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Wood-Polymer Composites

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1. Introduction

Wood has been an essential material for human survival since the primitive state, for its wide abundance, renewable and environmentally benign nature, relative ease of working it, and outstanding mechanical properties. With the development of technology, wood came to be used for shelter, fuel, tools, boats, vehicles, bridges, furniture, engineering materials, weapons, and even raw materials for energy (Li et al., 2011a). Now, wood is widely used in various corners of human life.

Wood possesses porous structures consisting of various cell walls, which are mainly composed of biopolymers, i.e., carbohydrate polymers of cellulose and hemicelluloses and phenolic polymers of lignin. The cellular structure of wood endows it with high strength-to-weight ratio. Because of this, some high-quality wood can be used as structural materials. However, wood components are easy to be degraded by microorganisms, and susceptible to damage by fire (Fuller et al., 1997). Besides, as the most abundant functional group in wood cell walls is the hydroxyl group, the hygroscopic character of these groups can render wood with poor dimensional stability. In other words, wood will shrink as it dries, while conversely swell when it is wetted (Alfered, 1977). All these disadvantages limit the application of wood as high-quality materials.

Furthermore, with the development of society, the consumption of wood has been rapidly increasing year by year. In contrast, however, the production of high-quality wood has been fleetly decreasing. The prominent contradiction has driven researchers to look for alternative low-quality resources for value-added applications. To achieve these goals, suitable technologies are needed to improve low-quality resources (especially specific wood quality) attributes (e.g., mechanical properties, dimensional stability, decay resistance and thermal stability) in order to meet end-use requirements (Wang et al. 2007; Zhang et al. 2006).

As the above unfavorable behaviors of wood are fundamentally ascribed to the presence of numerous hydroxyl groups (reactive sites) in the wood major components and various cell cavities (major paths for moisture movement) within wood (Couturier et al. 1996; Yildiz et al. 2005), blocking these reactive sites or plugging the cavities could not only make the wood more resistant to moisture, but also improve its dimensional stability and physical as well as biodegradation properties. Consequently, treatment of wood to modify its structure and thus improve its physical and mechanical properties, as well as durability, has been carried out via chemical modification, chemical impregnation, compression during heating, and heating at high temperature (Handa et al.1976).

One of the techniques used to improve the properties of wood, which has received considerable attention in the past few decades, is the fabrication of wood-polymer composites (WPC) through in-situ formation of polymer from unsaturated monomers within wood pores (vessels, tracheids, capillaries and ray cells). The resultant polymer can both strength the mechanical properties of wood and defer or stop wood matrix from being attacked by water or microorganisms (Baysal et al. 2007; Hashizume et al. 1988; Yalinkilic et al. 1999). Such multifunctional treatment can help avoid the potential damage of leached preservatives from chemically treated wood on environment (Obanda et al. 2008), strengthen the wood (Soulounganga et al. 2004), avoid dimensional deformation of compressed wood (Ellis et al. 1999) and color change of heat-treated wood (González-Peña et al. 2009). Thus, such treatment became an environmentally friendly wood modification process.

On the consideration of importance of such wood modification and development of researches on wood-polymer composite, this article presents an overall review on preparation, performance and application of wood-polymer composites. Prior to the detailed introductions, general knowledge on wood structure and components are first given for readers clearly understanding the principle of formation of wood-polymer composites.

2. Wood structure and components

Wood is, perhaps, nature's most wonderful gift to humanity, which versatile character providing unlimited scope for property manipulation and product development to suit diverse applications. In today's world, parallel to the technological developments, the number of fields where the raw material of wood is usage increased and it has not lost its importance as a raw material. The reason for the diversity of why the fields where wood is used too much is related to its anatomical structure, physical and mechanical properties and its chemical composition. The properties which make wood important among other raw material sources are its widespread occurrence, stability, hardness, lightness, elasticity and being a renewable source (Şolpan & Güven, 1999a).

2.1 Wood structure
2.1.1 Macro structure of wood
The three dimensional section of a tree trunk (Fig. 1) shows well defined concentric subdivisions. From the outside to the center: periderm, bark, vascular cambium, sapwood, heartwood and the pith. In a tree trunk, all the tissue inside the cambium layer to the center of the tree is xylem or wood. The wood of a tree trunk is mostly dead xylem tissue. The darker, scentral region is called heartwood. The lighter, younger region of wood closer to the cambium is called sapwood. Wood in most species is clearly differentiated into sapwood and heartwood. Softwood (Fig. 2a), which have needle-like or scale-like leaves, belongs to gymnosperms and hardwoods (Fig. 2c), which have broad leaves, belongs to angiosperms. Distinct anatomical differences exist between the gymnosperms (softwoods) and angiosperms (hardwoods) (Peydecastaing, 2008). The softwoods are fairly homogeneous as they consist basically of only two cell types, the longitudinal tracheids and ray cells. Hardwoods, on the other hand, are composed of mixtures of four or five cell forms and are thus relatively heterogeneous in structure (Patrice, et al. 1997; Stubičar, et al. 1998). The different cells that comprise xylem are alive when they are initially produced by the meristematic cambium, but when they actually become functioning water-conducting cells (tracheids and vessels), they lose their cell contents and become hollow, microscopic tubes with lignified walls.
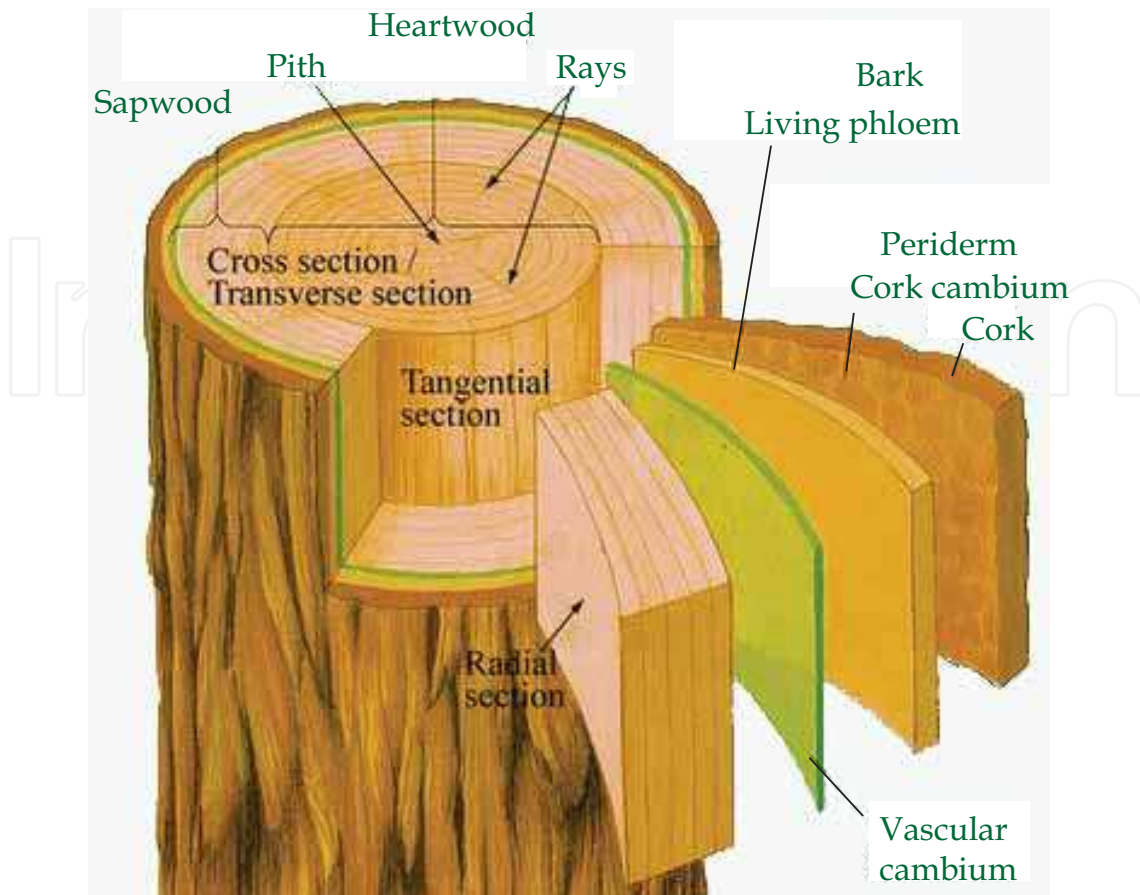
Heartwood
Pith
Rays
Bark
Living phloem
Sapwood

Cross section /
Transverse section

Periderm
Cork cambium
Cork

Tangential
section

Radial
section

Vascular
cambium

Fig. 1. The three dimensional section of a tree trunk

2.1.2 Micro structure of wood

Wood is composed of millions of individual units called cells, which differ in shape and size, depending on the tree's physiological function (Young & Rowell, 1986). The cells that make up the xylem of conifers have structures simpler than those of the dicotyledons. Conifers are composed mainly of cells that are tubular, elongated, pointed and closed at the ends, called tracheids (Hon, 1996). The dicotyledons, on the other hand, are composed of cells of more varying shapes and sizes. Most dicotyledon cells are long and narrow, with pointed and closed ends – the fibers. The tracheids in conifers and the fibers in dicotyledons constitute the greatest part of the cell wall and can be credited with most of the wood's physical and chemical properties (Hon, 1996). Other important constituents are the parenchyma and, in relatively small quantities, the vessels that, in transversal cuts, are called pores (Plackett & Dunningham, 1992). These cells have open ends and are usually shorter than fibers, varying considerably in shape and size.

Wood cells are connected to each other through a cemented substance called intercellular layer or medium lamella. A mature cell is made up of two layers: the primary wall (P)– a thin external layer, and the secondary wall (S)– a thicker internal layer composed of three other layers. The interior of the cell contains the cellular lumen which, in most mature cells, is completely empty (Young & Rowell, 1986). Thus, in whole, wood is a very porous material, about 70% of the volume is made up of air-filled cells. The remaining 30% is wood substance, or cell walls (wood constituents) (Fig. 2b and 2d). Although wood is considered a

highly porous material, it is not always highly permeable and shows great variability in permeability both within and between species. Important existing processes that are strongly influenced by wood permeability are seasoning, wood preservative, wood chemical modification and fire retardant treatments as well as pulping. The efficiency of these treatments, which in turn is related to cost, is largely controlled by the anatomical structure of the wood.
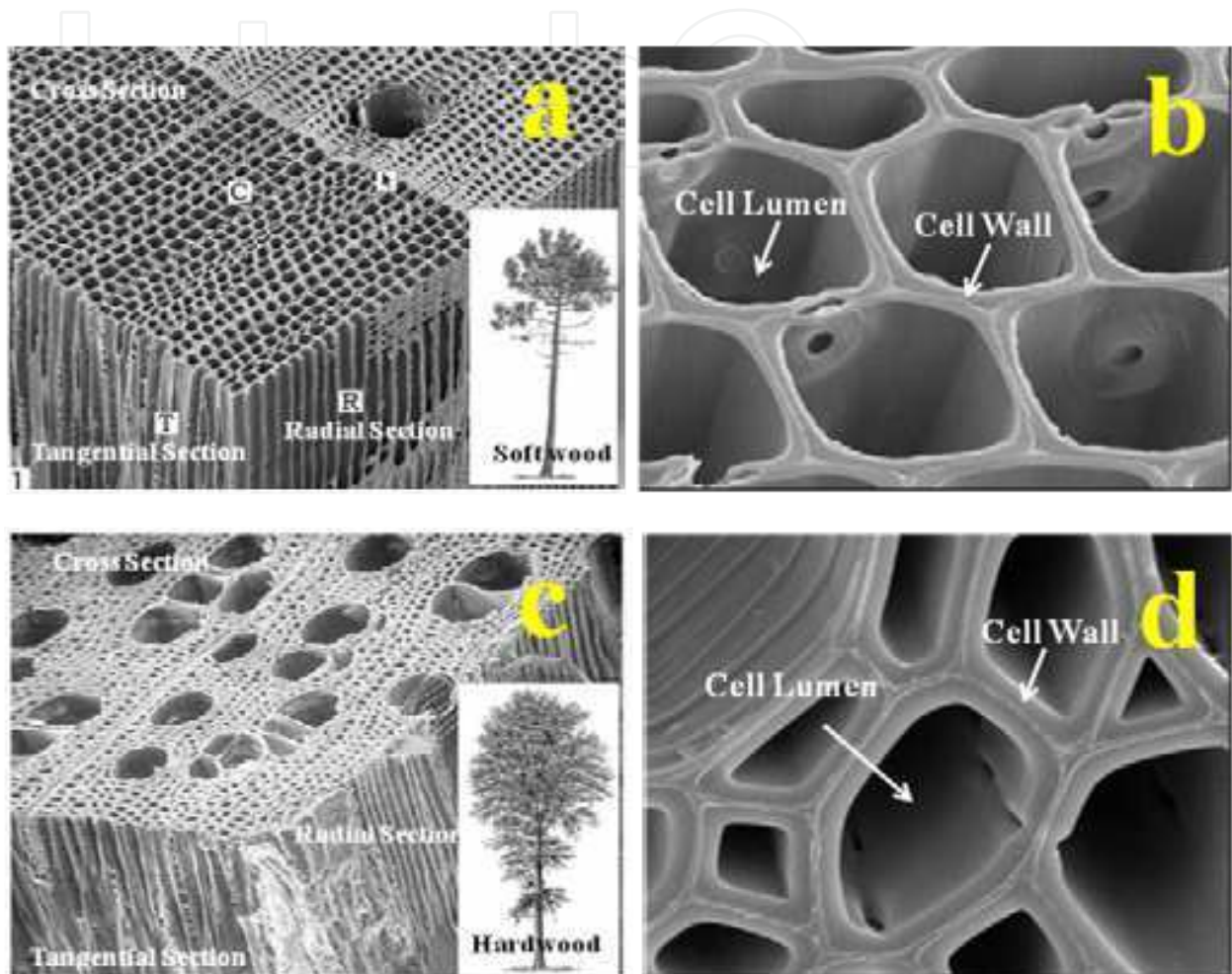

Fig. 2. SEM morphologies of wood porous structure: a) three-dimensional micrograph of softwood, b) the corresponding cross-section micrograph of softwood; c) three-dimensional micrograph of hardwood, d) the corresponding cross-section micrograph of hardwood

In detail, as Fig. 3 shown, the primary layer is the first to be laid down when the cell is formed and is composed of microfibrils, which have an essentially random orientation that allows expansion as cell growths. The secondary layer is subsequently formed, with each of the sub-layers exhibiting different patterns in the microfibrils orientation. From these, the S2 layer occupies the greatest volume of the wall. Consequently it has the greatest influence on the properties of the cell and hence of the wood. The S2 layer exhibits a definite microfibrillar orientation, and is itself composed of many lamellae consisting of numerous closely associated microfibrils that exhibit a helical winding pattern. The space between the cell fibers is occupied by the middle lamella. But micropores are still present permitting under certain conditions accessibility to the cell wall.
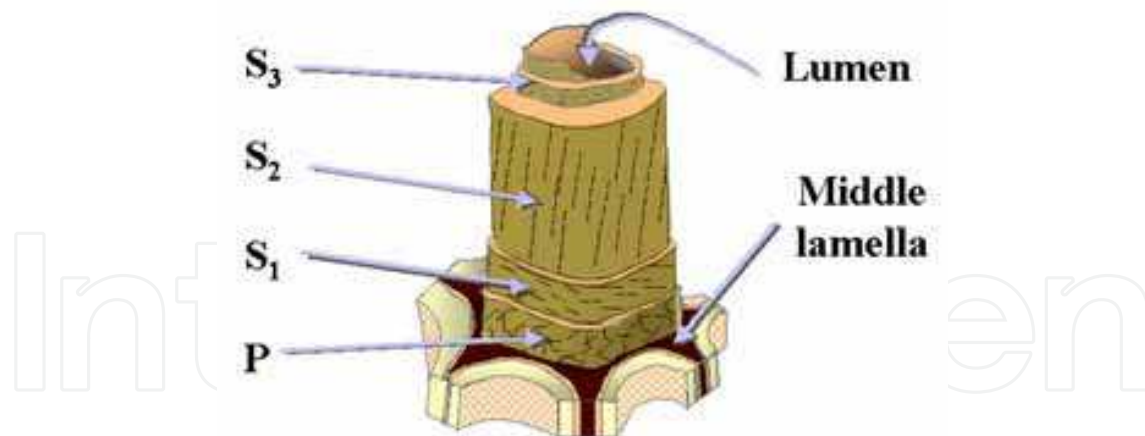
Fig. 3. Ultrastructure of the wood cell wall

2.1.3 Nanodimensional structure and chemical components of wood

Wood is a cellular hierarchical biocomposite (Fig. 4) made up of cellulose, hemicellulose, lignin, extractives and trace elements. Cellulose is the major carbohydrate component of wood along with the hemicelluloses (20–35% by weight). Lignin, extractives, and trace amounts of other materials make up the remaining portion of wood. Wood like many other biological tissues including bones and teeth are hierarchically structured composites in order to provide maximum strength with a minimum of material. Many of the physical, chemical and biological properties of wood can be understood by referring to the polymeric chemical constituents of the cell wall. At the nanoscale level, wood is a cellulosic fibrillar composite. Wood is approximately 30–40% cellulose by weight with about half of the cellulose in nanocrystalline form and half in amorphous form (Fig. 4g).

The hierarchical structure of wood, based on its elementary nanofibrilar components, leads to the unique strength and high performance properties of different species of wood. While a great deal of valuable study has led to an understanding of many mechanisms relating to the properties of wood, the overall complexity of wood's structure has limited discovery. Today we have the tools used in other areas of nanotechnology to look at structures down to the atomic scale. While this is fueling discovery in a wide range of biomimetic materials, studies on wood are only now beginning (Lucia & Rojas, 2009).

2.2 Wood components
2.2.1 Cellulose

The cellulose is a polymer of D-glucopyranose units (Fig. 4h). These monomeric units (anhydroglucose units, AGU) are alternately inverted in the plane of the ring. The AGU are linked together by β(1→4) glucosidic bonds forming the linear polymer cellulose. Cellulose is expressed from enzyme rosettes as 3–5 nm diameter fibrils that aggregate into larger microfibrils up to 20 nm in diameter (Figure 4g and 4f). These fibrils self-assemble in a manner similar to liquid crystals leading to nanodimensional and larger structures seen in typical plant cell walls (de Rodriguez et al. 2006). The theoretical modulus of a cellulose molecule is around 250 GPa, but measurements for the stiffness of cellulose in the cell wall are around 130 GPa. This means that cellulose is a high performance material comparable with the best fibers technology can produce (Vincent, 2002). Due to its crystallinity, cellulose

is relatively unreactive and thermally stable. It is difficult to isolate cellulose from wood in a pure form because it is intimately associated with lignin and hemicelluloses.
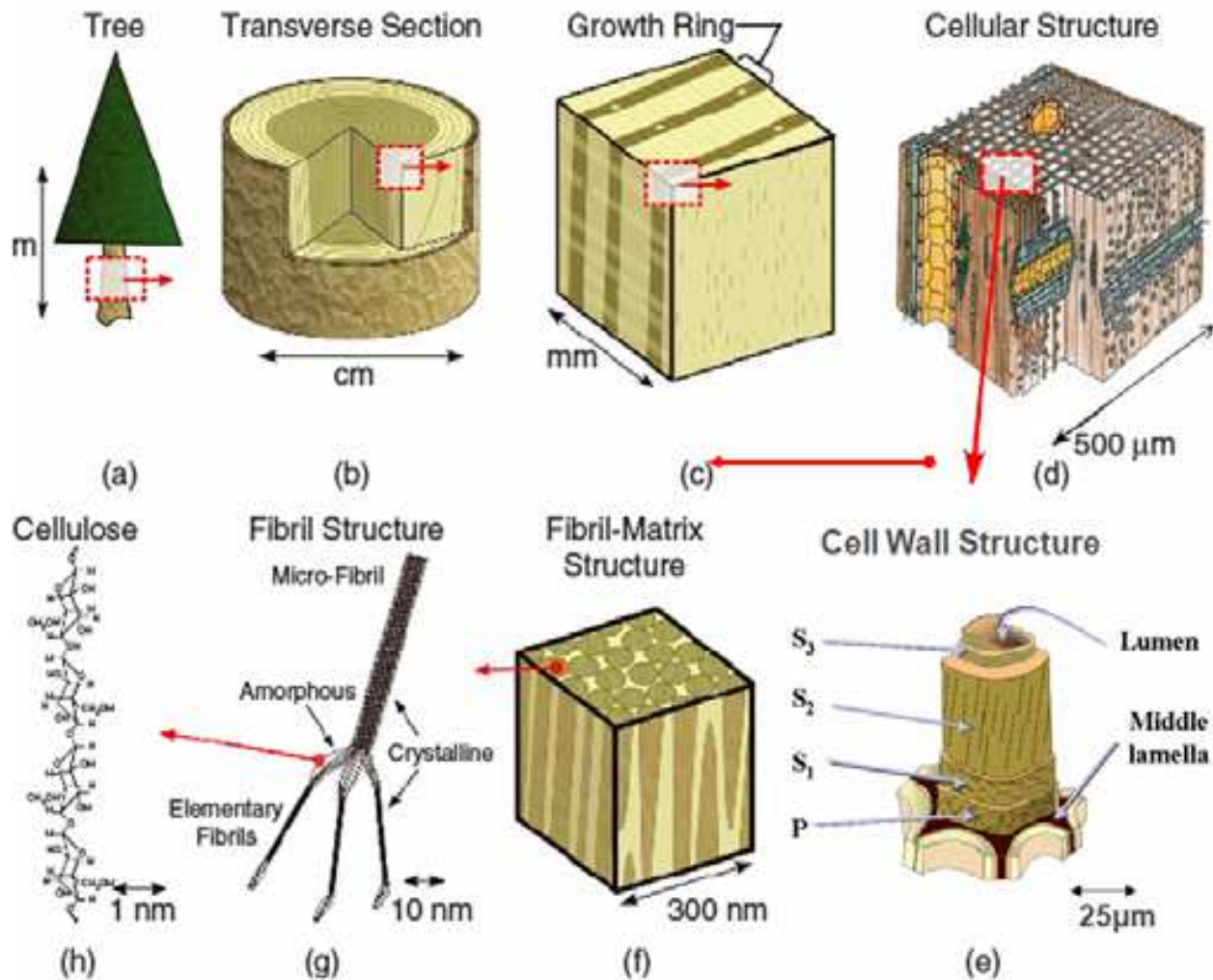
Fig. 4. Wood hierarchical structure: from tree to cellulose (Moon, 2008)

2.2.2 Hemicelluloses

Hemicelluloses are heteropolysaccharides with a lower DP than cellulose of about 100-300. They are also less ordered than cellulose, although some can form crystalline units. Hemicelluloses are referred to by the sugars they contain. The hemicelluloses also may contain carboxyl, acetyl- and methyl-substituted groups. The detailed structures of most wood hemicelluloses have not been determined, only the ratios of sugars that these polysaccharides contain have been determined. Hemicelluloses appear to act as interfacial coupling agents between the highly polar surface of the microfibrils and the much less polar lignin matrix.

2.2.3 Lignin

Lignin is a complex amorphous phenolic polymer of intermediate molecular weight. It is responsible for providing stiffness to the cell wall and also serves to bond individual cells

together in the middle lamella region. The precursors of lignin biosynthesis are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Fig. 5).
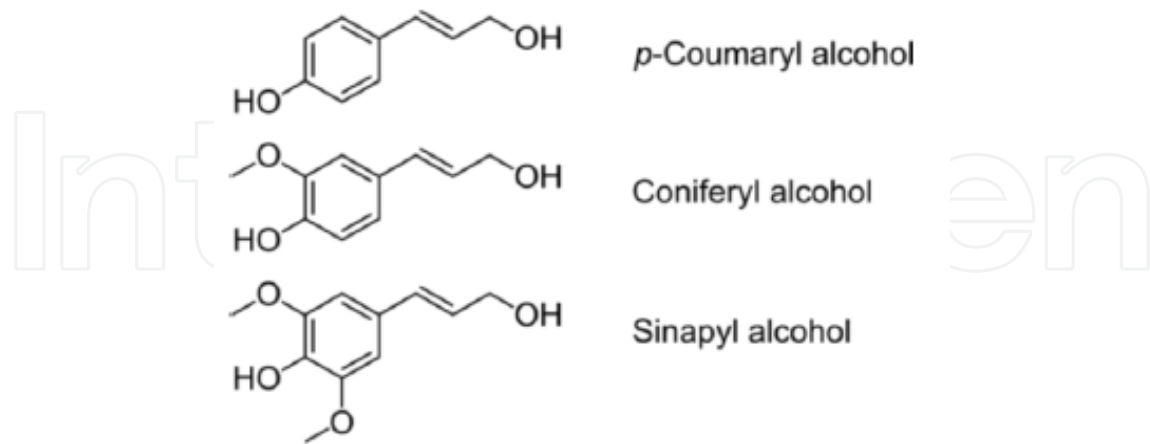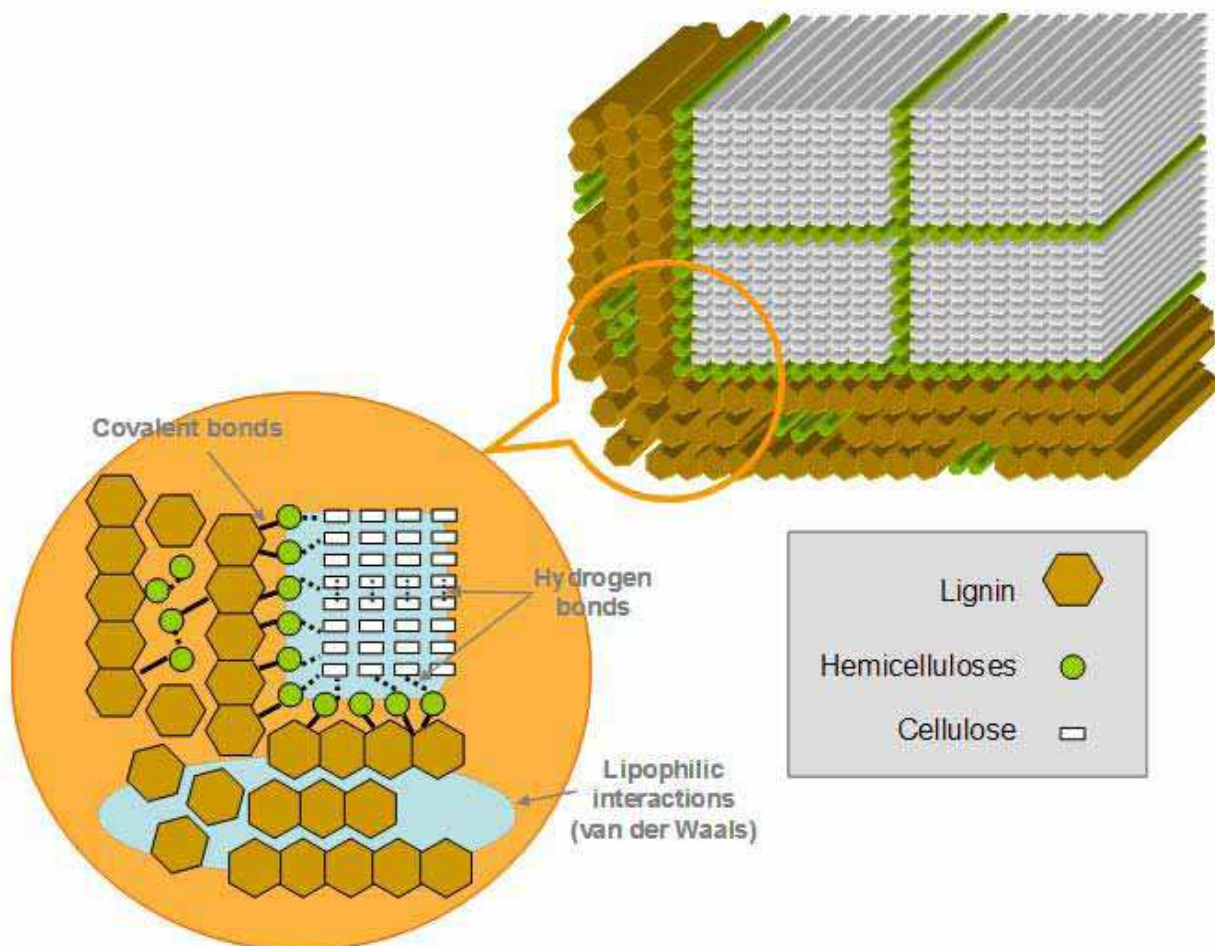

Fig. 5. Monolignol structures

Fig. 6. Schematic representation of the lignin-carbohydrate complex (LCC) and its interaction with cellulose microfibrils

There is a wide variation of structures within different wood species. The lignin content of hardwoods is usually in the range of 18-25%, whereas its content in softwoods varies between 25 and 35%. Lignin from softwoods is mainly a polymerization product of coniferyl alcohol and is called guaiacyl lignin. Hardwood lignin is mainly syringyl-guaiacyl lignin, because they are a copolymer of coniferyl and sinapyl alcohols.

Lignin is associated by covalent bonding (ester and ether) with hemicelluloses forming lignin-carbohydrate complexes. There is no evidence that lignin is associated with cellulose but hydrogen bonds are certainly established within hemicelluloses (Fig. 6) (Peydecastaing, 2008).

In conclusion, for wood cell wall, the hydroxyl groups they contain are the most abundant reactive chemical sites. For the cell lumen, it can be viewed as bulk storage reservoirs for chemicals. For example, the void volume of southern pine springwood or earlywood with a density of 0.33 g/cm^3 is 0.77 cm^3 voids/cm^3 wood or 2.3 cm^3/g. For summer-wood or latewood with a density of 0.70 g/cm^3, the void volume is 0.52 cm^3/cm^3 wood or 0.74 cm^3/g. The cell wall can also swell and act as a chemical storage reservoir. For southern pine the cell wall storage volume from oven dry to water swollen is 0.077 cm^3/cm^3 wood (Rowell & Ellis, 1981). On the basis of the abundant hydroxyl groups and various pores with partly permeable, wood chemical modification can be commonly achieved.

3. Wood-polymer composites

A composite is any combination of two or more materials in any form and for any use. Composites take advantages of the beneficial characteristics of each component material, and often have more useful properties than any of the constituents on its isolation (Haque, 1997).

Progress in the field of polymer chemistry led to the development of a new class of wood products with substantially improved physical, chemical, mechanical, and biological properties. Aesthetic superiority, uniform finish, property enhancement, and reduced maintenance also made modified wood attractive for large-scale application in many industrial uses as substitutes for costly metals and alloys (Deka & Saikia, 2000).

Just under such background, the term Wood-Polymer Composite (WPC) emerges, as the times require. WPC can be any combination of wood and polymer, from polymer filled with wood fiber to solid pieces of wood filled with polymer. This chapter denotes the material formed when wood is impregnated with unsaturated monomers which are then polymerized (Fig. 7). The polymerization may be initiated by treatment with high energy radiation, either from a cobalt source or from an electron accelerator, or by the action of polymerization catalyst and heat (Haque, 1997).
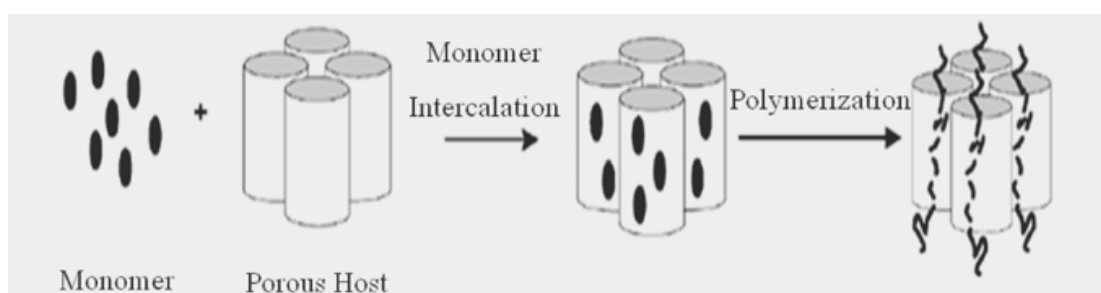

Fig. 7. Schematic view of production process of Wood-Polymer Composite

Generally, WPC involved bulk polymerization of vinyl type monomer(s) in the void spaces of solid wood. The void places (Fig. 8) include vessels, capillaries, ray cells etc., and perhaps to some extent in the cell wall through the assistance of swelling agents (Persenaire et al., 2004). The WPC production necessarily goes through two different phases: monomer(s) is(are) first introduced into the wood pores by various methods depending on the properties of the wood being treated, followed by its(their) polymerization inside the wood (Din, 1989). The resulting product resembles natural wood, and its properties are a combination of wood and polymer material, i.e., applied to the wood components: improved hardness, abrasion resistance, compressive and bending strength, dimensional stability, resistance to biological degradation and others (Schaudy & Proksch, 1982). Such WPC typically find applications in high value wood products where their use may be justified in spite of their higher cost relative to wood. In general, WPC are made from hardwoods and low-cost monomers such as styrene and methyl methacrylate (MMA), but other wood species and chemicals have also been used successfully (Noah & Foudjet, 1988; Couturier et al., 1996). This material has been known and available in small quantities for years since the 1960s. Among them, some specialty products have found commercial applications.

Over the years, several review articles on wood-polymer composites have been published (Stamm, 1977; Witt, 1977; Hamed & Coran, 1978; Meyer, 1977, 1981, 1982, 1984; Rowell & Konkol, 1987; Schneider, 1994; Youngquist, 1995; Ellis, 2000; Persenaire et al., 2004; Schneider & Witt, 2004). These reviews cover from chemical modification, treatment of wood, plastics to production technologies and applications for various types of wood-polymer composites (table 1). This chapter is intended as an overall review for materials, production, properties, application and history of wood-polymer composite and an update and extension of reviews on WPC. The developing trend of wood-polymer composites in future is also recommended in the end.
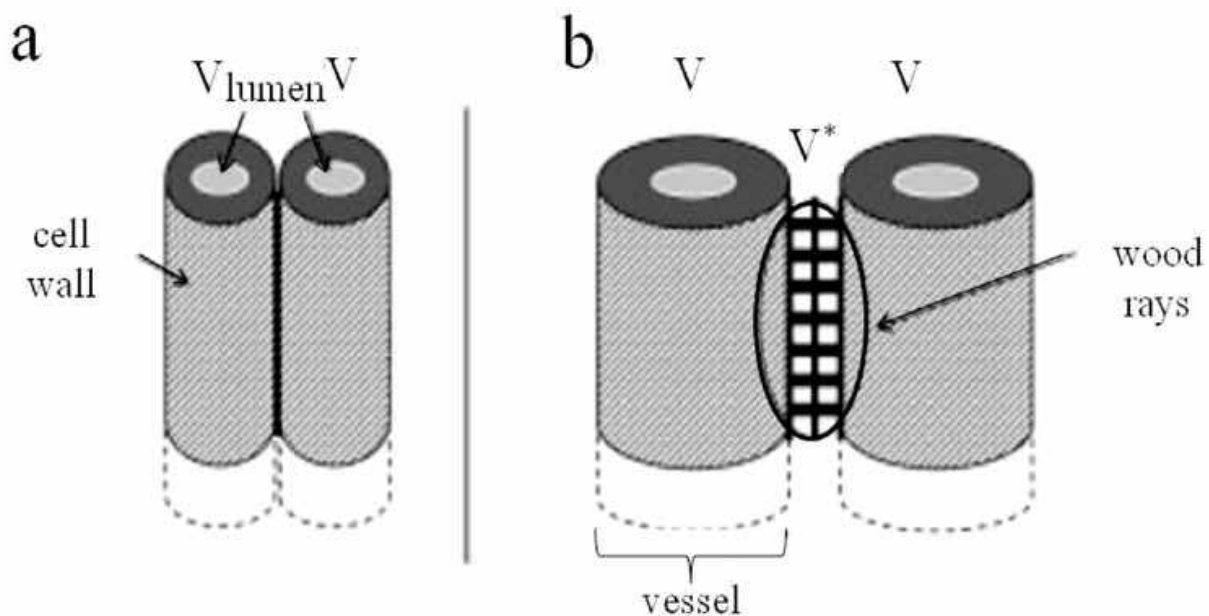

Fig. 8. Representation of two adjacent wood vessels in untreated wood (a) compared to WPC (b) and localization of the fracture propagation V and V*

Table 1. List of literatures of WPC

Authors	Title	Wood Species	Properties	Monomers	Initiators	Treating
Ergun Baysa, Mustafa Kemal Yalinkilic, Mustafa Altinok, Abdullah Sonmez, Hüseyin Peker, Mehmet Colak	Some physical, biological, mechanical, and fire properties of wood polymer composite (WPC) pretreated with boric acid and borax mixture	Sapwood of Scots pine (*Pinus sylvestris L.*) in Turkey	Some physical properties including ASE, specific gravity (SG), reduced WA, MOE and MOR; biological resistant against decay fungi, *Tyromycetes palustris* and *Coriolus versicolor* and fire resistance were evaluated	Styrene (St), methylmethacrylate (MMA), and their mixture (50:50; volume:volume); Boric acid (BA) and borax (BX) mixture at 1% concentration prior to monomer treatment. Divinyl benzene was used as a cross-linker	Benzoyl Peroxide	1% Boric was imp dring, sty and their volume/ under a v 30 min, f with alu
Ergun Baysal, Abdullah Sonmez, Mehmet Colak, Hilmi Toker	Amount of leachant and water absorption levels of wood treated with borates and water repellents	Douglas fir (Pseudotuga menziesii var. viridis) in Turkey	The amount of leachant and water absorption levels of wood after boron treatment was determined.	Vinyl monomers: styrene (St) and methyl methacrylate (MMA) containing divinyl benzene as a crosslinker	Benzoyl Peroxide	Boric aci weight to with their concentr polyethy prior to v with vin methyl m isocyana were eva Hg to ac soaking Impregn then wra before in in an ove
Kartal, S.; Yoshimura, T. & Imamura, Y.	Decay and termite resistance of boron-treated and chemically modified wood by in situ co-polymerization of allyl glycidyl ether (AGE) with methyl methacrylate (MMA)	Sugi wood (*Cryptomeria japonica* D. Don)	Dimensional stability, leachability, decay resistance, termite resistance	MMA+ allyl glycidyl ether (AGE) polymer mixtures (1:1, v:v)	2,2'-azobis-(isobutyronitrile) (AIBN)	In the sin treated v acid equ or with N mixtures processe firrst trea dried at 100°C fo then trea with MM
J. N. Noah, A. Foudjet	Wood-polymer composites from some tropical hardwoods	Three diffuse porous wood species: Movingui (*Distemonanthus bentharnianus*), Bilinga (*Nauclea diderrichii*) and Sapelli (*Entandrophragma cylindricum*) in Cameroon	The fractional volumetric retentions of monomer and polymer were determined and expressed in terms of the fraction of voids filled by the impregnant. According to these, the treatability of the three species was evaluated, respectively.	Methyl methacrylate (MMA) monomer containing 5% ethylene glycol dimethacrylate as crosslinker	2% benzyl peroxide	A vacuu then, a p was appi a period After wr polymer at 65°C o

Table 1. (continues) List of literatures of WPC

Authors	Title	Wood Species	Properties	Monomers	Initiators	Treating
Ümit C. Yildiz, Sibel Yildiz, Engin D. Gezer	Mechanical properties and decay resistance of wood–polymer composites prepared from fast growing species in Turkey	Maritime pine (*Pinus pinaster* Ait.) and poplar (*Populus x. euramericana cv.* I-214) in Turkey	Compression strength parallel to grain, static bending strength, decay resistance against *Coniophora puteana* and *Coriolus versicolor*	Styrene (St), methyl methacrylate (MMA) and styrene/methyl methacrylate (ST/MMA, 65/28 (w/w) %) mixture and 5% divinyl benzene as cross-linker (the cross-linker to adjust the three different polymer loading levels in WPCs)	2% benzyl peroxide	A full va and then solution condition impregn in alumi for 24h to
Rashmi R. Devi, Ilias Ali, T.K. Maji	Chemical modification of rubber wood with styrene in combination with a crosslinker: effect on dimensional stability and strength property	Rubber wood (*Hevea Brasiliensis*) in India.	Anti-shrink efficiency (ASE), water absorptivity (WA), modulus of rupture (MOR) and modulus of elasticity (MOE) as well as biodegradability	Styrene in combination with a crosslinker, Glycidyl Methacrylate (GMA)	2,2'-azobis-(isobutyronitrile) (AIBN)	Vacuum followed room ten after atta Then, the aluminu 24 h in a drying a
Rashmi R. Devi, T. K. Maji, A. N. Banerjee	Studies on dimensional stability and thermal properties of rubber wood chemically modified with styrene and glycidyl methacrylate	Rubber wood (*Hevea brasiliensis*) in India	Water uptake, water vapor exclusion, water-repellent effectiveness, and dimensional stability.	Styrene in combination with a crosslinker, Glycidyl Methacrylate (GMA)	2,2'-azobis-(isobutyronitrile) (AIBN)	Vacuum followed room ten after atta Then, the aluminu 24 h in a drying a
Rashmi R. Devi, T. K. Maji	Chemical modification of simul wood with styrene–acrylonitrile copolymer and organically modified nanoclay	Simul wood (*Salmalia malabarica*) in India	Physical properties including weight percent gain, density, hardness, water uptake, water-repellent effectiveness (WRE), chemical resistance)	Styrene–acrylonitrile copolymer (SAN), glycidyl methacrylate (GMA), and organically modified nanoclay	2,2'-azobis-(isobutyronitrile) (AIBN)	A mixtur acrylonit presence polymer min in ar heat-cata at 90°C f for 24hrs soxhlet-e

Table 1. (continues) List of literatures of WPC

Authors	Title	Wood Species	Properties	Monomers	Initiators	Treating
Shane B. Elvy, Gary R. Dennis, and Loo-Teck Ng	Effects of coupling agent on the physical properties of wood-polymer composites	Australian commercial popular timbers, radiate pine (*pinus radiata*)-a soft wood and fast growing plantation timber, and blackbutt (*eucalyptus piluliaris*)-a hard and plantation timber.	Hardness and compression tests as well as dimensional stability	Methyl methacrylate (MMA) containing benzoyl peroxide (1%) (BPO), lauroyl peroxide (0.5%) (LPO) and the accelerator-N, N-dimethylaniline (0.5%) (DMA). Vinyltriacetoxysilane (H$_2$C=CHSi (OOCH$_3$)$_3$) was used as a silane coupling agent	1% BPO	Vinyltria methano wood sa 5 mmHg continue overnigh under 70 monome introduc by a con temperat curing th and at 10
Dilek Şolpan, Olgun Güven	Preparation and properties of some wood/(co)polymer composites	Beech (*Fagus Orientalis* Lipsky) and Spruce (*Picea Orientalis* Lipsky) in Turkey	The dimensional stabilization (water uptake and artificial acid rain) and decay resistance against the biological attacks of microorganisms like mould and bacteria	Monomers-acrylonitrile (AN), methyl methacrylate (MMA), allyl glycidyl ether (AGE), and monomer mixtures-AGE + AN, AGE + MMA	Gamma radiation	The impr vacuum-wrapped irradiate
Dilek Şolpan, Olgun Güven	Preservation of beech and spruce wood by allyl alcohol-based copolymers	Beech (*Fagus Orientalis* Lipsky) and Spruce (*Picea Orientalis* Lipsky) in Turkey	Compressional strength, brinell hardness and water uptake capacity as well as biodegradation	Monomers-acrylonitrile (AN), methyl methacrylate (MMA), allyl glycidyl ether (AGE), and monomer mixtures-AGE + AN, AGE + MMA	Gamma irradiation	Vacuum 15min, a ^{60}Co-γ so 0.85 kGy
C. Roussel, V. Marchetti, A. Lemor, E. Wozniak, B. Loubinoux and P. Gérardin	Chemical modification of wood by polyglycerol/ maleic anhydride treatment	Pine Wood (*Picea abies*) and Beech Blocks (*Fagus sylvatica*) in France	Dimensional stability, compression, MOE and decay resistance against fungi (*Poria placenta* and *Coriolus versicolor*)	Synthesied PG/MA	Methylethyl ketone peroxide (2 wt%, MEKP), cobalt naphthenate (2 wt%)	Vacuum heat-cata
Denise Ortigosa Stolf, Francisco Antonio Rocco Lahr	Wood-polymer composite: physical and mechanical properties of some wood species impregnated with styrene and methyl methacrylate	Pine (*Pinus caribaea*) classified as a conifer and Eucalyptus (*Eucalyptus grandis*) within the class of the dicotyledons in Brazil	Most of the physical and mechanical properties and dimensional stability	Styrene and methyl methacrylate	Benzoyl peroxide (BPO)	Vacuum (a pressu and then aluminu 50°C for

Table 1. (continues) List of literatures of WPC

Authors	Title	Wood Species	Properties	Monomers	Initiators	Treating
W. Dwianto, M. K. Yalinkilic	Fixation of compressive deformation of wood by vinyl polymerization	Sugi (*Cryptomeria Japonica* D. Don.) sapwood	Specific Gravity (ρ) and Weight Gain (WG) and their relationship with MOR and MOE	MMA, St and MMA+St(7:3 in weight)	AIBN, 1%	Compres direction thickness press, th followed for 4h
L. H. L. Chia, P. H. Chua, E. E. N. Lee	A Preliminary study on the thermal conductivity and flammability of WPC based on some tropical woods	Kapur, Kempas, Keruing, Light Red Meranti, Seraya, and Chengal in Singapore	Thermal conductivity, flammability and the correlation of thermal conductivity to flammability.	Acrylonitrile (AN), 60% styrene-40%-acrylonitrile (STAN), MMA, 95% MMA--5% dioxane (MD), and vinylidene chloride (VDC).	BPO, 1%	Vacuum catalyst t
G. Scurfield, S. R. Silva, M. B. Wold	Failure of wood under load applied parallel to grain: A study using scanning electron microscopy	Wood of *Gonystylus sp.* in Australia	Compression and strain frature under load with SEM	MMA	γ-irradiation with a Co60 source	Impregn methacry for 3hr. T polymer impregn irradiatio
Jorge A. Duran, John A. Meyer	Exothermie heat released during catalytic polymerization of basswood-methyl methaerylate composites	Basswood (*Tilia americana* L.) in American	Effect of vazo catalyst and crosslink on exothermic heat of WPC	MMA containing trimethyl propane trimethacrylate (TMPTMA) as a crosslinker	Vazo	Vacuum dried wo wood wa under at hour. Po at 60°C i
M. H. Alma; H. Hafizolu; D. Maldas	Dimensional stability of several wood species treated with vinyl monomers and polyethylene glycol-1000	Black alder (*Alnus glutinosa* Mill, Gaertn.), scotch pine (*Pinus sylvesfris* L.), oriental spruce (*Picea orientalis* L.), and Caucasian fir (*Abies nordmanniana* L.) in Turkey	ASE and SEM observation	Styrene (St), and a mixture (5:2 weight ratio) of styrene and methylmethacrylate, (St-MMA), and 30% aqueous solution of PEG-1000 were used as bulking agents.	2,2'-azobisisobutyro nitrile (AIBN) , 0.1wt%	The viny 0.1wt% A wood un condition temperat polymer finally w (PEG100 were imp pressure
Wan Asma Ibrahim & Abdul Razak Mohd. All	The effect of chemical treatments on the dimensional stability of oil palm stem and rubberwood	Oil palm stem and solid rubberwood in Malaysia	Relationship between WPG and ASE	Analytical grade acetic anhydride, methyl methacrylate and glycidyl methacrylate	2,2'-Azobisisobutyro nitrile (AIBN)	The sam monome 1 hr, and gas, seal 120°C ar and mon curing ti and glyc

Table 1. (continues) List of literatures of WPC

Authors	Title	Wood Species	Properties	Monomers	Initiators	Treating
N. Sheikh and F. Afshar Taromi	Radiation induced polymerization of vinyl monomers and their application for preparation of wood-polymer composites	Beech and Hornbeam in Iran.	Physical and mechanical properties	Vinyl acetate, acrylic acid and acrylic acid/styrene mixture	Radiation source-a γ-ray from ^{60}Co with a dose rate of 4-5 kGy/hr	Vacuum the samp monome predeter.
M. F. Couturier, K. George, M. H. Schneider	Thermophysical properties of wood-polymer composites	Red maple in Canada	Theoretical models for the longitudinal and transverse thermal conductivities of wood-polymer composites prepared from maple boards	Styrene, methyl methacrylate or polyfurfuryl alcohol.	AIBN	Vacuum-heat-cata
Marc H. Schneider, Keith I. Brebner and Ian D. Hartley	Swelling of a Cell Lumen Filied and a Cell-wall Bulked Wood Polymer Composite in Water	Sugar maple (*Acer saccharum* Marsh.) in Canada	Ultimate swelling, moisture diffusion coefficient and fiber saturation points (FSP)	A nonswelling monomer similar to methyl methacrylate and the second monomer (FA) that swells the wood	AIBN	Vacuum-heat-cata
M. H. Schneider	New cell wall and cell lumen wood polymer composites	Sugar maple (*Acer saccharum* Marsh.) sapwood in Canada	Properties (density, hardness, anti swelling efficiency) gradients	FA containing 5% $ZnC1_2$ and 5% water; MMA containing 0.3% AIBN and 3% ethylene glycol dimethacrylate as a crosslinker	AIBN	The form MMA m polymer. was adde under va 1 hr and 8 atm (12 applied f heat-cata
Howal-d N. Rosen	Moisture adsorption and swelling in polyethylene glycol and polymethyl methacrylate treated wood at high relative humidity	Yellow-poplar (*Liriodenclron tulipifera* L.) sapwood and silver inaple (*Acer saccharinum* L.) heartwood in America	ASE and swelling efficiency	MMA monomer (0.2% Vazo catalyst) or 30% and 50% concentration of PEG-1000 treated wood	Vazo	A full cel (150 psi min at 22 treated w 67°C for

Table 1. (continues) List of literatures of WPC

| Authors	Title	Wood Species	Properties	Monomers	Initiators	Treating
Wesleye. Loos, Morgantown, West Virginia	Dimensional stability of wood-plastic combinations to moisture changes	loblolly pine (*Pinus taeda* L.) and yellow-poplar (*Liriodendron tulipifera*, L.) in America	Anti-shrinking efficiency (ASE)	Methyl methaerylate (MMA), and Styrene-Aerylonitrile (ST-ACN) (60%-40%)	WPC	Vacuum-heat-cata
M. H. Schneider and J. G. Phillips	Elasticity of wood and wood polymer composites in tension compression and bending	Sugar maple (*Acer saccharum* Marsh.) and basswood (*Tilia americana* L.) in Canada	The values in bending, tension and compression and the ratio of tensile to compressive modulus of elasticity	MMA	0.2% Vazo	Vacuum-heat-cata
Loo-Teck Ng, John L. Garnett, Shahroo Mohajerani	Role of additives in wood-polymer composites. Relationship to analogous radiation grafting and curing processes	Australian softwood, Pine wood (*Pinus radiata*) in Australian	Tensile strength and dimensional stability as well as comparising effect of radiation and heat-catalyst treatment on curing consolidation	MMA containing diethy-leneglycol dimethacrylate (DEGDMA) and divinyl benzene (DVB) as crossing-linkers, and urea for improving PL of WPC as well as oxygen scavenger (N,N-diethylaminoethyl methacrylate (DEAEMA)	Azobisisobutyro nitrile (AIBN)	γ-radiati method
H. Matsuda, M. Ueda and H. Mori	Preparation and crosslinking of oligoesterified woods based on maleic anhydride and allyl glycidyl ether	Red pine (*Pinus densiflora* Sieb. et Zucc.) in Japan.	heat distortion temperature (> 165°C) and compressive strength, flexural strength, Impact strength and hardness as well as water absorption	maleic anhydride and allyl glycidyl ether	2 wt-% of dicumyl peroxide (DCP) as initiator	Heat-cata for 8 h.
Baki Hazer, Yalcin Ors and M. Hakki Alma	Improvement of wood properties by impregnation with macromonomeric initiators (Macroinimers)	Scotch pine (*Pinus sylvestris* L.) , eastern spruce (*Picea orientalis* L.) , and eastern beech (*Fagus orientalis* L.) in Turkey	PAE was prepared by synthesis of azobisisobutyronitrile and polyethylene glycols (PEG-200) with molecular weight of 200	The mixture, containing 140 g PAE, 80 ml TDI, 70 ml HEMA, 400 ml St, and 5 ml SO as a catalyst	Synthetic macromonomeri c initiator	A vacuu at 40-50° wood sa aluminiu polymer unwrapp in a vacu

Table 1. (continues) List of literatures of WPC

Authors	Title	Wood Species	Properties	Monomers	Initiators	Treating
J. R. Wright and L. J. Mathias	New wood-polymer composites containing ethyl α-hydroxymethyl acrylate polymers	Southern pine in America	ASE, Compressive Strength	Ethyl acrylate, styrene, tetraethyleneglycol diacrylate (TEGDA), and 1,6-hexanediol diacrylate as well as 4-(N,N-dimethylamino) pyridine as catalyst.	AIBN	The samp of ≤3 mn then the mixture agent an soak for After imp wrapped at 50 to 6 (V-30) fo varying
Aikfei Ang, Zaidon Ashaari, Edi Suhaimi Bakar & Mohd Hamami Sahri	Enhancing the properties of mahang (*Macaranga* spp.) wood through acrylic treatment in combination with crosslinker	Mahang, *Macaranga* spp. in Malaysia	Mechanical strength containing specific strength (strength to density ratio), MOR, compressive stress and hardness, stiffness (MOE) as well as dimensional stability	Methyl methacrylate (MMA) in combination with a crosslinker-trimethylolpropane trimethacrylate (TMPTMA)-1~5 wt%	2% BPO	Vacuum-initial va a pressur ambient were the maintain at 103±2°
Elias Hanna Bakraji, Numan Salman	Properties of wood–plastic composites: effect of inorganic additives	White poplar (*Populus alba*), cypress (*Cupressus sempervirens*), and white willow *(Salix alba*) in Syrian	Polymer loading and compression strength as well as dimensional stabiltiy	The bulk monomers, AM and BMA, and the additives $LiNO_3$, $CuSO_4$ and H_2SO_4	γ-irradiation	γ-irradia
Zaki Ajji	Preparation of pinewood/polymer/composites using gamma irradiation	White poplar, cypress tree, and white willow	Tensile and compression strength	Butyl acrylate, butyl methacrylate, styrene, acrylamide, acrylonitrile, and unsaturated polyester styrene resin	[60]Co gamma source	The woo vacuum a pressur to remov The mon were intr the woo the comp samples temperat

3.1 Polymerization mechanism

The key point of WPC production is the in-situ formation of polymer from monomer(s) within wood pores. The polymerizing process is completed by monomer(s) on the basis of mechanism of free radical polymerization. It is a method of polymerization by which a polymer is formed from the successive addition of free radical building blocks. The free radicals ($R\bullet$) are commonly generated in two ways: by temperature-sensitive catalysts or by radiation curing. However, despite of the two different sources, the polymerization mechanism is the same after the free-radical creation, which can be presented as the following three steps:

$$\text{Chain Initiation Step: } R\bullet + M \text{ (monomer)} \to R\text{-}M \tag{1}$$

Chain initiation is the first step of the polymerization process. During initiation, an active center is created from which a polymer chain is generated. After which, it is the propagation step:

$$\text{Chain Propagation Step: } R\text{-}(M)_n\text{-}M\bullet + M \to R\text{-}(M)_{n+1}\text{-}M \tag{2}$$
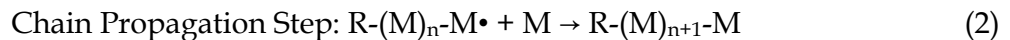
Once a chain has been initiated, the chain propagates until there is no more monomer (living polymerization) or until termination occurs. During the polymerization, a polymer spends most of its time in increasing its chain length.

In the final process of the polymerization, chain termination occurs as follow:

$$\text{Chain Termination Step: } R\text{-}(M)_n\text{-}M\bullet + R\text{-}(M)_n\text{-}M\bullet \to R\text{-}(M)_n\text{-}M\text{-}M\text{-}(M)_n\text{-}R \tag{3}$$
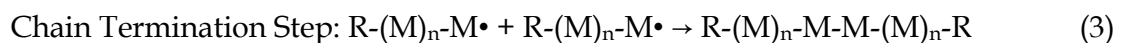
After this step, the polymer is resulted. For free radical polymerization, it is a key synthesis route for obtaining a wide variety of different polymers and material composites. The relatively non-specific nature of free radical chemical interactions makes this one of the most versatile forms of polymerization available and allows facile reactions of polymeric free radical chain ends. The free radical polymerization was an improvement over the condensation polymerization reaction because the free radical catalyst was neither acidic nor basic, nor does the reaction leave behind a reaction product, such as water, that must be removed from the final composite. The acid and base catalysts used with the other treatments degrade the cellulose chain and cause brittleness in the composite. Thus, on the basis of the free radical polymerization mechanism and wood porous structure, the wood-polymer composites were created by vinyl type monomers on 1960s. As the above mentioned two generation ways of free radicals in the WPC production, each process for generating free radicals has its own peculiarities, though the vinyl polymerization mechanism is the same after free-radical generation. Chemical curing is a more economical method for small-scale production, whereas gamma radiation is more economical on a larger scale (Ibach and Ellis 2005). However, both of them place an important role in the production of WPC.

3.1.1 Radiation-initiated polymerization

There are two main radiation-initiated polymerization methods used to cure monomers in wood (table 1): gamma radiation and electron beam.

3.1.1.1 Gamma radiation

When γ-radiation passes through a material such as wood or a vinyl monomer it leaves behind a series of ions and excited states as the energy of the γ-ray is absorbed through photoelectric, Compton, and pair production collisions (Fig. 9). (Cobalt-60 produces two γ-rays of 1.17 and 1.33 MeV. Approximately 30eV is required to rupture a covalent bond and to cause ionization.) The ions and excited states generated in the absorbing material immediately rearrange to form free radicals, which in turn initiate the polymerization process.

$$(Monomer)^* \rightarrow R\bullet + H \qquad (4)$$
$$\text{Excited State} \qquad \text{Free Radicals}$$
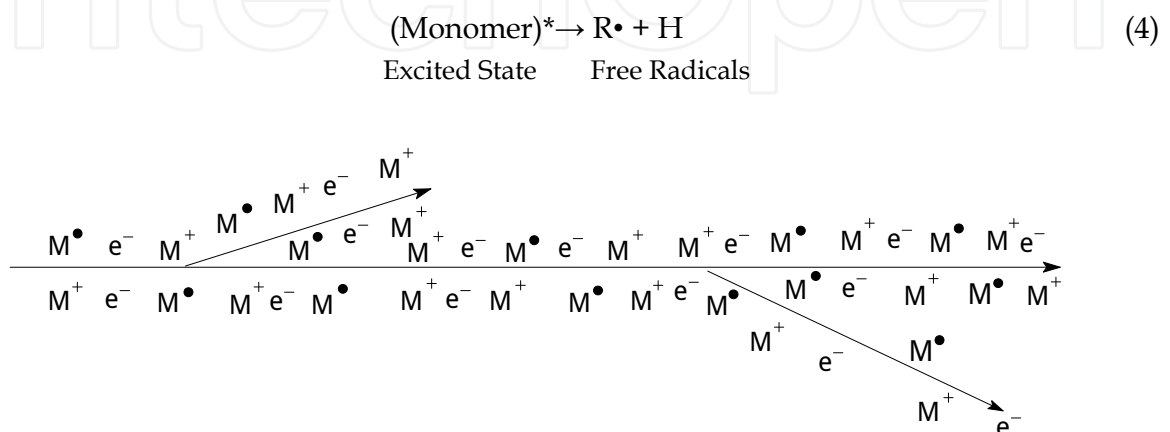
Fig. 9. Ionized and excited molecules along the path of a γ -ray

The free radicals usually consist of H* and the radical monomer. Once the free radical is generated, the polymerization reaction is the same as that o f the above normal free-radical-catalyzed, vinyl monomer bulk polymerization (Meyer, 1984).

With gamma radiation, polymerization rate and extent of polymerization within wood pores are dependent on the type of monomer, other chemical additives, wood species, and radiation dose rate. An example of radiation polymerization of the vinyl type monomer, MMA using cobalt 60 γ-ray dose rates of 56, 30, and 9 rad/s produced exotherms at 120°C, 90°C, and 70°C, respectively, with reaction times of 5, 7, and 12 h, respectively, produced 70–80% wood weight gain. A 1.5–2.5 Mrad dose of gamma irradiation from a cobalt-60 source of isotope activity 20,000 Ci can be used to polymerize MMA in wood. Polymerization rate of vinyl compounds in wood, by gamma-ray irradiation, decreases in the presence of oxygen giving 50–90% conversion for styrene, methyl-, ethyl-, propyl-, and butyl methacrylates, and 4–8% conversion of vinyl acetate. Radiation polymerization of the vinyl monomers butyl methacrylate and styrene in different wood species, using cobalt 60 γ-ray radiation at various doses at a dose rate of 100 rad/s exotherms with different monomer concentrations, produced 5–140 % polymer retention (Bakraji et al., 2001). The radiation dose required for complete conversion during polymerization in an inert atmosphere was 1.5–2 Mrad for spruce and 2.0–2.5 Mrad for pine, polar and beech (Ding, 2009; Pointing, 1998).

Wood as a mixture of high-molecular-weight polymers, when exposure to high-energy radiation, it will depolymerize the polymers by creating free radicals along the C-C backbone to initiate polymerization. If two free radicals are created on separate chains in close proximity, cross-linking will take place. Thus, when radiation exposure reaches 1.0 Mrad, some slight increase in mechanical properties and a decrease in hygroscopicity

normally take place. If the free radical is created near a reactive or functional group, other types of reactions, not cross-linking reaction, normally take place. When the free radical is on a tertiary carbon, disproportionation will occur with chain scission. The effect on wood properties was negligible up to a dose of 10.0 Mrad, but higher radiation doses led to strength and toughness losses (Šimunková et al. 1983). When radiation doses achieve 3×10^8 rd, the wood will be completely soluble (Meyer, 1984). Consequently, the theoretical radiation doses for polymerization of monomers and graft of wood consequents are normally below 10 Mrad.

However, as the vinyl monomers are normally nonpolar and the wood's cell wall structure is not swollen by the monomers, there is little opportunity for the monomer to reach the free-radical sites, generated by the γ-radiation on the cellulose, to form a vinyl polymer branch, and there is little if any interaction with the hydroxyl groups attached to the cellulose molecule. Consequently, in general, most vinyl polymers simply bulk the wood structure by filling the capillaries, vessels, and other voids within wood.

3.1.1.2 Electron beam

High-energy electrons are another way of generating free radicals to initiate polymerization, and have been used with some success. Electron-beam irradiation was used to make WPCs of beech sapwood veneers with styrene, MMA, acrylonitrile, butyl acrylate, acrylic acid, and unsaturated polyesters (Handa et al., 1983; Doss et al., 1991; Şolpan & Güven, 1995; 1996; Tang & Xu, 2004). Increasing the wood moisture content has a positive effect on electron curing. For example, the monomer conversion in the electron beam-induced polymerization of MMA pre-impregnated in beech veneer increases with increases of moisture content in the wood up to 20–30% moisture, and is proportional to the square root of the electron dosage. The polymerization of styrene and acrylonitrile in veneer is also affected similarly by moisture content (Ibach & Ellis, 2005).

Some studies have indicated that curing of monomer systems in wood causes some interaction of the polymer with the wood. WPCs made with MMA, MMA–5% dioxane, and vinyl acetate impregnation into the wood cellular structure, followed by electron-beam irradiation show an increase in the compressive and bending strength, indicating some interaction at the wood-polymer interface (Boey et al., 1985). A recent study (Tang & Xu, 2004) used resins including styrene alone, styrene/unsaturated polyester mixture, and styrene/acrylic epoxy ester mixture, respectively, with the help of electron irradiation of a dose of 56 kGy, to prepare a series of wood/polymer composites (WPCs) (Matsuda et al., 1988). The results showed that the curing degree of the impregnated resins could be greater than 90 % with the aid of electron irradiation; and the WPCs possessed much higher hardness and compression strength, and much lower water absorption, compared to untreated wood .

3.1.2 Heat-catalyst-initiated polymerization

As the radiation method has drawbacks such as safety concerns, cost considerations as well as special regulations, and certain monomers (e.g. MMA, St, acrylonitrile) with low boiling points, need low curing temperature to avoid significant monomer loss during their curing process, method of initiators sponsored polymerization as catalysts which can generate free radicals by self-decomposition under lower temperatures were developed.
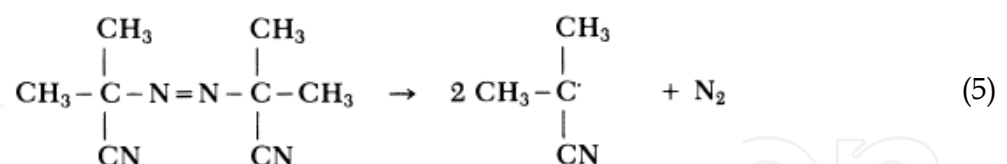
Two kinds of initiators as catalysts are commonly used in the heat-catalyst-initiated polymerization: Vazo series and Peroxide catalysts.

3.1.2.1 Peroxides

The commonly used peroxides for the polymerization of monomers in wood include dicumyl peroxide (DCP), t-butyl hydroperoxide (TBPB), methyl ethyl ketone peroxide (MEKP), lauroyl peroxide (LPO), isopropyl hydroperoxide (ISO-HPO), cyclohexanone peroxide (CHPO), hydrogen peroxide (HPO), and benzoyl peroxide (BPO) (table 1). Each of the radicals generated from these peroxides has a different reactivity. The phenyl radical is more reactive than the benzyl radical, and the allyl radical is unreactive. Thus, benzoyl peroxide is one of the most commonly used peroxides initiator. Usually the amount of peroxide added ranges from 0.2–3% by weight of monomer (Ibach & Ellis, 2005). Excess peroxide may adversely affect the mechanical properties of the composite because molecular chain scission of the polymer and cellulose occurs when peroxide is too abundant (Maldas and Kokta 1991a).

3.1.2.2 Vazo catalysts

Vazo or 2,2' -azobisisobutyronitrile series catalysts are solvent soluble and have a number of advantages over organic peroxides (Rowell, 2009). The catalysts are more stable than most peroxides, so they can be stored under milder conditions, and are not shock-sensitive. They decompose with first-order kinetics, resulting in faster polymerization in the presence of AIBN than with benzoyl peroxide; are not sensitive to metals, acids, and bases; and are not susceptible to radical-induced decompositions. The Vazo catalysts produce less energetic radicals than peroxides, so there is less branching and cross-linking. They are weak oxidizing agents, which allows them to be used to polymerize unsaturated amines, mercaptans, and aldehydes without affecting pigments and dyes. The catalysts are white crystalline solids that are soluble in most vinyl monomers. Upon thermal decomposition, the catalysts decompose to generate two free radicals per molecule. Nitrogen gas is also generated (5). The rate of decomposition is first-order and is unaffected by contaminants such as metal ions. This first-order reaction is independent of the concentration of vazo and the type of monomer (Meyer 1984).

$$
\begin{array}{ccccc}
& CH_3 & & CH_3 & CH_3 \\
& | & & | & | \\
CH_3-&C&-N=N-&C&-CH_3 \rightarrow \quad 2\ CH_3-C^{\cdot} \quad + N_2 \\
& | & & | & | \\
& CN & & CN & CN
\end{array} \qquad (5)
$$

The rapid decomposition of vazo catalyst with an increase in temperature (Table 2) can be used to advantage in the bulk vinyl polymerizations in wood. A moderate temperature of 60 °C can be used to initiate the reaction, and, because the half-life is more than 40,000,000 min or about 20 years at 0 °C, the catalyzed monomer can be stored safely for months. Catalyzed monomers have been stored for over a year at 5 °C. The cost of vazo catalyst is in the range of \$1-\$10 a pound depending upon the amount ordered. Theoretically, 1g will produce 7.4×10^{21} free radicals and at \$10/lb; this is 3.3×10^{23} free radicals per dollar, or about \$0.02/g (Meyer 1984). Consequently, the reaction of vazo-initiated polymerization is easier to control and cheaper than the radiation process.

Dupont manufactures a series of Vazo catalysts that are substituted azonitrile compounds. The grade number is the Celsius temperature at which the half-life in solution is 10 hours. The series consists of the following compounds (Ibach & Ellis, 2005):
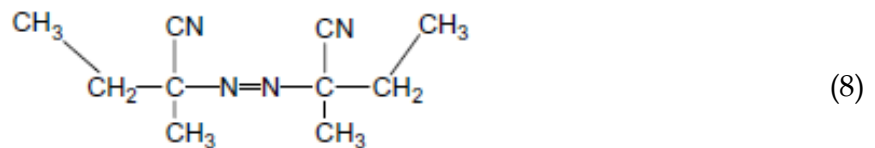
Vazo®52, the low-temperature polymerization initiator (2,2'-azobis-2,4-dimethylvaleronitrile),

$$ \text{(6)} $$
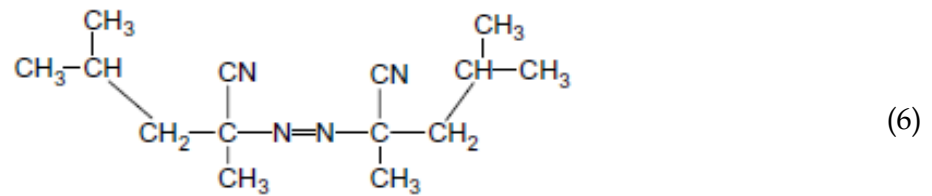
Vazo®64 (2,2'-azobisisobutyronitrile), also known as AIBN (toxic tetramethylsuccinonitrile (TMSN) is produced, therefore better to substitute Vazo 67),

$$ \text{(7)} $$
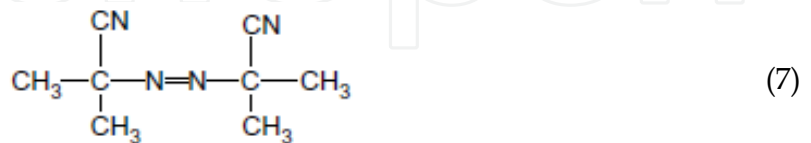
Vazo®67 (2,2'-azobis-(2-methylbutyronitrile)), best solubility in organic solvents and monomers,

$$ \text{(8)} $$

and Vazo®88 (1,1'-azobis-cyclohexanecarbonitrile),

$$ \text{(9)} $$

Temperature (°C)	$T_{1/2}$ (min)
0	4×10^7
7	1×10^7
18	1×10^6
30	1×10^5
46	1×10^4
70	270
100	5.5

Table 2. Half-life of Vazo Catalyst vs. Temperature

In addition to the Vazo series initiators, some macromonomeric initiators are also synthesized, which behave as macroinitiator, macromonomer and macrocrosslinker in thermal polymerization by themselves or copolymerization with vinyl monomers (Hazer, 1989; Matsumoto et al., 1989; Yamamoto et al., 2003). For example, a new macroinimers (Fig. 10) was prepared from the mixture of polyazoester (PAE-200), toluene diisocyanate (TDI) and hydroxyethyl methacrylate (HEMA) in the mol ratio of 1 : 2 : 2, respectively.

(Hazer et al., 1993). Such macromolecular initiator works more stable and normally has higher conversion rate as well as multifunction (Zhu & Guo, 1998).
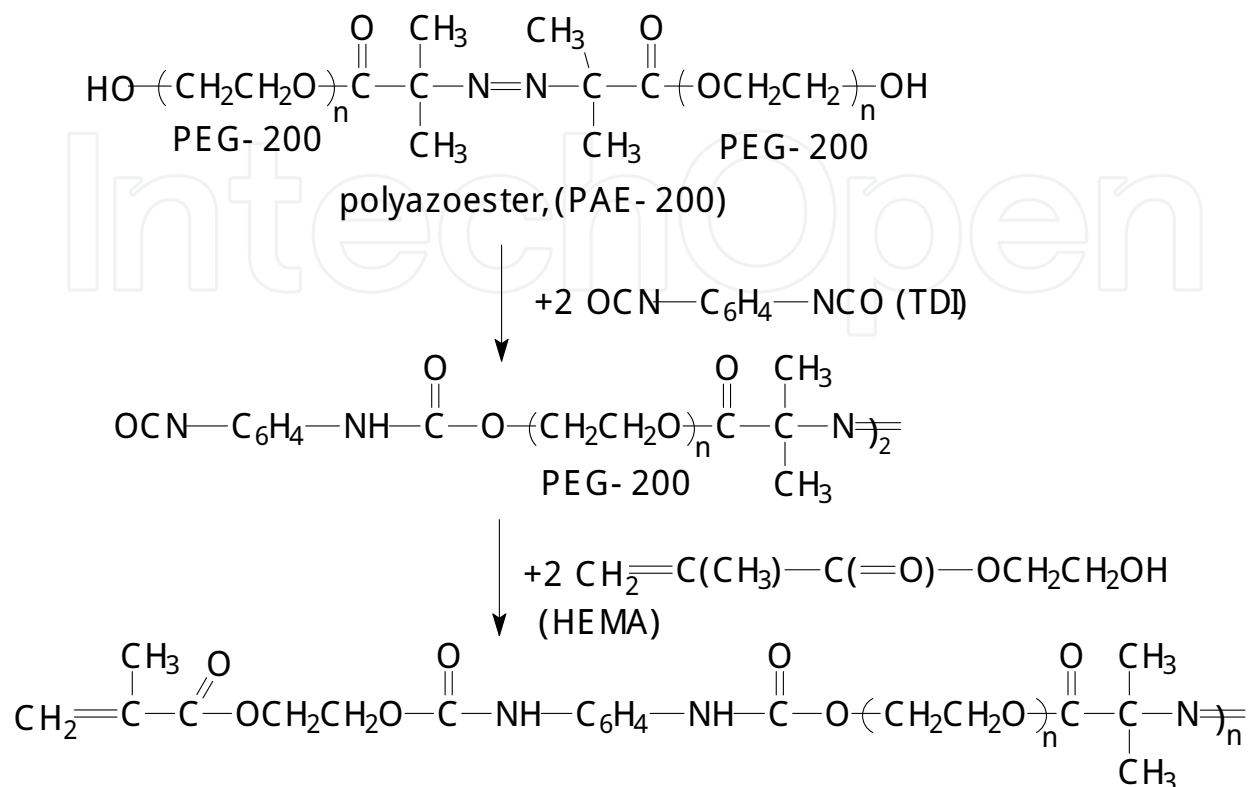

Fig. 10. Scheme of synthesis of the new macroinimer from mixture of PAE-200, TDI and HEMA

Vazo catalysts are most frequently used in concentrations of 1% or less by weight of the monomers. The rate of free radical formation is dependent on the catalyst used and is controlled by regulating the temperature. For Vazo 52, the temperature range is 35–80°C; for Vazo 64 and 67, 45–90°C; and for Vazo 88, 80–120°C (Ibach & Ellis, 2005). Benzoyl peroxide were used as initiators for beech wood impregnated with trimethylolpropane trimethacrylate (TMPTA) and polyethylene glycol dimethacrylate (PEGDMA), and cyclohexanone peroxide were used to initiate the polymerization of styrene in birch wood (Ibach & Ellis, 2005; Ang et al., 2009). AIBN was used as an initiator under 80~110ºC to initiate the polymerization of methyl methacrylate (MMA), styrene (St), glycidyl methacrylate (GMA) within poplar wood (Li et al., 2009; 2010a, 2010b; 2011a, 2011b).

3.2 Wood species

Many different wood species in the world have been reported to prepare WPC, e.g., maple (*acer pseudoplatanus*), spruce (*picea abies*), beech (*fagus silvatica*), white ash (*Fraxinus amerixans L*), white fir (*Abies alba*), lime (linden), abachi (*Triplochitin scleroxylon*), niangon (*Heritiera trifoliolata*), mutenye (*Guibourtia regia*), alder (*Alnus spp.A.cordata*), birch (*Betula pendula*), walnut (*Juglans nigra*), pear (*Pyrus sorotina*), hornbeam (*Acercarpinifolium*), larch (*Larix olgensis Henry*), ramin (*Gonystylus* spp.), redwood (*Seqyiua senoervurebs Endl*), red lauan (*Shorea* spp.), African rosewood (*Dalbergia melanoxylon Guill. & Perr.*), Brazilian rosewood (*Dalbergia Nigra*) and iroko (*Chorophora excelsa*) (Schaudy and Proksch, 1982).

Theoretically, both hardwood and softwood can be prepared into wood-polymer composites. However, most researches for WPCs mainly focused on hardwood. And in application, WPCs are traditionally made from hardwoods. Several reasons may contribute to this situation. One reason is that WPC is used for finished products, which are traditionally made from hardwoods. Another is that sapwood of most species (hardwoods and softwoods) treats well, but heartwood treatability is species-dependent. In hardwoods, pores (vessels) provide major longitudinal flow paths for fluids, while in softwoods, pits between pores and fibers, fiber lumens, and rays also play important roles in fluid flow, which commonly results in the poor impregnation of softwoods. Also, softwoods usually have lower density than hardwoods, requiring more treating chemical for comparable properties (Schaudy & Proksch, 1982; Schneider, 1994; Stolf & Lahr, 2004; Witt et al., 1977, 1981). In other words, most of hardwoods have the common denominator that they have a relatively open pore structure and minimum anmunt of pore blockage so that impregnant can be forced into the cell structure in a cost effective time frame. However, over all, a great many wood species in the world containing North America, South America, Asia, Europe, Africa and Australia, from softwoods to hardwoods even tropical woods, have been extensively investigated to be sutiable for WPCs Production (table 1).

In total, with the decrease of wood availability and the increase of less durable, younger and faster-growing trees, it seems a good way to replace expensive hardwoods with less expensive softwoods and low-quality faster-growing woods by producing WPCs, but to use wood to its best advantage and most effectively in structural or nonstructural applications, specific characteristics or physical properties must be considered.

3.3 Monomers

In WPCs, vinyl type monomers are polymerised into the solid polymer by means of a free radical mechanism, like the polymerisation of pure monomers. This vinyl polymerization is an improvement over the condensation polymerization reaction because the free radical catalyst was neither acidic nor basic which degrades the cellulose chain and causes brittleness of the composite, nor does the reaction leave behind a reaction product that must be removed from the final composite, such as water (Meyer, 1977). Vinyl polymers have large range of properties from soft rubber to hard, brittle solids depending upon the groups attached to the Carbon-Carbon backbone. Some examples of vinyl monomers used in WPC are styrene, vinyl chloride, vinyl acetate, ethylene oxide, many of the acrylates especially methyl methacrylate, acrylonitrile, t-butyl styrene and cholorostyrene. Since vinyl monomers are non-polar there is little if any interaction with the OH groups attached to the cellulose molecule. In general, vinyl polymers simply fill the capillaries, vessels and other void spaces in the wood structure (Meyer, 1981). However, there are cases where vinyl polymers bulk and graft with cell wall components (Li et al., 2011a). Vinyl monomers were used to stabilise wood in the presence of moisture and to increase the mechanical properties, while at the same time retaining the aesthetic qualities of wood that make it so desirable. Unlike deep coloured PF based thermosetting polymers, the vinyl polymers are clear, colourless and hard thermoplastic materials. The process of polymerising the vinyl monomers is the void spaces of wood does not discolour the wood or alter in any way its eye appealing nature (Haque, 1997)

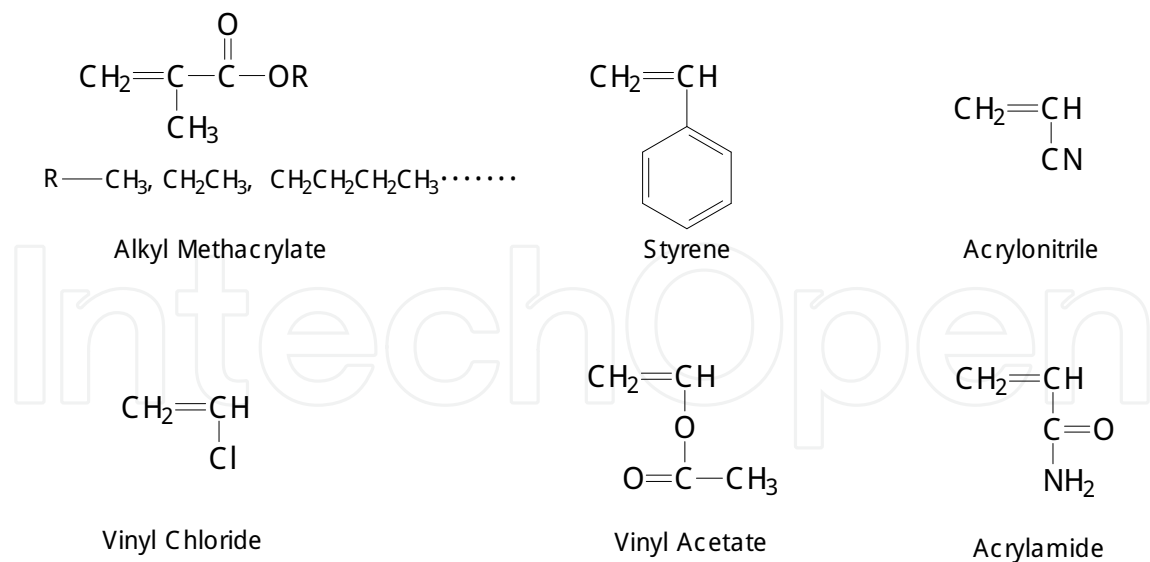Most of vinyl monomers are lised in table 1. Some of them are shown below:

Fig. 11. Structure of the commonly vinyl monomers for WPCs

3.3.1 Methyl methacrylate

Methyl methacrylate (MMA) is shown in Fig. 11. It is one of the least expensive and most readily available monomers and is used alone or in combination with other monomers to crosslink the polymer system (Li et al., 2011b). MMA has a low boiling point (101˚C) that can result in significant loss of monomer during curing and it is mostly cured in an inert atmosphere. The PMMA is resistant to aliphatic hydrocarbons, cycloaliphatic compounds, fats and oils, and also to weak acids and bases at temperatures of up to 60 ℃. The resistance to weathering of PMMA is very good. PMMA has good insulating properties, a high dielectric strength and high tracking resistance. PMMA is naturally transparent and colorless. The transmission for visible light is 92%. The refractive index is 1.492 for PMMA. There are types that transmit UV rays, and types that absorb it almost completely, as a result of which sensitive dyes on painted surfaces behind are protected from fading. Consequently, it is the most commonly used monomer for WPCs (Ibach & Ellis, 2005). MMA shrinks about 21% by volume after polymerization, which results in some void space (seen in Fig. 12a) at the interface between the cell wall of the wood and the polymer (Li et al., 2010a, 2011a). Adding crosslinking monomers such as di- and tri-methacrylates decreases the shrinkage of the polymer, which improves the compatibility between the polymer and cell walls (Fig. 12b). Oak and maple are often dyed to resemble walnut.

3.3.2 Styrene

Styrene (Fig. 11) is another monomer that is commonly used for WPCs (Ibach & Ellis, 2005). It normally relusts in poor interaction between polymer and wood cell walls because of its lower polarity (Fig. 13a). Other monomers are commonly added to control the polymerization rate, extent of polymerization, and to crosslink the styrene for improved physical properties of the WPCs (Fig. 13b) (Li et al., 2009; 2011a).

Hardness, compression and shear strength, wearability and bending strengths of styrene-treated wood are better than those of untreated samples. However, commonly, its impact strength sharply decreases over untreated wood, as seen of the clear cracks (Fig. 14a) and smooth fracture section (Fig. 14b) in the SEM morphologies of styrene-treated wood (Razi & Raman, 2000; Li et al., 2009; 2011a).

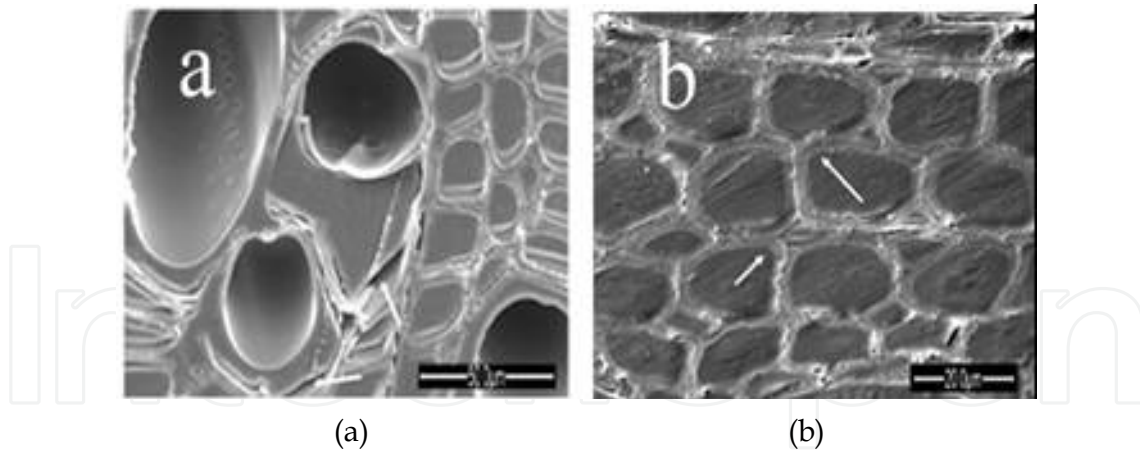(a)   (b)

Fig. 12. SEM morphologies of WPCs prepared from MMA monomer(s) (a) WPC made with MMA monomer (b) WPC made with MMA with GMA or/and anhydride as cross-linker

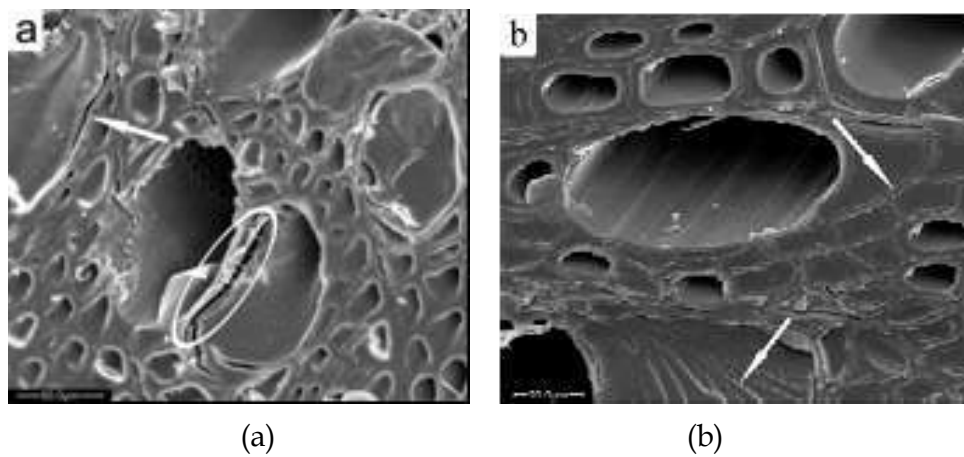(a)   (b)

Fig. 13. SEM morphologies of WPCs prepared from St monomer(s) (a) WPC made by St monomer (b) WPC made by St with GMA or/and anhydride as cross-linker
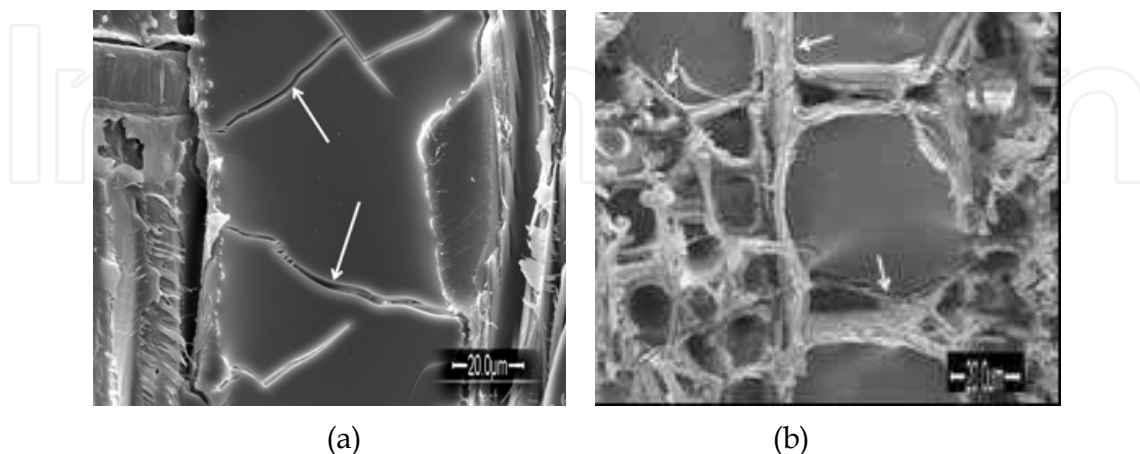

(a)   (b)

Fig. 14. SEM morphologies of impact fracture section of styrene treated wood (a) Vertical section of styrene treated wood after impact fracture (b) Cross section of styrene treated wood after impact fracture

3.3.3 Acrylonitrile

Acrylonitrile (Fig.11) is used in the production of WPCs mostly in combination with other monomers because the polymer does not improve properties by itself (Persenaire et al., 2004; Şolpan & Güven, 1999b). It is most frequently used with styrene, and less frequently with MMA, methyl acrylate, unsaturated polyester, diallyl phthalate, and vinylidene chloride. WPCs made with MMA-acrylonitrile or styrene-acrylonitrile mixtures were cured using either gamma radiation or catalyst (table.1), and the resultant composites were found to be very similar (Yap et al. 1990; Yap et al. 1991a, b, c).

Acrylonitrile is highly toxic and is a carcinogen; therefore attempts have been made to find chemicals that can be substituted for acrylonitrile in the treating solutions. These attempts have been only partially successful. N-vinyl carbazol can be used as a partial replacement of acrylonitrile. Several other compounds including acryloamide, N-hydroxy acryloamide, and 1-vinyl-2-pyrrolidone were tried unsuccessfully (Bakraji et al., 2001; Ibach & Ellis, 2005).

3.3.4 Vinyl chloride

Vinyl chloride is the organochloride with the formula CH_2-CHCl, which has a sickly sweet odor at ambient pressure and temperature. It is also called vinyl chloride monomer, or VCl. This colorless compound is an important vinyl monomerl chiefly used to produce the WPC because of its high reactivity (Calleton et al., 1970). However, recently, it has been rarely used in the production of WPC for its highly toxic and carcinogenic characteristic.

3.3.5 Vinyl acetate

Vinyl acetate (VAc) monomer with the formula $CH_3COOCH=CH_2$ is a versatile and economically important chemical building block used in a wide variety of industrial and consumer applications, such as: Plastics, films, lacquers, elastomers, inks, water-based emulsion paints, adhesives, finishing and impregnation materials, paper coatings, floor tiling, safety glass, building construction, acrylic fibers, glue, cosmetics and personal care products, textile finishing and non-wovens and so on. Among, about 83% of the VAc manufactured is used to produce polyvinyl acetate emulsions and resins for its lower toxicity and good reactivity. Thus, vinyl acetate is often used as active vinyl monomer to produce WPCs. However, it is commonly used in combination with other monomers such as methyl methacryalte, styrene, acrylonitrile, vinyl chloride, glycidyl methacrylate and so on (Baysal et al., 2007; Deka & Saikia, 2000; Li et al., 2010c). The resultant WPCs exhibit excellent mechanical properties and good durability (Sheikh & Taromi, 1993).

3.3.6 Acrylamide

Acrylamide (or acrylic amide) is a chemical compound with the chemical formula C_3H_5NO. It is a white odourless crystalline solid, soluble in water, ethanol, ether, and chloroform. Acrylamide is incompatible with acids, bases, oxidizing agents, iron, and iron salts. Acrylamide is prepared on an industrial scale by the hydrolysis of acrylonitrile by nitrile hydratase.

As the conjugated effect of acrylamide, it is one of the most active acrylic-based monomers. Thus, it is universally used by itself or in combiniation with other vinyl monomers to prepare WPCs (Bakraji et al., 2001, 2002, 2003). The resultant physical and mechanical properties of acrylamide treated wood were significantly improved for the higher polymer loading in the presence of acrylamide (Bakraji & Salman, 2003).

3.4 Additives

Additive is a substance added to another substance or material to improve its properties or impart functions to it in some way. Additives are often present in small amounts and are used for a variety of purposes, as in preventing corrosion, stabilizing and strengthing polymers, preserving and coloring material, promoting reaction, controlled release of biocides, repellenting water or other functions.

Additives designed or suitable for wood-polymer composites are wholly classified two categories. One is normal additives, including crosslinkers, coupling agents and curatives. The other is functional additives, including fungicides, fire retardants, hydrophobic agents, pigments and UV stabilizers.

3.4.1 Normal additives

The normal additives are commonly used to improve the properties of polymer for wood-polymer composites.

3.4.1.1 Crosslinkers

Crosslinkers are additives used to enhance crosslinking or bonding between polymer chains, so that the resultant polymer mainly exists in a 3D network form in wood pores, which could increase reaction rate and significantly improve the mechanical properties of WPCs. The studied crosslinkers in WPCs include glycidyl methacrylate (GMA), ethylene glycol dimethacrylate (EGDMA), polyethylene glycol dimethacrylate (PEGDMA), 1,6-hexanediol diacrylate (HDDA), trimethylene glycol dimethacrylate (TMEGDMA), tetraethylene glycol dimethacrylate (TTEGDMA), trimethylolpropane triacrylate (TMPTA), trimethylolpropane trimethacrylate (TMPTMA), triallyl phosphate (TAP), trivinyl isocyanurate (TVI), unsaturated polyester (UP) and divinylbenzene (DVB) (table 1). The crosslinking agents are normally used with MMA, St, or other vinyl monomers. The addition of 1.0% divinylbenzene, triallyl phosphate, or trimethylolpropane trimethacrylate crosslinking agent to styrene results in an increased polymerization rate, with divinylbenzene having the most pronounced effect on the polymerization rate (Lawniczak & Szwarc 1987). Generally 10% or more crosslinking agent is needed to give the best improvement in physical or mechanical properties, such as hardness, abrasion resistance, and compression strength as well as bend strength. Composite materials obtained by evacuation of wood (beech, spruce, ash, and tropical wood *Pterocarpus vermalis*) followed by its impregnation with an unsaturated polyester-MMA-styrene mixture or unsaturated polyester-acrylonitrile-styrene mixture and gamma irradiation-induced curing exhibit decreased water vapor absorption and improved dimensional stability, hardness, compression strength, and wear resistance, compared to untreated wood (Ibach & Ellis, 2005; Ng et al. 1999).

WPCs with only MMA show a void space at the interface between cell wall and polymer (Fig. 12a). With addition of polar crosslinking esters, such as EGDMA, PEGDMA, the shrinkage (and hence void spaces) of the polymer during polymerization is reduced (Fig. 15), suggesting better adhesion of the polymer to the inner surface of cell wall.

In addition, some crosslinkers in certain contents can also improve the impact strength. In theory, the embrittlement may be due to the short inflexible unit of polymer in WPCs. If the inner unit of polymer has more flexibility, the embrittlement should be reduced. For example, wood-polystyrene composite has lower impact strength for the stereo-hindrance effect of bezene ring of polystyrene, as evidenced by the smooth impact fracture section (Fig. 14b). However, it would be useful to reduce the brittleness by addition of reactive

(a)   (b)

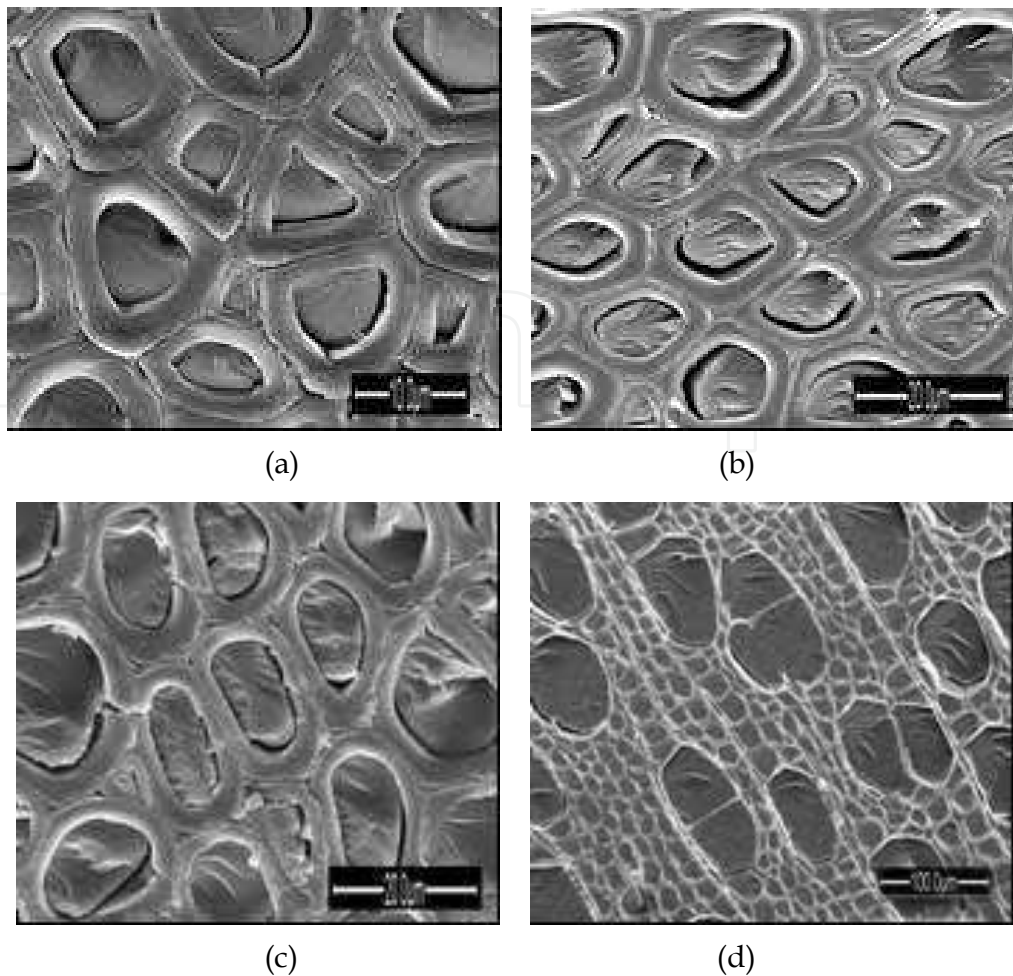(c)   (d)

Fig. 15. SEM morphologies of WPCs prepared with addition of crosslinkers (a) WPC made by MMA and EGDMA (b) WPC made by St and EGDMA (c) WPC made by EGDMA (d) WPC made by PEGDMA
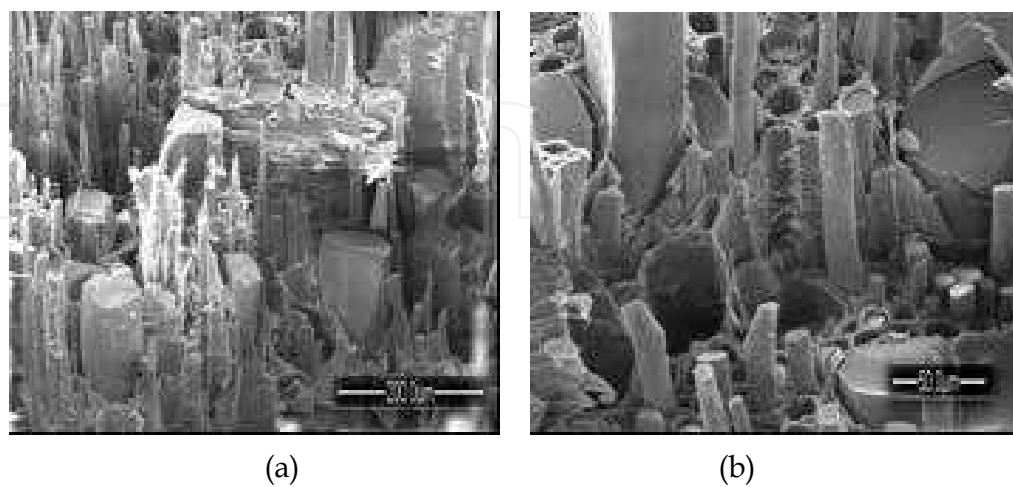

(a)   (b)

Fig. 16. SEM morphologies of impact fracture section of WPCs with PEGDMA as crosslinker (a) Cross-section suface of WPCs with PEGDMA after impact fracture (b) Cross-section of WPCs with PEGDMA and St after impact fracture

difunctional chemicals with long ether chains. For example, the addition of EGDMA or PEGDMA containing 4 to 10 units of ethelene glycol can help wood-polystyrene composite achieving good toughness, as evidenced by the rough impact fracture section (Fig. 16). The addition of isocyanate compounds with acrylic monomers reduces the brittleness of WPCs consisting only of acrylic compounds (Schaudy & Proksch, 1982). The toughness of Wood-Polystyrene Composites modified by GMA and anhydride as crosslinkers and other mechanical properties as well as dimensional stability were all improved (Li et al. 2011a).

3.4.1.2 Coupling agents

Coupling agents are substances that are used in small quantities to treat a surface so that bonding occurs between it and other surfaces, e.g., wood and polymer resulted in WPCs (Chen et al. 1998). Generally, coupling agents act as bridges that link wood matrix and resulting polymers by one or more of the following mechanisms: covalent bonding, polymer chain entanglement, and strong secondary interactions as in the case of hydrogen bonding (Lu et al. 2000).

Over forty coupling agents have been used in WPCs, which are classified into organic, inorganic, and organic-inorganic groups. Organic agents include isocyanates, anhydrides, acrylates, epoxides, organic acids, monomers, polymers, and copolymers. Only a few inorganic coupling agents, such as silicates, are used in WPC. Organic-inorganic agents include silanes and titanates (Lu et al. 2000).
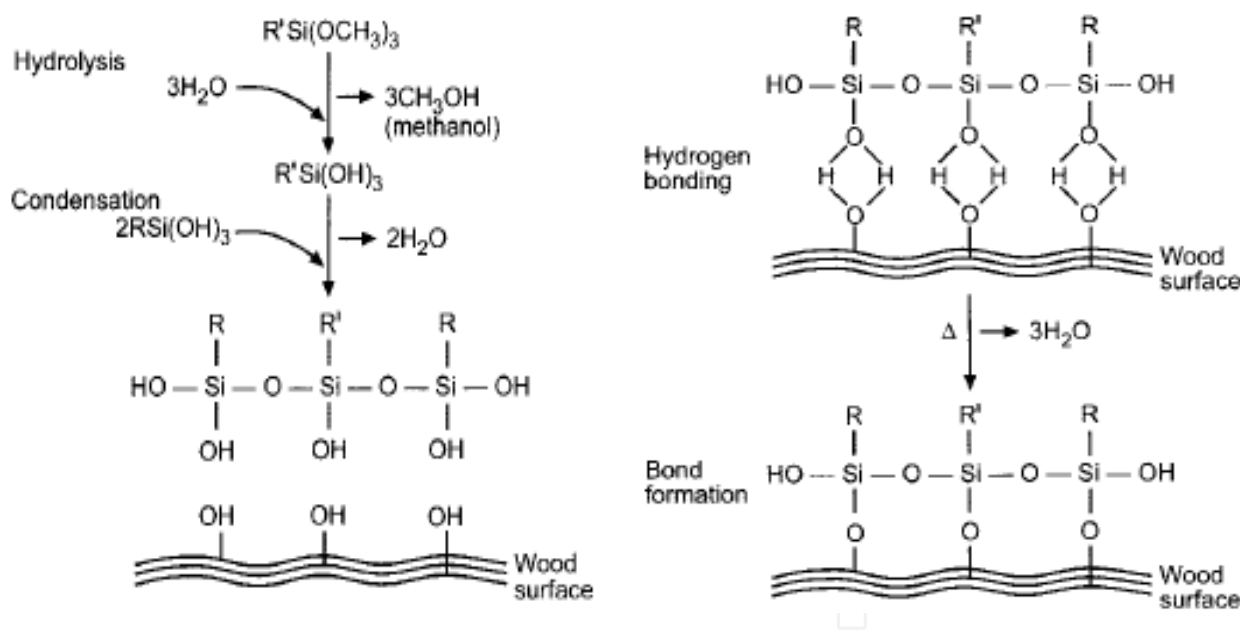

Fig. 17. Scheme for chemical coupling of alkoxysilane onto wood surface

Organic coupling agents in WPCs normally have bi- or multifunctional groups in their molecular structure. These functional groups, such as (-N=C=O) of isocyanates, [-(CO),O-] of maleic anhydrides, and (-C1-) of diclorotriazine derivatives, interact with the polar groups [mainly hydroxyl groups (-OH)] of cellulose and lignin to form covalent or hydrogen bonding (Lu et al. 2000). Alternatively, organic coupling agents can modify the polymer matrix by graft copolymerization, thus resulting in strong adhesion, even crosslinking, at the interface. The normally used organic coupling agents include glycidyl methacryalte (GMA) (Li et al. 2009a; Westin et al. 2006), allyl glycidyl ether (AGE) (Şolpan &

Güven, 1999a), isopropyl glycidyl ether (IPG) (Chang & Chang, 2006), hexanediol diacrylate (HDDA) (Ibach & Ellis, 2005), hydroxyethyl methacrylate (HEMA) (Hazer et al. 1993; Zhang et al. 2006), maleic anhydride (MA) (Li et al. 2011a; Mohamad et al. 2007) and N-vinyl pyrrolidone (NVP) (Husain et al. 1995; 1996; Bakraji et al. 2002). In principle, the acrylic coupling agents commonly bear similar structure with the chief components of wood, i.e. cellulose and lignin, thus such coupling agents have been played an important role in wood-polymer composites (Baysal et al. 2007).

Inorganic coupling agents possibly act as dispersing agents to counteract the surface polarity of wood and improve the conlpatibility between wood and polymer (Lu et al. 2000; Mai & Militz, 2004a). Organic-inorganic agents are hybrid compounds in structure. For example, titanates usually contain a titanium center and an organic part surrounding this inorganic atom. The functionality of the organic part in these agents determines their coupling effectiveness in WPCs (Bengtsson et al. 2007). Organic-inorganic coupling agents are between organic and inorganic agents in function (Lu et al. 2000; Mai & Militz, 2004b). One of most important organic-inorganic coupling agents is silicone organic silicon compound (Brebner & Schneider, 1985; Elvy et al. 1993; Mai & Militz, 2004b; Schneider & Brebner, 1985; Sèbe & Brook, 2001). The mechanism of such organic coupling agent for wood modification is schemed as Fig. 17 (Tshabalala et al. 2003). For example, wood fiber surface was effectively modified by triethoxyvinylsilane (TEVS) (Fig. 18) (Gwon et al. 2010). The normally used organic silicone coupling agents included triethoxyvinylsilane (TEVS), γ-Aminopropyltriethoxysilane (KH550), γ-Glycidoxypropy1 trimethoxysilane (560), γ-Methacryloxypropyl trimethoxysilane (KH570), 3,3,3-trifluoropropyltrimethoxysilane (TFPTMOS), 2-heptadecafluorooctylethyltrimethoxysilane (HFOETMOS) and decyltrimethoxysilane (DTMOS) (Mai & Militz, 2004b; Hansmann et al., 2005).

3.4.1.3 Catalysts

Catalysts normally play an important role in proceeding reaction or activating chemicals. Some catalysts have been reported in accelerating reactions of monomers or activating wood components in wood-polymer composites. For example, N, N-dimethylaniline is used as an accelerator to improve the reaction of monomers within wood under lower temperature (Hazer et al. 1993). When Maleic anhydride (MAN) is used as a coupling agent of WPCs, adding a moderate amount of MgO can improve the performance of MAN because MgO reacts with water and the acid group to yield carboxylate ions (-COO-). Concurrently, Mg^{2+} interacts with two carboxylate ions as a crosslinking agent and yields ionomer systems (Lu et al. 2000). Lithium nitrate ($LiNO_3$), copper sulfate ($CuSO_4$) and sulfuric acid (H_2SO_4) are found to be useful for improving the polymer loading and partly enhancing the mechanical properties (Bakraji et al. 2002; Bakraji & Salman, 2003; Husain et al. 1996).

3.4.2 Functional agents

3.4.2.1 Fungicides

Fungicides are designed to kill and prevent the growth of fungi. There are two normal ways favorating the decay resistance of wood-polymer composites. One is inorganic compounds like boron compounds as wood preservatives being added into wood pores before formation of WPCs (Kartal et al., 2004; Baysal et al. 2007). Boron mixture of Boric acid (BA) and borax (BX) are used as preservatives for its sufficient protection against wood destroying organisms, low mammalian toxicity, and low volatility as well as colorless and

odorless characteristic. The polymerization of monomers in wood cell lumen further improves the leachability of the boron compounds. Thus, the combination treatment synergeticly improves the mechanical properties, dimensional stability, decay resistance and fire resistance (Baysal et al. 2007). The other way is fabrication of bioactive wood-polymer composites. The basic approach is still in situ polymerization of vinyl monomers in wood, with the appropriate choice of a bioactive, toxic, functional group incorporated in the monomer, and with other modifications based on wood-polymer reactions (Subramanian, 1984). Organotin monomers carrying the bioactive tributyltin group are considered to be the effective monomers for bioactive wood-polymer composites. Tri-n-butyltin methacrylatemaleic anhydride and tri-n-butyltin methacrylate—glycidyl methacrylate are examples of suitable monomer combinations for in situ copolymerization. SEM-EDX proves that a detectable portion of tin copolymer is located in cell walls, and the test results indicate that the treated wood is effective in providing resistance against white rot and brown rot
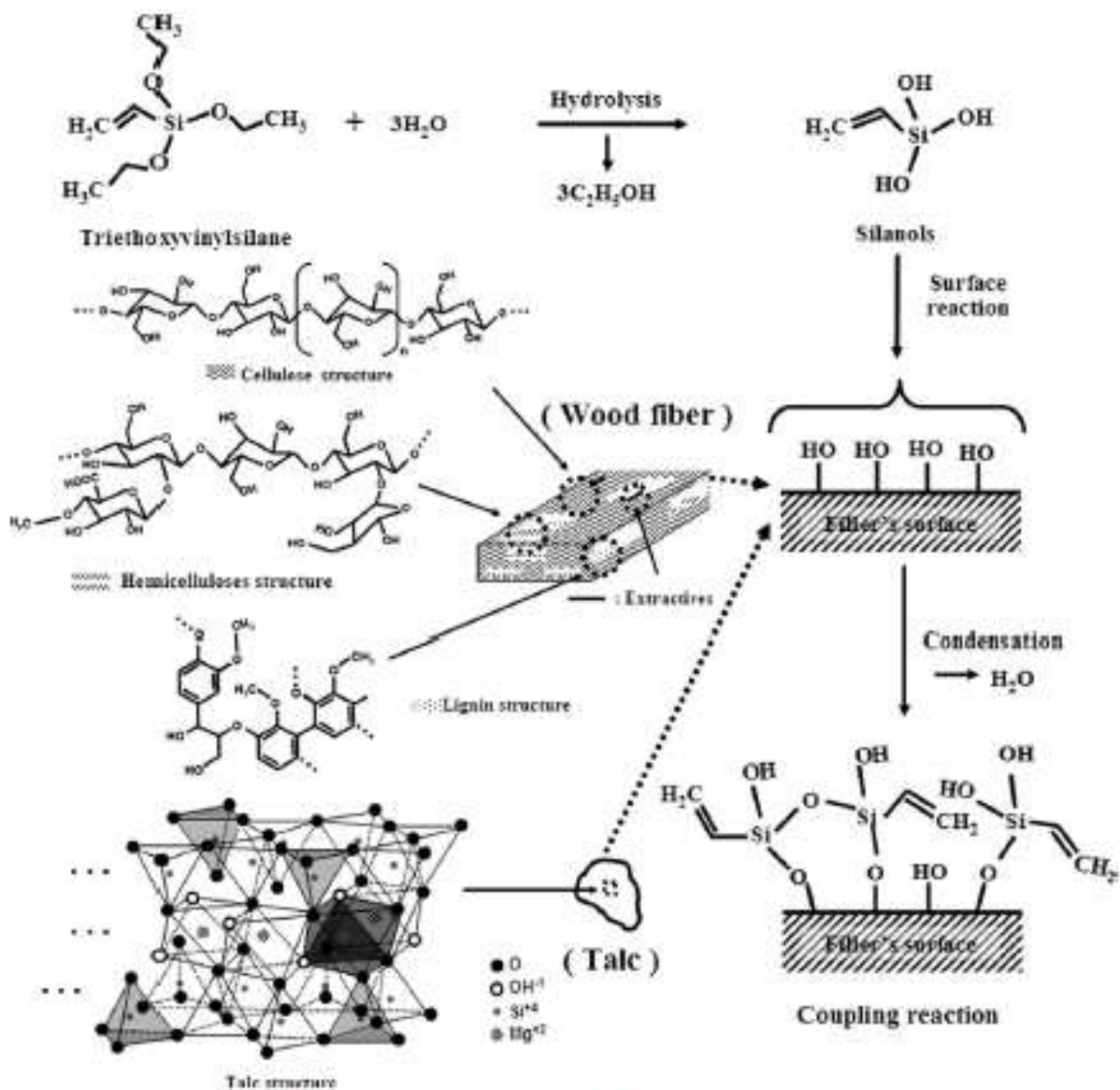

Fig. 18. Schematics of the triethoxyvinylsilane coupling reactions on the wood matrix

fungi as well as marine organisms; notable improvements in flexural and impact strength and significant reduction in moisture absorption are also observed (Subramanian, 1984). Such bioactive monomers are normally synthesized before impregnated into wood pores, thus, the additives here refer to the tin materials.

3.4.2.2 Fire retardants (thermal stabilizer)

Fire retardants (thermal stabilizer) are additives added to improve fire resistance (or thermal stability) of wood-polymer composites. They are normally applied to pretreat wood or mixed into monomers before impregnating wood. Such additives include silicone dioxide (SiO_2), alumina trihydrate ($Al(OH)_3$), magnesium oxide (MgO), boric acid (H_3BO_3), or/and borax ($Na_2B_4O_7$), tributyl phosphate and alkenyl esters of phosphorus acids (Baysal et al. 2007; Ibach & Ellis, 2005; Lu et al. 2000). The addition of magnesium oxide and boron compounds can protect wood fiber from thermal decomposition and degradation during high-temperature composite processing (Lu et al. 2000).

Addition of a solid organic halogen-compound with a high content of Cl or Br, accelerates the polymerization (Pesek et al. 1969). Addition of tributyl phosphate accelerates the polymerization rate of MMA 2.5 times and decreases the required radiation dosage. Addition of alkenyl phosphonates or alkenyl esters of phosphorus acids increases the polymerization rate and imparts fire resistance and bioresistance to the resultant WPC (Schneider et al., 1994).

3.4.2.3 Hydrophobic agents

Hydrophobic agents are substances that are used in small quantities to impart hydrophobicity to materials so that the contact angle is biger than 90º (Baysal et al. 2006; Sèbe & Brook, 2001; Tshabalala et al. 2003). The normal ways to endow wood-polymer composites with hydrophobic property include pretreatment of wood substance by organic silicone compounds (Fig. 19) and in situ polymerization of special monomers bearing fluorin (F) element within wood pores (Fig. 20). From the figures, it can be known that both methods impart hydrophobic property to wood. The hydrophobic agents, i.e. water repellent agents are organic silicone compound and 2,2,3,3,4,4,5,5,6,6,7,7-Dodecafluoroheptyl methacrylate (G04), respectively.

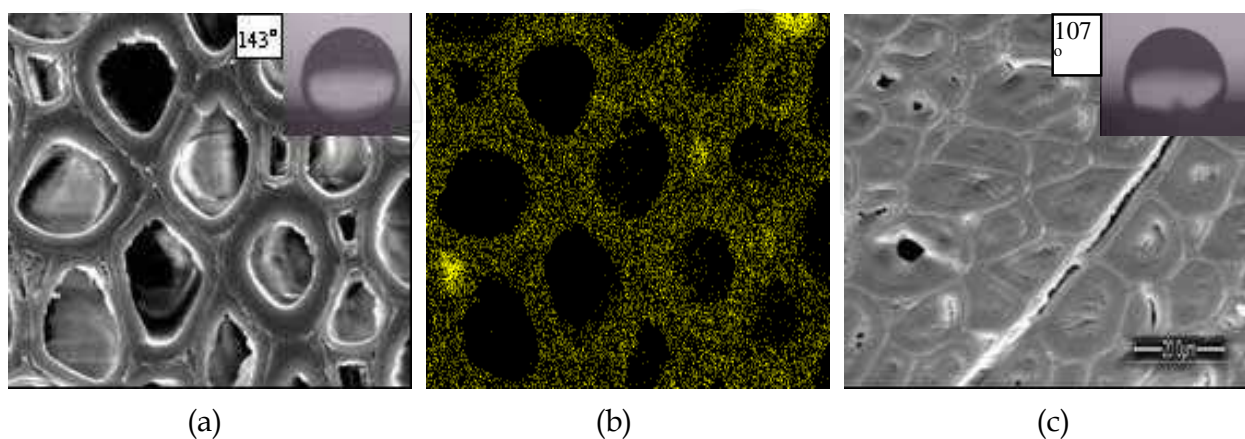(a)   (b)   (c)

Fig. 19. SEM morphologies of silicone compounds pretreated wood with contact angle (a) Wood pretreated with organic silicone compound (b) Si element distribution corresponding to micrograph (a) (c) WPC pretreated with silicone compound
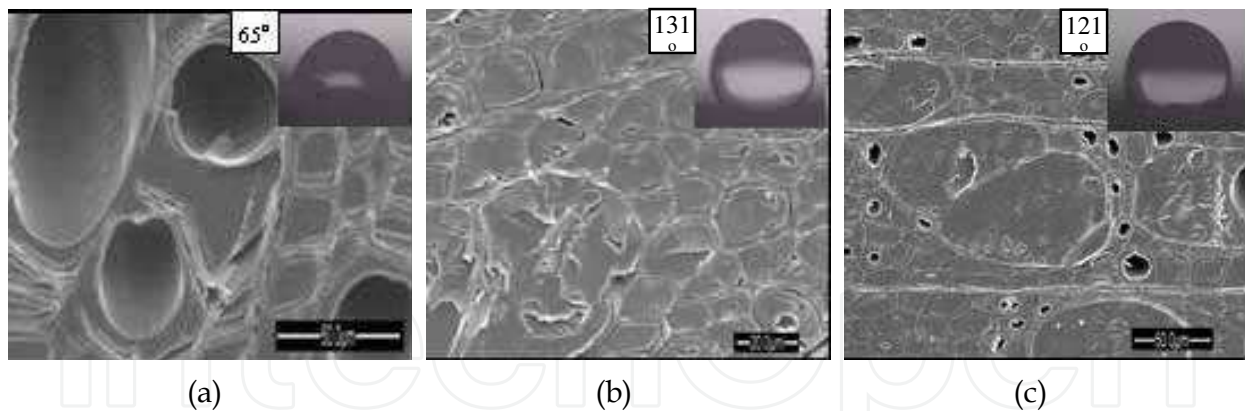
Fig. 20. SEM morphologies of wood-polymer composites with contact angles (a) WPC prepared by MMA (b) WPC prepared by G04 (c) WPC prepared by G04 and GMA

3.4.2.4 Pigments

Pigment additives, i.e. dyes, are substance being used to impart color to materials (WPCs). They can be added to change the color of the impregnated wood with the darker browns the most popular (Fig. 21). Oak and maple are often dyed to resemble walnut. Veneers can be treated with MMA and a dye to give veneers of different colors which are laminated into custom knife handles (Fig. 22) (Rowell, 2009).

Fig. 21. Comparison of the colors of WPCs with different dyes

Fig. 22. Colored knife handles from veneers with MMA monomer and dyes

3.4.2.5 UV Stabilizers

UV stabilizing agents are used to increase the ultraviolet (UV) and sunlight exposure resistance of plastics, elastomers, paints, coatings, adhesives and other polymeric materials (e.g. WPCs). The normal ways also contain pretreatment with inorganic additives (Fig. 19c) and in-situ polymerization of inorganic additives with monomers (Fig. 23) (Li et al. 2009b).
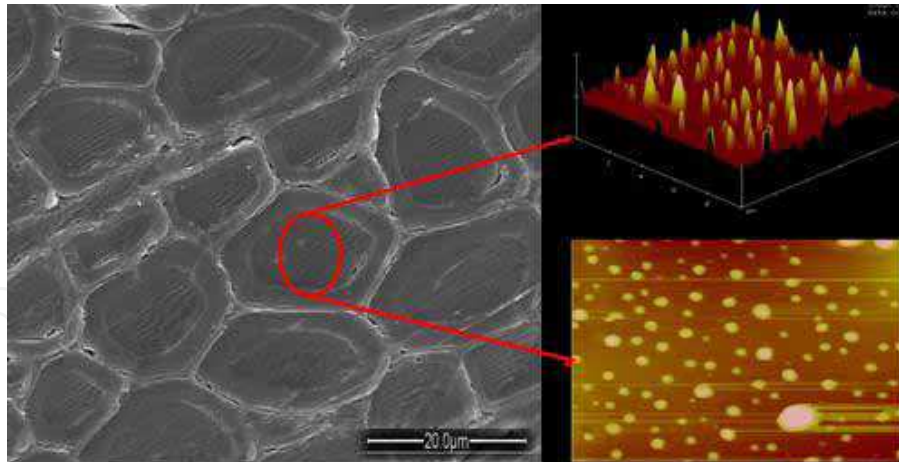
Fig. 23. WPC added with nano-SiO$_2$

3.5 Impregnation style

Wood is impregnated by various monomers, which can be done by diffusion, vacuum immersion and vacuum-pressure (Husain et al. 1996). The final way can be conducted depending on the variation in permeability of wood, containing the broadly variation between species, between sapwood and heartwood, variation in wet and dry condition, and the availability of facilities as well as the experimenter's preferences. Vacuum or/and pressure is usually applied during impregnation because simple diffusion of wood in a treating solution under normal atmospheric pressure requires a lengthy time and usually leads to incomplete absorption. Vacuum immersion of monomer consists of evacuating the air and moisture from wood vessels and lumens using a vacuum pump and then introducing the monomer from a reservoir maintained at atmospheric pressure (Fig. 24). Vacuum-pressure method uses a combination of vacuum and pressure (Zhang et al. 2006). Both the vacuum immersion and vacuum-pressure treatments are widely used in preparation of WPCs (Fig.25) (Ding, 2009).

3.6 Polymerization style

The impregnated monomer can be polymerized through two different processes: by the incidence of radiation or by the thermal decomposition of initiators, which have been introduced above (Meyer, 1984).

The U.S. Atomic Energy Commission sponsored research that used gamma radiation to make WPCs in the early 1960s. The cobalt-60 radiation process does have some distinct advantages in making WPCs, such as the monomer can be stored at ambient conditions, as long as inhibitor is included, and the rate of free radical generation is constant for cobalt-60 and does not increase with temperature; terilization can be achieved simultaneously by gamma irradiation; the gamma radiation technique can be applied to any size of material due to its high penetration; natural wood grain and colour are retained, or an artificial, uniform colouring the material is possible.(Şolpan & Güven, 1999a; 1999b). However, drawbacks include safety concerns, cost considerations and regulations needed when using radiation. Safety requirements must be satisfied before a cobalt-60 source can be installed and licensed. Radiation-trained personnel must be on the staff before a license can be issued. At least 500,000-1,000,000, Ci (curies) of cobalt-60 are required in a production source for making wood-polymer composites, and at \$1.00 or more per curie, a considerable investment must be made before production can begin (Ibach & Ellis, 2005).
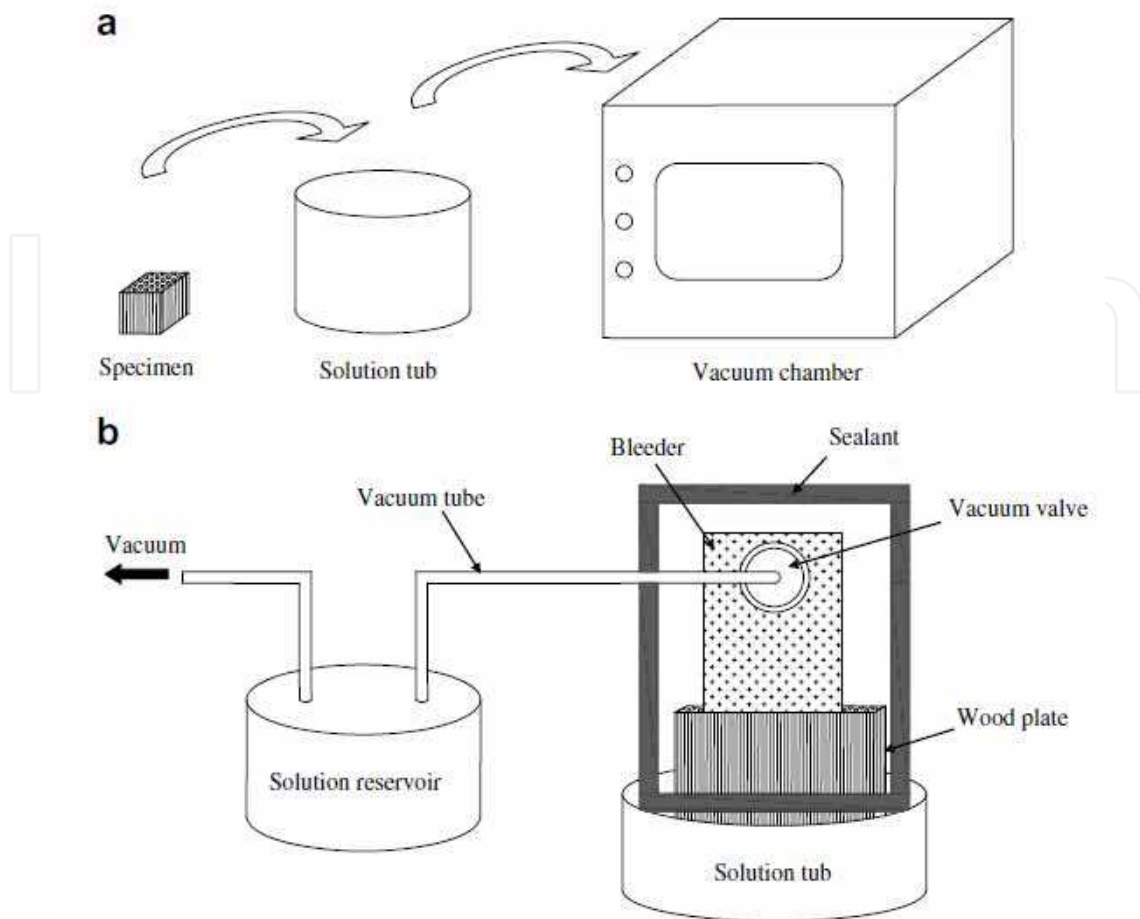
Fig. 24. Impregnating methods for wood-polymer composites: (a) natural soaking method, and (b) vacuum bag method (Kim et al. 2008)

(a)   (b)

Fig. 25. Systems used to impregnate the wood (a) impregnating equement in experimental use (b) impregnating equement in plant use

The heat-catalyst-initiated method is now widely used by researchers (El-Awady 1999; Yildiz et al. 2005; Zhang et al. 2006; Li et al., 2009; 2010a; 2011a, 2011b) and in industrial production, for it is less cost and easier operation; and the improvements in the physical and mechanical properties of wood species combined with anti-shrink efficiency make this method preferable to the γ-radiation method (El-Awady 1999). But, it also has some shortcomings such as longer reaction time over gamma radiation, sealed container requirement and releasing nitrogen during decomposition which normally results in void spaces in the resultant polymers within wood pores and thus decreases by the mechanical properties of wood-polymer composites. However, despite all that, during the past 50 years the industrial development has been slow but steady for bothγ-radiation and catalyst-heat processes.

3.7 WPC types

There are two orders of porosity in wood: cavities for the cell lumen and micropores within the cell walls. Normally, as the monomers are nonpolar, they maninly exist in cell lumen, and the resulting WPC belongs to cell-lumen WPC. While the cell lumen and cell wall being combinely treated by monomer with other chemical reagents, the resulting WPC belongs to combined cell-wall-lumen WPC. However, there is another treatment for WPC which is different from the above two WPC types. It is considered to be compressed WPC for the wood being compressed before or after the monomers penetrating wood.

3.7.1 Cell-lumen WPC

If a chemical introduced into dry wood does not cause swelling, the chemical remains in cell lumens. Most ofthe common vinyl monomers (such as styrene and methyl methacrylate) are in the nonswelling or little-swelling category over normal treating times (Schneider, 1994) and so produce essentially cell-lumen WPC. When a nonswelling chemical is changed into a polymer, the polymer will occupy the cell cavities but not the cell walls. Since the cell cavities are a major path for moisture movement in wood (Li et al, 2011c), plugging them with a polymer makes the wood more resistant to rapid changes in moisture content, especially along the grain. The effect is greater dimensional stability over the short term. There is speculation that physical restraint by polymers in cell lumens reduces swelling at a given moisture condition (Schneider et al. 1994). This would contribute to dimensional stability. Similar to this, by adding bulk vinyl monomers to the void spaces in wood; compression strength, hardness, and abrasion resistance greatly improved In the homo-polymerization process, the polymer is located almost completely in the lumen; only minor amounts are polymerized in the cell wall. Thus, most of the WPCs are cell-lumen type WPCs (Schneider et al., 1994).

3.7.2 Combined cell-wall-lumen WPC

Cell-wall micropores are transient. They are at maximum volume in fully water-swollen wood and disappear nearly linearly with moisture content as wood dries below the fiber saturation point. They can be largely (there is some hysteresis) restored by re-exposing to moisture or another polar fluid. The cyclic moistening and drying wood undergoes in use, increasing and decreasing micropore volume, are the reason for its dimensional instability. If a chemical reagent can bulk and/or react with wood cell wall, it may inhibit the cell wall from swelling and slow down the movement of moisture into wood cell wall, particularly in the liquid form. Consequently, the combined treatment of bulking wood cell wall and filling

wood cell lumen may impart both improved mechanical properties and durability to wood. The bulking reagents include silicon compound, maleic anhydride, PEG1000 and so on (Fig. 19 and Fig. 26); and the filling reagents could be most of vinyl monomers and functional monomers, such as GMA, EGDMA, PEG(200)DMA and so on (Keskin et al., 2008; Persenaire et al., 2004; Rodrigues et al., 2004; Roussel et al., 2001; Schneider et al.; 1991; 1995; WallstroÈm & Lindberg, 1999)

(a)   (b)   (c)

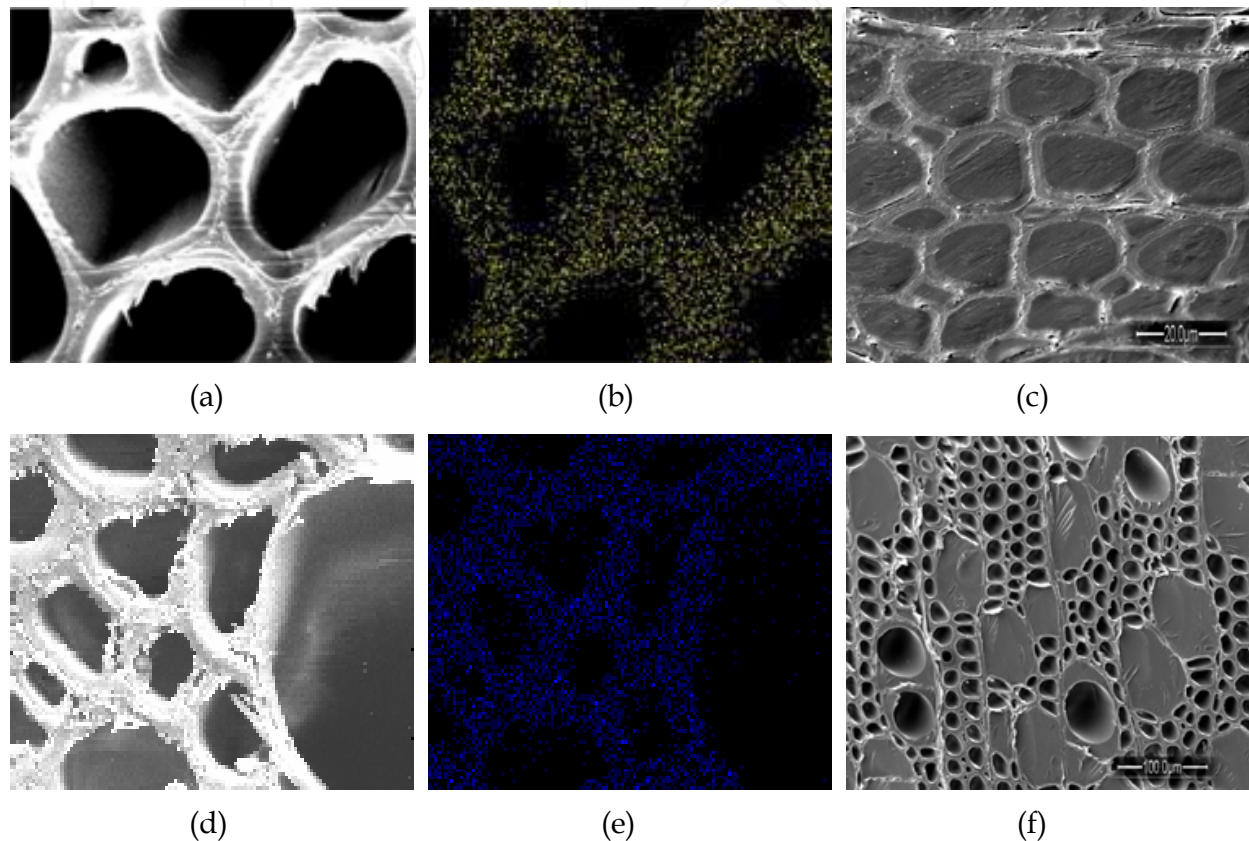(d)   (e)   (f)

Fig. 26. SEM morphologies of wood and bulked wood as well as cell-wall-lumen WPC (a) Wood (b) Wood bulked with maleic anhydride marked by Diacetone acrylamide (DAAM) (c) Combined cell-wall-lumen WPC (d) Wood (e) Wood bulked with PEG1000 marked by silicon element (f) Combined cell-wall-lumen WPC

For the bulking treatment, one way is the bulking agents in liquid form directly move into and thus swell the cell wall; another way is the bulking agents as nonpolar or weak polar molecules swell the cell wall by diluting in polar solvents, such as methanol acetone, tetrahydrofuran (THF), ethanol, dimethyl sulfoxide and so on (Meyer, 1981). The solvents evaporate during cure, which limits solids retention. Cell-wall followed by cell-lumen treatments, neat (100% active ingredient), swelling monomers or mixtures of swelling and nonswelling monomers (Rowel1 et al., 1982) and silane coupling agents combined with nonswelling monomers have shown improved dimensional stability over cell-lumen treatments (Brebner & Schneider, 1985; Schneider & Brebner, 1985). Considering the large number of chemicals available, combination formulations that develop desirable properties of both cell-wall and cell-lumen treatments have promise (Schneider et al., 1994).

3.7.3 Compressive WPC

The compressive-wood polymer composite (CWPC) was developed based on combination of compression technique and vinyl polymerization. One way is compressing wood followed by vinyl polymerization; the other way is one-step combination of compressing wood and vinyl polymerization. For the prior way, vinyl monomers such as MMA, St, combination of MMA and St, are impregnated into a drying set of deformed wood and further polymerized to fix the compressive deformation. Resultantly, increasing MOR and MOE as well as superior dimensional stability are finally obtained (Dwianto & Yalinkilic, 2000). For the latter way, vinyl monomers with functional groups, such as GMA, AGE, Maleic Anhydride (MAN) are impregnated into wood and then the impregnated wood (or veneer) are further hot-compressed under temperature of 70~120°C depending on the activity of monomers (Fig. 27).
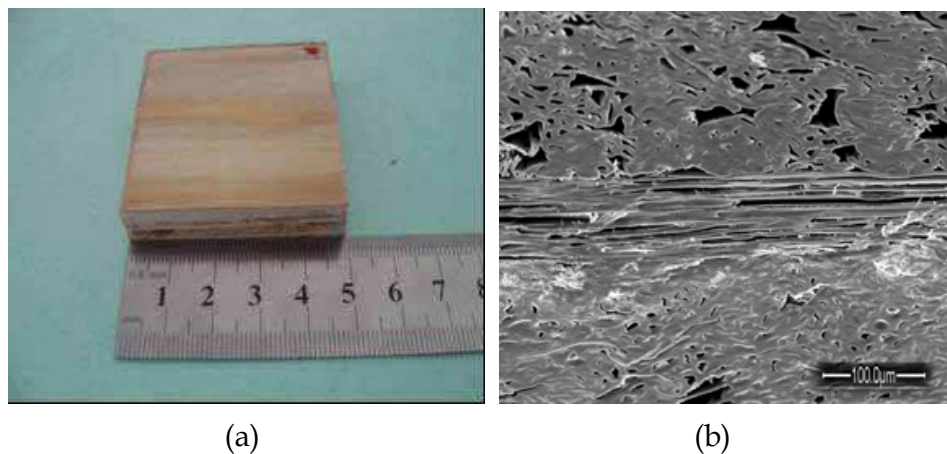

|(a)|(b)|

Fig. 27. Compressive WPC veneer covered plywood and its SEM morphology (a) Compressive WPC veneer covered plywood (b) SEM morphology of sample (a)

3.8 WPC properties

In-situ formation of polymer within wood pores improves the physical properties of the wood, allowing the composite to be tailored for specific applications. Frequently targeted properties are most mechanical properties, hardness, dimensional stability and resistance to abrasion, decay, weather and fire. Other important propertics are toughness, strength, thermal conductivity and appearance.

3.8.1 Mechanical properties

It was found that most of the mechanical properties of WPC are improved over untreated wood. The normal including properties are MOE, MOR and compressive strength (Li et al. 2009a; 2010a; 2011a). The mechanical properties of WPC are almost the same for Cell-lumen WPC and Cell-wall-lumen WPC. But where WPC is impregnated into the cell wall it imparts better dimensional stability than in a lumen only treatment. In addition, the toughness and impact strength of WPCs are variable depending on the style of monomers. Increasing the toughness of wood with polymer increases the crack resistance and brittleness at room temperature. Impact strength and toughness are closely related; both refer to the ability of WPCs to resist fracturing. Measurements of impact strength are made using the Izod and the Charpy impact test instruments. The test involves striking the specimen with a

pendulum and measuring the impact energy necessary to initiate fracture. Microscopy indicates brittle polymer fracture extends across lumens but stops at the polymer and cell wall interface (Schneider, 1994). Brittleness of a composite can be severely increased by increasing the amount of a crosslinker such as ethylene glycol dimethacrylate even to as little as 1.5% in MMA. WPCs with high toughness (low brittleness) have been prepared by using a treating mixture consisting of MMA and an isocyanate that has an acrylic functionality. This treating mixture increased the impact bending strength of the WPC by about 100% (Ibach & Ellis, 2005).

WPCs formed by St, GMA monomers possess decreased toughness and impact strength. While WPCs impregnated with MMA or/with EGDMA or PEGDMA as crosslinkers, normally has improved impact strength (Fig. 14 and Fig. 16). Figure 28 shows different fracture pattern between control and MMA treated wood. The control samples break deep within the sample and it looks more like a brittle failure. In the case of the MMA treated wood, the break is confined to the outer surface and failure is more in the longitudinal direction. This indicates that the MMA polymer is acting as a reinforcing element in the longitudinal direction (Rowell, 2009).
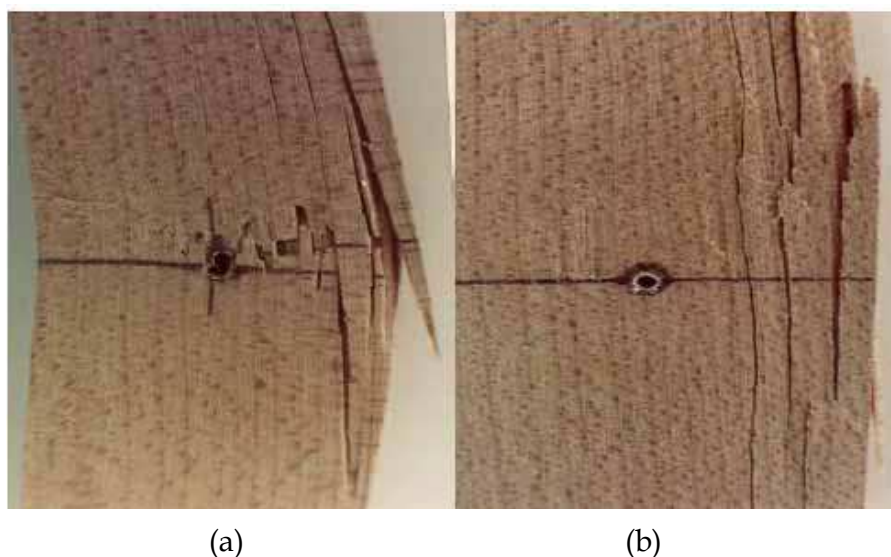

(a)   (b)

Fig. 28. Failure pattern of control (a) and MMA treated wood (b) for toughness

3.8.2 Hardness

Hardness implies the ability of a material to resist deformation. There is a wide variety of hardness assessment procedures available, including static indentation, scratch, plowing, rebound, damping, cutting, abrasion and erosion tests. Recently, nanoindentation techniques have also been used for the investigation of hardness of wood. Hardness is a routinely measured mechanical characteristic that is sensitive to structural parameters as well as to mechanical behavior. A classical method used to measure hardness is the static indentation test, which involves forcing a hard tool of known geometry into the sample body. The hardness of the sample is then defined as the ratio of the applied force to the size of the resulting indentation. Brinell hardness is defined as the ratio of the applied force to the actual area of surface contact, whereas Meyer hardness is the ratio of the applied force to the projected contact area (Zhang et al., 2006).

Hardness of a WPC depends on polymer hardness and loading. Polymer hardness is affected by the type of polymer, presence of crosslinking chemicals, and method and extent of polymerization. Polyner loading is affected by wood porosity and density; porous, low-density wood requires a high polymer load. Conversely, dense wood, such as the latewood of oak, accepts a very low polymer load. In general, the higher the polymer load the greater the WPC hardness. Polymer loading is also affected by impregnation method and monomer properties, such as viscosity, boiling point (evaporation during cure), polarity, molecular weight, and shrinkage with polymerization (Ellis, 2000). However, all WPC samples tested in these studies were found to be harder than their corresponding untreated wood samples (Şolpan & Güven, 1999b; Li et al., 2009a, 2010a, 2011a).

3.8.3 Abrasion resistance

Abrasion resistance is determined by the Taber wear index, which is the weight loss (mg/1000 cycles) caused by an abrasive wheel turning on a specimen. The lower the weight loss value, the better the resistance to wear. In general, abrasion resistance increases with increasing polymer content in the wood. Softwood species such as birch, gray and black alder, and spruce when made into a composite with polystyrene have abrasion resistance comparable to that of natural oak wood. Alder wood and birch wood impregnated with MMA had up to 85% less weight loss than untreated wood (Ibach & Ellis, 2005). In our previos studies, the poplar wood impregnated with MAN and GMA as well as MMA has significant improvement of abrasion resistance over untreated poplar wood (Li et al, 2009a, 2011a).

3.8.4 Dimensional stability

Dimensional stability is the property of wood that allows it to resist changes in dimensions when exposed to various moisture conditions. Dimensional stability is reported as percent volumetric swelling, moisture exclusion efficiency (MEE) or as antishrink efficiency (ASE). ASE is the percent reduction in volumetric swelling of treated wood compared to untreated wood at equilibrium water- or moisture-saturated conditions. Moisture exclusion efficiency, the ability to exclude moisture, is related to the rate at which the composite absorbs moisture and swells and not to the maximum extent of swelling or moisture uptake. MEE has been used to represent dimensional stability when the composite reached equilibrium with respect to moisture or water. In WPC, the large void volume of wood filled with polymer reduces pathways for entrance of water and moisture; thus, ASE and MEE are normally used to represent dimensional stability.

As many vinyl monomers are just confined in cell lumen for polymerization without reacting with wood cell wall, they are rarely dimensionally stable so that with time in water or high humidity, they will swell to the same amount as untreated wood (Li et al., 2009a; 2010b; 2011a). While the monomers possessing functional groups (e.g. hydroxylethyl acrylate, glycidyl methacrylate, isocyanate acrylate) or some reactive chemicals (e.g. anhydride, isocyanates, epoxides, alkoxysilane coupling agents) being incorporated with vinyl monomers, the resulting WPCs will hve excellent dimensional stability (Deka & Saikia, 2000; Ibach & Ellis, 2005; Li et al., 2011a).

3.8.5 Decay resistance

Brown-, white-, and soft-rot fungi all contribute to the decay of wood. The conditions essential for fungal growth in wood are food, sufficient oxygen, suitable temperature, and

adequate moisture. Wood itself provides the necessary food, and oxygen is readily available in the environment. A wood moisture content of approximately 20% is required for decay. Below this level degradation due to fungal attack will not occur, and fungi that may have already begun to grow will cease growing (Şolpan & Güven, 1999a). As a general rule, if wood is kept dry, i.e. moisture content below 20% then fungi typically will not attack wood. However, in unprotected outdoor or marine exposures, wood can be exposed to high levels of moisture that provide the necessary conditions for biological attack. Although, many poisonous chemicals are effective for biological resistance of wood, their toxicity to environment is normally questionable. Increased public concern on the environmental effect of many wood preservatives has rendered a special importance to wood-polymer composite as an environmentally friendly way for wood protection. Several reasons contribute to the effectiveness of WPCs on wood protection against microorganisms. It is speculated that the biological resistance of chemically modified wood by in-situ polymerization of monomers is due to chemical alteration of cellulosic substrate so that the very specific hydrolytic enzymatic reactions cannot take place. Resistance may also be due, in part, to reducing the available cell wall moisture to below a level required for biological attack. The decrease in swelling of wood in contact with moisture--that is, dimensional stability--which results from chemical modification of wood is due to the bulking action of the added chemical to the cell wall or the reduced availability of hydroxyl groups on cell wall. The bulked wood cell walls are kept in a swollen state as long as the bonded chemical is retained. In this swollen condition, wood cannot expand in response to water. And the chemical modification of hydroxyl groups increases the repellency of wood against water (Rowell & Ellis, 1981).

WPCs prepared by vinyl monomers are not decay-resistant because the polymer merely fills the lumens and does not enter the cell walls, which makes the cell walls accessible to moisture and decay organisms. WPCs prepared using vinyl monomers and several kinds of crosslinking monomers (e.g. ethylglycol dimethacrylate, polyethylglycol dimethacrylate, trimethylolpropane trimethacrylate) and polar monomers (2-hydroxyethyl methacrylate and glycidyl methacrylate) added at 5–20% concentration have excellent resistance to brown rot decay (Ibach & Ellis, 2005). Actually, the crucial point of WPCs for wood protection is the selection of a monomer which can protect and consolidate the wood. In principle, the consolidating action can best be obtained if a polymer is fully compatible with the chemical constituents of the wood. The structures of cellulose and lignin, chief constituents of wood, led us to select glycidyl methacrylate, allyl glycidyl ether (AGE), ethylglycol dimethacrylate and polyethylglycol dimethacrylate as potential monomers for the conservation of wood. Due to resonance stability of allylic radicals, chain polymerization of allyl monomers does not take place efficiently and products obtained have very low molecular weight. Thus, these functional monomers are normally used with MMA, St and other monomers (Yildiz et al., 2005; Şolpan & Güven, 1999a).

In addition, using methanol with MMA or St allows the polymer to penetrate the cell walls. The amount of polymer in the cell wall is important for decay resistance. Some protection against biological degradation is possible at cell wall polymer contents of 10% or more. Acrylate monomers with various bioactive moieties such as boron compounds, can also effectively improve decay resistance of wood (Baysal et al. 2007).

Another basic, effective approach to bring about simultaneous improvements in decay resistance, dimensional stability, and mechanical behavior of wood is in situ polymerization and copolymerization of organotin monomers carrying the bioactive tributyltin group. Tri-n-butyltin methacrylatemaleic anhydride and tri-n-butyltin methacrylate-glycidyl

methacrylate are examples of suitable monomer combinations for in situ copolymerization. Comonomers that carry anhydride or epoxy functional groups graft to wood through esterification or etherification of wood hydroxyls. Pentachlorophenol acrylate and Fyrol 6 acrylate polymers provided no protection against decay, whereas tributyltin acrylate, 8-hydroxyquinolyl acrylate, and 5,7-dibromo-8-hydroxyquinolyl acrylate were found to be resistant to the brown-rot fungus, *Gloeophyllum trabeum,* at low polymer loading of 2–5% retention (Matsuda , 1987; Subramanian, 1984; Ibach & Ellis, 2005; Matsuda et al., 2003).

3.8.6 Weather resistance

WPCs made with birch and pine impregnated with MMA or styrene-acrylonitrile were exposed in a weatherometer for 1000 hours and became more resistant to surface checking than untreated controls. Wood-polymer composites made with styrene and acrylonitrile performed better than those made with MMA. A combination of cell wall-modifying treatments (butylene oxide or methyl isocyanate) with MMA lumen-filled treatments results in a dual treatment that resists the degradative effects of accelerated weathering in a weatherometer. The use of MMA in addition to the cell wall-modifying chemical treatments provides added dimensional stability and lignin stabilization and has a significant effect on weatherability (Rowell, 1981). The combination use of monomers of MANwith GMA or AGE and compression treatment for WPC can impart wood excellent weather resistance (Timara et al., 1999). The combination treatment of inorganic compounds such as silicon compounds, titanic compounds, aluminous compounds with monomers can also remarkably improve the weather resistance of wood (Fig. 19 and 23).

3.8.7 Fire resistance

Wood and wood-polymer composites consist of organic compounds are composed mainly of carbon and hydrogen, for this reason, they are combustible. It is impossible to make wood and WPCs incombustible but it is possible to make it fire retardant. It is well known that boron compounds work efficiently as fire retardant chemicals for cellulosic materials. Boric acid and borax mixtures have some efficacy in retarding flame spread on wood surfaces. In addition to the usual char-forming catalytic effect, they have a rather low melting point and form glassy films when exposed to high temperatures in fires. Borax tends to reduce flame-spread but can promote smoldering or glowing. On the other hand, boric acid suppresses smoldering but has little effect on flame spread. Therefore, these compounds are usually used together to pretreat wood, followed by polymerization of monomers within woor pores for fire resistant improvement of WPCs (Baysal et al. 2007; Couturier et al., 1996; Deka & Saikia, 2000).

There are several methods of measuring different aspects of the property of fire retardancy. Thermogravimetry measures char formation and decomposition temperatures by heating small specimens in an inert atmosphere. More char generally indicates greater fire retardancy. The oxygen index test measures the minimum concentration of oxygen, in an oxygen and nitrogen atmosphere, that will just support flaming combustion. Highly flammable materials are likely to have a low oxygen index. Flame spread tests are those in which the duration of flaming and extent of flame spread are measured. The results of any of the test methods that use small specimens often do not correlate with the actual performance of materials in a real fire situation. The surface burning characteristics of WPCs used as building materials are best measured by flame spread tests that use large specimens,

such as the ASTM E84 test that requires specimens approximately 514 mm wide by 7.3 m long. The test chamber in this test also has a photometer system built in to measure smoke and particulate density. Smoke evolution is very important because many fire deaths are due to smoke inhalation.

Bis(2-chloroethyl)vinyl phosphonate with vinyl acetate or acrylonitrile improves the fire retardancy, but is less effective than poly(dichlorovinyl phosphate) or poly(diethyl vinyl phosphonate). Wood impregnated with dimethylaminoethyl methacrylate phosphate salt and then polymerized in the presence of crosslinking agents has high fire retardancy as does trichloroethyl phosphate. The addition of chlorinated paraffin oil to monomer systems imparts fire retardancy to composites. The limiting oxygen index values of the MMA-bis(2-chloroethyl)vinyl phosphonate copolymer and MMA-bis(chloropropyl)-2-propene phosphonate copolymer wood composites are much higher than that of untreated wood and other composites, indicating the effectiveness of the phosphonates as fire retardants (Yap et al. 1991). WPC specimens made with MMA are smoke-free, but styrene-type monomers create dense smoke. The presence of aromatic polymers, such as poly(chlorostyrene), and fire retardants having aromatic benzene rings in wood increase the smoke evolution, flame spread, and fuel contribution in a modified tunnel furnace test. In all specimens tested, the smoke evolution increased markedly after the flame is extinguished (Ibach & Ellis, 2005). The addition of magnesium oxide and boron compounds can protect wood fiber from thermal decomposition and degradation during high-temperature composite processing (Lu et al. 2000). Addition of alkenyl phosphonates or alkenyl esters of phosphorus acids increases the polymerization rate and imparts fire resistance and bioresistance to the resultant WPC (Schneider et al., 1994).

3.8.8 Thermal conductivity

Thermophysical properties such as thermal conductivity and thermal diffusivity which influence the insulating and fire retardant characteristics of wood-polymer composites have received comparatively little attention. In a preliminary study, researchers found that wood-polymer composites prepared using tropical woods have a lower longitudinal thermal conductivity than untreated woods (Chia et al., 1985). While another research (Couturier et al., 1996) made different conclusions: the addition of polystyrene and polymethyl-methacrylate to red maple boards increased the thermal conductivity of the boards in both the longitudinal and transverse directions. However because the increase in the thermal conductivity was less than the increase in the volumetric heat capacity, the thermal diffusivity of the wood-polymer composites was in all cases less than that of the parent wood. The proposed theoretical models (Fig. 29) for the longitudinal and transverse thermal conductivities of wood polymer composites have been shown to give reliable predictions. The models apply to both cell-wall and cell-lumen composites and the inputs of the model are simply the thermal conductivity of the constituent materials, the fractional volumetric expansion observed during treatment and the porosities of the composite and parent wood. On average the thermal diffusivity of the composites was 26% smaller than that of the parent wood.

3.9 Application of WPC

The potential uses for WPC fall into four main categories: construction materials, traffic materials, military materials and furniture materials (Fig. 30). Wood-polymer composites are becoming more accepted in advanced engineering applications. The latest generation of
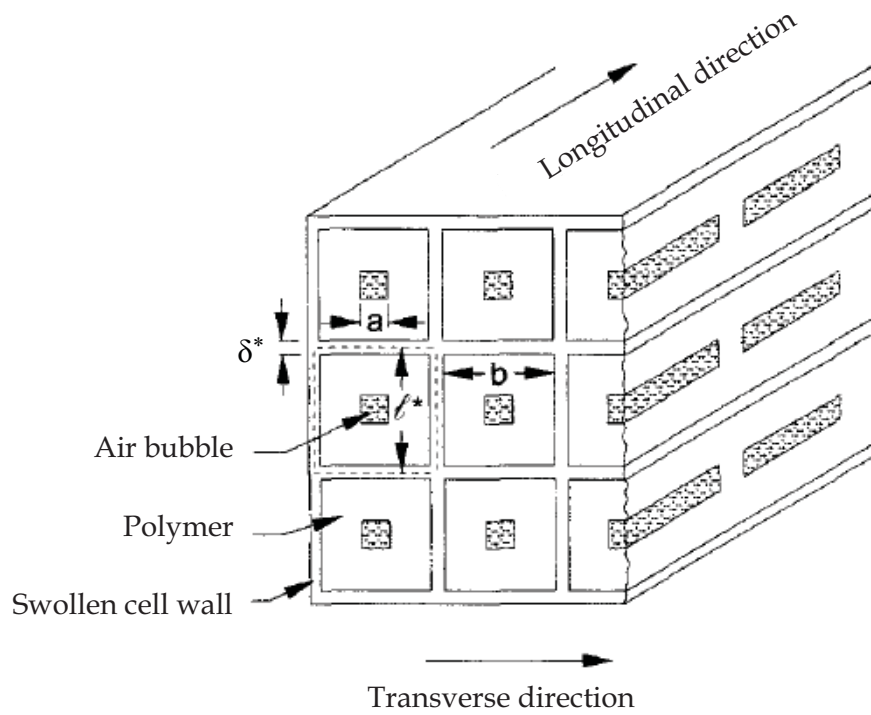
Fig. 29. Geometrical model for the cellular structure of wood-polymer composites
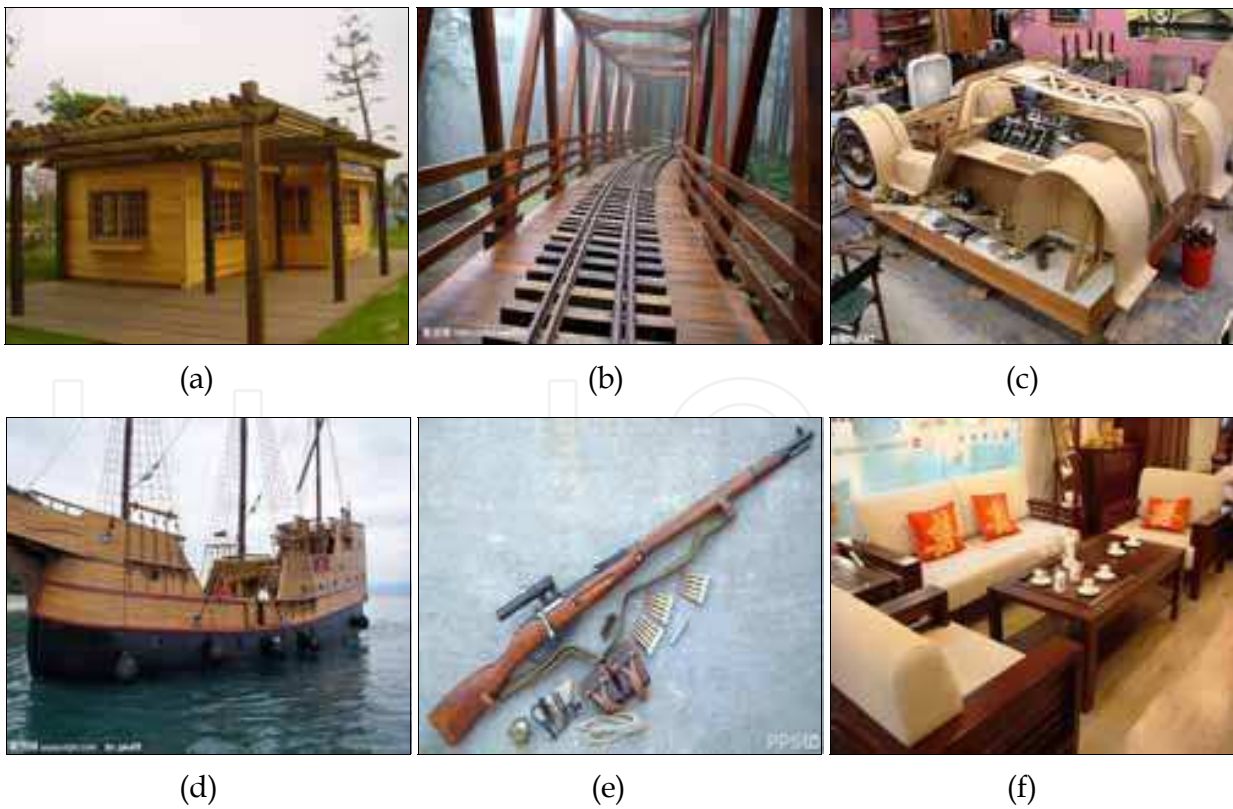

Fig. 30. Major uses for WPCs (a) Construction Material (b) Traffic Material- Crosstie (c) Traffic Material for car beds (d) Traffic Material for ship uses (e) Military Materials (f) Furniture Materials

wood-polymer composites is being used in automotive, civil and marine engineering. Advances in durability, mechanical properties and materials used in their production have allowed a significant increase in their use in outdoor applications such as decking, fencing, utility poles and exterior woodwork on buildings. Wood-polymer composites also benefit from being more sustainable than other, traditional, composites and possess a consistency in quality that cannot be achieved by wood alone. Flooring, the largest volume use for WPC, includes solid plank flooring, top veneers of laminated flooring, and fillets for parquet flooring (Rowell, 2009). The major raw materials for the above floorings have been primarily red oak, ash, maple, and walnut. As for sports equipment, patents have been issued for golf club heads, bows, baseball bats, hockey sticks, and parts of laminated skis, gun stocks. WPC is used for wind instruments, bagpipe chanters, mouthpieces of flutes and trumpets and finger boards of stringed instruments. Another huge potential use is veneer laminates for scratch resistant furniture (such as desk writing surfaces, tabletops), decorative products (knife handles, clock faces, plaques) and recreational equipment (Ellis, 2000). Another smaller application, in relation to volume, would be handrails. These handrails are used primarily for commercial type installations, such as malls, department stores, and airports, for their strength improvements, aesthetics, as well as the ease of maintenance (Schaudy & Proksch, 1982; Kim et al. 2008).

3.10 History

This material has been known and available in small quantities for years made from lumber since 1960s. After the Second World War, the United States government worked very hard to erase the atomic bomb from peoples' minds. One result was President Eisenhower's Atoms for Peace program designed to find peaceful uses of nuclear energy. A project under that program impregnated vinyl-group-containing monomers into wood and cured them using gamma radiation from Cobalt 60 produced in nuclear fission reactors. The process dramatically improved some wood properties. Initial work was done at Brookhaven National Laboratories in the early 1960s. A pilot plant funded by the program was set up at Lockheed to run test materials for anyone that made a wood product. Then the program funded a multiyear project at West Virginia Technological University to study the properties of WPCs. This work started around 1963. The Research Triangle Institute in North Carolina was awarded funds to summarize all of the work in a report. Considerable money and effort went into developing the product. The project was the beginning of the new material: solid-wood-based WPCs. The low viscosity of the treating monomer allowed lumber and other solid wood products to be made into WPCs. The virtually 100 percent solids of the vinyl monomers used (all of the treating solution except that lost through evaporation became solid polymer) allowed very high wood loadings. Since no solvent was needed for the treating solution, dry wood was the preferred raw material. Thus wood could be dried and pre-shaped before treatment (Schneider & Witt, 2004).

During the 1960's support for making wood-plastics by the radiation process was available from the various Atomic Energy Agencies. This support resulted in a great amount of research in Canada, Finland, Sweden, Japan, and South America, and commercial amounts of wood-plastic flooring were produced for airport terminals and office buildings. Today there is no known commercial gamma radiation production of wood-plastics outside of the United States.

The catalyst-heat system for making wood-plastics is used on a commercial scale in Japan, Germany and Italy. Few details are available on the German production of shuttle cocks for the textile industry. In Italy a plant in the Bologna area is producing about three cubic meters a day using styrene monomer. This polystyrene wood-plastic is used for buttons, desk sets and other high cost low volume items. The same organization is planning a future plant in Spain. The Japanese have been very active in research and the production of wood-plastics using the catalyst-heat system with MMA and styrene mixtures. Applications research at the Government Forest Experiment Station in Tokyo has been carried through to production by the Iwaso Company, Ltd. in Ishikawa, Japan. Iwaso Ltd. produces a range of wood-plastic colors for industry including the Pilot Pen Co. Pilot pen and pencil sets with solid dyed wood-plastic bodies are available in U.S.A. at most stationery stores. Iwaso Ltd. produces wood-plastics for vases, bowls, desk caddies, unusual paper weights, letter holders and the ancient abacus.

Over the years wood has been treated with variety of chemicals to change its physical characteristics. A great deal of effort has been put into attempts to make wood plastics or structural board from comminuted wood. Now the physical properties of wood-polymer composites are better known, specific commercial products are being produced which take the advantage of the desirable aesthetic appearance, the high compression strength, increased hardness and abrasion resistance, and improved dimensional stability as well as decay resistance. In total, recent interest in environmentally friendly biodeterioration-resistant wood products has caused new interest in WPC material, which may lead to more use of it. This material, a composite of wood and polymer, can be considered a "value-added" product of wood. However, compared to the amount of wood and plastic products used, WPC sales are small for its higher price (Schneider & Witt, 2004). Future use of wood-polymer composites will depend upon the imagination of the producer and the market place.

4. Conclusion and future recommendation

With the demand of environmentally benign nature and good value-added uses for wood material, WPC are likely to be found applications in broad fields. However, considering its high cost, the market for WPCs may continue to grow slowly in a long term (Schneider & Witt, 2004). In addition, there are much more fundamental works remaining to be done before more satisfactory processes being practiced in the industries. There is yet to be learned about chemical formulations, treating and curing, and their relationships to property enhancements, WPC recyclability, and chemicals from renewable sources for making WPC. Consequently, with the purpose of enhancing the cost effectiveness of WPCs, some technologies need to be further incorporated with in-situ polymerization of monomers within wood pores: foaming technology, nanotechnology and organic-inorganic hybrid technology.

4.1 Wood-polymer composite foams

Foamed solid polymers, also referred as microcellular composites or expanded composites or sponge materials are a class of materials that are extensively used in everyday applications because of their outstanding cost-to-performance and favorable strength-to-weight ratios. Recently, nanocomposite foams produced by introducing nanometer-sized

elements such as layered silicates, carbon nanofibers, or metal nanoparticles to the cell walls of the foam have received a great deal of attention for their large specific surface area and high aspect ratio, which will impart materials good thermal properties, sound insulation properties, excellent strength-to-weight ratio, and energy-absorbing capacity as well as some functional properties. According to some estimates, the market of foam products in the world stands at 14 billion US Dollars and is expected to grow at a phenomenal rate of 14% for the next 5 years. Thus, this kind of polymer exhibits promising and wide applications in future (Svagan et al., 2008).

The foam style is normally classified as two categories: physical foam and chemical foam. Physical foaming agents including water, argon, nitrogen, and carbon dioxide are compounds that liberate gases as a result of physical processes (evaporation, desorption) at elevated temperatures or reduced pressures; Chemical foaming agents (CFAs) such as azodicarbonamide and sodium bicarbonate are substances that decompose at processing temperatures thus liberate gases like CO_2 and/or nitrogen. Despite of all, combination of polymer foam and wood-polymer composite has been rarely reported (Faruk et al., 2007). One of successful reports on wood-polymer composite foams showed that in-situ foaming polyurethane resins within wood pores remarkably improved the mechanical properties and dimensional stability of wood without high density (Gao & Li, 2007). Consequently, wood-polymer composite foams or combinating with nanotechnology seems a novel promising field for development of WPCs in future.

4.2 Wood-nanofiller reinforced polymer composites

Nanocomposite technology with silicon dioxide or layered silicate nanoclays as in situ reinforcement has been intensively investigated in recent years (Fig. 23). Essential improvements of physical and mechanical properties including tensile modulus and strength, flexural modulus and strength, thermal stability, flame resistance, and barrier resistance have been observed for various thermoplastic and thermoset nanocomposites at low silicate content (Kiliaris & Papaspyrides, 2010). Barrier properties, fire resistance and mechanical properties are of great importance for the successful application of selected wood products. However, few efforts based on such technology have been made in the formation of wood polymer composite (WPC), to improve such properties so as to meet specific end-use requirements (Cai et al., 2008; Devi & Maji, 2011). It seems to be a promising way to further improve the comprehensive performance of wood.

4.3 Wood-organic-inorganic hybrid nanocomposites

Hybrid organic–inorganic nanomaterials with remarkable improvement in properties such as mechanical, thermal, electrical, and magnetic compared to pure organic polymers, are promising systems for a variety of applications due to their extraordinary properties based on the combination of the different building blocks and synergism between the properties of the components, and thus are attracted a lot of attention during the last years. The most commonly employed preparation procedures for these materials are the use of the sol–gel process for the formation of interpenetrating networks (IPNs) between inorganic and organic moieties (Kickelbick, 2003).

We recently used sol-gel approach to form organic-inorganic nanopolymer within wood pores and successfully improved the thermal stability and mechanical properties as well as

dimensional stability of wood. Consequently, it also seems to be a wonderful way to form wood to be a novel value-added composite-Wood-organic-inorganic hybrid nanocomposites (Fig. 31).

In addition, recently, with much attention payed on bionanocomposites, incorporation of bioactive wood-polymer composites (Subramanian, 1984) with nanotechnology seems to be a potential and promising direction for value-addition of wood-polymer composites.

In conclusion, a new generation of hybrid nanostructured materials signifies an emerging field in the frontier between chemistry, nanotechnology and biomass materials. An expanding exploration with the novel interdisciplinary technology may be advisable for development of wood-polymer composites so that it can continue to find a place in the commercial market where the improved and novel conveyed functional properties justify the additional cost.

Element	Wt%	At%
C K	46.52	56.07
O K	42.03	38.03
Si K	11.45	05.90
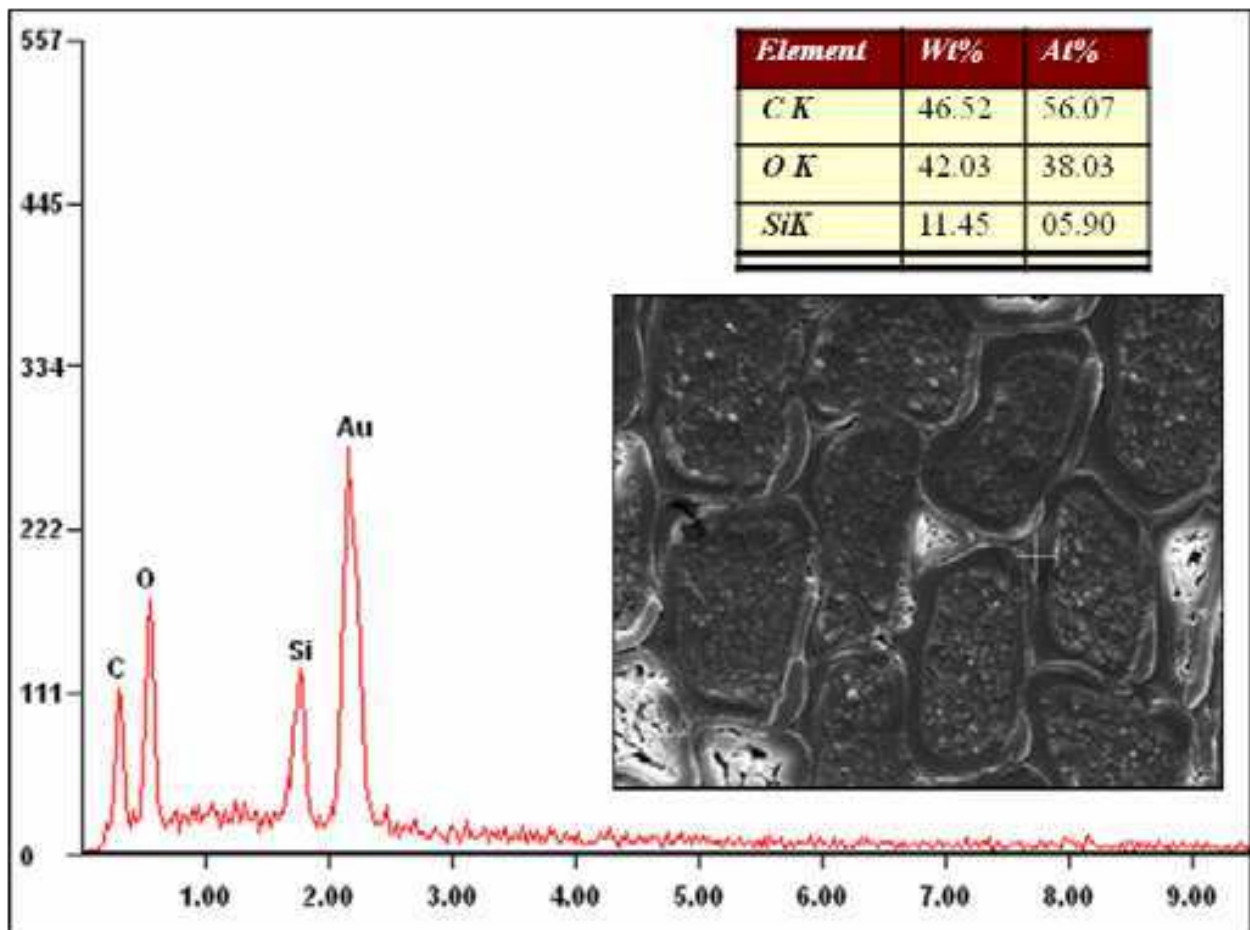
Fig. 31. SEM-EDX of wood-organic-inorganic hybrid nanocomposites

5. Acknowledgements

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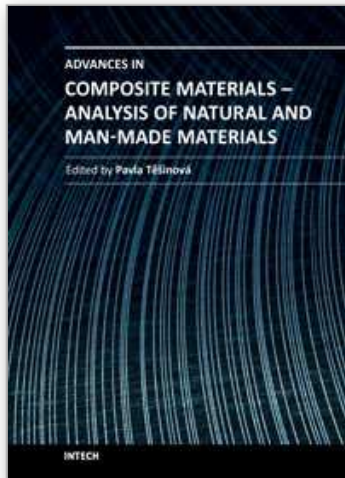
Advances in Composite Materials - Analysis of Natural and Man-Made Materials

Edited by Dr. Pavla Tesinova

Composites are made up of constituent materials with high engineering potential. This potential is wide as wide is the variation of materials and structure constructions when new updates are invented every day. Technological advances in composite field are included in the equipment surrounding us daily; our lives are becoming safer, hand in hand with economical and ecological advantages. This book collects original studies concerning composite materials, their properties and testing from various points of view. Chapters are divided into groups according to their main aim. Material properties are described in innovative way either for standard components as glass, epoxy, carbon, etc. or biomaterials and natural sources materials as ramie, bone, wood, etc. Manufacturing processes are represented by moulding methods; lamination process includes monitoring during process. Innovative testing procedures are described in electrochemistry, pulse velocity, fracture toughness in macro-micro mechanical behaviour and more.

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