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COMPOSITES BASED ON LIGNOCELLULOSIC RAW MATERIALS

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Lignocellulosic natural fibres are an excellent raw materials for production of wide range of composites. Generally, composites based on lignocellulosic particles or fibres can be divided into the following groups:

- conventional panel-type composites like particleboards, fibreboards, insulating boards, etc.,*
- lignocellulosic-mineral composites, which are based on inorganic binders,*
- natural fibres reinforced polymers,*
- nonwoven textile-type composites.*

Some data regarding above mentioned composites were presented during the Fourth ICFPAM, which took place in 1997 in Cairo, Egypt [1]. However, from that time progress in utilization of wider range of lignocellulosic raw materials for composites, and in technologies of their manufacturing have been observed. Moreover, taking into consideration ecological aspects, new gluing systems for conventional lignocellulosic composites were developed – e.g., enzymatic system.

This paper together with paper on Potential of Lignocellulosic Raw Materials gives a general view on present situation and prospects for development of lignocellulosic based composites.

Keywords: composites; lignocellulosic raw materials; natural fibres

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INTRODUCTION

Natural fibers have been used as a reinforcement in composite materials since the beginning of our civilization, when grass and straw or animal hair were used to reinforce mud bricks, also known as adobe [2]. In ancient Egypt, some 3000 years ago, pharaoh mummies were wrapped in linen cloth impregnated with Dead Sea salts, natural resins and honey in order to protect and reinforce them. These were, most likely, the first known man-made material composites in human history [3]. To improve properties of materials, man imitated patterns occurring in nature.

Composite is a material that contains at least two different components, clearly separated one from another and uniformly filling its volume, produced in order of creating particular properties.

Plywood, which is made of thin wood layers, glued together and usually crosswise arranged, can be regarded as the first modern laminar composite, the use of which began at least 100 years ago. However, only the manufacture of glass and carbon fibers on a commercial scale and the discovery of synthetic resins (alkyd, melamine, polyester and epoxy resins – 1924–1952) have resulted in the formation of dynamically developing new industry of composite materials. Increase in the consumption of plastics and consumption-oriented economy have resulted in a change in the approach to renewable raw materials as a reinforcement for polymers, due to both the depletion of resources and increasing ecological hazards.

Ecological balances of natural fiber-containing composites point to their lower environmental noxiousness compared to the reinforcing materials used hitherto. Increase in the production of natural fiber-containing composites makes also an economic chance for the agriculture and rural areas in particular.

Natural fiber reinforced composites can be divided into groups as follows:

- conventional panel-type composites – particleboards, fiberboards, insulation boards based on organic binding materials, including natural binders like lignin, tannin, where the lignocellulosics serve as the main ingredient of a composite,
- lignocellulosic-mineral composites which are based on inorganic binding materials,
- natural fiber reinforced polymers – in which the lignocellulosics serve as reinforcing fillers within a matrix material such as thermoplastics, thermosetting plastics, rubbers,
- nonwoven textile-type composites.

The properties of composites depend on those of individual components and on their interfacial compatibility.

CONVENTIONAL LIGNOCELLULOSIC COMPOSITES – BOARDS

Conventional composites fall into two main categories based on physical configuration of the lignocellulosics: particleboards and fiberboards. Within these categories are low, medium, and high-density classifications. Within the fiberboard category, both wet and dry processes exist. Conventional composites typically use a heat curing adhesive to hold the lignocellulosic component together [4].

Particleboards

The main lignocellulosic raw material used for particle and fiberboard industry is wood, but in many countries other agro-based materials are successfully utilized. Annual plant waste such as flax and hemp shives, jute stalks, bagasse, reed stalks, cotton stalks, grass-like *Miscantus*, vetiver roots, rape straw, oil flax straw, small grain straw, peanut husks, rice husks, grape-vine stalks and palm stalks are cheap and valuable raw materials for lignocellulosic board production. It is worth to add that production technology is similar to the lignocellulosic board production from wood particles. All particleboards are currently made using the dry process, in which air is used to randomize and distribute the particles prior to pressing. The specificity of board production from annual plant waste consists in raw material preparation, including purification and sorting of the material [1].

One of the most important advantages of these boards is the possibility of board production in a wide spectrum of densities from 300–750 kg/m³. Density ranges for individual residue materials are given in Table 1. Main fields of the application of annual plant waste boards are building and furniture-making industries as well as transportation [5].

TABLE 1 The Density Range of Particleboards from Different Annual Plant Refuse [5].

Specific weight (kg/m ³)	Low density		Medium density			
	300	400	500	600	700	800
Flax						
Hemp						
Jute						
Bagasse						
Flax + saw dust						
Rape						

Table 2 displays physical and mechanical properties of boards made of jute stalks, cotton stalks, bagasse, bamboo and peanut husks [6]. The results shown refer to the three-layer boards, 19 mm thick.

The particleboards and fiberboards have found very wide application, especially to building and construction industry (panels, ceiling paneling, partition boards, etc.), transportation, packaging, automobile and railway coach interiors and storage devices.

Fiberboards

There are several differences between fiberboards from particleboards, the most notable of which is physical configuration of disintegrated material. Because lignocellulosics are fibrous by nature, fiberboards exploit their inherent strength to a higher degree than particleboards.

Fiberboards are normally classified by density and can be made by either dry or wet processes. Dry processes are applicable to high density and low density insulation boards as well [4].

Among fiberboards, the most popular, especially in furniture industry is MDF. They are used particularly for those purposes, where particleboards cannot be employed, e.g., for molding of edges, varnishing of surfaces and edges, veneering of surfaces and edges with thin foil, etc. A high rate of MDF production increase occurred in the late 1980's in the whole world and since then it regularly goes up [4].

The production of MDF from fibers of annual plants started in 1985, when the Sunds Defibrator company in Thailand developed the process of MDF manufacture from bagasse. Next factories based on bagasse were built in Pakistan, China and India. There is growing interest in using annual plants to make boards because annual plants are renewed each year, and produce three times more cellulose per year than ring-growth in tree [7].

Properties of MDF based on natural fibers are shown in Table 3.

TABLE 2 Physical and Mechanical Properties of Particleboards Made of Annual Plant Waste [6]

Properties	Unit	Bagasse	Cotton stalks	Jute	Reed	Bamboo	Peanut husks
Density	kg/m ³	600	600	580	730	625	750
Modulus of rupture	MPa	20–21	16–17	15–16	22–23	18–19	17–18
Internal bond strength	MPa	0.4–0.5	0.4–0.5	0.5–0.7	0.4–0.5	0.6–0.7	0.5–0.6
Swelling thickness after 24 h	%	6–7	– 6	12–15	6–7	6–8	–

TABLE 3 Physical and Mechanical Properties of MDF Based on Bast Fibers [8]

Property	Flax	Hemp	Kenaf	Cotton	Straw	Bamboo	Reed	Bagasse
Density kg/m ³	785	880	817	—	—	—	—	—
Board thickness mm	—	—	—	18	9	9	9	9
Internal bond strength [IBS] MPa	0.55	0.21–0.59	0.75	0.5–0.6	0.6–0.65	0.5	0.45–0.55	0.60–0.65
Modulus of rupture [MOR] MPa	29.0–35.4	7.8–20.8	19.3	30–40	32–36	25	26–30	30–35
Water absorption %	—	—	—	14–17	22–26	20	16–20	12

New Systems for Binding Conventional Lignocellulosic Composites

Recently, research was carried on the possibility of using biotic factors for the activation of natural bonding forces present in lignocellulosic materials in order to reduce or eliminate the use of synthetic binders. Among the methods of activation, the enzymatic treatment seems to be particularly promising. The concept of enzyme-catalysed bonding of lignocellulosic materials is based on the reactivity of functional groups of the aromatic compounds, such as lignin, which are generated by oxidoreductases (laccase, peroxidase) [9,10].

The idea of bonding wood fibres via laccase-catalysed activation of the intercellular lamella was first conceived by Körner and the relevant process was described in a patent application by Kharazipour *et al.* [11,12].

The laccase enzyme can be used for bonding lignocellulosic materials by oxidation of phenol compounds, in accordance with the reaction equation given in Figure 1.

In the course of an enzyme-initiated recombination of radicals, the lignin monomers undergo polymerization to form a three-dimensional conjugated aromatic polymer.

Bonding of lignocellulosic materials can be performed either by means of a one-component system, which activates lignin contained in a raw material or by two-component system in which enzymatically activated technical lignins are mixed with the raw material, similar to conventional binding agent system.

Currently, at the Institute of Natural Fibres the studies are carried out on the possibility of using for that purpose two different bacterial laccase from *Aspergillus sp.*, with Novo Nordisk [13,14].

The experiments by the two-component system included:

- Development of bonding agents based on enzyme-activated technical lignin: pH 4,5, temperature 20°C, time 1 hr and consumption of Laccase

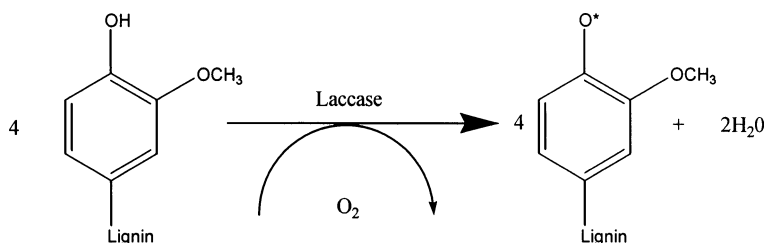


FIGURE 1 Mechanism of lignin activation by laccase enzyme.

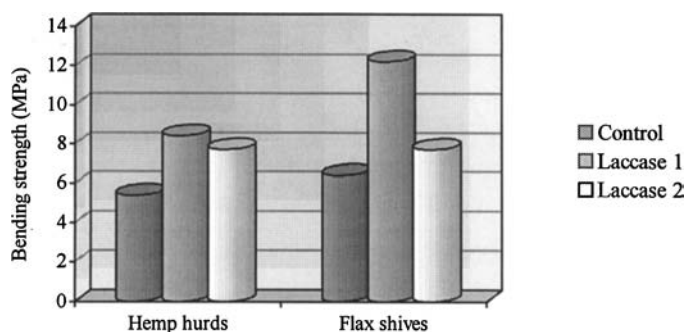


FIGURE 2 The influence of laccase type on the bonding strength of hemp and flax particleboards.

1-3LACU/g d.s., Laccase 2-6LAMU/g d.s. (LACU and LAMU – the activity of Laccase 1 and 2)

- Combination of the obtained bonding agents with the raw materials (hemp, flax) into composite boards (temperature 140°C, pressure 2 MPa, time 20 min.)

Results are presented in the Figure 2.

Considerable increase in bending strength of the boards was achieved by the activation of technical lignins with Laccase 1, whereas the performance of lignins activated by Laccase 2 was lower, particularly in the case of flax shives.

The advantage of replacing synthetic binding agents with enzymatic system of bonding lies in environmental protection and economic production. Clear advantage of the process of manufacturing natural binding agents, in comparison with synthetic resins, is the absence of emission of harmful substances from the boards, both on the site of their production and on that of their prolonged use.

This system of bonding is developing now for both fibreboards and particleboards by several research centres. This system is not commercialized yet, but results of conducted research give a promising future for industrial application.

LIGNOCELLULOSIC-MINERAL COMPOSITES

Inorganic-bonded wood composites have a long history. They can be divided as follows:

- cement bonded composites (magnesia cement and Portland cement),
- gypsum bonded composites,

- other mineral adhesive bonded composites (sodium glass, lime),
- organic resin bonded composites based on lignocellulosic and mineral particles,
- paper and another lignocellulosic material-covered gypsum boards.

Cement bonded lignocellulosic composites are building materials suitable for exterior and interior use. They are more resistant to fire, possess very good sound attenuation properties and can be made resistant to rotting after a special treatment of lignocellulosic material with fungicides.

Lignocellulosic fibers are frequently employed as a substitute for asbestos. One of the areas of their application were asbestos-cement boards, which in the past were commonly used for roofing. Paper waste and short fibers can be used as substitutes for asbestos. [15].

The process of manufacturing gypsum bonded composites could utilize wood waste and other lignocellulosic waste as well as “chemical” gypsum obtained as a result of chemical reaction proceeding during desulfurization of combustion gas [16]. Gypsum-bonded composites are widely used in building industry, however, they are not resistant to water [17,18].

An example of lignocellulosic-mineral composite bonded with a polymer (typical of particleboard adhesives) is a three-layer incombustible particleboard VERCOR[®], developed by the INF [19,20]. These particleboards are characterized by the presence of lignocellulosic particles in the core, whereas, their faces are made of vermiculite.

NATURAL FIBER REINFORCED COMPOSITES

The interest in natural fiber reinforced polymer composite materials is rapidly growing both in terms of industrial applications and fundamental research. They are renewable, cheap, completely or partially recyclable and biodegradable. These fibers are incorporated into a matrix material such as thermosetting plastics, thermoplastics or rubber. The significant weight savings and the ease and low cost of the raw constituent materials make this composite an attractive alternative material to glass and carbon fibers.

The combination of a plastic matrix and reinforcing fibers give rise to composites having the best properties of each component. Since the plastics are soft, flexible and lightweight compared to fibers, their combination provides a high strength to weight ratio to the resulting composite.

In natural fiber composite materials natural fibers are used as reinforced elements. The most commonly used natural fibers and matrices for natural fiber composites are shown schematically in Figure 3. The properties of composites depend on those of the individual components and on their

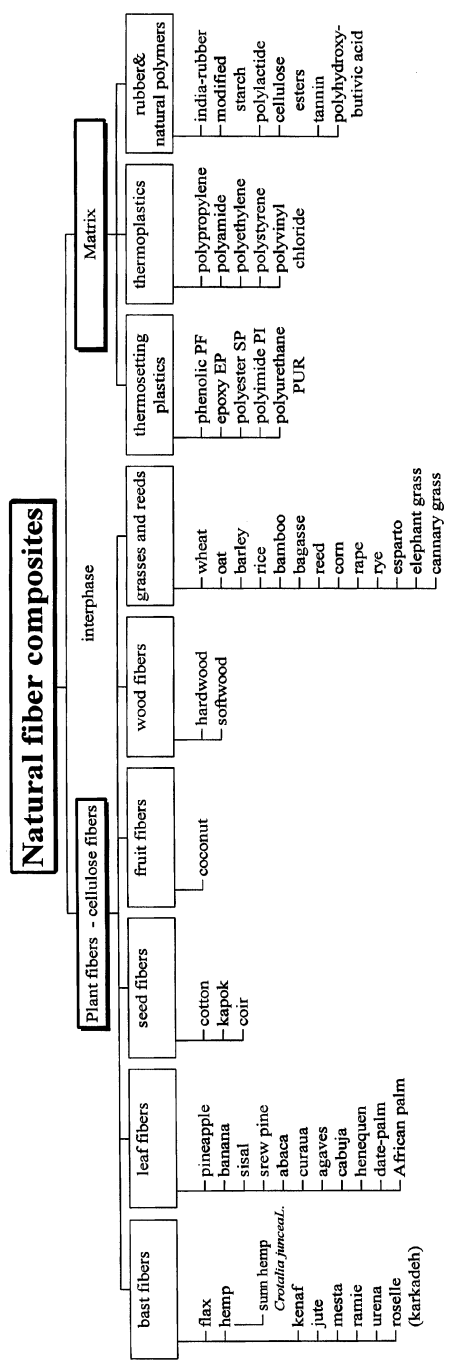


FIGURE 3 Constituents of natural fibre reinforced polymeric composite materials.

interfacial compatibility. The stress transfer at the interface to different phases is determined by the degree of adhesion [21].

A strong adhesion at the interface is needed for an effective transfer of stress and load distribution throughout the interface [22]. This situation calls for the development of strategies for the modification of cellulosic surfaces, thereby in composites a coating is applied which generally consists of coupling agents or compatibilizing agents which introduce chemical bonds between the fiber and matrix [22].

Advantages of Composites Containing Natural Vegetable Fibers

- They are environmentally friendly materials at the stage of production, processing and waste.
- Environmentally friendly production of natural vegetable fibers – annual renewability and lower energy inputs in production per unit.
- Commonly known processing methods.
- Properties comparable to those of materials reinforced with glass fiber.
- Better elasticity of polymer composites reinforced with natural fibers, especially when modified with crushed fibers, embroidered and 3-D weaved fibers.
- They display acoustic insulation and absorb vibrations and large quantities of energy when subjected to destruction.
- Lower density of polymer composites reinforced with natural fiber than those reinforced with glass fiber.
- The price of polymer composites reinforced with natural fibers is from two to three times lower than that of polymers reinforced with glass fiber.
- Natural vegetable fibers can be applied to the reinforcement of the natural polymers such as starch, lignin, hemicellulose and India-rubber and the material obtained in this way is 100% biodegradable.
- Reaction of fire of composites based on lignocellulosic fibres is much more beneficial comparing to polymers – significant reduction of heat release rate and emission of CO and CO₂ [23,24].

Limitations of Vegetable Fiber Applications to Composites

- Quality production efficiency depends on natural conditions.
- Non-homogeneity of natural fibrous raw materials, associated with cultivars and growing, harvesting and primary processing conditions.
- Preparation of fiber is time and labor consuming.
- Changes in properties and dimensions of polymer composites reinforced with natural fibers depend on inherent physical properties of the latter.
- Large areas for cultivation, if big amounts of raw materials are required.

- Low density of natural vegetable fibers can be disadvantageous in processing due to the necessity of pressure application (the fiber tends to emerge on the surface).
- Knowledge of the best properties used for composites and the best modification methods is still not sufficient.
- Weak bonding of natural fibers to polymers.

Fiber Modification

Reinforcing fibers can be modified by physical and chemical methods. Chemical and physical modifications of natural fibers are usually performed to correct for the deficiencies (described above) of these materials, especially to impart bonding and adhesion, dimensional stability and thermoplasticity. Surface modification of natural fibers can be used to optimize properties of the interface.

Physical methods involve surface fibrillation, electric discharge (corona, cold plasma), etc. Cold plasma is already a very effective method to modify the surface of natural polymers without changing their bulk properties. This method has been used for increasing adhesion and compatibility between two polymers [25–27].

Physical treatments change structural and surface properties of the fiber and thereby influence the mechanical bonding with the matrix.

There some treatment methods of partially physical and chemical in nature, among which mercerization [3,28,29] and liquid ammonia treatment [3,30] should be mentioned.

Mercerization leads to the increase in the amount of amorphous cellulose at the expense of crystalline cellulose. The important modification expected here is the removal of hydrogen bonding in the network structure. As a result of sodium hydroxide penetration into crystalline regions of parent cellulose (cellulose I), alkali cellulose is formed. Then, after washing out unreacted NaOH, the formation of regenerated cellulose (cellulose II) takes place.

The treatment with **liquid ammonia** has been used mainly for cotton. Its development occurred since the late 1960s as an alternative to mercerization. Liquid ammonia, due to its low viscosity and surface tension, penetrates quickly the interior of cellulose fibers, forming a complex compound after the rupture of hydrogen bonds. The molecule of ammonia is relatively small and is able to increase distances between cellulose chains and penetrate crystalline regions.

The original crystal structure of cellulose I changes to cellulose III after liquid ammonia treatment, and at the next stage, cellulose III changes to cellulose I again after hot water treatment [30]. Liquid ammonia treatment of natural fibers results in their deconvolution and smoothing their

surfaces. At the same time, fiber cross-section becomes round and lumens decrease.

Conventional chemical modification is usually carried out through typical **esterification** and **etherifications** reactions of lignocellulose hydroxyl groups.

Esterification usually involves the reactions with organic acids or anhydrides. Many esters are possible depending on the nature of organic acid (anhydride) used in the reaction. Esters containing from 1 to 4 carbon atoms are formate, acetate, propionate and butyrate; laurate has 12 carbon atoms and stearate 18 carbon atoms. Maleate and fumarate are esters of dicarboxylic acids containing double bonds in the carbon chain. Double bond-containing esters with longer chains confer thermoplasticity on the lignocellulosic materials [31].

The most popular esterification method is **acetylation**, which has already been developed in commercial scale, first in the United States [32], than in Russia [33]. Within the UK, BP chemicals performed an economic appraisal of the process and built a small pilot plant to modify fibres, but have now discontinued this work [34]. Within Europe several groups are working towards a scale up of the process [35–37].

In Sweden, a continuous process of acetylation has been recently developed. The pilot plant for wood fibre or particles acetylation of capacity 500 kg/h is jointly owned by A-Cell and GEA Evaporation Technology AB, and located in Kvarntorp [38].

Substitution of hydrophilic hydroxyl groups in lignocellulose by hydrophobic radicals alters properties of fibers, especially equilibrium moisture content (EMC), depending of degree of substitution. Modification alters polarization of fibers and make them more compatible to non-polar matrix.

Organosilanes are the main group of coupling agents for glass fiber-reinforced polymers. **Silanization** of natural fibers minimizes disadvantages effect of moisture on properties of composites and at the same time increases adhesion between fibers and polymer matrix which results in upgrading composite strength. The effectiveness of the modification depends, among others, on the type of silane used, its concentration in solution, temperature and time of fiber silanization, moisture content and volume contribution of fibers to composite [39–41].

The surface of natural fibers can be modified by **grafting copolymerization**. Grafting efficiency, grafting proportion and grafting frequency determine the degree of compatibility of cellulose fibers with a polymer matrix. The grafting parameters are influenced by the type and concentration of initiator, by the monomer to be grafted and the reaction conditions [22]. the polymerization reaction is initiated at the surface of the fibers by incorporation of peroxides or oxidation – reduction agents, or treatment with gamma radiation or cold plasmas.

The cellulose is treated with an aqueous solution containing selected ions and is exposed to a high-energy radiation. Then, cellulose molecules crack and radicals are formed [41]. Afterwards, the radical sites of the cellulose are treated with a suitable solution (compatible with the polymer matrix), for example vinyl monomer [42], acrylonitrile [43], methyl methacrylate [44], polystyrene [45]. The resulting copolymer possesses properties characteristic of both fibrous cellulose and grafted polymer [41].

The lignin content in the fiber is a governing factor on the extent of acrylonitrile grafting. The accessibility of the monomer molecules to the active centers of cellulose is easier in water than in an organic solvent. It was found that without the presence of lignin, the grafting reaction could favorably proceed between cellulose and acrylonitrile.

The treatment of cellulose fibers with hot polypropylene-maleic anhydride (MAPP) copolymers provides covalent bonds across the interface [46].

There are two ways of obtaining biocomposites from natural fibres and polymer. In the first one, pretreated fibres with maleated polymer are reinforced with desired polymer matrix. In the second method, fibres, polymer and maleic anhydride with addition of peroxide initiator in one step processing are reactively extruded and then proceed with molding or injection to obtain a final composite.

Manufacture of Composites

Natural fiber-containing composites can be manufactured by almost all production techniques. Resins used for the manufacture of composites can be hardened without using elevated temperatures and products can be obtained by laying layers of mats of fabrics made of reinforcing fibers on a simple one-sided mold, followed by saturation with a resin composition, performed e.g. by brushing. Such a simple, manual method of product formation, which consist in contacting starting materials with uncomplicated one-sided mold, without applying high temperature and pressure, is called the contact method or hand lay-up method. This is the most popular method of manufacturing products made of polymer-containing composites. The simplicity of this method enables fast start of the production of new products at low cost. It is enough to make the model of a product designed. The advantage of the method is the absence of limitations concerning dimensions of a product and the possibility of manufacturing products having quite a complicated shape. The contact method can be used for the manufacture of a variety of products, e.g. cases for laboratory and electronic equipment, machine housing, elements of car body and whole body of a car, sail boats and fish cutters, swimming pools, chemical apparatus, tanks and silos.

The contact method imposes, however, some limitations on the quality and construction of products. Only one surface of product manufactured by this method is smooth. Thickness of product walls, formed by hand and consisting of many layers is not uniform. It should be kept in mind, that the quality of a product manufactured by the contact method depends, to a considerable extent, on well-designed production technology, complying with procedures and operation contained therein as well as on self-observation, craftsman's skills and reliability of a worker involved in the production.

A variant of the contact method is the spray method. In the latter method filament fibers are used, instead of reinforcing fibers in the form of mats and fabrics. The filament fibers are cut with the help of special devices and sprayed on a mold together with a resin composition covering the mold with a kind of a loose scum. Then the latter is pressed down towards the mold by means of brushes and rollers, i.e. in the way similar to that used in the contact method. The spray technique enables to obtain fiber-reinforced composites in a cheaper way and to mechanize some stages of manufacturing process as well as it forces to set the manufacturing process in order.

The manufacture of goods made of chemosetting resins is often vacuum-aided and this requires an air-tight mold composed of two parts. By forming composites in the vacuum-aided way it is possible to gain such advantages as better resin penetration and better product deaeration, higher content of reinforcing fibers, smoother internal surface of a product, air-tight sealing of the process.

For the manufacture of closed-shape products the method of press molding with flexible punch is applied as well. A protective helmet or head-piece can be molded by using a punch made of e.g. polyurethane, flexibility of which enables to press the composite to the walls of a matrix.

Another, widely used manufacturing method of goods made of polymer composites is so-called **RTM** (Resin Transfer Molding). In this method a resin composition is forced under a slight overpressure into a tight mold which was loaded with reinforcing fibers. Sometimes, in addition to the pressure necessary to force resin into mold, a vacuum is employed in order to close the mold and to increase penetration of the reinforcement. The two-part molds used in the RTM method have to be more rigid and made with greater accuracy than those used when applying vacuum only and this fact enables to obtain better quality and repeatability of products. The RTM method is more effective and it makes possible to manufacture composites of higher quality and better repeatability than the contact method. In the former method, the compositions of resin can be, to a considerably larger extent, modified by adding fillers.

Of particular importance to the manufacture of composites is the **pultrusion method** [47].

Pultrusion is a manufacturing process for producing continuous lengths of reinforced plastic structural shapes with constant cross-sections. Raw materials are a liquid resin mixture (containing resin, fillers and specialized additives) and flexible textile reinforcing fibers. The process involves pulling these raw materials (rather than pushing, as is the case in extrusion) through a heated steel forming die using a continuous pulling device. The reinforcement materials are in continuous forms such as rolls of fiber mat and natural fiber. As the reinforcements are saturated with the resin mixture ("wet-out") in the resin bath and pulled through the die, the gelation, or hardening, of the resin is initiated by the heat from the die and a rigid, cured profile is formed that corresponds to the shape of the die [48] (Figure 4).

Products manufactured by the above method are characterized by a high content of reinforcing fibers (of order of 70% and in some special products even as much as 90%) and the fibers are orderly laid out. The strength of the products is very high, oriented and programmable. The pultrusion method enables to manufacture bars and sections as well. Fibers are pulled through a tank filled with a resin composition or melted polymer and then they pass through forming dies which serve also for resin excess removal as well as through a heating zone in which hardening occurs (in the case of thermoplastics a cooling zone is applied).

In the method of **filament winding** a bundle of filament fibers is pulled through binder-containing tank and then wound round a rotating core (the role of which is to give shape to a product). By appropriate programming of the movements of the tank and the core on a special device (a winder), a desired arrangement of reinforcing fibers in the product can be achieved. This technique makes it possible to manufacture pipes, tanks and other products in the form of solids of revolution. By using special fibers and resins, elements of rocket launchers and ballistic missiles can be produced by the filament winding method. The last two of the discussed methods are

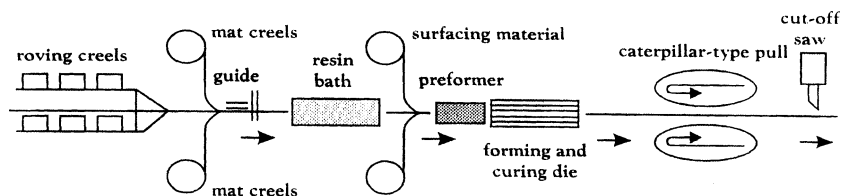


FIGURE 4 Schematic diagram of pultrusion process and reciprocating pulling system [47].

characterized by very high effectiveness due to high mechanization of the processes of saturating and forming.

The above review points to a rich variety of manufacturing techniques of polymer composites containing chemosetting resins.

The choice of thermoplastics which can make matrices for natural fiber-reinforced composites is limited, because above 230°C a fast deterioration of fiber strength occurs. For this reason thermoplastics which can be processed below that temperature are applied. Composites based upon a thermoplastic matrix are manufactured, among other, by press molding method. Moreover, more complex methods are used to make products known under acronyms **SMC** (Sheet Molding Compound) and **BMC** (Bulk Molding Compound). While in the former case the molding compound is in the form of sheets, in the latter it makes a shapeless mass or loose granulated product. Properties of SMC and BMC products can be modified by using different kinds and combinations of resins and reinforcing fibers, hardeners, fillers and upgrading additives. These composites have found application to automotive industry, where prototype bumper, elements of truck driver's cabs, etc., are produced by using flax fibers and polyester resin.

Bulk molding compound make also suitable materials for the manufacture of products of smaller dimensions and lower strength requirements, such as structural elements and housings of office machines, elements of tape recorders and video recorders, circuit-breakers, controllers, household equipment, street light housings, etc.

Sheet molding compounds can be applied to the production of bumpers and body elements, particularly for tractors and vehicles manufactured in limited series (trucks, delivery vans, special cars). They have found application also to railway and air transportation (window frames, partition walls, passenger compartment ceilings, luggage racks, etc. Their other applications include benches for parks, seats for amphitheaters and stadiums, bill-posts, traffic limiting elements such as barriers, road guards.

NONWOVEN TEXTILE-TYPE COMPOSITES

Nonwovens technologies, which appeared in the 1940s, were later developing with different dynamics in various countries. At first these new types of textile products were made on basis of low-grade materials and waste of natural textile raw materials, mostly cotton. Also in the USA, where this new branch of textile industry was started and was developing dynamically, it was mainly regarded as a possibility for utilization of less valuable and waste fibers. However, already in the second half of 1950s, with the appearance of new fibers, the technology of nonwovens was further improved and

developed, particularly as concerns bonded nonwovens based on valuable chemical fibers and synthetic binding agents, facilitating the manufacture of better and more useful products for technical application as well as for clothing and household use.

The application of nonwovens is ranging widely from furniture to the geo- and chemotextiles. The latter are used for insulation and reinforcement of earth structures such as landfills, slopes and embankments. Although they are primarily manufactured from synthetic fibers, the research is conducted on the utilization of natural ones. For instance geotextiles contain a special mineral fraction that, when in contact with water, becomes waterproof and do not allow water to penetrate through the nonwovens. This is of particular importance to the insulation of landfills which, when become closed, can undergo an easier reclamation due to slow decomposition of lignocellulosic skeleton of nonwovens.

An example of a special utilization of nonwovens can be geotextiles for the reinforcement earth structures by using grass mats. The grass seed mat (sometimes including flower seeds) can be produced from rettery waste, particularly from hemp after its defibration to the state resembling the structure of cotton wool. After defibration, the waste is pressed into felt of 4–5 mm in thickness. This felt constitutes a cover for the base consisting of jute fabric onto which a mixture of fertilizer, peat and grass seeds are placed during the production process. All layers are put together by needling on a stitcher. In this way a grass seed mat is produced. It is 220 cm wide and 6 mm thick and contains everything that is necessary for grass growth. The mat is very simple in using; it is just enough to place it on a desired area, adjust to fit, level it up and irrigate. The germination of seeds and root development in favorable conditions take place within 8–12 days, while the complete decorative effect on the slope is obtained in 2–4 weeks after germination.

The lawn of natural grass seed mat can be used for consolidating of slopes, reinforcement of road and railroad embankments, consolidation of banks of water reservoirs and rivers, for decorative gardens and sports fields, as well as for interior decoration and verdure establishment on hardened surfaces between buildings. Most frequently applied methods of slope surface consolidation include placing openwork concrete slabs on the slope surface and sowing the open areas with grass or planting with perennials. Sometimes weeds are also allowed to grow in the openwork of the concrete slabs.

The surface of the newly formed slope can be mulched with bark, cut straw, sawdust or their mixture with peat, and the mulched surface is covered with a fine net until it becomes naturally strong.

Another method consists in making fastened revetments or reinforcing the slope with strips to form horizontal thresholds in the form of steps where the rainwater easily penetrates to the ground without causing

erosion. Such thresholds can be also formed with the help of stones, and the horizontal surfaces are planted with perennial plants. This method gives particularly valuable decorative effects and it is recommended in verdure terrain for arranging ornamental slopes.

However, most frequently on the surface of newly formed slopes, sod is placed being taken from meadows or grown in another place on fertile soil. This method is expensive and complicated in practice. Transportable sod can be also prepared on a thin layer of sphagnum peat. Using this method, sod is placed on the slope in the form of a skew chessboard design.

However, so far, the least known method of protecting newly formed shaped against erosion is spreading a textile lawn mat on the slope. Such mat plays originally a protective role by supplying a cover, and after the germination of grass and plant seeds, it reinforces the root system.

GENERAL CONCLUSIONS

1. Fiber plants such as flax, hemp, ramie, kenaf, jute, abaca, sisal, coir, curaua are seen as promising lignocellulosic raw materials for the manufacture of natural fiber reinforced composites for different applications.
2. The natural fiber-containing composites include a wide range of products for different applications ranging from construction and insulation panels made of wood pieces, particles and fibers, through special textiles (geo-textiles and non-woven textiles) to plastic products based on polymers filled with natural fibers or lignocellulosic particles.
3. Their great advantage is biodegradability and the fact that when combined with polymers or natural resins they are as strong as steel yet of lower density. Such composites may be used for vehicles, building elements, furniture, machine constructions, insulating materials, gardening and agriculture equipment, tropical housing and even grape holding structures.
4. In conventional lignocellulosic board composites a new bonding systems based on enzymatic activation of lignin will play an advanced role in the future, replacing synthetic non-ecological resins.
5. Recycling of natural fiber-reinforced composites is relatively easy and convenient. This fact makes one of the most important factors in forecasting the future growth of production and consumption of these materials.
6. When preparation of natural fibers from the point of view of their homogeneity and quality would be improved, a new big potential market for natural fibers can emerge.

REFERENCES

- [1] Kozłowski, R. & Helwig, M. (1998). Lignocellulosic Polymer Composites. Fourth International Conference on Frontiers of Polymers and Advanced Materials, Cairo, Egypt, 4–9 January 1997, Prasad, P. N. *et al.* Ed.: Science and Technology of Polymers and Advanced Materials, Plenum Press, New York, 679–698.
- [2] Cook, D. J. (1980). International Fibrous Concrete. C180:99.
- [3] Kozłowski, R. & Władysław-Przybylak, M. Natural Fiber Reinforced Composites. General Applications. *Chapter 15 in Natural Fibers, Polymers and Composites—Recent Advances*, Wallenberger, F. T. & Kandachar, P. V. (Eds.), Kluwer Academic Publishers, Boston, Dordrecht, London (in press).
- [4] English, B., Chow, P., & Bajwa, D. S. (1997). Processing into Composites. In *Paper and Composites from Agro-Based Resources*, Roger M Rowell *et al.* (Eds.), CRC Press, Inc. Lewis Publishers.
- [5] Kozłowski, R., Mieleniak, B., & Przepiera, A. (1994). Plant Residues as Raw Materials for Particleboards. Proceedings of the 28th International Particleboard/Composite Materials Symposium. Washington State University, Pullman, WA, USA, 181–197.
- [6] Niedermaier Information Materials of Siempelkamp Company.
- [7] Kozłowski, R., Mieleniak, B., & Przepiera, A. (1997). Hemp Straw and Hemp Shives as a Raw Material for the Production of Particleboards and Insulating Boards. Proceedings of the Commercial and Industrial Hemp Symposium: Vancouver, Canada.
- [8] Lloyd, E. H. Bast Fibres Application for Composites. Proceedings of 30th Particleboard/Composite Materials Symposium 1996: Washington State University, Pullman, WA, USA.
- [9] Kharazipour, A. *et al.* (1991). Ensymgebundene Holzwerkstoffe auf der Basis von Lignin und Phenoloxidasen. *Adhasion Jg* 35 H.5: 30, 33–34, 36.
- [10] Yaropolov, A. I., Skorobogatko, O. V., Vartanov, S. S., & Varfolomeyev, S. D. (1994). Laccase-Properties, Catalytic Mechanism and Applicability. *Applied Biochemistry and Biotechnology*, 49, 257–280.
- [11] Körner, S. (1990). Verfahren zur Stofflichen Modifikation des Rohholzes für die Holzwerkstoffherstellung. *Dissertation*, Technischen Universität Dresden.
- [12] Kharazipour, A., Hüttermann, A., Kühne, G., & Rong, M. (1993). Verfahren zum Verkleben von Holzfragmenten und nach dem Verfahren Hergestellte Formkörper. *German Patent DE 4305411*.
- [13] Kozłowski, R., Batog, J., Przepiera, A., & Kinastowski, S. (2001). Lignocellulosic Composite Materials Bonded by Enzymatic System. Proceedings of the 8th International Conference on Biotechnology in the Pulp and Paper Industry, Helsinki, Finland, 257–258.
- [14] Kozłowski, R., Batog, J., & Przepiera, A. (2003). Lignocellulosic Composite Materials Bound by Natural Adhesives. Proceeding of the 1st European Conference on Wood Modification, Ghent, Belgium, 411–414.
- [15] Mankowski, J., Rynduch, W., & Baraniecki, P. Substytucja azbestu odpadowym włóknem lniwym w produkcji pokryć dachowych. (Asbestos Substitution by Waste Flax Fibers in Roof Coverings Production), Non-textile Applications of Flax, Natural Fibers Poznań Poland: 1994 special edition.
- [16] Lawniczak, M., Kozłowski, R., & Helwig, M. (1995). Effect of Accelerators on Properties of Semi-Dry Process Gypsum Particleboards. *Proceedings of the 4th International Inorganic-Bonded Wood and Fiber Composite Materials Conference 1994*, Spokane, USA, Moslemi, A. A. (Ed.), Inorganic-Bonded Wood and Fiber Composite Materials, Vol. 4, 75–82.

- [17] Lempfer, K. H. (1995). Technology Trends in Gypsum Fiberboard. *Proceedings of the 4th International Inorganic-Bonded Wood and Fiber Composite Materials Conference 1994*, Spokane, USA, Moslemi, A. A. (Ed.), Inorganic-Bonded Wood and Fiber Composite Materials, Vol. 4, 41–46.
- [18] Englert, M. H., Miller, D. P., & Lynn, M. R. (1995). Properties of Gypsum Fiberboard Made by the USG Porcess. *Proceedings of the 4th International Inorganic-Bonded Wood and Fiber Composite Materials Conference 1994*, Spokane, USA, Moslemi, A. A. (Ed.), Inorganic-Bonded Wood and Fiber Composite Materials, Vol. 4, 52–58.
- [19] Kozłowski, R., Helwig, M., & Przepiera, A. (1995). Influence of Adhesives on the Properties of Composite Materials Based on Lignocellulosic Particles and Some Mineral Compounds. *Natural Fibers – Włókna Naturalne*, Poznań, Poland, Vol. XXXIX, 169–176.
- [20] Kozłowski, R., Mieleniak, B., Przepiera, A., & Helwig, M. (1996). Composite, Non-Flammable and Non-Toxic Particleboards Based on Lignocellulosic and Mineral Particles. *Proceedings of the 4th European Regional Workshop on Flax*, Rouen, France.
- [21] Garbarczyk, J., Paukszta, D., & Borysiak, S. (2002). Polymorphism of Isotactic Polypropylene in Presence of Additives, in Blends and in Composites. *Journal of Macromolecular Science, Part B-Physics*, B41 (4–6), 1267–1278.
- [22] Thomas, S. (2002). Cellulose Fiber Reinforced Composites: New Challenges and Opportunities. *4th International Wood and Natural Fibre Composites Symposium*, Kassel/Germany, April 10–11.
- [23] Helwig, M. & Paukszta, D. (2000). Flammability of Composite Based on Polypropylene and Flax Fibres. *Molecular Crystals and Liquid Crystals*, Gordon & Breach Science Publishers: Philadelphia, USA, Vol. 354, 373–380.
- [24] Helwig, M., Paukszta, D., Garbarczyk, J., Borysiak, S. Composites Based on Polypropylene and Flax Fibres – A Study of Fire Performance and Some Physical and Mechanical Properties. *Proceedings from the Third Int. Symposium on Natural Polymers and Composites ISNaPol/2000*, 14–17.05.2000, Sao Pedro, Brazil, 520–526.
- [25] Iorio, I., Leone, C., Nele, L., & Tagliaferri, V. (1997). Plasma treatments of polymeric materials and Al alloy for adhesive bonding. *Journal of Materials Processing Technology*, 68, 179–183.
- [26] Petash, W., Räuchle, E., Walker, M., & Elsner, P. (1995). Improvement of the adhesion of low energy polymers by a short time plasma treatment. *Surf. Coat. Technol.*, 74–75, 682–688.
- [27] Tu, X., Young, R. A., & Denes, F. (1994). Improvement of Bonding Between Cellulose and Polypropylene by Plasma Treatment. *Cellulose*, 1, 87–106.
- [28] Bledzki, A., Gassan, J., & Lucka, M. (2000). (in Polish) Renesans tworzyw sztucznych wzmocnionych włóknami naturalnymi. (Natural Fiber – Reinforced Polymers Come Back). *Polimery*, 45(2), 98–108.
- [29] Paukszta, D. (2000). The structure of Modified Natural Fibers Used for the Preparation the Composites with Polypropylene. *SPIE – The International Society for Optical Engineering*, 4240, 38–41.
- [30] Yanai, Y. Non-Resin Shrink-Proof Process, Celtopia. Nisshinbo Industries Inc. Miai Plant, Aichi, Japan (unpublished).
- [31] Young, R. A. (1996). Utilization of Natuaral Fibers: Characterization, Modification and Applications. In: *Lignocellulosic-Plastics Composites*, Lea, A. L. et al. (Eds.), UNESP, Sao Paulo, Brazil.
- [32] Koppers' Acetylated Wood. *New Materials Technical Information* No. (RDW-400), E-106 (1961).
- [33] Otlesnov, Y. & Nikitina, N. (1977). *Latvijas Lauksaimniecības Akademijas Raksti*, 130, 50.

- [34] Sheen, A. D. The preparation of Acetylated Wood Fibre on a Commercial Scale. Pacific Rim Bio-Based Composites Symposium; Chemical Modification of Lignocellulosics, FRI Bulletin, 176, 1–8 (1992).
- [35] Beckers, E. P. J. & Militz, H. (1994). Acetylation of Solid Wood. *Second Pacific Rim-Based Composites Symposium, Vancouver Canada*, 125–134.
- [36] Militz, H., Beckers, E. P. J., & Homan, W. J. (1997). Int. Res. Group Wood Pres., Doc. No. IRG/WP 97-40098.
- [37] Rowell, R. M. Chemical Modification of Natural Fibres to Improve Performance. This proceedings.
- [38] *Wood Modification Thematic Network Newsletter*, Issue 3: April 2002.
- [39] Abdalla, A. & Pickering, K. (2002). The use of silane as a coupling agent for wood fibre composites. Proceedings of the 3rd Asian-Australasian Conference on Composite Materials (ACCM-3), Auckland, New Zealand.
- [40] Abdalla, A., Pickering, K., & MacDonald, A. G. (2002). Mechanical Properties of Thermo-plastic Matrix Composites with Silane-Treated Wood Fibre. *Proceedings of the 6rd International Conference on Flow Processes in Composite Materials*, Auckland, New Zealand.
- [41] Bledzki, A. K. & Gassan, J. (1997). Natural Fiber Reinforced Plastics. In: *Handbook of Engineering Polymeric Materials*, Cheremisinoff, N. P. (Ed.), Marcel Dekker, Inc.
- [42] Kroschwitz, J. I. (1990). *Polymers: Fibers and Textiles*. John Wiley & Sons: New York.
- [43] Mohanty, A. K., Patmaik, S., & Singh, B. C. (1989). *Journal of Applied Polymer Science*, 37, 1171.
- [44] Escamila, G., Trugillo, G. R., Franco, P. J. H., Mendizabal, E., & Puig, J. E. (1970). *Journal of Polymer Science*, 66, 339.
- [45] Maldas, D., Kokta, B. V., & Daneaulf, C. (1989). *Journal of Applied Polymer Science*, 37, 751.
- [46] Han, G. S., Saka, S., & Shiraisi, N. (1991). Composites of wood and polypropylene. *Morphological study of composites by TEM-EDXA*, *Mokuzai Gakkaishi*, 3, 241.
- [47] Young, R. A. (1996). Utilization of Natural Fibers: Characterization, Modification and Applications In: *Lignocellulosic-Plastics Composites*, Lea, A. L. et al. (Eds.), UNESP, Sao Paulo, Brazil.
- [48] www.strongwell.com