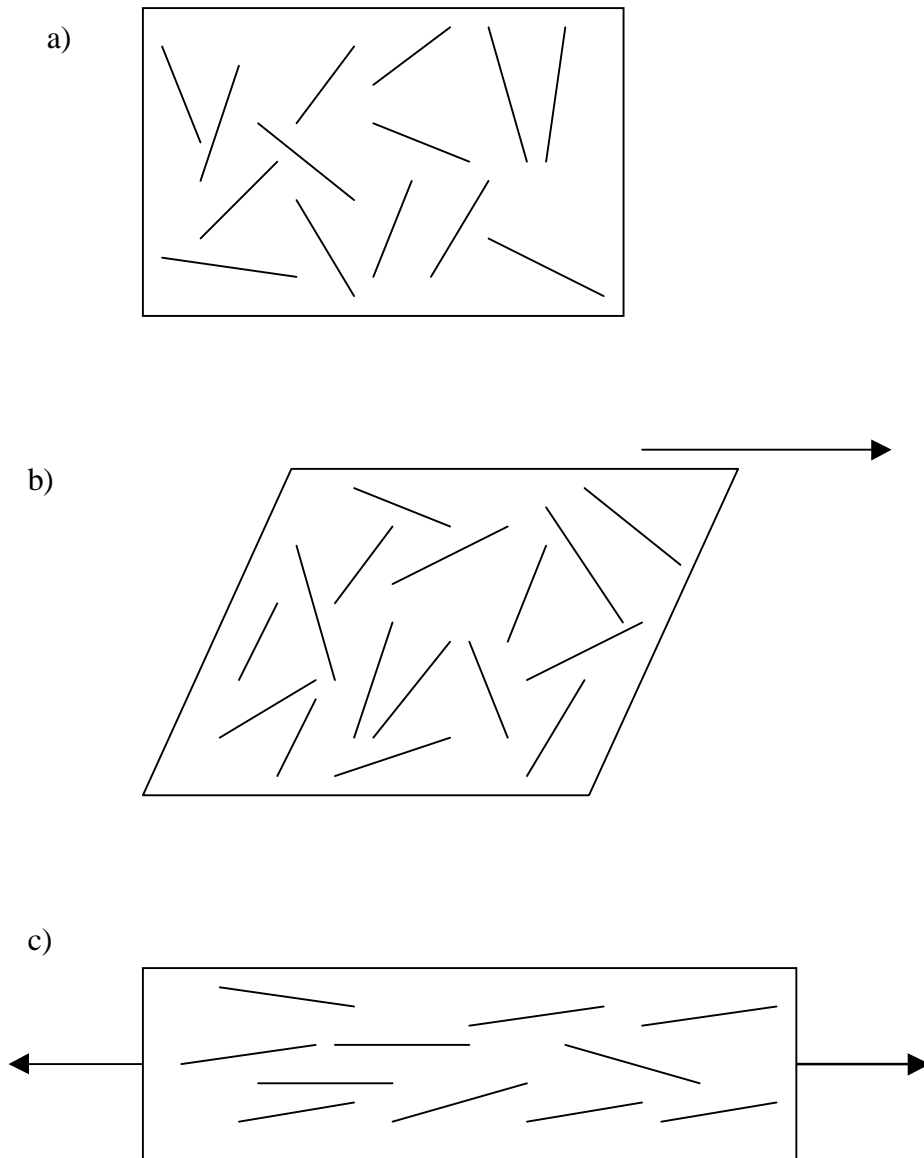


Figure 2.5 Schematic representation of the changes in fiber orientation occurring during flow. a) Initial random distribution, b) rotation during shear flow, and c) alignment during elongational flow [Taken from Hull *et al.*, ref. 2].

The same results were also found by Pavithran *et al.* (1993) who studied the mechanical properties of sisal fiber-reinforced polyethylene composites [47].

#### 2.2.5 *Fiber volume fraction*

Like other composite systems, the properties of short-fiber composites are also crucially determined by fiber concentration. Variation of composite properties, particularly tensile strength, with fiber content can be predicted by using several models such as the ‘Rule of Mixtures’ (Figure 2.6), which involves extrapolation of matrix and fiber strength to fiber volume fractions of 0 and 1. At low fiber volume fraction, a drastic decrease in tensile strength is usually observed. This has been explained with dilution of the matrix and introduction of flaws at the fiber ends where high stress concentrations occur, causing the bond between fiber and matrix to break [44]. At high fiber volume fraction, the matrix is sufficiently restrained and the stress is more evenly distributed. This results in the reinforcement effect outweighing the dilution effect [6, 44]. As the volume fraction of fibers is increased to a higher level, the tensile properties gradually improve to give a strength higher than that of the matrix. The corresponding fiber volume fraction in which the strength properties of the composite cease to decline with fiber addition, and begin to again to improve, is known as the optimum or critical fiber volume fraction,  $V_{crit}$  [6, 44]. For short-fiber composites to perform well during service, the matrix must be loaded with fibers beyond this critical value [6]. At very high fiber volume fraction, the strength again decreases due to insufficient matrix material [6, 44].

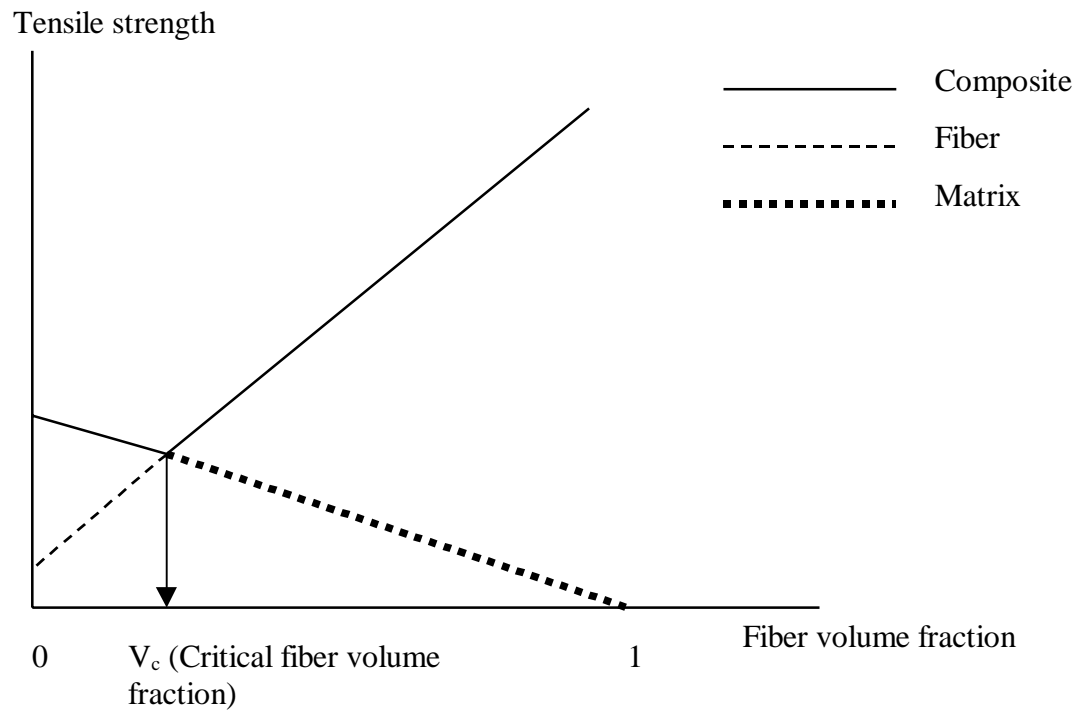


Figure 2.6 Typical relationship between tensile strength and fiber volume fraction for short fiber-reinforced composites.

Thomas *et al.* (1997) [48] investigated the mechanical behavior of pineapple leaf fiber-reinforced polyester composites as a function of fiber loading, fiber length, and fiber surface modification. Tensile strength and modulus were found to increase linearly with fiber content. The impact strength was also found to follow the same trend. But in the case of flexural strength, there was a leveling off beyond 30 % fiber content. A significant improvement in the mechanical properties was observed when treated fibers were used to reinforce the composite.

### **2.3 Nondestructive Analysis of Fiber Dispersion**

The success of reinforcing composites with short fibers depends on a few key requirements such as good and uniform fiber dispersion in the polymer matrix. Variability of fiber dispersion gives rise to differences in properties throughout the material that may lead to composite properties falling short of the true fiber reinforcing potential. Hence, it is important to examine, control and quantify fiber dispersion.

There are several reported techniques that can be adopted to determine fiber dispersion either qualitatively using ultrasonic or film-based radiographic imaging, or quantitatively using computed tomography techniques [11]. These techniques, however, have not been used extensively either because they are relatively slow, expensive or highly subjective. In 1994, Scott (1994) [10, 11] successfully patented a new nondestructive technique that can be used to determine fiber dispersion as well as fiber loading within a composite material quantitatively [10, 11]. This technique is based on real-time

radiographic imaging, and it uses image processing to obtain results instantaneously (10 s). The technique also can be easily automated to analyze multiple samples, and it has been demonstrated to work well with a wide variety of composite systems. Samples in the form of test coupons or finished parts can be used with this technique.

A schematic illustration of the instrument used by Scott (1994) [10, 11] to determine fiber dispersion and fiber loading is shown in Figure 2.7. In this test, at least one test coupon or finished part of known thickness is placed on an X-Y table located directly below the radiation source. Radiation from the source passes through the sample and then enters the image intensifier, which converts the transmitted radiation to a visible pattern of photographic image. This image is captured from the intensifier's output screen by a charged-couple device (CCD) camera. Here, an image signal is generated. The image signal is digitized in a frame buffer, stored and analyzed by the computer. A typical digitized electronic image generally consists of 512 x 512 pixels or 'picture elements'. Each pixel of the image is examined separately by the computer and described by its X and Y co-ordinates plus a digitized gray level that describes its shade in 256 steps between black (0) and white (255).

The computer uses the following equations to determine fiber loading:

$$\mu = - \ln (I / I_o) / t \quad (1)$$

$$\alpha = (\mu_s - \mu_n) / (\mu_g - \mu_n) \quad (2)$$

$$\beta = \alpha / [\alpha(1 - R) + R] \quad (3)$$

where:

$\alpha$  = volume loading ( fiber fraction by volume)

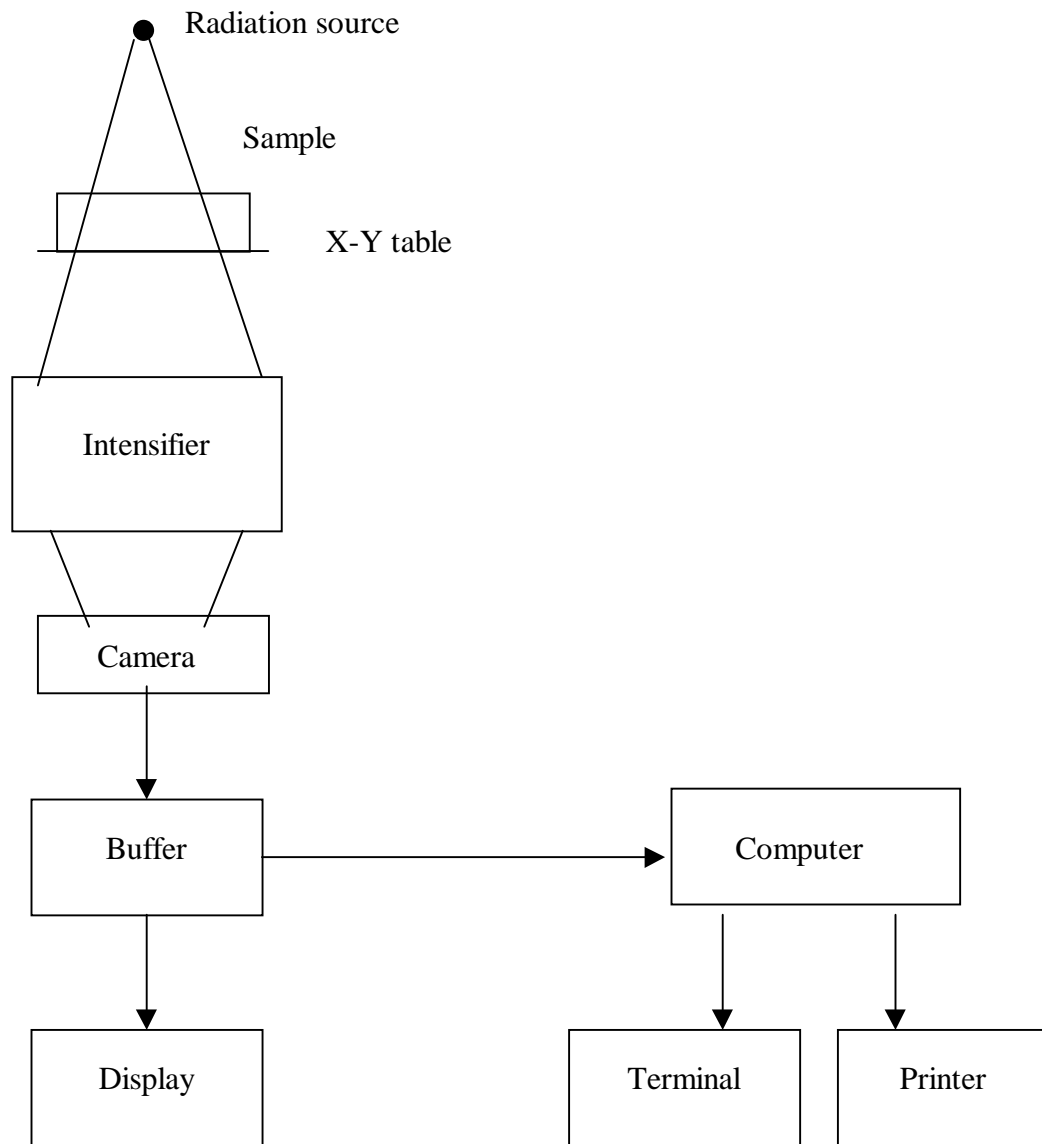


Figure 2.7 Schematic illustration of the instrument used by Scott (1994) [10,11]

$\beta$  = weight loading (fiber fraction by weight)

$t$  = sample thickness

$\mu$  = linear attenuation coefficient ( $\text{cm}^{-1}$ )

$\mu_s$  = calculated linear attenuation coefficient of the sample ( $\text{cm}^{-1}$ )

$\mu_g$  = linear attenuation coefficient of fiber ( $\text{cm}^{-1}$ )

$\mu_n$  = linear attenuation coefficient of matrix ( $\text{cm}^{-1}$ )

$R$  = density ratio ( $\rho$  of composite material /  $\rho$  of fiber)

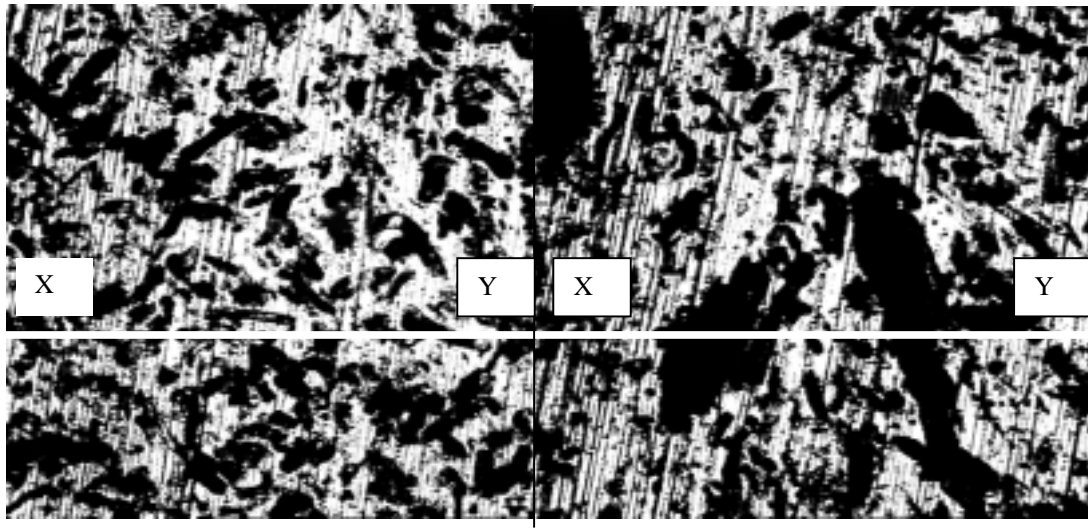
$I$  = average gray level value; and

$I_0$  = reference level (gray level with no sample)

These equations can be applied to the gray level value of each individual test specimen to determine the amount of fiber loading. The average of the fiber loading values can be taken to determine the loading of the sample. In practice, it has been found that this loading value correlates well with the average gray level value of all the pixels that comprise the sample. Therefore, instead of applying equations # (1) – (3) to determine the exact value of fiber loading, the average gray level value of all pixels may be used to represent the value. Fiber loading in a region of interest within an image can then be simply determined from the average gray level of the pixels comprising the region. To determine fiber dispersion, pixels that comprise the image of interest are analyzed to determine both the average and standard deviation of the gray levels. For a sample with substantially uniform thickness, the more evenly distributed the fibers are, the more

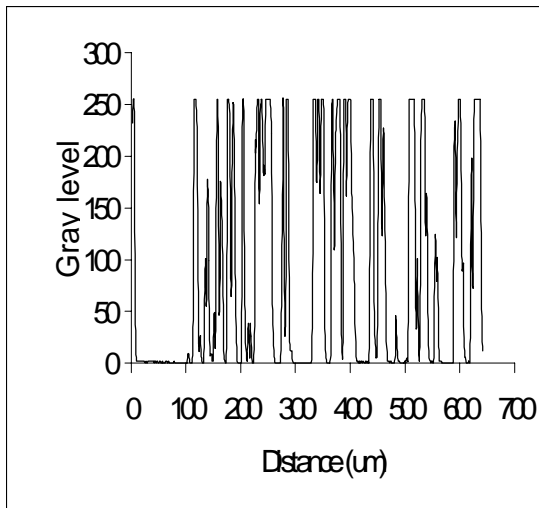
uniformly gray will be the digitized image. The values of 'standard deviation of the gray level' then will be small for samples with uniform fiber dispersion (Figure 2.8)



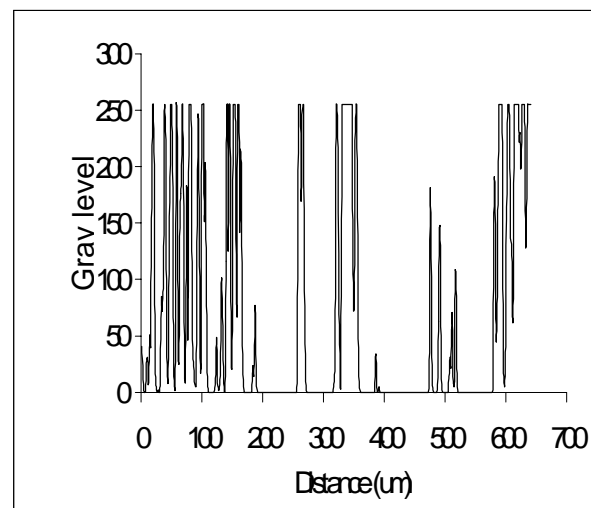


A

B



C



D

Average gray level = 117.502

Average gray level = 64.905

Std. dev. of gray level = 96.186

Std. dev. of gray level = 108.916

Figure 2.8 Images of good (A) and bad (B) fiber dispersion. C and D show variations of gray level from X to Y for image A and B respectively.