MODIFICATION OF SOFTWOOD WITH IMPREGNATION OF POLYMERS

A thesis submitted
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

By

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CERTIFICATE

This is to certify that the thesis entitled "**MODIFICATION OF SOFTWOOD WITH IMPREGNATION OF POLYMERS**" submitted by Ms. Rashmi Rekha Devi, Senior Research Scholar of Department of Chemical Sciences, Tezpur University, Assam for the award of degree of Doctor of Philosophy in Science, is a record of bonafide research work done under my supervision and guidance at Department of Chemical Sciences, Tezpur University, Assam-784028. Ms. Devi has explored the possibility of obtaining chemically modified wood with improved dimensional stability and other mechanical properties. She has successfully completed the work. A few scientific papers related to the subject have been published/ accepted for publication in international and national journals of repute. A few are also under communication and under preparation.

She has fulfilled all the requirements for submitting the thesis for award of the degree of Doctor of Philosophy in Science

The results embodied in the thesis have not been submitted to any other University or Institution for award of any degree or diploma.

Tarun K Maji
(T.K.Maji)

Preface

Wood has been used as an engineering material for centuries. Despite of its various useful properties, wood also possesses some disadvantages as showing dimensional instability, anisotropic mechanical properties, susceptible to biodegradation and catches fire. Impregnating wood with a polymerizable monomer formulation and then polymerizing it in place produces a wood polymer composite (WPC). WPC could be more useful for more products, and have a longer life, because it is less susceptible to moisture induced swelling, shrinking and biodeterioration and has a harder surface.

The north eastern part of India is bestowed with a huge storage of trees. Varieties of hardwood and soft woods are available in this region and the use of wood products is widespread. Again the area is flood prone area. Softwoods are mainly used for fuel purposes due to poor strength and dimensional instability. But their growth rate is fast compared to hardwood and also less costly. Although many research works have been carried out to modify wood with different chemicals, yet, the work on chemical modification of Indian wood for use in constructional purposes is very less. Hence softwoods like pine and rubber can be modified with polymers to increase the strength and dimensional stability.

In the conservation studies, the selection of the monomers is of importance to protect and consolidate the wood. The consolidant action can be improved if the polymer is fully compatible with the chemical constituents of the wood which are cellulose, lignin and hemicelluloses.

Therefore, in our experiments attempts were made to modify softwood like rubber and pine woods generally not employed for constructional purposes, by treatment with styrene as the impregnating monomer and glycidyl methacrylate as the crosslinking monomer.

Flame retardancy is generally imparted into woods by incorporating either chlorine or phosphorous containing polymer, or the copolymerization product of these with more flammable polymers like PMMA, PS etc. Few literatures are available in this regard. But still there is wide scope to further work in this area by exploring the possibility of synthesizing and incorporating new chlorine or phosphorous containing monomers into wood. Attempt was made to use diethyl allyl phosphate (DEAP) as potent flame retardant monomer with flammable monomer styrene to improve flame retardancy of rubber wood.

This research was carried out in the Department of Chemical Sciences, Tezpur University with financial support from Council of Scientific and Industrial Research (CSIR), New Delhi, Govt. of India.

Rashmi Rekha Devi
(Rashmi Rekha Devi) 22\11\05

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I fall short of vocabulary to express my feelings towards my parents, who have been a constant source of my inspiration, courage, support and eternal love and who have done everything to enable me to concentrate on my research work single-mindly. The feelings of love, blessings and well wishes of my loving sisters Majani and Bhon, brother Babu and also Momiba, Nami, Junmahi, Mayamami and Jitenmama were the sources of inspiration for my whole course of work.

Last, but not least, I thank almighty for blessing my life with such wonderful people. Without his blessings, the thesis would certainly have not seen the light of the day.

Rashmi Rekha Devi
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ABSTRACT

ABSTRACT

Wood a natural, cellular, composite material of botanical origin possesses unique structural and chemical characteristics that render it desirable for a broad variety of end uses. Wood is a renewable source and abundantly available in North -Eastern part of India. It has wide spectrum of applications as construction materials, pulp, paper, and fire- board products as well as source of energy and raw material for various industrially important chemicals.

Solid wood in its many forms and adaptations has been used as the most versatile material for buildings, constructions, or furnitures because of superior material properties; e.g. pleasing optical appearance, favourable mass/strength ratio, low thermal conductance, biodegradability and its neutral carbon dioxide balance. There are, however, solid wood properties that are often perceived as negative by the end user, such as dimensional instability with moisture content, low natural durability of many species, expressed photoyellowing, or unsatisfying mechanical properties. A promising way to improve wood properties is through controlled chemical modification. Many research papers and literature reviews have been published on chemical modification of wood. Chemical modification of wood is any chemical reaction between same reactive part of a wood component and a simple single chemical reagent, with or without catalyst that forms a covalent bond between the two components. The most abundant reactive chemical sites of wood are the hydroxyl groups on cellulose, hemicellulose and lignin.

Wood Polymer Composites (WPC) are made by impregnating wood with a polymerizable monomer or prepolymer and then curing the monomer or prepolymer to a

solid. Solid wood (lumber) or any wood composite (such as water board and medium density fiberboard) can be used to make WPC, although solid wood is usually used. WPC has polymer in cell lumens or in cell lumens and walls. WPC has many changed and improved physical properties compared with the parent wood. Notable are an increase in surface hardness, dimensional stability and the possibility of fine finishing without surface coating.

In this part of work, softwoods like rubber and pine were impregnated with styrene as the impregnating monomer and glycidylmethacrylate (GMA) as the crosslinking monomer which reacts with hydroxyl groups of wood and double bond of styrene. Almost all the physical, mechanical, thermal and biodegradation properties of WPC improved. Diethyl allyl phosphate (DEAP) monomer was used with styrene to see its effect on the thermal stability of rubber wood.

Chapter I Chapter I includes introduction part. This covers the origin of wood, chemical composition, properties such as physical (hygroscopicity, shrinkage and swelling, permeability etc), mechanical, thermal, chemical (corrosiveness, chemical resistance, and biological deterioration) and applications of wood. Chemical modification, impregnation of monomers that covers types of monomers, techniques, vinyl polymerization and lastly applications and properties of WPC has also been incorporated.

Chapter II This chapter covers the available literatures involving the chemical modification of wood based on a) impregnation systems that covers polymerization using catalyst heat treatment and gamma radiation technique and b) analysis of wood polymer composites in the light of dimensional stability, physical and mechanical properties, thermal and biodegradation properties, FT-IR spectroscopy and surface morphology. The objectives and plan and of work have also been included in this chapter.

Chapter III This chapter covers the materials and methods which includes the raw materials used, sample preparation, impregnation procedure, different measurements used to characterize the WPC.

Chapter IV This chapter includes results and discussion part. This chapter is divided into three parts.

Part I Modification of rubber wood with impregnation of styrene as the monomer and GMA as the crosslinking monomer using 2,2′-Azobis isobutyronitrile (AIBN) catalyst

In this part of work rubber wood (Hevea brasiliensis) was impregnated with styrene monomer and glycidyl methacrylate (GMA) as the crosslinking monomer. Polymerization was accomplished by catalyst heat treatment using AIBN. Different parameters like monomer concentration, vacuum, catalyst concentration, time of impregnation etc. were varied.

The best condition for highest polymer loading, which showed maximum overall improvement in properties, was found at 5″ Hg vacuum , 1:1 (Styrene-GMA) monomer concentration, 0.5% of AIBN (concentration by weight) and 4h of impregnation time.

Water uptake capacity (%) and water vapour exclusion (%) decreased on treatment. Dimensional stability and anti swell efficiency, hardness, bending strength in terms of modulus of elasticity and modulus of rupture, compressive strength in both perpendicular and parallel to fibre direction and resistance to biodegradation improved on impregnation. Thermal stability was also improved. FT-IR spectroscopy and scanning electron microscopy study indicated the interaction between wood, styrene and GMA. In general maximum overall improvements in properties were obtained for treatment with (1:1) styrene-GMA.

Part II Modification of Pine wood with impregnation of styrene as the monomer and GMA as the crosslinking monomer using AIBN catalyst

Chemical modification of pinewood was carried out by impregnating the wood with styrene and Glycidyl methacrylate (GMA) as a crosslinking monomer. Polymerization was carried out by catalyst heat treatment (AIBN as the catalyst). The best condition for highest polymer loading, which showed maximum improvement in properties, was found at 5" Hg vacuum ,1:1 (styrene: GMA) monomer concentration , 2.0% of AIBN (concentration by weight) and 4h of impregnation time.

In the case of pine wood, also all the properties improved more or lesss on treatment. The highest improvement was obtained with styrene-GMA (1:1) treatment. Water uptake capacity (%); water vapour exclusion (%); dimensional stability; antiswell efficiency; hardness, MOE , MOR, compressive strength and resistance to biodegradation improved maximum for (1:1) styrene-GMA treatment. Thermal properties improved on treatment. SEM and FT-IR study revealed the interaction between wood and the polymers.

Part III: Modification of rubber wood with impregnation of styrene as the monomer and diethyl allyl phosphate (DEAP) as the comonomer to improve the thermal stability

Rubber wood was impregnated with styrene as the monomer and diethyl allyl phosphate (DEAP) as the comonomer. Diethyl allyl phosphate was first synthesized and then characterized.

The best condition for impregnation, at which highest improvement in the properties was obtained, was achieved using styrene: DEAP [88:1.5 (v/v)], 0.5% AIBN, 5" Hg vacuum, 4h of impregnation time and tetrahydrofuran (THF) as solvent. On treatment with DEAP-styrene system water uptake capacity (%), swelling in water (%), hardness and MOE values improved. Thermal stability increased with the increase in the concentration of DEAP as evident from decrease in temperature of initiation and the formation of higher char yield (%). The improvement in flame retardancy is also evident from the increase in value of limiting oxygen index (LOI) for styrene-DEAP-THF system over untreated or styrene treated samples.

ChapterV This chapter includes summary and conclusion part of the present work.

In the present experimental work, it was found that the maximum improvement in the properties of WPC took place at 1:1 styrene: GMA concentration, 5" Hg vacuum and 4h of impregnation time. Optimum concentration of AIBN required for rubber and pine wood composites were 0.5% and 2% respectively. These were the optimum conditions at which maximum interaction between wood and the polymers was found. For DEAP-styrene system, the maximum improvement in the properties was obtained at styrene-DEAP concentration of 88:1.5 (v/v).

It could be concluded that almost all the physical and mechanical properties of WPC improved on impregnation with styrene-GMA. DEAP could be used as potent flame retardant comonomer for production of WPCs. This is followed by future scope of the work.

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List of abbreviations

1	AIBN	2,2′-azobis-(isobutyronitrile)
2	ASE	Anti-swell efficiency
3	ASTM	American Society for Testing Materials
4	^{0}C	Degree centrigrade
5	cm	Centi meter
6	DEAP	Diethyl allyl phosphate
7	DSC	Differential scanning calorimetry
8	DTG	Differential thermogravimetry
9	Fig	Figure
10	FT-IR	Fourier Transform Infra red
11	GMA	Glycidyl methacrylate
12	h	Hour
13	m	Meter
14	MOE	Modulus of elasticity
15	MOR	Modulus of rupture
16	MPa	Mega Pascal
17	NMR	Nuclear Magnetic Resonance
18	SEM	Scanning electron microscopy
19	TG	Thermogravimetry
20	TGA	Thermogravimetric analysis
21	µm	Micro meter
22	v/v	Volume/volume
23	WPG	Weight percent gain
24	WRE	Water repellent effectiveness

CHAPTER I

INTRODUCTION

CHAPTER I

INTRODUCTION

1. Origin, structure and chemical composition of wood

1.1. Origin

Wood a natural, cellular, composite material of botanical origin possesses unique structural and chemical characteristics that render it desirable for a broad variety of end uses. Wood is a renewable source and abundantly available in North -Eastern part of India. It has a wide spectrum of applications as construction materials, pulp, paper, and fire-board products as well as source of energy and raw material for various industrially important chemicals. Wood is obtained from two broad categories of plants known commercially as softwoods and hardwoods. These general names cannot be used universally to refer to the actual physical hardness or density of all woods because some softwoods are quite hard (e.g. Douglas-fir and southern yellow pines) and some hardwoods are soft (e.g. aspen, cotton wood etc). From a more scientific perspective, softwoods are tree species of a class of plants called gymnosperms (seeds are borne naked) and hardwoods are woody, dicotyledenous (two seed leaves) angiosperms (seeds are borne in a fruit structure).

1.2. Structure

1.2.1. Softwoods

The wood or secondary xylem of gymnosperms is composed of relatively few cell types. The predominant cell type in softwoods is the vertically oriented longitudinal tracheid. More commonly known as fibres, these tracheids are hollow, square to rectangular in cross section, have closed and tapering ends and are arranged so that their ends overlap adjacent fibres. They are also arranged into well-aligned radial rows.

Widths of longitudinal tracheid are generally range from 35 to 50 μm and average lengths are between 3 and 5 mm. These cells serve a duel role of providing strength and mechanical support as well as being the pathway by which water and dissolved minerals are translocated from the tree's root system upward to the tree crown. Also axial parenchyma, epithelial cells, ray tracheids and ray parenchyma are found in softwood cells (fig. 1.2.1.)

1.2.2. Hardwoods

Various cell types are found in hardwoods. Hardwood anatomy is more varied or complicated than that of the softwoods, but most structural concepts are analogous.

Hardwood contains a substantial volume of fibre cells, but the distinguishing feature of angiosperm xylem is the occurance of vessels. These vessels are seen on the wood cross section as holes or pores in various patterns. Thus all hardwoods are referred to as porous woods, in contrast to the soft woods that are technically non porous. An individual vessel or pore consists of short (0.02-0.5 mm) vessel segments, which are joined end-to-end along the grain. Individual vessels can mender to a limited extent in the radial or tangential direction to join, terminate in, or depart from other vessels, but their major function is the vertical translocation of sap. Hardwood fibres, because of presence of vessels, occupy a proportionally smaller volume of wood tissue than softwood fibres do. The fibers are also smaller and average width and lengths are about one half the width and one third of those of softwood tracheids (fig 1.2.2.)

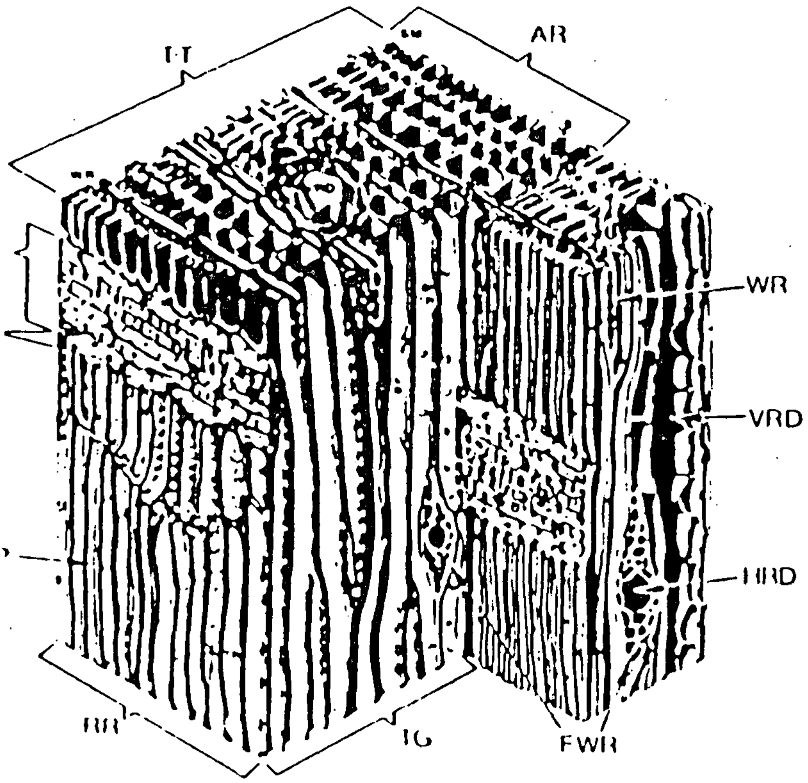


Fig. 1.2.1. Cellular structure of a softwood (white pine), enlargement of a block of 1mm high. AR, annual rings; BP, border pit; FWR, fusiform wood rays; HRD horizontal resin duct; RR, edge grain; S,early wood; SM, latewood; SP, simple pits; TG, flat grain; TR, tracheid; TT, end-grain; VRD, vertical resin duct; WR, wood rays.

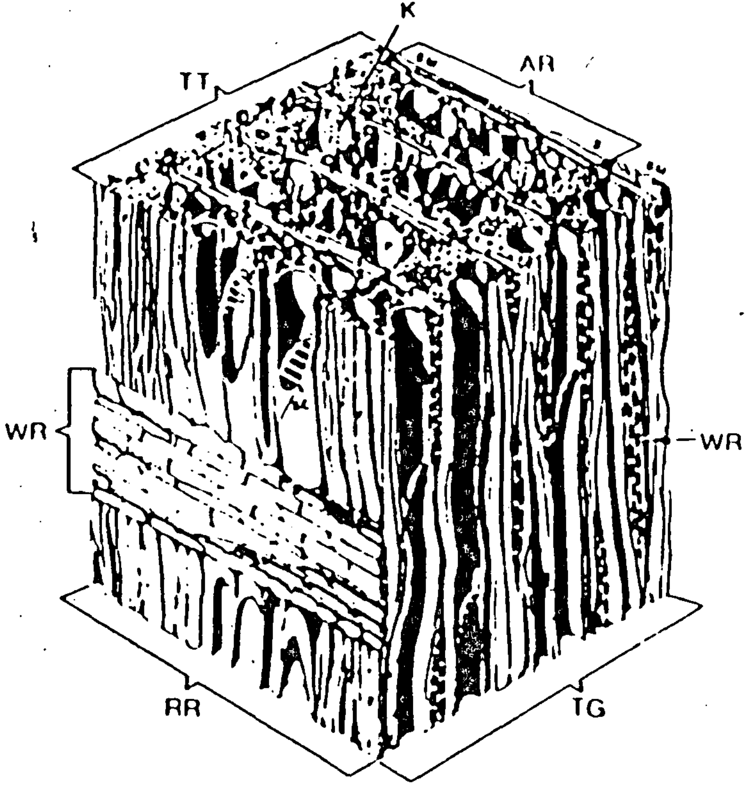


Fig. 1.2.2. Cellular structure of a hardwood (yellow poplar), enlargement of a block of 1mm high. AR, annual rings; F, fibre; K, pits; P, pores; RR, edge grain; S, earlywood; SC, grating separating vessels; SM, latewood; TG, flat grain; TT, end grain; WR, wood rays.

1.3. Chemical composition of wood

The principal chemical components of wood are carbohydrates (70-80%), lignin (20-30%) and extraneous materials (5-10%). Because the chemical composition varies between and among species, it is impossible to define absolute compositions. Nevertheless, the following generalizations can be made: ranges of composition values can be defined within species, and the average lignin content of softwood is slightly higher than that of hardwood.

1.3.1. Carbohydrates

The carbohydrate portion of wood can be isolated as a white fluffy material called holocellulose, by dissolving the lignin. (holocellulose consists of cellulose and hemicellulose). The carbohydrate of wood polymers are built up from five sugars: glucose, xylose, manose, galactose and arabinose.

Cellulose is the principal component of wood carbohydrate (40-50% of the total wood). A cellulose molecule is a linear, straight chain polymer of up to 10,000 anhydroglucose units. X-ray diffraction studies have shown that much of wood cellulose is crystalline and resists attack from mild chemicals such as dilute acid. The length of a cellulose polymer chain (degree of polymerization) in wood is between 7,000 and 10,000 glucose units. Hemicelluloses are sugar polymers with a degree of polymerization of 200 or less. They have normally monomeric substituents or, in some cases, branched oligomer chains, and vary in composition and structure.

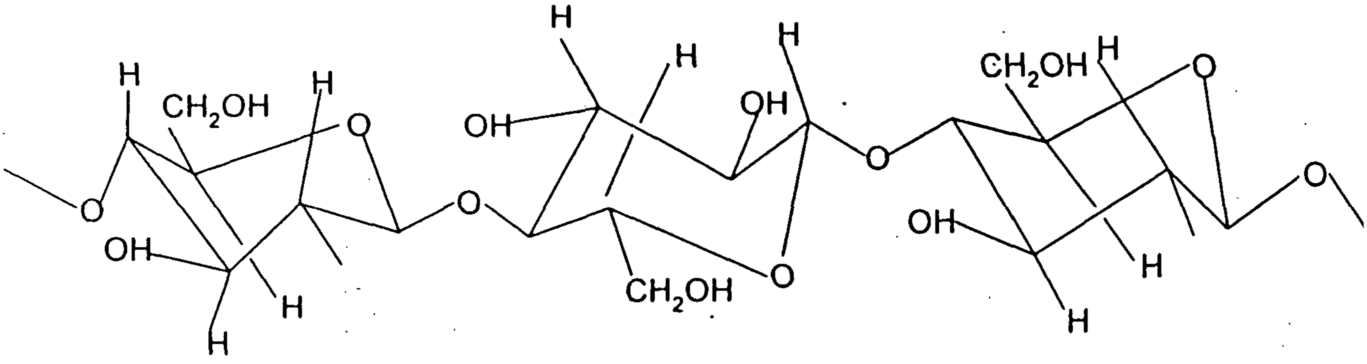
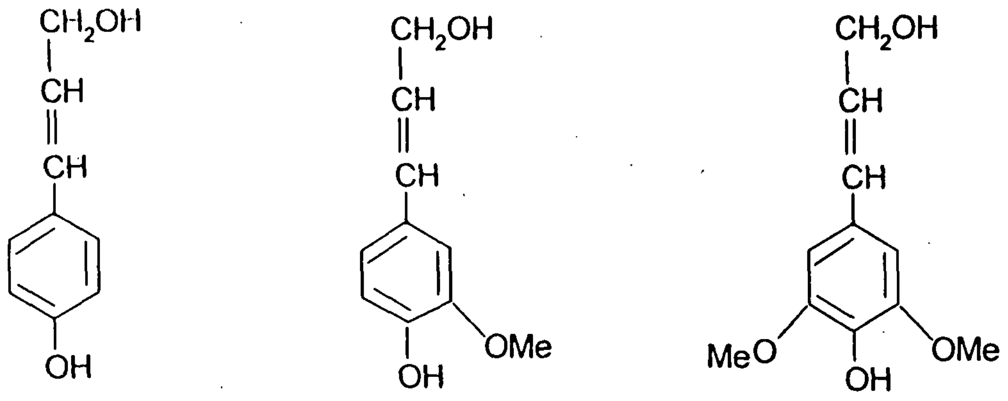


Fig. 1.3.1. A partial molecules structure of cellulose $[(C_6H_{10}O_5)_x]$ in the 1,4 β- D glucopyranose form.

1.3.2. Lignin

Wood lignin is an irregular, complex polymer consisting of methoxy- and hydroxy-substituted phenyl propane units. The lignin's building in the biosynthetic pathway is p-coumaryl alcohol (I), coniferyl alcohol (II), and syringyl alcohol (III). Softwood lignins result from the polymerization of II with very minor amounts of I and III. Hardwood lignins contain large amounts of II and III and traces of I. The most frequent bonds occured between monomers are ether bonds and carbon-carbon single bonds. Lignin is present in both the cell wall and the middle lamella between fibres. It imparts such strength to the wood that trees are able to grow to enormous heights (upto 100m). Such heights are not possible in plants lacking lignin.



(I) (II) (III)

Fig. 1.3.2. Precursors of lignin, p-coumaryl alcohol (I), coniferyl alcohol (II), and syringyl alcohol (III)

1.3.3. Extraneous Components

The extraneous components (extractive and ash) in wood are the substances other than cellulose, hemicelluloses and lignin. They don't contribute to the cell wall structure , and most are soluble in neutral solvents. Extractives are a variety of organic compounds including fats, waxes, alkaloids, proteins, simple and complex phenolics, simple sugars, pectins, mucilages, gums, resins, terpenes, starches, glycosides, saponins and essential oils. Many of these function as intermediates tree metabolism, are energy reservoirs or as part of the tree's defence mechanism against microbial attack. They contribute to wood properties such as colour, odor and decay resistance.

1.4. Properties

1.4.1. Physical properties

Wood is characterized by hygroscopicity, shrinking and swelling and water transport.

1.4.1.1. Hygroscopicity

Dry wood is highly hygroscopic. The amount of moisture adsorbed depends mainly on the relative humidity and temperature. The cell walls of green wood are saturated; some cell cavities are completely filled, others may be completely empty. Moisture in the cell cavities is called free or capillary water. Moisture in the cell cavities is distinguished from moisture in the cell walls because, under ordinary conditions, removing free water has little or no effect on many wood properties. On the other hand removing cell water has a pronounced effect.

1.4.1.2. Shrinking and swelling

The adsorption and desorption of water in wood are accompanied by external volume change. At moisture contents below the fibre saturation point, the relationship may be simple, merely because the adsorbed water adds its volume to that of the wood or the desorbed water subtracts its volume from that of the wood. As with all wood properties, swelling or shrinking is highly anisotropic.

1.4.1.3. Permeability

Although wood is porous (60-70% void volume), its permeability (fluid flow under pressure) varies. Permeability is 50 to 100 times higher in the longitudinal than in the transverse direction. Sapwood is considerably more permeable than heartwood.

Variability in permeability is due to the highly anisotropic shape and arrangement of the component cells and the microscopic channels between cells.

1.4.1.4. Mechanical

The source of wood strength and stiffness is the fibre. The use of wood as a structural material is influenced by environmental factors such as temperature and moisture content. These factors have direct effect on mechanical properties and promote the growth of decay fungi that degrade wood. Mechanical properties may be further altered by chemical treatments used to protect wood from decay and fire. Mechanical properties of clear wood increase markedly as moisture content is reduced below the fiber saturation point. Clear wood mechanical properties tend to deteriorate when wood is heated and improve when it is cooled. The effect of treatments on strength properties largely depend on the chemical nature and reactivity of the absorbed liquid. Decay or wood destroying fungi may seriously reduce strength.

1.4.1.5. Thermal properties

Thermal properties include specific heat, thermal conductivity, coefficient of thermal expansion, thermal degradation and fire resistance. Specific heat varies from species to species. The thermal conductivity of wood is low compared to most other structural material. The thermal expansion of wood is negligible compared to that of moisture-induced swelling and shrinking.

1.4.2. Chemical properties

1.4.2.1. Corrosiveness

Wood and metal are compatible in most construction and furniture uses. However if there is sufficient moisture at the wood-metal interface, some corrosion can be expected with susceptible metals.

1.4.2.2. Chemical resistance

Wood is widely used in the chemical industry as a structural material because of its resistance to a variety of chemicals. Different species vary in their resistance, depending on wood structure and cell wall composition.

1.4.2.3. Biological deterioration

Microorganisms (fungi and to a relatively minor extent, bacteria), insects and marine borers attack wood. Fungal damage may result in decay or rot, soft rot, stain and mold. The sapwood of all species has little resistance to decay. The heartwood of many tree species is naturally resistant to decay and gives long service under conditions that promote decay.

1.5. Chemical modification

Solid wood in its many forms and adaptations has been the most versatile material for buildings, constructions, or furnitures because of superior material properties; e.g. pleasing optical appearance, favourable mass/strength ratio, low thermal conductance, biodegradability and last, but not least, due to its neutral carbon dioxide balance. There are however, solid wood properties such as dimensional instability with moisture content, low natural durability of many species, expressed photoyellowing,unsatisfying mechanical properties etc. that are often perceived as negative by the end user. A promising way to improve wood properties is through controlled chemical modification. Many research papers and literature reviews have been published on chemical modification of wood. Chemical modification of wood is any chemical reaction between same reactive part of a wood component and a simple single chemical reagent, with or without catalyst that forms a covalent bond between the two components. The most abundant reactive chemical sites of wood are the hydroxyl groups on cellulose, hemicellulose and lignin.

The properties of wood can be modified for the purposes other than preservation or protection from fire. Different methods can be used to reduce swelling and shrinking under conditions of fluctuating relative humidity by bulking the cell wall with leachable and nonleachable, or bonded chemicals that leave the wood in a swollen state.

1.5.1. Treatment with leachable agents

Poly (ethylene glycol) (PEG) in a water solution can be used to permeate the lumens and penetrate the cell wall. A 30-50% solution of PEG in water is generally used on green wood; no pressure is required. Treatment times are adjusted so that uniform uptakes of 25-30% of PEG are achieved based on the dry weight of the wood. The wood may require weeks of soaking, depending on species, density and thickness. After treatment the wood is dried in a well-ventilized space, preferably by heating. The PEG is not fixed or cured in the wood and leaches out if the wood contacts water.

1.5.2. Treatment with Nonleachable Agents

Resin impregnation can be used to add bulking agents to the cell wall. These resins have a low degree of polymerization or the monomers are polymerized after impregnation. The best fibre penetrating thermosetting resins are highly water soluble phenol-formaldehyde, resin forming systems with low initial molecular weights. Compreg is a highly dense product obtained by applying pressure to dry, resin treated veneers during heat cure (Compreg can be used also as it offers most of the advantages of Impreg). Wood and plastic combinations are becoming commercially available. Wood is treated with a nonswelling vinyl type monomer and cured by radiation or by heat and a catalyst.

1.5.3. Bonded treatment

Through chemical reactions, an organic chemical can be added to the cell wall. This treatment confers bulk to the cell wall with the help of permanently bonded chemical. For best results, the chemicals should be capable of reacting with the wood hydroxyl groups under neutral or mildly alkaline conditions. The chemical system should be simple and must be capable of swelling the wood structure to facilitate penetration. The complete molecule must reacts quickly with wood components and yield stable chemical bonds.

1.5.4. Composites

Wood can be modified by chemically changing the wood element itself or by adding chemicals to improve resistance to decay, insect attack, and fire. Such modifications are easily made when wood is in the comminuted form, before it is converted into the final product. A number of wood components or elements can be used to produce wood based composite products. The categories of composite materials may be logs, lumber, thin lumber, vineer, long flakes, chips, flakes, excelsior, strands, particles, fibre bundles, paper fibre and wood flour etc.

1.5.5. Treatment with impregnation of monomers/ or oligomers and crosslinker

Wood can be modified by impregnating some monomer or oligomer having low viscosity along with a crosslinker into the cell wall or lumens under vacuum or high pressure of wood followed by polymerization and crosslinking with the help of catalyst or radiation. By this process, the various physical and chemical properties of wood are improved. Many different vinyl monomers such as styrene, methyl methacrylate, acrylonitrile have been used to make wood polymer composites, but methyl methacrylatte appears to be the preferred monomer for both the catalyst heat and radiation processes. In many countries styrene and styrene-MMA mixtures are used with vazo or peroxide catalysts.

In order to enhance the properties crosslinking of polymer with the wood are done by employing various crosslinking agents.Soluble dyes are added to the catalyzed monomer solution to color the final wood polymer composite. Fire retardants based on phosphorous and the halogens can also be added directly to the monomer solution. Most of the fire retardants are based on benzene ring structures such as triphenyl phosphate and Santicizer-140.

To improve antishrink efficiency (ASE), some polar solvents may be added with non polar monomer. This may help to swell the cell wall structure more and incorporate monomer to a swollen state.

When gamma radiation passes through the vinyl monomer, it leaves behind a trait of ions and excited molecules which in turn produces free radicals. These free radicals initiate the vinyl monomer polymerization reaction.

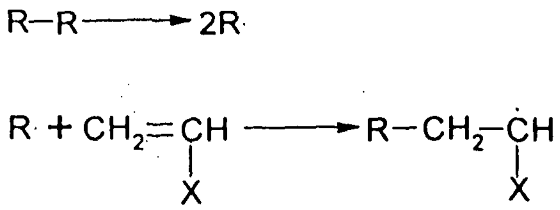
Various catalysts such as AIBN, peroxide etc. are generally employed. Among the chemical catalysts vazo or 2,2'-azobisisobutyronitrile (AIBN) catalyst is preferred over peroxide catalysts because of its low decomposition temperature and its nonoxidizing nature. Vazo will not bleach dyes dissolved in the monomer during polymerization.

Heat of polymerization is released rapidly in catalytic curing compared to gamma radiation curing. Due to that the water from cell walls drives out fast in catalytic curing which leads to changes in dimensions. Therefore the composites cured by catalytic heat process must be machined to the final stage after treatment. Although curing by gamma radiation has the above advantage yet it has many inherent complications. Safety requirements must be satisfied before installation of a gamma radiation source. Capital investment is also high.

1.5.5.1. Vinyl polymerization

In WPCs , vinyl type monomers are polymerized into the solid polymer by means of free radical mechanism, like the polymerization of pure monomers. Free radical of vinyl monomers consists of three steps, initiation, propagation and termination.

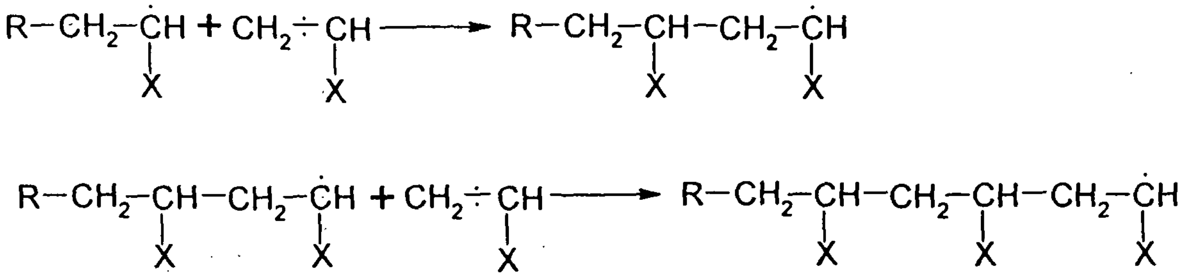
Initiation



$$R-R \longrightarrow 2R\cdot$$

$$R\cdot + CH_2=\underset{X}{CH} \longrightarrow R-CH_2-\underset{X}{\dot{C}H}$$

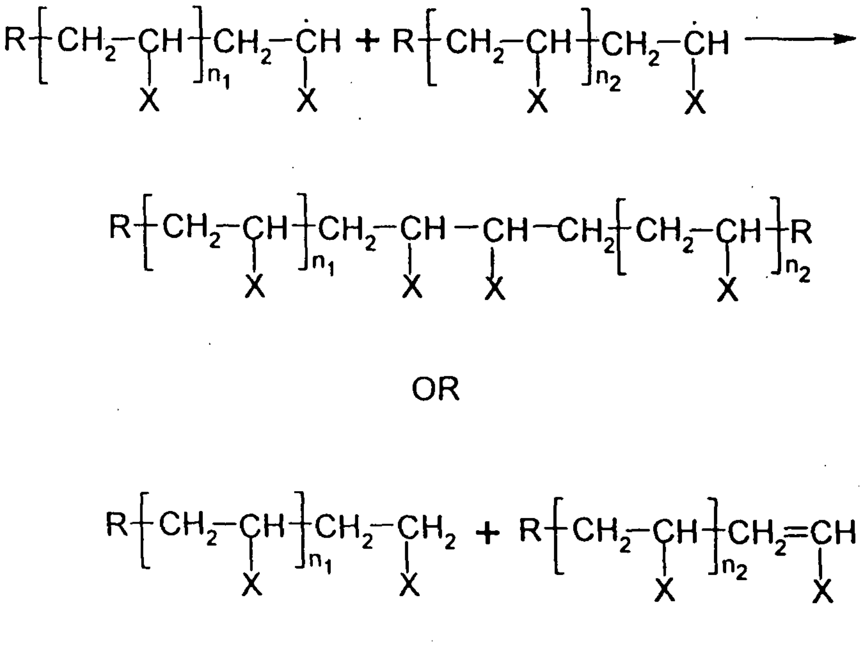
Propagation



$$R-CH_2-\underset{X}{\dot{C}H} + CH_2\div\underset{X}{CH} \longrightarrow R-CH_2-\underset{X}{CH}-CH_2-\underset{X}{\dot{C}H}$$

$$R-CH_2-\underset{X}{CH}-CH_2-\underset{X}{\dot{C}H} + CH_2\div\underset{X}{CH} \longrightarrow R-CH_2-\underset{X}{CH}-CH_2-\underset{X}{CH}-CH_2-\underset{X}{\dot{C}H}$$

Termination



$$R\left[CH_2-\underset{X}{CH}\right]_{n_1}CH_2-\underset{X}{\dot{C}H} + R\left[CH_2-\underset{X}{CH}\right]_{n_2}CH_2-\underset{X}{\dot{C}H} \longrightarrow$$

$$R\left[CH_2-\underset{X}{CH}\right]_{n_1}CH_2-\underset{X}{CH}-\underset{X}{CH}-CH_2\left[CH_2-\underset{X}{CH}\right]_{n_2}R$$

OR

$$R\left[CH_2-\underset{X}{CH}\right]_{n_1}CH_2-\underset{X}{CH_2} + R\left[CH_2-\underset{X}{CH}\right]_{n_2}CH_2=\underset{X}{CH}$$

1.6. Properties and applications of wood polymer composites

Wood Polymer Composites (WPC) are made by impregnating wood with a polymerizable monomer or prepolymer and then curing the monomer or prepolymer to a solid. Solid wood (lumber) or any wood composite (such as water board and medium density fiberboard) can be used to make WPC, although solid wood is usually used. WPC has polymer in cell lumens or in cell lumens and walls. WPC has many changed and improved physical properties compared with the parent wood. Notable are an increase in surface hardness, dimensional stability and the possibility of fine finishing without surface coating.

It has been found that most of the WPC properties are improved over untreated wood. Certain properties of WPC like modulus of elasticity (MOE), modulus of rupture (MOR), hardness and other elastic properties are better than those of parent wood. Polymer may be impregnated either into the lumen or the lumen/cell wall of the wood. The mechanical properties of WPC are the same for these two systems. But when polymer is impregnated into the cell wall it imparts better dimensional stability compared to impregnation in lumen only. Wood treated with vinyl type monomer followed by curing (radiation or catalyst) significantly improves the moisture resistance, hardness, water repellency, compression, bending strength etc.

Commercial production of wood polymer composites (WPC) has started in the mid 1969s using the radiation process. Parquet flooring is the principal product, where the increased in hardness and abrasion resistance offered an advantage in high traffic commercial installations. The long life and ease of maintenance have justified the increased cost over conventional flooring. Perma Grain products Inc. has been producing radiation cured, solid acrylic wood flooring since the 1960s and at present produces about 46× 10^3 m^2/yr. Perma Grain also produces a smaller volume acrylic wood for other uses, such as maple and ash hand railings, black walnut knife handles, stain treads, windowsills and golf clubs. Tebbles Flooring Co. is marketing a line of catalyst -heat cured acrylic wood flooring under the Hartco trade name. The flooring unlike Perma Grain consists of a plywood sandwich with a thick veneer of wood plastic composite on the wear surface. Since late 1980s, the catalyst heat process has been widely used for making wood polymer composites, but in smaller volume than the radiation process. Because of the simplicity of the catalyst heat process and the low capital investment, these products are used by small companies that make high cost, low volume articles. AMF Bowling division is producing Billicard and experimental bowling alley flooring. In the late 1960s and 1970s, Bear archery is also producing wood polymer composites archery bows of dyed maple, replacing tropical hardwoods. Dunbar of Canada and the War pipes of Vermont produced bagpipes and chanters of maple wood-polymer composites. Kelly Putters of Oregon has been producing golf putters of maple and myrtte wood polymer composites for the past 20 years. Ovation Musical Instruments Co produces black walnut wood polymer composites fret boards for guitters replacing ebony. Other products include drum-sticks, shuttle cocks, picker sticks and jwellery where the dyed wood polymer composite is invalid in sterling silver etc.

A research group at the University of New Brunswick Canada is assisting industry in setting up the catalyst-heat process to produce knife handles and other articles. In Poland, large production facilities have been constructed for making styrene wood polymer composite called lignomers by the catalyst heat process. The Japanese products include pen and pencil sets, office equipment, wall panels and flooring under the trade name of Aploid. In Taiwan a number of wood polymer composites are made with mixtures of styrene-polyester, MMA-styrene and MMA-polyester as the monomers in the catalyst heat process. Some wood polymer composites are made in Australia and Newzealand.

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CHAPTER II

LITERATURE REVIEW

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2.1. Introduction

The present thesis on modification of softwood by impregnation of polymers embodies the results of investigation on a) improvement of properties of pinewood by chemical modification with styrene b) improvement of properties of rubber wood by chemical modification with styrene. Many literature and research papers have been published on chemical modification of wood.

It would therefore be meaningful to make a review of the literature involving chemical modification of wood on i) impregnation system that covers polymerization using catalyst heat treatment and gamma radiation technique and ii) analysis of wood polymer composites in the light of dimensional stability, physical and mechanical properties, thermal and biodegradation properties and surface morphology.

2.2. Literatures based on impregnation system

2.2.1. Modification of properties of wood using different methods of polymerization

Wood polymer composites (WPC) are materials which may be prepared by impregnating wood with a variety of monomers which are subsequently polymerized either by conventional free radical catalyst or by gamma radiation

2.2.1.1. Polymerization using catalyst heat treatment method

For comparison among eight species of wood, composites were prepared using methyl methacrylate as monomer and azobis butyronitrile as catalyst [1].

Another widely studied system was the crosslinking of wood via impregnation with formaldehyde in the presence of acid catalyst [2]. It was reported that WPC made with vinyl monomer followed by curing (radiation or catalyst) significantly improved the moisture resistance [3].

Wood polymer composites (WPC) of rubber wood were prepared by impregnating the wood with methyl methacrylate (MMA) and the combinations of MMA and diallyl phthalate mixture (MMA/DAP). Polymerization was carried out by catalyst heat treatment [4].

Rubber wood-polymer composites were prepared by employing benzoyl peroxide, as initiator [5]. Indonesian pine, jabon and USA southern yellow pine were *in-situ* polymerized by catalyst heat treatment using tri-n-butyltin methacrylate (TBTMA) as monomer [6]. The properties of white pine wood was studied by treating it with a mixture of styrene, four different types of polyester resins and with varying percentage of bromine based on poly (polyethylene glycol-maleate phthalate) [7].

Impregnation of pine and eucalyptus with monomers like styrene and methyl methacrylate and their polymerization by using 0.2% benzoyl peroxide catalyst were reported in literature [8].

Sugar maple was treated with MMA, hydroxy ethylene methacrylate (HEMA), ethylene glycol dimethacrylate (EGDMA). Polymerization was carried out using catalyst heat treatment process [9].

Treatment of poplar wood with acrylonitrile as the monomer and benzoyl peroxide as the catalyst was reported by Joshi et al., [10].

2.2.1.2. Polymerization using γ-radiation method

Wood polymer composites were prepared using methyl methacrylate or its mixture with some other specific multifunctional monomers such as ethylene glycol dimethacrylate (EGDMA) and tetrahydrofurfurylmethacrylate (THFMA). Polymerization was achieved by gamma radiation or by catalyst heat treatment [11] Wood polymer composites prepared by impregnating polymeric monomer (methyl methacrylate, methyl methacrylate- 5% dioxane and vinyl acetate) into wood cellular structure followed by irradiation for investigation of compressive and bending strength was reported in literature [12].

In one study rubber wood-polymer composites was prepared by using gamma radiation from a ^{60}Co source and five different type of monomer formulations [13]. Tropical wood polymer composites (geronggang, a light hardwood) was prepared by *in-situ* polymerization of monomers like methyl methacrylate, styrene-co-acrylonitrile, MMA-co-bis (2-chloroethyl) vinyl phosphonate and MMA-co-bis(chloropropyl)-2-propene phosphonate and employing either gamma radiation or catalyst [14].

Solpan and Guven [15] modofied Beech and Spruce wood was studied by treating with allyl alcohol (AA), acrylonitrile (AN), methyl methacrylate (MMA) and employing γ- radiation for polymerization.

Wood plastic composites from Syrian tree species (white poplar, cypress and white willow) were prepared using gamma radiation. Dry wood was impregnated with acrylamide or butyl methacrylate and different inorganic additives at various methanol compositions. Polymerization was done by using gamma radiation [16].

An attempt was made to by Gupta et al [17] improve various physical properties via preparation of WPC using various monomers like methyl methacrylate, butyl methacrylate, acrylonitrile and styrene. Polymerization was accomplished by gamma radiation from ^{60}Co source.

2.3. Literatures based on analysis of wood polymer composites

2.3.1. Improvement on dimensional stability of wood by chemical modification

Many research and developmental works had been carried out in past in order to improve the dimensional stability of wood materials in past decades.

Many researchers studied the mechanism of the effect of bulking treatments on dimensional stability. They reported that increase in wood volume due to bulking treatments was directly proportional to the theoretical volume of chemicals added [18-21].

Impregnation of wood with vinyl or acrylic monomer showed less dimensional stability in the presence of moisture. This might be due to the confinement of monomer in cell lumen instead of cell wall was reported by Rowell and Ellis [2].

A number of chemical treatments to improve the dimensional stability of wood had been tried. One way to obtain a good stabilizing effect was to bulk or fill the wood cell wall with a chemical and thus prevent shrinkage or swelling [22, 23]. It was reported that WPC made with vinyl monomer followed by curing (radiation or catalyst) significantly improved the moisture resistance [3].

Geibeler [24] investigated the effect of treatment with moisture, heat and pressure on dimensional stability of beech, birch, poplar, pine and spruce wood and reported that treatment at 180^0-200^0C under inert gas pressure reduced shrinkage and swelling of treated wood .

One method of impregnation of wood with amino resins was patented with a view to improve some properties of wood for using in constructional purposes [25].

The effect of high temperature and chemical concentration on dimensional stability of treated wood and also the chemistry of changes in wood volume in detail was reported by Hillis [26].

A simple acetylation process by dipping in acetic anhydride had been widely used to reduce swellability of wood in water [27].

Compounds such as epoxides, isocyanates, anhydrides , lactones and diols, which were highly reactive to the hydroxyl groups of cellulose, hemicellulose and lignin components of wood, were utilized for the reduction of equilibrium moisture content, one of the most important factors related to dimensional stability of wood [28].

When wood took moisture into the cell wall, the cell walls of wood due to absorption of moisture swelled in proportion to the volume of the water absorbed [29].

It was reported in literature [30-34] that dimensional stability of WPC improved due to the restriction of access of water into wood.

Work was done on chemical modification of wood for improvement of dimensional stability and acoustic properties by non-formaldehyde crosslinking agents viz. glyoxal, glutaraldehyde and dimethyloldihydroxyethyleneurea. It was found that ethylene urea did not give sufficiently high anti-shrink efficiency like those of glyoxal and glutaradehyde which caused 70% ASE. It was also suggested that the improvement of dimensional stability and acoustic properties could partly be attributed to the formation of cross links [35]. Mathias and coworkers [36] reported that cross linking of material in wood samples provided better dimensional stability to the wood polymer composite .

Numerous reports regarding improvement of quality of wood by chemical modification were available in literature [37-41]. A study was conducted by Filonov et al., [42] to investigate the effect of new oligomeric compounds on water absorption and swelling of wood.

Different types of wood impregnated with a polymer mixture containing macro ionomer and styrene improved the water repellency [43].

A method was developed by Minoru et al., [44] for preparation of crosslinked oligoesterified wood by hot pressing the wood blocks. They impregnated wood with a reactant solution of maleic anhydride and glycidyl methacrylate, for improvement of dimensional stability and surface property. The treatment method resulted in the cross linked oligoesterified wood with hard and smooth surface.

Wallstorm et al., [23] carried out work on surface stabilization of wood surface with polyethylene glycol (PEG) and studied the possibilities of interaction between wood (viz. *Pinus sylvestris*) and K-stained PEG using scanning electron microscope (EDS-anal), dynamic mechanical analysis (DMTA) and wide angle X-ray scattering (WAXS).

Wood polymer composites (WPC) of rubber wood were prepared by impregnating the wood with either methyl methacrylate (MMA) or mixture of MMA and diallyl phthalate (MMA/DAP) showed improvement in dimensional stability over the untreated wood [5].

WPC made with MMA and vinyl triacetoxy silane as coupling agent improved the dimensional stability of pinewood (positive effects both in anti-shrink efficiency and anti absorption efficiencies) [45].

It was reported that the difference in biological resistance of glyoxal, glutaraldehyde and dimethylol dihydroxy ethylene urea treated wood to white, brown rot fungus and subterranean termite was related to dimensional stability of wood resulting from the treatments [46]. The effect of heat on the dimensional stability of compressed wood was evaluated and reported by Dwianto et al., [47].

Characterization of chemically modified wood with elaborate discussion was reported in literature [48]. The chemical reaction between some reactive part of wood cell wall components and a simple single chemical reagent with or without catalyst for evaluation of physico-mechanical properties of modified wood was discussed [49].

Effect of organic solvents on wood substrate matrix hydrogen bond structures was studied and reported [50]. It was reported that rubber wood treated with glycidyl methacrylate (GMA) and diallyl phthalate (DAP) showed improvement in dimensional stability. WPC based on GMA exhibited greater dimensional stability compared to DAP alone [5].

Effect of temperature on dimensional stability of wood in which green planks of Norway spruce were dried either at 50 or 110^{0}C and then exposed to 5 climate cycles with wet and dry period was reported in literature. It was observed that the moisture contents and dimensional changes were lower in wood exposed to higher temperature [51].

Ellis and O'Dell [52] studied and reported that WPC made with combinations of hexane diol diacrylate, hydroxyethyl methacrylate, hexamethylene diisocyanate and maleic anhydride reduced the rate of swelling in water as well as in water vapour. Dimensional Stability of beech and spruce wood increased when treated with allyl alcohol, acrylonitrile and methyl methacrylate monomers [15].

Boric acid and phenylboric acid (PBA) were added into aqueous solutions of non or low formaldehyde reagents; dimethylol dihydroxyethylene urea (DMDHEU), glutaraldehyde (GA) and glyoxal (GX) in order to check their potential synergistic effects in wood. Boron addition to GA improved the ASE of wood while other combinations resulted in some decrease in the value of ASE [53]. Mahmoud et al., [54] investigated the effect of phosphoric acid on thioureaformaldehyde impregnated pine wood and reported that H_3PO_4 having concentration of 85% resulted in 18% anti-shrink efficiency in the treated wood.

The wood treated with silicone resin followed by curing resulted dimensionally stable and rot resistant wood [55]. A method was developed to improve the strength, moisture resistance and fire resistance to wood and timber to be used as building material by treating with water-soluble Na-silicate/borate mixture and employing vacuum or pressure techniques [56].

Dimensional stability of white pine wood improved on treatment with unsaturated polyester resin in admixture with styrene and varying bromine content. It was also reported that ASE properties were excellent for wood samples impregnated with resin without bromine [7].

Dimensional stability and moisture excluding efficiency (MEE) of wood after acetylation, butyrylation and hexanolylation were evaluated in one study. Moisture content of acetylated wood at three different relative humidities (RH) (33%, 65% and 93%) was significantly reduced. MEE of acetylated wood was greatly improved [57].

Chemical Modification of a soft wood kadam (*Anthocephalus Cadamba* Miq.) using different concentrations of urea-formaldehyde (UF) resin was carried out and their strength properties and ASE values were reported [58]. ASE of the treated samples was found to increase with the increase in the amounts of polymer loading.

Caribean Pine impregnated by the full cell treatment schedule with styrene, furfuryl alcohol (FFA) and styrene-furfuryl alcohol showed that permanent volumetric swelling was attained with only for samples treated with FFA, which was caused by cell wall impregnation. The dimensional stability of the treated wood samples evaluated in terms of anti swell efficiency (ASE) was found to be improved on double treatment [59].

An increase in dimensional stability of wood polymer composites, made by using styrene, methyl methacrylate and eucalyptus or pine wood, rendered it more impermeable to moisture absorption and retention [8].

Gupta & coworkers [17] reported that dimensional stability in terms of ASE of rubber wood (*Hevea brasiliensis*) was improved by impregnation and polymerization of methyl methacrylate, butyl methacrylate, acrylonitrile and styrene on to wood. They also reported that rubber wood on treatment with styrene produced maximum ASE compared to other monomers.

2.3.2. Development of physical and mechanical properties of wood by chemical treatment

From constructive point of view it is necessary to improve physical and mechanical properties of wood.

Wood polymer composites prepared by using methyl methacrylate or its mixture with some other specific multifunctional monomers such as ethylene glycol dimethacrylate (EGDMA), triethyleneglycoldimethacrylate (TEGDMA), trimethylol propane trimethacrylate (TMPTMA) and tetrahydro furfuryl methacrylate (THFMA) followed by γ radiation or by catalyst heat treatment increased the compressive strength and modified Janka Hardness [11].

A study was performed to see the dependence of physico mechanical characteristics of chemically and radiation modified birch wood on its moisture content and the types of modifying polymers [60].

The changes in mechanical properties of wood through cross lamination with phenolic resin and polyethylene glycol impregnation was reported in literature [61].

Kapur (*Dryobalanop sp.*) wood when impregnated with vinyl acetate, methyl methacrylate and methyl methacrylate-5% dioxane, the compressive strength, bending strength and impact strengths of the wood increased [12]

The reaction mechanism, physical and mechanical properties of wood modified chemically with thioacetic acid was studied and reported [62]. Ignatovich and coworkers [63] reported that the impregnation of wood with urea formaldehyde resin under pressure resulted in an improvement of mechanical properties of wood. They recommended the treated wood for the manufacture of furniture and parquet floors. Enhancement of physical properties of wood by resorcinol/formaldehyde treatment was observed by Yano et al., [64]. They reported that the treatment increased bending strength in longitudinal direction. A remarkable decrease in abrasion resistance and linear increase of the surface hardness with increase in concentration were also reported [65].

Different types of wood impregnated with a polymer mixture containing macro ionomer and styrene improved compressive and bending strength [43].

A method was put forwarded for densification of wood by impregnating with a solution containing unsaturated carboxylic acid, phosphonic acid and /or sulfonic acid followed by curing [38].

WPC prepared from radiata pine and eucalyptus using methyl methacrylate with vinyl triacetoxy silane as coupling agent led to an improvement in compressive strength and hardness values [45]

Rozman et al., studied the properties of wood polymer composites (WPC) of rubber wood prepared by impregnating the wood with methyl methacrylate (MMA) and the combinations of MMA and diallyl phthalate (MMA/DAP) and found a significant improvements in compressive strength, impact strength and hardness values over the untreated wood [4].

Glycidyl methacrylate and diallyl phthalate treated rubber wood showed an improvement in modulus of elasticity (MOE), modulus of rupture (MOR), toughness, compressive strength and impact properties over untreated ones [5].

An improvement in compressive strength, hardness values of beech and spruce wood on treatment with allyl alcohol, acrylonitrile and methyl methacrylate monomers and their mixtures were reported by Solpan and Guven [15]. The compressive strength and hardness of artificially aged wood samples showed values similar to those of before ageing.

An increase in compressive strength of thiourea formaldehyde resin and orthophosphoric acid treated white pine wood was reported by Mahmoud et al., [54]. The effect of impregnation of white pine wood with unsaturated polyester resin in admixture with styrene was studied by Mahmoud and co workers [7]. An improvement in compression strength was reported due to treatment.

Hardness of wood composites of Sugi (*Cryptomeria japonica*) made by using the colloidal silica-boric acid system was increased upto 22% compared to untreated wood [66]. *Anthocephalus cadamba* Miq. was chemically modified with urea formaldehyde (UF), MOR value increased on treatment [58].

A study on Syrian tree species poplar, cypress and white willow treated with aryl amide or butyl methacrylate with different inorganic additives and co additives such as lithium nitrate, copper sulfate and sulfuric acid showed that sulfuric acid decreased compressive strength while Li^+ had a positive effect on compressive strength [16].

The mechanical and physical properties of pine (*Pinus caribaea*) and eucalyptus (*Eucalyptus grandis*) treated with styrene and methylmethacrylate was studied. Benzyol peroxide (BPO) was used as the initiator using vacuum pressure method. In Eucalyptus-wood composite hardness was improved in both parallel and perpendicular to grain direction. Dimensional stability was improved for pine wood composites [8].

Mechanical properties like compressive and impact strength were improved for poplar wood on treatment with acrylonitrile as the monomer [10].

2.3.3. Improvement of biodegradation property of wood by chemical modification

The polymerization of vinyl monomers in void spaces of bulk wood resulted in wood polymer composites of increased strength properties and dimensional stability. Timber is attacked by numerous wood deteriorating microorganisms during service due to exposure in different environmental conditions. So it is desirable to enhance the biodegradation resistance of wood, with simultaneous improvements in mechanical properties.

Efforts were made to incorporate of triallyl tin group in to monomers used for *in-situ* polymerization in wood. Triallyl tin compounds had emerged as broad spectrum toxicants having high toxicity toward marine fouling organisms [67] as well as wood destroying organisms [68-70].It was reported that tri-allyl tin compounds eventually degraded to harmless inorganic oxides of tin by the action of UV light, microbes etc. and thus formed a minimal environmental hazard.

Biodegradation of wood, whether it is above ground, by soil contact or in marine applications was brought about by fungi, bacteria, insects and marine borers [71].

Non toxic preservative treatment was studied for chemical modification of wood to improve biological resistance [19, 72]. Some researchers used copolymers of tri-n-butyltin methacrylate (TBTMA) and glycidyl methacrylate against *Pseudomonas nigrifacieums* (marine bacterium), *Sarcina lutea* (soil fungus) and *Giomeralla cingulata* (soil fungus). The leaching rate was determined by the nature and extent of crosslinking of the polymers [73, 74].

Degradation of wood caused by actions of fungi, insects and matrix borers and the effects of chemical treatments in preventing wood degradation by these agents was studied in detail [75]. Chemical modification with thioacetic acid on biological resistance of wood were also reported [62].

It was reported that the durability of beech wood (*Fagus sylvatica*) against fungi was improved due to treatment with acetic acid anhydride without using any catalysts [76]. Using aqueous solution of D-glucose and optionally fungicides and termicides a process was developed for improvement of dimensional stability of wood [77].

The plastic component in the original WPC's was presumed to protect the wood against biological attack, but several reports had suggested that the wood remained susceptible to fungal degradation despite its close association with the plastic [78-81]

Solpan and coworkers [82] reported that beech wood and spruce wood treated by allyl alcohol, acrylonitrile, and methyl methacrylate monomers and monomer mixtures increased the resistance to *Bacillus spp.* bacteria after 30 days exposure to nutrient agar medium.

Boric acid and phenylboric acid (PBA) were added into aqueous solutions of formaldehyde reagents; dimethyloldihydroxyethyleneurea (DMDHEU), glutaraldehyde (GA) and glyoxal (GX) to see their effect on wood. Boron addition to these reagents considerably improved the decay resistance against *Tyromyces pulustris* and *Coriolus versicolor* which were the representative fungi of white and brown rot. Mass loss due to the farmosan termite (*Coptotermes formosantes*) attack could be reduced to a minimum with total inactivation of termites by PBA addition [53].

Indonesian pine, Indonesian jabon and USA southern yellow pine were either in situ polymerized with tri-n-butyltin methacrylate (TBTMA) or acrylated and then exposed to termite and fungal degradation both in laboratory and field. All levels of

TBTMA and acetylation treatments were effective against the brown rot fungus *Tryomyces plustris* and white rot fungus *Coriolus vernicolar* in the laboratory testing. Resistance to subterrenean termites and dry wood termites at all treatments was reported [6].

Rubber wood was treated to prepare WPC using methyl methacrylate (MMA), butyl methacrylate, acrylonitrile and styrene. Gamma radiation from a ^{60}Co source was used for polymerization. Bio deterioration in terms of weight loss caused by white and brown rot fungi was measured during a period of 12 weeks exposure. Maximum resistance against fungus was found with styrene [17].

The presence of boron compounds in wood plastic composites increased the resistance to biodegradation by brown rot fungus *Glyoeophyllum trabeum* [83].

2.3.4 Improvement of thermal property of wood by chemical modification

Increased efforts to expand the use of wood products in institutional and commercial structures may require wood to be treated with fire retardant. Therefore research on fire retardant treatments for wood has accelerated. It was reported in the literature [54] that the improvement in fire retardancy of wood compressive strength and anti-swell efficiency were obtained on treatment with thiourea-formaldehyde resins and orthophosphoric acid.

Flame retardancy had been imparted to woods that were incorporated with phosphorous or chlorine containing polymers, or flammable polymers like polymethyl methacrylate, polyacrylonitrile and polystyrene [84-88].

Eickner and Schaffer [89] found that monoammonium phosphate was the most effective among different fire -retardant chemicals in reducing the flame spread index of Douglas-fir plywood. Zinc chloride was next in terms of effectiveness but required higher retention levels to reduce the flame spread index values equivalent to monoammonium phosphate. Ammonium sulfate and borates were as effective as zinc chloride at retentions of about 4.5 pounds per cubic foot and lower but not as effective at higher retention levels. Boric acid had some effectiveness in reducing flame spread.

Char development rate in the three species of wood namely, Douglas-fir; southern pine and white oak was studied and reported by Schaffer [90]. Charring rate decreased with increase in dry specific gravity and moisture content. He also found that growth ring orientation parallel to the exposed face resulted in higher charring rates compared to perpendicular to the exposed face.

Schaffer [91] found that impregnation of southern pine with certain fire retardant and other chemicals did not significantly change the rate of charring. Boric acid, borax, ammonium sulfate, monosodium phosphate, potassium carbonate and sodium hydroxide reduced the rate of charring by about 20 percent over untreated wood after 20 minutes of fire exposure. Only polyethylene glycol 1,000 reduced the rate of charring over the entire period of fire exposure by about 25 percent over untreated wood. Tetrakis-(hydroxy methyl) phosphoniumchloride with urea, dicyandiamide with phosphoric acid, monoammonium phosphate, zinc chloride, and sodium chloride had no effect on charring rate [91].

Various thermal analytical techniques had been developed for the study of thermal degradation of wood [92-94] and wood impregnated with polymers [95, 96]

The weight loss of wood at different temperatures due to thermal degradation was reported in the literature [92, 93]. A small weight loss prior to 100^0C was attributed to the evaporation of moisture. The pyrolysis took place between 150 and 200^0C, with the hemicellulose starting to decompose at about 200^0C, followed by lignin at about 220^0C, and subsequently by cellulose at 250^0C. At temperature higher than 250^0C, rapid weight loss was observed which is due to the volatilization of the wood components was observed. Pyrolysis was considered to be completed at around 360^0C as indicated indicated by a small shoulder in the TG curve around this temperature. The next phase of weight loss around 400^0C could be attributed to the oxidative combustion of the non-volatile pyrolysis products. Complete decomposition was achieved at around 480^0C.

When potassium aluminium sulfate alum was used as a flame retardant for some Nigerian timbers, it was observed that flame spread rate and after glow time were drastically decreased. Thermogravometric analysis (TGA) showed that alum acted as a flame retardant (FR) by a complex process [97].

Wood polymer composites (WPC) of geronggang (GE: *Cratoxylon arborescens*), a light tropical hardwood, impregnated with MMA; styrene-co-acrylonitrile (3:2STAN); MMA-Co-bis (2-chloroethyl) vinyl phosphonate (3:1 MVP) were prepared by *in-situ* polymerization using γ radiation or catalyst heat treatment. Thermal characterization of these WPC by oxygen index measurements (LOI), TG and DSC showed that the impregnation greatly modified the wood properties. The LOI values of the GE-MVP and GE-MVP composites were much higher than those for GE and other composites [14]

Determination of the oxygen index and thermogravimetric analysis were used to evaluate the flammability of wood by Saka et al., [98, 99]. Enhancement of fire resistance properties by addition of tetraethyl ortho silicate (TEOS) with trimethyl phosphite (TMP) or/and trimethylborate was reported in literature [100, 101].

The method for enhancing fire resistance to wood and timber to be used as building material by treating with water-soluble Na-silicate/ borate mixture by using vacuum/ pressure techniques was reported [56].

The thermal properties of five types of wood polymer composites based on rubber wood (*Hevea brasilliensis*) was studied by limiting oxygen index measurements (LOI), differential thermal analysis (DTA) and thermogravimetry (TG). Of the five components, the impregnated one with bis (2-chloroethyl) vinyl phosphonate (MVP) reduced the initial temperatures of decomposition, increased the peak temperature of exothermic reactions and char yield [13].

Thermal properties of poplar wood composites with acrylonitrile as the monomer was evaluated using simultaneous differential thermogravimetric analysis (DTG-TG-DTA) in air. Wood composites showed resistance against thermo oxidation [10].

2.3.5. Effect of chemical modification on the surface morphology and FT-IR spectroscopy of wood

A SEM study on radiata pine and blackbut showed that the presence of silane coupling agent increased the adhesion of the polymer to the cellulose fibres of the wood [45].

The fine structures of wood-polymer (copolymer) composites were investigated by scanning electron microscopy (SEM). The photographs were taken from the cross-sectional surface of wood samples [15].

Indonesian pine, jabon and USA southern pine were treated with tributyltin acryalte (TBTA) and then exposed to termite colony. SEM of the treated samples before and after exposure to termite colony showed the presence of polymer in the lumen [6].

Stolf et al., [8] investigated and compared the microscopic structure of non-impregnated samples of *Pinus caribea* with those of styrene and methyl methacrylate impregnated monomers. They reported that the penetration and subsequent polymerization of the monomers occurred inside the anatomical structure of wood.

Rozman et al., [102] used the FT-IR to see the interaction of rubber wood with glycidylmethacrylate (GMA) and diallylphthalate (DAP). The peaks obtained clearly showed the interaction between wood and the polymers.

A study of chemical structure of softwood and hardwood and the wood polymers with the help of FT-IR spectroscopy were carried out and reported by Pandey [103].

The adhesion of urea formaldehyde (UF), melamine formaldehyde (MF) and phenol formaldehyde (PF) resins to the wood substrate was observed by scanning electron microscopy [104].

Study of the fracture surfaces of basswood and yellow birch showed that WPC made with different polymers fractured differently. Especially noticeable were stretching and tearing of the soft polymer. Samples containing a coupling agent showed evidence of bonding to the cell wall [105]

2.4 Objectives and plan of work

The north eastern part of India is bestowed with huge storage of trees. Out of two varieties available hardwoods are being used mainly for construction purposes. Softwoods are mostly used for fuel purposes due to their poor strength and dimensional stability compared to hardwoods. These softwoods can have value added by being made into wood suitable for different applications like furniture, office equipment and in construction through proper treatment such as chemical modification. Modification through impregnation has drawn the attention of researchers in the past and studies in this area are still being persued with great interest.

The chemicals to be used for modification should penetrate easily into the cell wall and must react with hydroxyl group of wood for improvement of strength, dimensional stability and other allied properties.

There are limited information regarding the use of styrene and glycidyl methacrylate (GMA) in combination as chemicals for modification of wood. GMA contains both glycidyl groups and double bond. The glycidyl group and double bond can be exploited for reaction with hydroxyl group of cellulose present in wood and for copolymerization with vinyl or acrylic monomers.

The impregnation of vinyl monomer followed by *in-situ* polymerization is known to enhance the strength, dimensional stability and thermal properties. In order to impart flame retardancy, solutions of flame retardant chemicals are used to impregnate into wood under pressure and then dried to obtain retention of chemicals. This process does not improve the strength and stability to a large extent.

Flame retardancy are generally imparted into woods by incorporating either chlorine or phosphorous containing polymer, or the copolymerization product of these with more flammamble polymers like PMMA, PS etc. Few literatures are available in this regard. But still there are wide scope to further work in this area by exploring the possibility of synthesizing and incorporating new chlorine or phosphorous containing monomers into wood.

Diethyl allyl phosphate (DEAP) can be used as a potent flame retardant monomer as it has double bond and alkoxy linkage. The alkoxy linkage and double bond can be used for reaction with hydroxyl group of wood and for copolymerization with vinyl or acrylic monomers.

Studies of various properties of impregnated wood and their characterization are essential. It is assumed that these studies may provide some important and valuable information for detailed understanding and further development of the current techniques of impregnation.

With all these above background and possibilities in view, the present work has been under taken. Therefore the aim of the present work is to determine the effect of impregnation with styrene in the presence of i) difunctional crosslinker, GMA and ii) flame retardant monomer DEAP on the various properties of rubber wood and pine wood.

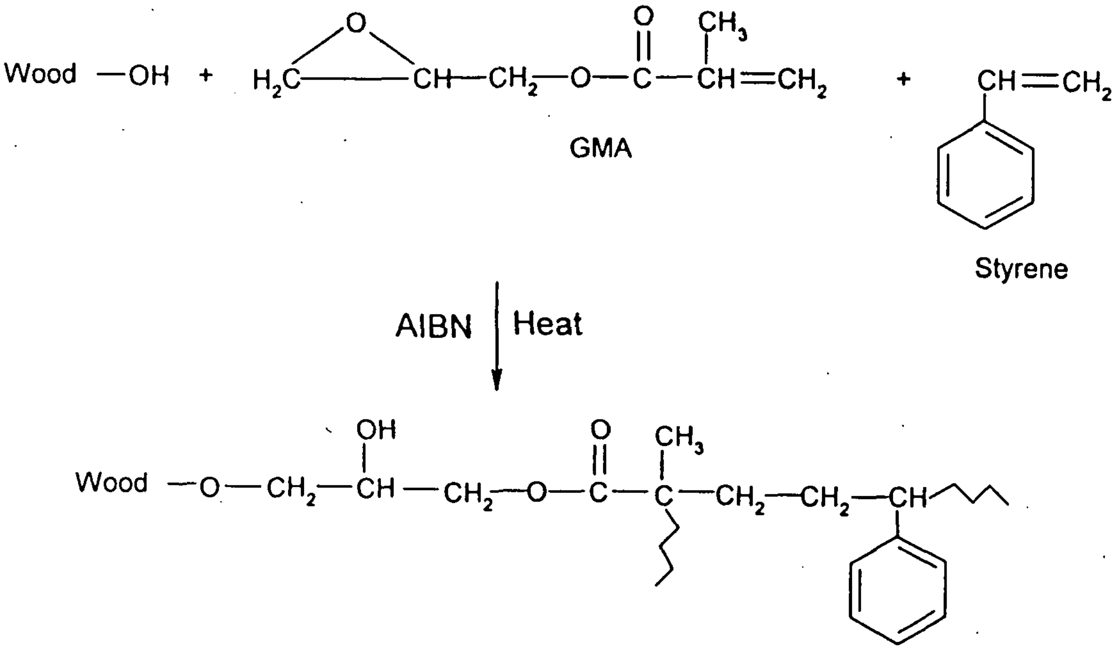
The splitting of the overall studies is presented as below

i) a) Modification of rubber wood and pine wood with impregnation of styrene and GMA as the monomer and crosslinker using 2,2′-azobis isobutyronitrile

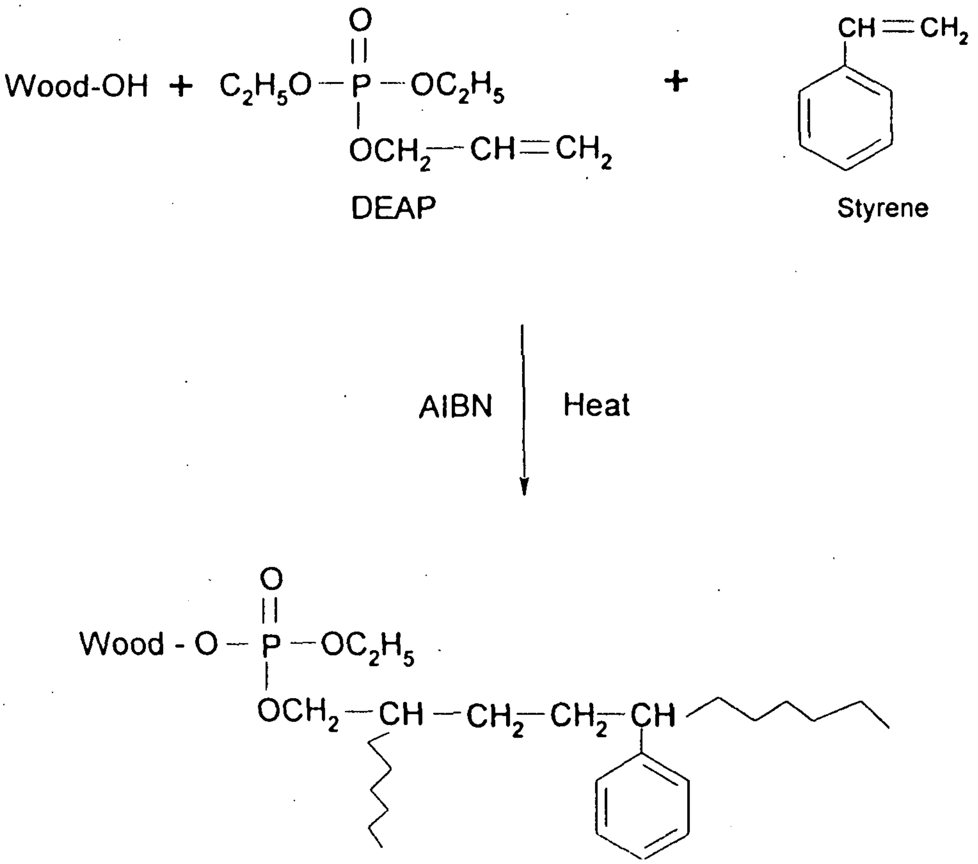
(AIBN) catalyst b) Modification of rubber wood with impregnation of styrene and diethyl allyl phosphate (DEAP) as the monomer and comonomers using 2,2'- Azobis isobutyronitrile (AIBN) catalyst.

ii) Studies of the various properties of impregnated wood samples and their characterization by using FT-IR spectrophotometer, scanning electron microscope, thermo gravimetric analyzer and differential scanning calorimeter.

Scheme I and scheme II represents the possible reaction between wood, styrene, GMA and wood, styrene and DEAP.



Scheme 1. Probable reaction between wood, styrene and GMA



Scheme II. Probable reaction between wood, DEAP and styrene

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CHAPTER III

EXPERIMENTAL

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3.1. Materials

Two kinds of softwoods namely rubber and pine wood along with the following materials were used in the present study.

Rubber wood (*Hevea brasiliensis*)

Rubber wood was collected locally from Assam. The wood is soft to moderately hard with an average weight of 515 Kg m^{-3} at 12% moisture content. Pores on the cross section are diffused and of medium to large size, mostly solitary, but sometimes in short multiples of two to three, filled with tyloses. Vessel tissues are conspicuous in radial and tangential faces and are of the order of about 200μ in diameter. Wood parenchyma is abundantly visible to the naked eye appearing as narrow, irregular and somewhat closely spaced bands forming a net like pattern with rays. The rays of the wood are moderately broad, rather few and fairly widespread. There are very few natural defects in rubber wood capable of making it unsuitable for general purpose applications. Due to the presence of growth stresses and induced drying stresses, a few defects such as splits, cracks and checks are usually observed. Being non homogeneous in its structure, its density varies from site to site inside the material.

Pine wood (*Pinus khasya*, Royle)

Pine, a large evergreen tree having thick bark with deep cracks was collected from a local forest in Assam. The annular rings are very distinct. The medullary rays are fine and irregularly distinguished. Resin ducts are moderate sized; numerous in the outer and middle ebelt of each annual ring is prominent on vertical sections.

Styrene, glycidyl methacrylate (GMA), 2,2'-azobis-(isobutyronitrile) (AIBN), allyl alcohol, phosphoryl chloride ($POCl_3$) were obtained from Merck, India. Tetrahydrofuran (THF), Benzene, ethanol and other reagents used were of analytical grade.

3.2. Purification and preparation

3.2.1. Purification of monomer (Styrene)

Styrene was freed from inhibitor by repeated washing with 4% aqueous NaOH solution followed by washing with distilled water. The inhibitor free monomer was then dried over fused calcium chloride, distilled under reduced pressure and middle fraction was collected. It was stored in a dark coloured bottle in the refrigerator at a temperature of 5^0C.

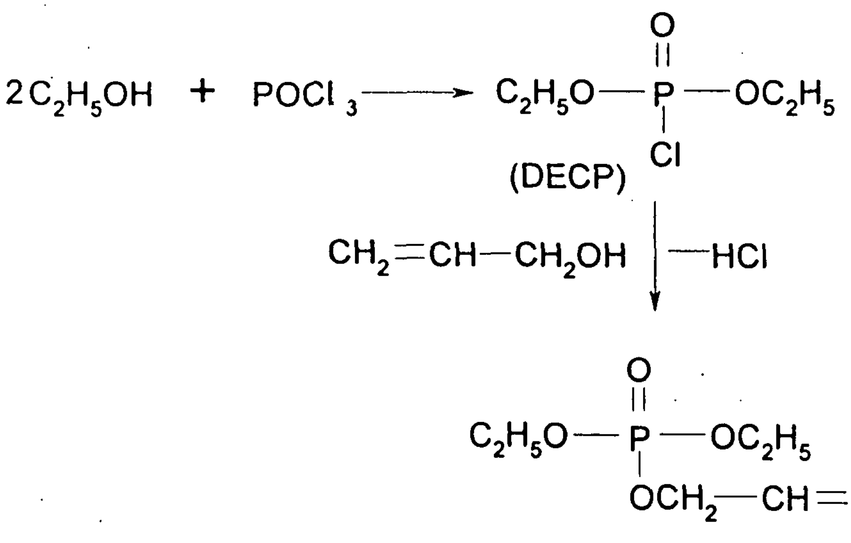
3.2.2. Purification of allyl alcohol

Allyl alcohol was distilled under reduced pressure and the middle fraction was collected. It was stored in a bottle containing molecular sieve and kept in the refrigerator.

3.2.3. Preparation of diethyl allyl phosphate (DEAP) monomer

DEAP was prepared according to the procedure given in literature[1].Freshly distilled ethanol (18.4 g, 0.4mol) was slowly added from a dropping funnel to ice-cold

$POCl_3$ (34.4 g , 0.2 mol) in a 100 ml round bottom flask fitted with a condenser, mechanical stirrer and a $CaCl_2$ guard tube. The reaction mixture was stirred at room temperature for 5h. Diethyl chloro phosphate (DECP) thus formed was vacuum distilled. Dried allyl alcohol (4.04 g, 0.07 mol) was added drop wise to the ice cold diethyl chloro phosphate (12.09 g, 0.07 mol) under constant stirring and the reaction mixture was kept at room temperature for 5 h to yield the diethyl allyl phosphate (DEAP) monomer.



(DEAP)

Scheme 3.1. Reaction Scheme for preparation of DEAP

3.2.4. Preparation of wood sample

The wood samples used for the study were prepared from clear defect free wood cut into blocks of different sizes for different experiments. The blocks having dimensions

$2.5\times1\times2.5$ cm^3 (radial × tangential × longitudinal) were used for water repellency, hardness, water uptake, dimensional stability and water vapour exclusion test.

$1\times1\times10$ cm^3 (radial × tangential × longitudinal) and $2\times2\times3$ cm^3 (radial × tangential × longitudinal) for bending strength and compressive strength experiments and

$(0.65\times0.3\times10)$ cm^3 (radial × tangential ×longitudinal) were used for Limiting oxygen index test.

3.2.5. Impregnation Procedure

All the samples were oven dried at 105^0C to constant weight before treatment and dimensions and weights were measured. The samples were then placed in an impregnation chamber followed by application of load over each sample in order to prevent them from floatation during addition of monomers. Vacuum was applied for a specific time period for removing the air from the pores of the wood before addition of monomers. Now sufficient mixture of styrene and initiator or that of styrene-GMA and initiator or styrene-diethyl allyl phosphate (DEAP) and initiator was added from a dropping funnel to completely immerse the wood samples. The samples were then kept in the chamber at room temperature for another 4h after attaining atmospheric pressure. This was the minimum time to get an optimum polymer loading which showed maximum improvement in properties. The condition of impregnation was varied by changing different parameters like monomer concentration, initiator concentration, time of impregnation, vacuum etc. After impregnation samples were taken out of the chamber and excess chemicals were wiped from the wood surfaces. The samples were then wrapped in aluminum foil and cured in an oven at 90^0C for 24h. This was followed by drying at 105^0C in an oven for 24h. The cured samples were then soxhlet extracted to remove homopolymers, if any, formed during impregnation. Finally the samples were dried and dimension was measured using a slide caliper and weights were taken.

3.3. Characterization

Density

For determination of density, the dimension of each test specimen was measured to accuracy not less than ± 0.3 percent and the mass to an accuracy of ± 0.2 percent. The density was measured using the relation [2].

$$\text{Density } (g.cm^{-3}) = M/V$$

Where M is the mass of the test specimen in g and V is the volume of the test specimen in cm^3

Void volume

Void volume of wood was calculated using the following relation

$$v_v = (1 - S_0) / 1.50$$

Where, $S_0/1.50$ is the solid volume of wood, where S_0 is the specific gravity of oven dry species and 1.50 is the specific gravity of oven dry wood substance.

Weight Percent Gain (WPG)

WPG after polymer loading was calculated according to the formula

$$WPG\ (\%) = (W_2 - W_1) / W_1 \times 100$$

Where W_1 is oven dry weight of wood blocks before polymer treatment and W_2 is oven dry weight of blocks after polymer treatment.

Volume Increase (%) after impregnation

Percentage volume increase after curing of wood samples was calculated as follows:

$$\%\text{Volume increase} = (V_t - V_o)/V_o \times 100$$

Where V_o is the oven dry volume of the untreated wood and V_t is the oven dry volume of the treated wood.

Water uptake test

Both untreated and treated wood samples were immersed in distilled water at room temperature (30°C) and weights were taken after 0.5,2,6,24,48,96,120, 144 and 168h. It is expressed as

$$\text{Water uptake (\%)} = (W_t - W_d)/W_d \times 100$$

Where W_d is the oven dry weight of the sample and W_t is the weight after immersion in distilled water for specified time period.

Water vapour exclusion test

Oven dried samples were conditioned at 30°C and 30% relative humidity (RH) and weighed. Samples were then placed in a chamber where temperature and relative humidity (RH) were maintained at 30°C and 90% respectively and weights were measured after 0.5, 2, 4, 8, 24, 48, 96, 120 and 168h. It is expressed as percentage of moisture absorbed based on oven dry weight.

Water Repellent Effectiveness (WRE)

WRE was measured for different soaking periods. Resistance to water uptake is expressed as WRE and calculated as follows

$$WRE = (D_0 - D_t)/ D_0 \times 100$$

Where D_0 is the water uptake capacity of untreated samples immersed for 0.5, 2, 6, 24, 48, 96, 120, 144, 168h. D_t is the water uptake capacity of treated wood samples immersed for the same periods.

Dimensional stability test

Dimensional stability test was performed in terms of swelling in water vapour and swelling in water. The procedure was similar to that of used in literature [3].

Swelling in water vapour

Samples were first dried at 105^{0}C followed by measuring the dimensions in radial as well as tangential directions. Samples were then conditioned at 30^{0}C and 30% RH. Finally the samples were placed in a chamber where relative humidity and temperature were maintained at 90% and 30^{0}C respectively. Now the dimensions were remeasured after 0.5, 2,4, 8, 24, 48, 96, 120 and 168h.

Swelling in Water

Dimensions of the oven dried samples were measured and conditioned at room temperature (30^0C) and 30% RH. Final placements of the samples were done in distilled water and then dimensions were remeasured after 0.5, 2, 6, 24, 48, 96, 120,144 and 168h. In both the cases swelling was considered as change in volume and expressed as the percentage of volume increase compared to oven-dried samples.

$$\text{Swelling (\%)} = (V_{t,u} - V_0)/V_0 \times 100$$

Where $V_{t,u}$ is the volume of the untreated or treated wood after water absorption and V_o is the volume of the untreated or treated wood before water absorption

Anti swell efficiency (ASE)

ASE index was determined in order to evaluate dimensional stability of treated wood specimens. The specimens were submerged in distilled water at 30^0C for different time periods after conditioning at 30% RH and 30^0C. Volumetric swelling coefficients in percentage (%) were calculated according to the formula:

$$S\ (\%) = (V_2\text{-}V_1/V_1) \times 100$$

Where V_2 is the volume of the water saturated blocks and V_1 is the volume of the oven dried blocks.

The percentage of ASE was calculated from the wet and oven dried volumes of treated and untreated wood specimens according to the formula:

$$\text{ASE (\%)} = (S_c\text{-}\ S_t)/S_c \times 100$$

Where S_c is the volumetric swelling co efficient of untreated blocks and S_t is the volumetric swelling coefficient of the treated blocks.

Hardness

The hardness of the samples was measured according to ASTM D2240 method using a durometer (model RR12) and expressed as shore D hardness.

FT-IR Study

The treated and untreated samples were grounded and FT-IR spectra were recorded using KBr pellet in a Nicolet Impact 410 spectrophotometer. In some cases FT-IR spectra was directly taken in liquid form.

NMR study

^{1}H NMR spectra of diethyl allyl phthalate (DEAP) was measured in $CDCl_3$ on a 400MHz Varian Mercury NMR spectrometer

Bending Strength Test

Bending strength test was performed by using Zwick Tensile Tester (model Z010) with a crosshead speed of 2mm/min and by calculating modulus of rupture (MOR) and modulus of elasticity (MOE) of the wood samples according to ASTM D790 method.

$$\text{MOR (MPa)} = 3WL/\, 2bd^2$$

Where W is the ultimate failure load (N), L is the span between centers of support (m), b is the mean width (tangential direction) of the sample (m) and d is the mean thickness (radial direction) of the sample (m).

Compressive Strength Test

Compressive strength test was carried out in a load frame attached to a CBR test machine (model AIM-049, 10t) by maintaining a cross head speed of 1.25 mm/ min. The compressive strength (σ) was determined along directions both in perpendicular and parallel to fiber directions by using the equation $\sigma = P/A$, where P is the maximum external force (Kg) and A is the cross sectional area of the sample (cm^2)

Thermal study

Thermal properties of the untreated and treated wood samples were measured by Differential Scanning Calorimeter (DSC) and Thermogravimetric Analyser (TGA). DSC study was carried out in an instrument (model Metler TA 4000) at a heating rate of 10^0C/min upto 500^0C. TGA study was carried out using a thermo gravimetric analyzer (model Metler TA 4000) at a heating rate of 20^0C/min upto 500^0C. TGA of some samples was carried out in a thermogravimetric analyzer (model Universal V2. 5H) instruments at a heating rate of 20^0C/ min upto 800^0C. In both the cases nitrogen atmosphere was used.

Limiting Oxygen Index

Limiting oxygen index (LOI) is defined as the minimum concentration of oxygen, expressed as percent volume, in a flowing mixture of oxygen and nitrogen that will support flaming combustion of a material initially at room temperature. The method was according to ASTM D-2863. The sample was placed vertically in the sample holder of the LOI apparatus. The total volume of the gas mixture (N_2+ O_2) was kept fixed at 300cc. To begin with experiment, the volume of nitrogen gas and that of oxygen gas were kept initially at a maximum and minimum level. Now the volume of nitrogen gas was decreased and that of oxygen gas was increased gradually. However the total volume of gas mixture was kept fixed at 300cc during the experiment. The ratio of nitrogen and oxygen at which the sample continued to burn for at least 30sec was recorded.

$$\text{Limiting oxygen index (LOI)} = \text{volume of } O_2 \,/\, \text{Volume of } (O_2 + N_2)$$

Scanning Electron Microscopy (SEM) study

The compatibility between wood and polymers was monitored using a scanning electron microscope (model JEOL, JSM-5200) at an accelerating voltage of 15 kV. The electron microscopy photographs were taken from the fracture surfaces of some of the selected wood samples. The samples were coated with a thin layer of gold using a sputter coater.

Biodegradation Test

The wood samples showing improved dimensional stability and improved strength properties were subjected to biodegradation tests using a procedure described in literature [4]. An appropriate nutrient agar media for the growth of fungus, microorganisms, moulds etc. was prepared. The untreated and treated wood samples were stored in agar medium and then kept in vacuum desicator for 30 days. The samples were removed after the stipulated time and examined microscopically to access the growth of microorganisms.

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CHAPTER IV

RESULTS AND DISCUSSION

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RESULTS AND DISCUSSION

4.1. Modification of rubber wood with impregnation of styrene as the monomer and GMA as the crosslinking monomer taking 2,2′–azobis isobutyronitrile (AIBN) catalyst

Introduction

Improvement of wood properties by chemical modification has been the subject matter of many investigations in recent years. Various chemical methods have been employed to enhance the wood properties.

In this part, the author has reported and explained the effect of impregnation of styrene and glycidyl methacrylate (GMA) on various properties of rubber wood.

Treated samples for conducting different tests chosen were more or less similar polymer loading. Each result presented in either figure or tables was taken from the average of five samples.

4.1.1. Results

4.1.1.1. Properties of rubber wood

The density and void volume of rubber wood was determined and given in table 4.1.1. The measurements were done in triplicate and the reported results were the mean value.

Table 4.1.1. Properties of rubber wood

Properties	values
Density (g/cm^3)	0.54
Void volume	0.64

Table 4.1.2. Effect of variation of initiator (AIBN) concentration on polymer loading (WPG) (%) of pinewood [AIBN: 0.2-5% (by weight), Styrene-GMA= 100:20, Time: 4h, Temperature: 30± 1° C, Vacuum: 5" Hg]

Initiator Concentration (%)	0.2	0.5	2	5
WPG (%)	25.1	49.8	13.3	21.5
Volume increase (%) after curing	-	3.9	1.2	1.8
Water uptake (%)	22.3	20.0	53.1	40.3
Swelling in water (%)	3.9	7.8	10.4	10.3
Hardness	60.0	61.5	62.9	65.3

4.1.1.2. Standardization of impregnation conditions

The conditions of impregnations to get the highest polymer loading at which maximum improvement in properties obtained were optimized

Preliminary studies indicated that the best condition of polymer loading occurred at 5" Hg vacuum, 1:1 (Styrene-GMA) monomer concentration, 0.5% AIBN and 4 h of impregnation time.

4.1.1.3 Effect of variation of initiator concentration

Table 4.1.2. shows the results of variation of initiator concentration on polymer loading (WPG) using styrene-GMA system. The maximum polymer loading of 49.8% was found with 0.5% AIBN catalyst concentration (by weight), which showed maximum improvement in properties with more increase in the volume after curing. At 0.5% AIBN concentration, hardness and water absorption value were found to be 61.5 was 20% respectively.

4.1.1.4. Effect of variation of monomer concentration

Rubber wood samples showed negligible change in volume on impregnation with styrene. But significant change in volume (%) of wood samples was noticed when GMA was introduced (table 4.1.3.). At 1:1 Styrene-GMA concentration the highest improvements in the properties were obtained. Water uptake capacity (%) increased in the order untreated > styrene treated > styrene-GMA (5:1) treated > styrene-GMA (2:1) treated > styrene-GMA (1:1) wood samples. Improvement in hardness values [69.9 for Styrene: GMA (1:1) treated samples while for untreated samples the value was 46.6] was also observed.

Table 4.1.3. Effect of variation of monomer concentration on polymer Loading WPG (%) and other properties: [Styrene: GMA= 100:0 to 100: 100, AIBN: 0.5% (by weight), *Time*: 4h, *Temperature*: 30±1°C, *Vacuum*: 5" Hg]

Samples particulars		WPG (%)	Volume increase after curing (%)	Water uptake (%)	Swelling in water (%)	Hardness (Shore D)
Untreated		-	-	104.4	3.9	46.6
Treated with						
Styrene	GMA					
100	0	33.3	-	40.1	3.4	61.9
100	20	49.8	3.9	26.8	1.5	61.5
100	50	52.1	5.1	16.5	1.1	65.2
100	100	61.4	9.1	10.9	0.6	69.9

Table 4.1.4. Effect of variation of vacuum on loading and other properties: [Styrene-GMA= 100:100, Vacuum: 1-15"Hg, AIBN: 0.5% (by weight), Time: 4h, Temperature: 30±1°C]

Vacuum applied (Inches of Hg)	WPG (%)	Volume increase(%) after curing	Water uptake (%)	Swelling in water (%)
1	30.1	1.5	30.5	4.5
5	61.4	9.1	10.9	0.6
10	51.4	7.4	20.8	2.4
15	45.0	7.5	24.3	3.1

Table 4.1.5. Effect of variation of time on loading and other properties: [Styrene-GMA= 100:50, AIBN: 0.5 %(by weight), Time: 2-20h, Vacuum: 5"Hg, Temperature: 30±1°C]

Time (h)	WPG (%)	Volume increase (%) after curing	Water uptake (%)	Swelling (%) in water
2	35.4	1.4	25.6	3.9
4	46.3	3.9	21.3	2.1
6	46.8	4.0	25.0	2.4
8	47.9	4.3	27.4	3.2
20	53.2	3.8	22.0	2.8

4.1.1.5. Effect of variation of vacuum

Vacuum during impregnation was varied from 1″ Hg to 15″ Hg keeping the others parameters constant. When effect of variation of vacuum (1″ – 15″Hg) on impregnation was studied it was found that with increasing vacuum polymer loading increased first and then it decreased (table 4.1.4.). Maximum improvements in the properties were obtained at 5″ Hg with 61.4% polymer loading.

4.1.1.6. Effect of variation of time

The results showing the effect of variation of impregnation time on polymer loading are presented in table 4.1.5. Loading was found to be increased throughout the time period studied (upto 20h). Both water uptake and swelling in water decreased with increase in polymer loading. Overall improvements in properties were obtained when impregnation was done for 4h.

4.1.2. Characterization

4.1.2.1. Water uptake test

The results of water uptake for treated and untreated samples are shown in fig. 4.1.1. and table 4.1.6. Water uptake capacity of both the treated and untreated samples increased with increase in time throughout the time period studied. Untreated samples absorbed more water compared to treated samples. Styrene-GMA (1:1) treated samples showed least water uptake throughout the time period studied. After 168h, untreated wood absorbed 149.3% water. The value for styrene, styrene-GMA (5:1), styrene-GMA (2:1) and styrene-GMA (1:1) treated samples were 99%, 73.5%, 53.2% and 31.3% respectively.

4.1.2.2 Water Repellent Effectiveness (WRE)

Water repellent effectiveness (WRE) of treated and untreated wood samples was calculated as per the relation given in experimental part. Table 4.1.7 showed the results of the water repellent effectiveness (WRE) values for treated and untreated wood samples in water at room temperature (30^0C). An improvement in WRE values was observed for treated samples particularly on incorporation of GMA. In all the cases, water repellency decreased with time initially at a faster rate and finally at a slower rate. Styrene-GMA (1:1) treated samples showed 79% WRE value after 168 h of water absorption. At the same condition, the WRE value for styrene-GMA (2:1), Styrene-GMA (5:1) and styrene treated samples were 64.4, 50.8 and 33.6%.

Table 4.1.6. Water uptake test (%) at room temperature (30^0C)

Time (h)	0.5	2	6	24	48	96	120	144	168
Untreated	57.9	65.8	83.3	104.4	115.0	127.9	138	142.8	149.3
<u>Treated with</u>									
Styrene-GMA (1:0)	15.1	20.8	27.9	40.1	60.5	86.0	91.0	98.6	99.0
Styrene-GMA (5:1)	5.7	7.2	10.1	26.8	39.8	60.0	65.9	72.5	73.5
Styrene-GMA (2:1)	4.1	6.0	8.3	16.5	22.4	40.1	44.6	52.8	53.2
Styrene-GMA (1:1)	2.5	3.9	5.2	10.9	16.2	23.9	26.6	28.2	31.3

Table 4.1.7. Water repellent effectiveness (WRE) (%) of Wood Polymer Composites at room temperature

Time	0.5	2	6	24	48	96	144	168
<u>Treated with</u>								
Styrene-GMA (1:0)	73.9	68.3	66.5	61.5	47.4	32.7	30.9	33.6
Styrene-GMA (5:1)	90.2	89.1	87.9	74.3	65.4	53.1	49.3	50.8
Styrene-GMA (2:1)	92.9	90.9	90.0	84.2	80.5	68.6	63.0	64.4
Styrene-GMA (1:1)	95.7	94.1	93.8	89.5	85.9	81.3	80.3	79.0

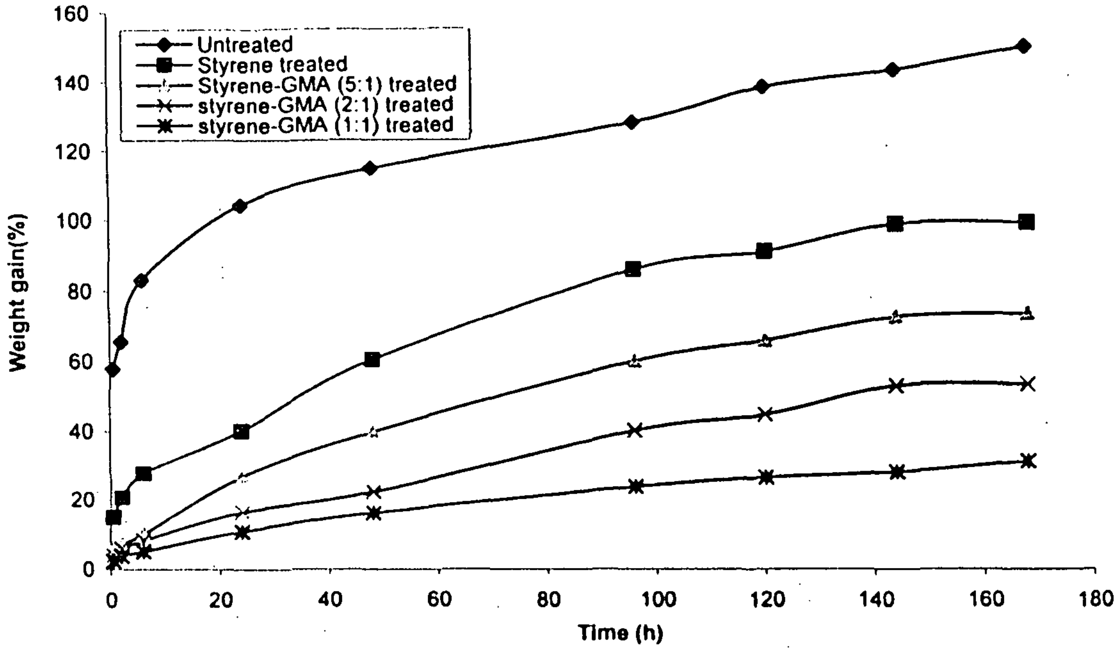


Fig. 4.1.1. Weight gain of WPC in water at 30^0C

4.1.2.3. Water vapour exclusion test

The water vapour exclusion (%) of the untreated and treated wood samples were calculated from the relation given in experimental part. The results are summarized in table 4.1.8 and figure 4.1.2. In a series of water vapour exclusion study in 90% RH and at 30^0C for various time periods, treated samples absorbed less water vapour than untreated samples. The absorption of water vapour followed the trend: untreated> styrene treated > Styrene-GMA (5:1) treated > Styrene-GMA (2:1) treated >Styrene-GMA (1:1) treated samples. After 168h untreated wood absorbed 13.9% water vapour compared to 8.2% for styrene-GMA (1:0) treated, 5.8% for styrene-GMA (5:1), 5.1% for styrene-GMA (2:1) treated and 4.9% for styrene-GMA (1:1) treated samples.

Table 4.1.8. Weight gain in 90% RH at room temperature

Time (h)	0.5	2	4	8	24	48	96	120	168
Untreated	5.1	5.6	5.7	6.6	9.6	10.7	12.4	13.0	13.9
Treated with									
Styrene-GMA (1:0)	1.3	1.4	1.6	2.1	3.7	4.9	6.7	7.2	8.2
Styrene-GMA (5:1)	1.2	1.2	1.3	1.5	2.5	4.3	4.8	5.6	5.8
Styrene-GMA (2:1)	1.0	1.0	1.2	1.3	2.0	3.5	4.1	4.9	5.0
Styrene-GMA (1:1)	0.8	0.8	0.9	1.1	1.8	2.5	3.7	4.2	4.9

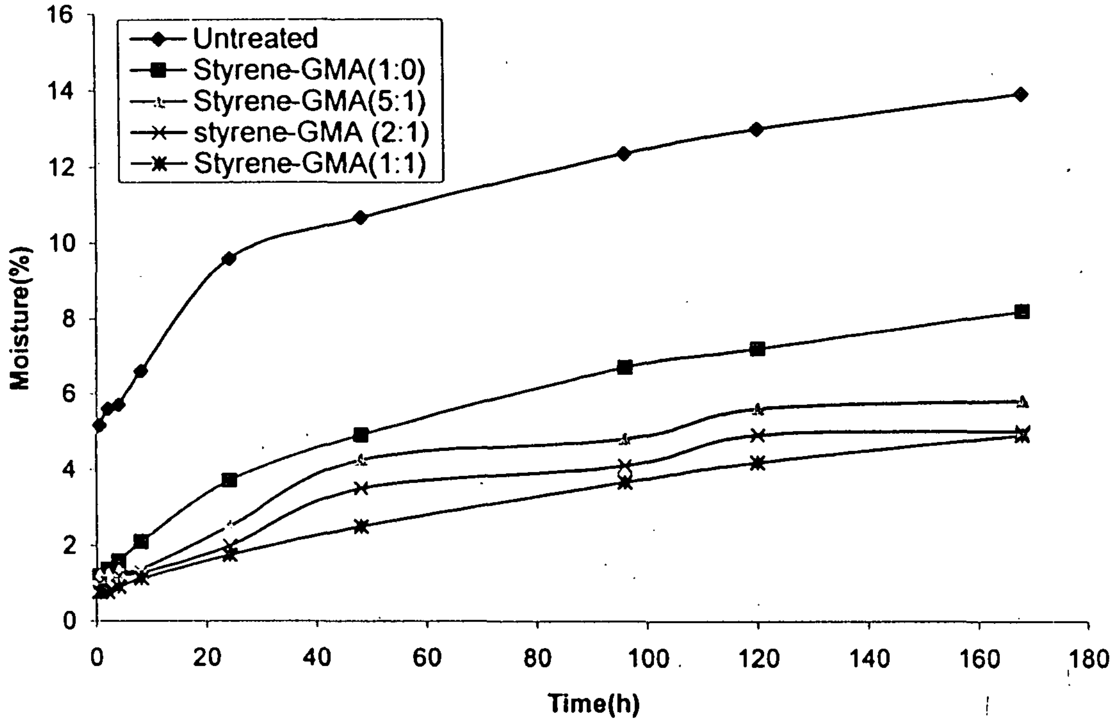


Fig. 4.1.2. Weight gain of WPC in water vapour at 90% RH and 30^0C

4.1.2.4. Dimensional stability study

Dimensional stability test at room temperature was performed in terms of volumetric swelling in liquid water and water vapour at 90% RH.

The volumetric swelling percentage in liquid water of wood samples were calculated using the relation given in experimental part. The effect of swelling in liquid water at room temperature (30^0C) for untreated and treated wood samples for different time periods are shown in table 4.1.9. and fig. 4.1.3. Samples treated with styrene-GMA (1:1) combination showed least swelling compared to either untreated or other treated samples. Samples treated with styrene or styrene-GMA (5:1) showed less swelling than the untreated samples upto 120 h beyond that swelling increased. The value for untreated wood after 168h immersion in liquid water was 5.1%. The value varied in the range 4.6-6.7% for different styrene-GMA treated samples.

The volumetric swelling (%) in 90% RH was calculated according to the formula given in experimental part. The results showing the effect of swelling in water vapour at 90%RH and room temperature (30^0C) upto 168h are presented in table 4.1.10. and fig. 4.1.4. As expected treated samples particularly those where GMA was incorporated showed more reduction in swelling. After 168 h treatment in water vapour untreated samples swelled upto 4.4%, which decreased to 1.2% on treatment with styrene. Further decrease in the value of swelling occurred with increase in GMA concentration. Styrene-GMA (5:1) treated samples showed 0.5% swelling compared to 0.5% and 0.4% for (2:1) styrene-GMA and 1:1 styrene-GMA treated samples respectively.

Table 4.1.9. Volumetric Swelling of Liquid water at room temperature (30^0C)

Time (h)	0.5	2	6	24	48	96	120	144	168
Untreated	0.4	1.0	3.5	3.9	4.9	5.0	5.3	4.9	5.1
Treated with									
Styrene-GMA (1:0)	0.3	0.9	3.3	3.4	4.6	4.7	5.0	5.6	6.7
Styrene-GMA (5:1)	0.1	0.1	0.2	1.5	4.0	4.2	4.4	6.0	6.4
Styrene-GMA (2:1)	0.2	0.2	0.3	1.1	4.0	4.1	4.2	4.6	4.9
Styrene-GMA (1:1)	0.3	0.3	0.4	0.6	3.5	4.0	4.1	4.2	4.6

Table 4.1.10. Volumetric swelling in 90% RH at room temperature

Time (h)	0.5	2	4	8	24	48	96	120	168
Untreated	1.8	1.9	2.6	2.7	3.9	4.2	4.2	4.3	4.4
Treated with									
Styrene-GMA (1:0)	0.2	0.2	0.2	0.2	0.4	0.4	0.5	0.7	1.2
Styrene-GMA (5:1)	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.5	0.5
Styrene-GMA (2:1)	0.1	0.1	0.1	0.2	0.2	0.3	0.3	0.4	0.5
Styrene-GMA (1:1)	0.0	0.0	0.0	0.1	0.1	0.1	0.2	0.4	0.4

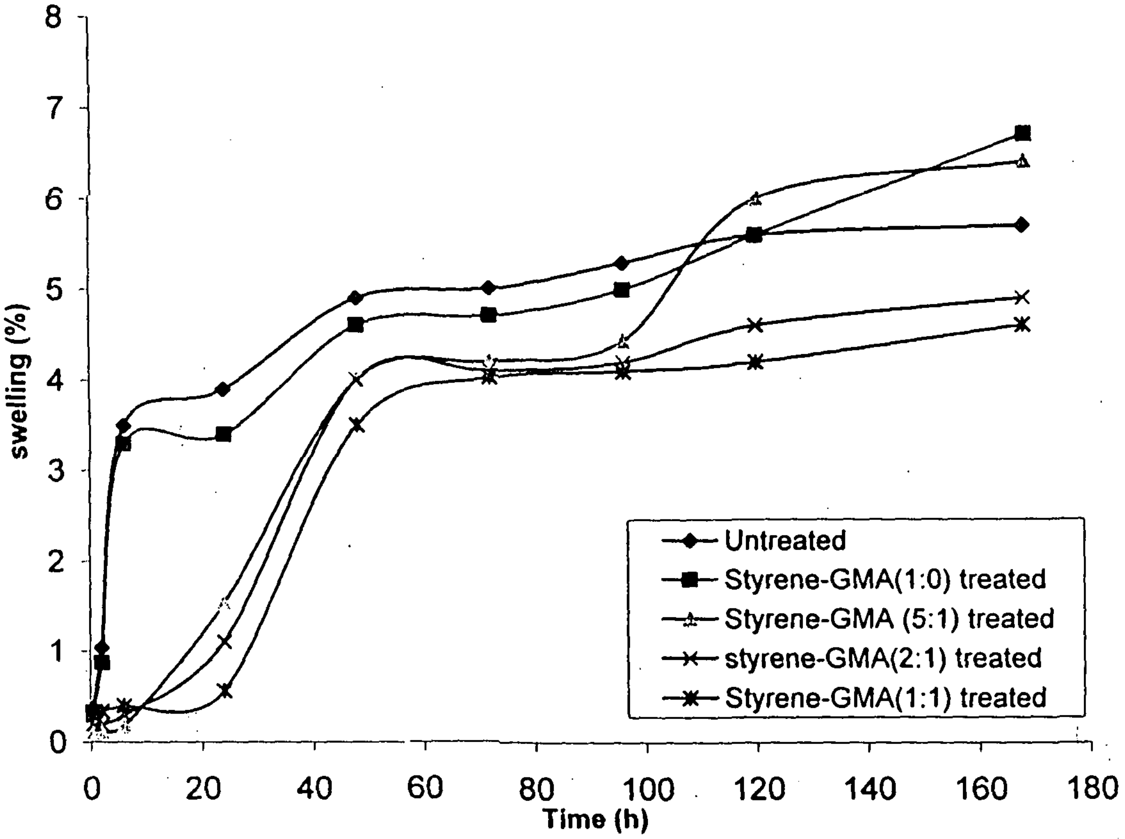


Fig. 4.1.3. Volumetric swelling of WPC in water

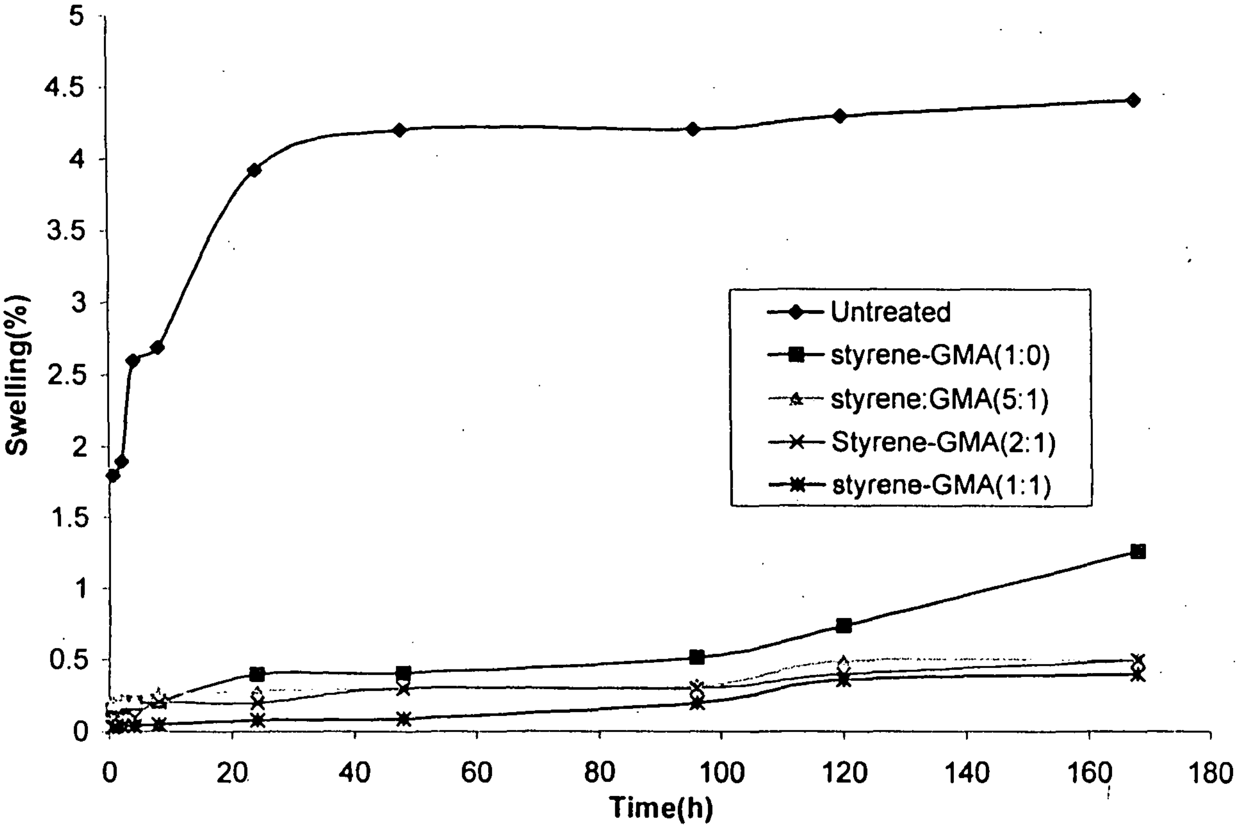


Fig. 4.1.4. Swelling of WPC conditioned at 90% RH and at 30^{0}C

4.1.2.5. Anti swell efficiency (ASE) study

Anti shrink Efficiencies (ASE) of the untreated and treated samples were evaluated according to the formula given in the experimental section.

Table 4.1.11.summarizes the results of anti-swell efficiency (ASE) of WPC and untreated samples. ASE values obtained were based on the measurement of the changes in longitudinal, tangential and radial dimensions using a vernier caliper and expressed to the nearest 0.01 cm. These results showed that ASE of styrene-GMA treated samples were better than untreated or styrene treated samples upto 168h in water. After 168h styrene-GMA (1:1) treated samples showed an ASE value of 9.8% while untreated or styrene treated samples showed a negative value.

4.1.2.6. Hardness study

Hardness values of the untreated and treated wood samples (of similar polymer loading) were measured using a Durometer (Shore D) and the values are summarized in table 4.1.12. Untreated samples showed a hardness value of 46.6 while on treatment it increased upto 69.9. Hardness values increased with increase in GMA value.

Table 4.1.11. Anti-Swell Efficiencies of the wood polymer composites

Time (h)	0.5	2	6	24	48	72	96	120	168
Treated with									
Styrene-GMA (1:0)	25.0	10.0	5.7	12.8	6.5	6.0	5.6	-	-
Styrene-GMA (5:1)	75.0	90.0	94.2	18.4	16.0	16.9	-	-	-
Styrene-GMA (2:1)	50.0	80.0	91.4	71.7	18.4	16.0	20.8	6.1	3.9
Styrene-GMA (1:1)	25.0	70.0	88.6	84.6	28.6	20.0	22.6	14.3	9.8

Table 4.1.12. Hardness values of the treated and untreated wood samples

Sample particulars	WPG (%)	Hardness (Shore D)
Untreated	-	46.6
Treated with		
Styrene: GMA (1:0)	33.3	61.9
Styrene: GMA (5:1)	35.4	61.5
Styrene: GMA (2:1)	36.1	63.0
Styrene: GMA (1:1)	37.5	69.9

4.1.2.7. Bending strength Test

Bending strength of the wood samples in terms of MOE and MOR were calculated using the relation given in experimental section.

Table 4.1.13 shows the values of MOE and MOR for untreated and treated wood samples. Both MOE and MOR values were found to increase due to treatment. Styrene treated samples showed higher MOR values (127.2 MPa) over the styrene: GMA (5:1) treated (120.0MPa) or styrene: GMA (2:1) treated (125.8 MPa) samples. But this value again increased for styrene: GMA (1:1) treated samples (138.6 MPa).

4.1.2.8. Compressive strength test

Compressive strength both in parallel and perpendicular to fibre directions were calculated using the relation given in experimental section. The results of compressive strengths of treated and untreated samples are shown in table 4.1.14. Compressive strength increased both in parallel and perpendicular to fibre directions on treatment. The value increased from 90.1 Kg/cm^2 for untreated samples to 152.2 Kg/cm^2 for styrene-GMA (1:1) treated samples. Similarly in parallel direction it increased from a value of 260.2 Kg/cm^2 for untreated samples to 329.0 Kg/cm^2 for styrene-GMA (1:1) treated samples. In general, the compressive strength was higher in parallel direction over the perpendicular direction for all the samples.

Table 4.1.13. MOE and MOR values of treated and untreated wood samples

Samples	WPG (%)	MOE (MPa)	MOR (MPa)
Untreated	-	3031.2	64.6
Treated with			
Styrene: GMA (1:0)	32.0	6718.4	127.2
Styrene: GMA (5:1)	39.9	7288.9	120.0
Styrene: GMA (2:1)	40.2	9132.4	125.8
Styrene: GMA (1:1)	41.5	12,341.5	138.6

Table 4.1.14. Compressive strengths of untreated and treated rubber wood samples

Samples	WPG (%)	Compressive strengths (Kg/cm^2)	
		Perpendicular to fibre direction	Parallel to fibre direction
Untreated	-	90.1	260.2
Treated with			
Styrene-GMA (1:0)	30.7	98.1	296.5
Styrene- GMA (5:1)	32.8	111.6	302.9
Styrene-GMA (2:1)	33.1	131.2	312.8
Styrene-GMA (1:1)	34.4	152.2	329.0

4.1.2.9. FT-IR Study

The FT-IR spectra of untreated and treated wood samples are presented in fig. 4.1.5. (I-III). From the FT-IR spectra it was found that the peak at 1733cm^{-1}, which was due to carbonyl stretching vibration, became more pronounced on treatment with styrene-GMA. The position of the peak at 3428.38cm^{-1} (OH stretching) for untreated wood remained unchanged by incorporation of styrene. The peak shifted to 3432.39cm^{-1} for styrene-GMA (1:1). The intensity of C-O stretching vibration (1113.56cm^{-1}) of untreated wood had also been found to increase on treatment with styrene and GMA.

4.1.2.10. Thermogravimetric analysis (TGA)

Table 4.1.15. shows the initial decomposition temperature (T_i), maximum pyrolysis temperature (T_m) and residual weight (%) (RW) for untreated and polymer treated wood samples. Table 4.1.16. showed the temperature of decomposition (T_D) at different weight loss percentages. T_i and T_m values for both the stages of pyrolysis in treated samples were higher than untreated samples. RW value is observed higher in the case of untreated wood samples compared to those of treated ones. It was also observed that T_D values of treated wood samples were higher than the untreated samples upto 60% decomposition, beyond that the value decreased. Besides this, a small weight loss was observed at different temperatures before the onset of major decomposition (270^{0}C) (not shown in table 4.1.16.).

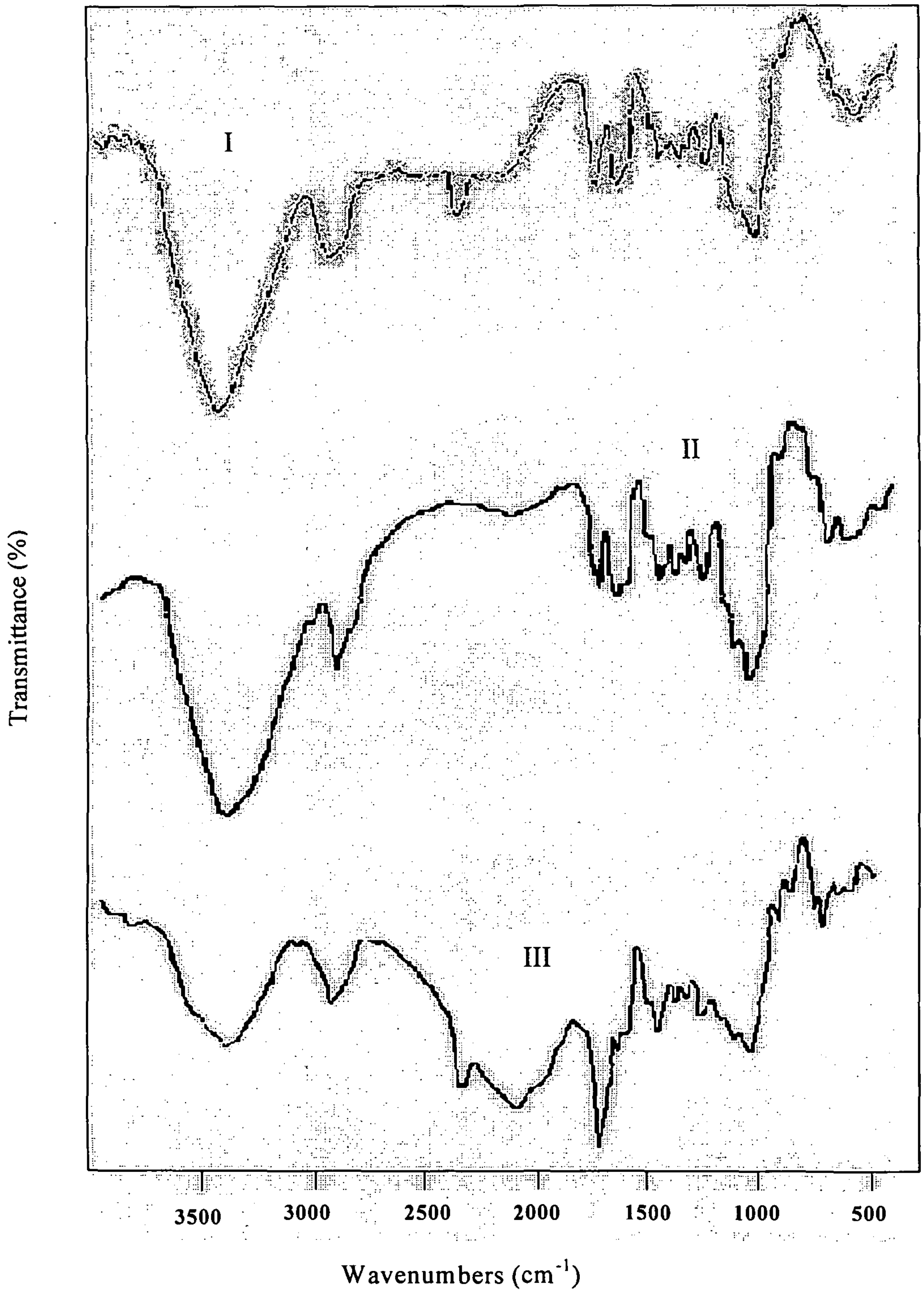


Fig. 4.1.5. FT-IR spectra of Untreated (I), styrene treated (II) and styrene – GMA treated (1:1) (III) rubber wood samples

Table 4.1.15. Thermal Analytical data for untreated wood and polymer treated wood samples

Sample particulars	T_i (^{0}C)	$Tm_i{}^a$(^{0}C)	$Tm_{ii}{}^b$(^{0}C)	RW (%)
Untreated	270	315	368	31.55
Treated with				
Styrene-GMA (1:0)	272	363	433	27.39
Styrene-GMA (5:1)	280	356.3	414.7	28.05
Styrene: GMA (2:1)	290	350.0	404.1	25.3
Styrene-GMA (1:1)	295	341.3	384.7	23.84
Styrene-GMA (0:1)	289	349	418	16.83

a: T_m value for first step b: T_m value for second step

Table 4.1.16. Temperature of decomposition (T_D) at different weight losses of untreated and treated wood samples

Sample particulars	Temperature of Decomposition (T_D) in ^0C at different weight loss (%)						
	20	30	40	50	60	65	70
Untreated	302	326	350	363	380	430	--
Treated with							
Styrene- GMA (1:0)	303	330	352	370	417	432	455
Styrene-GMA (5:1)	308	328	350	364	405	420	440
Styrene- GMA (2:1)	309	328	350	365	394	411	423
Styrene-GMA (1:1)	310	330	348	369	390	396	414
Styrene-GMA (0:1)	310	328	344	350	372	389	400

4.1.2.11. Differential scanning calorimetric (DSC) Study

Fig. 4.1.6. (I-VI) shows the DSC results of untreated and treated wood samples. Untreated wood (curve I) showed a single endothermic peak at 360^0C. Wood treated with GMA (curve V) also showed one endothermic peak at around 351^0C. Styrene and styrene-GMA impregnated wood samples (curve II-IV) and physical mixture of styrene-GMA (curve VI) showed one endothermic peak in the range $354\text{-}370^0$C and another endothermic peak in the range $416\text{-}432^0$C. The polystyrene and polyGMA was mixed in the ratio of 5:1 and mixed with wood flour similar to that of polymer loading in sample (curve III) to prepare the physical mixture.

4.1.2.12. Scanning Electron Microscopy Study

The fine structure of wood and wood polymer composite was investigated by Scanning electron microscopy (SEM). To investigate the interaction and compatibility between wood and polymer, detail SEM studies were carried out on some selected fractured surface samples obtained after bending test. Fig. 4.1.7. (a-d) shows the photographs of untreated, styrene treated, styrene-GMA (5:1) treated and styrene-GMA (1:1) treated rubber wood samples. These photographs (arrow marked) showed that either the cell wall or cavities were filled up with styrene-GMA (1:1) treated samples

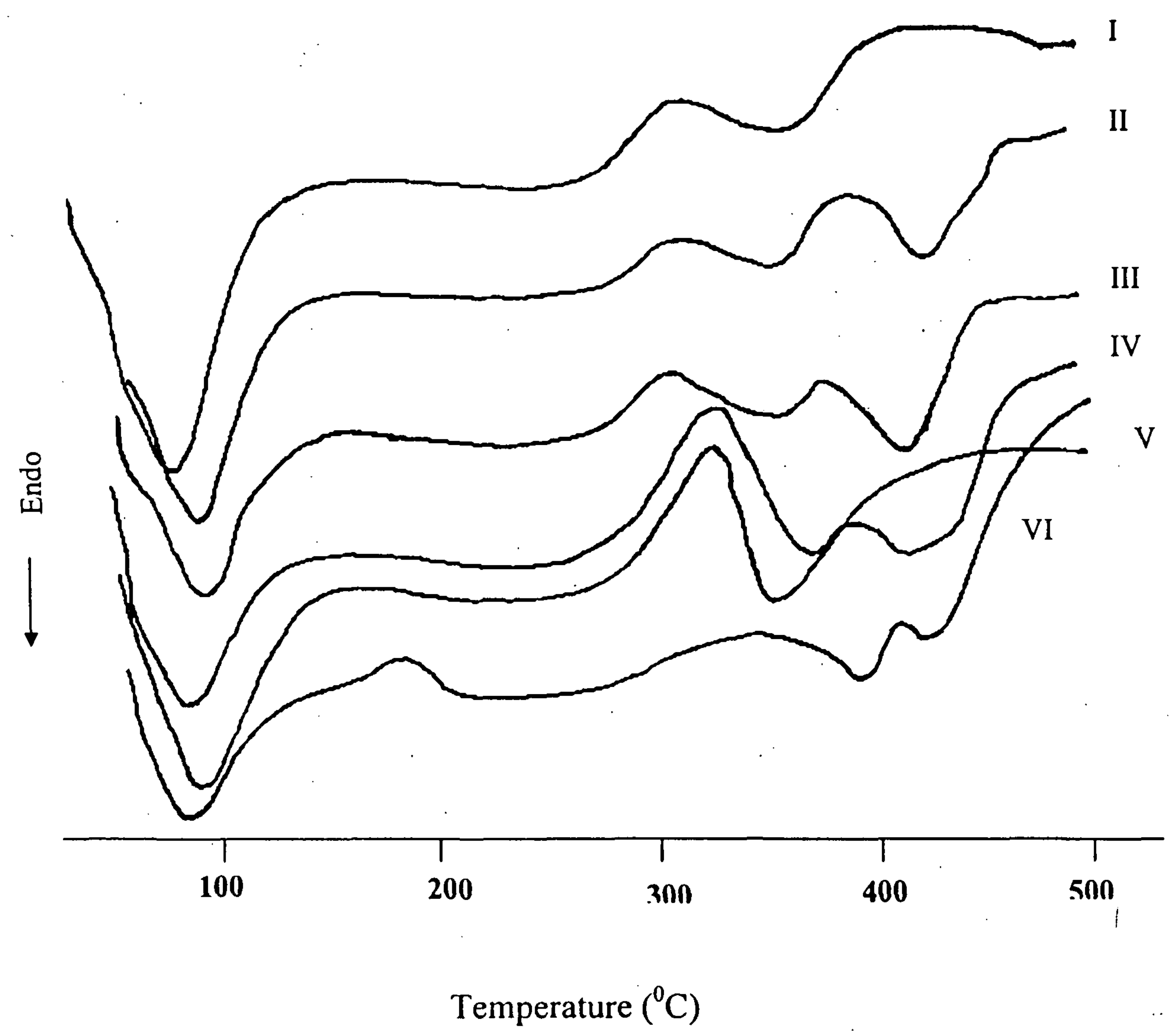


Fig. 4.1.6. DSC thermograms of untreated (I), styrene treated (II), styrene-GMA (5:1) treated (III), styrene-GMA (1:1) treated (IV), and GMA treated (V) and physical mixture of styrene-GMA (5:1) treated (VI) rubber wood samples.

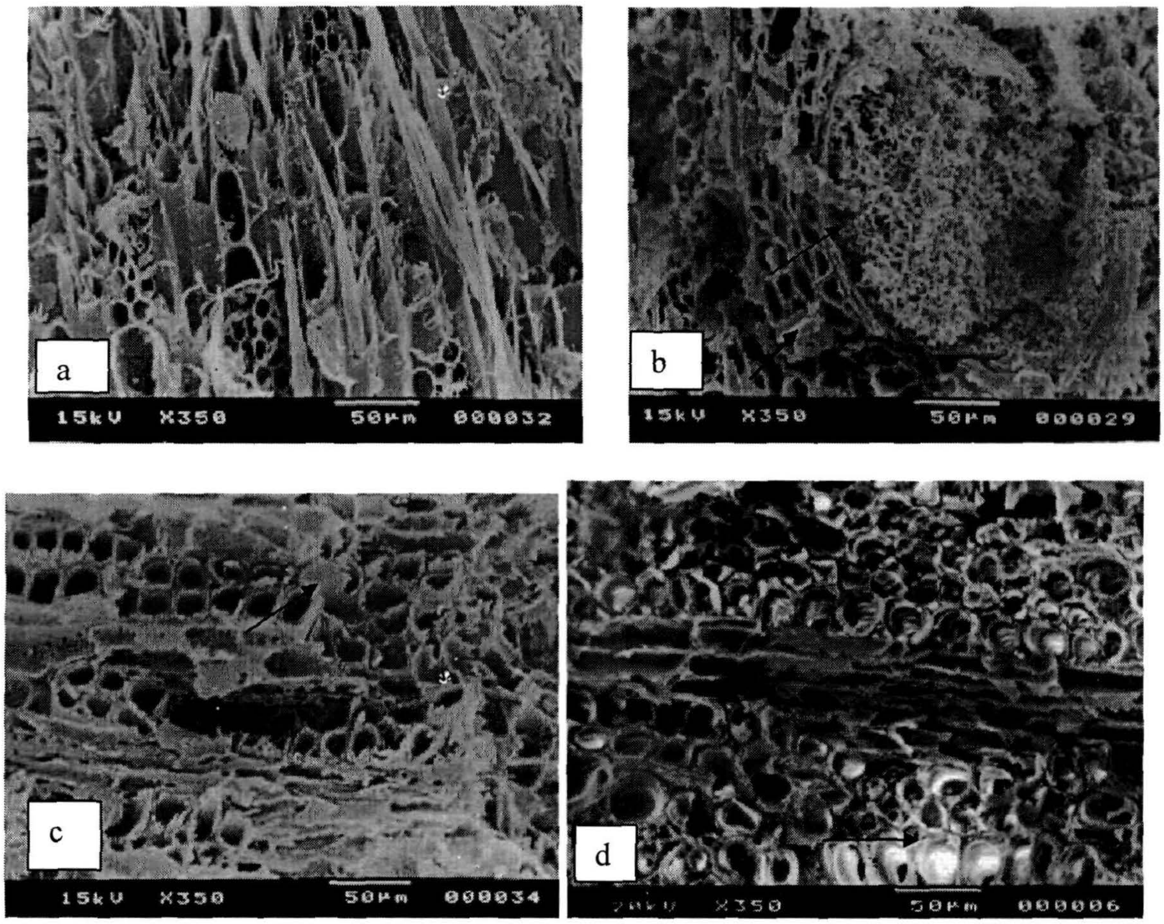
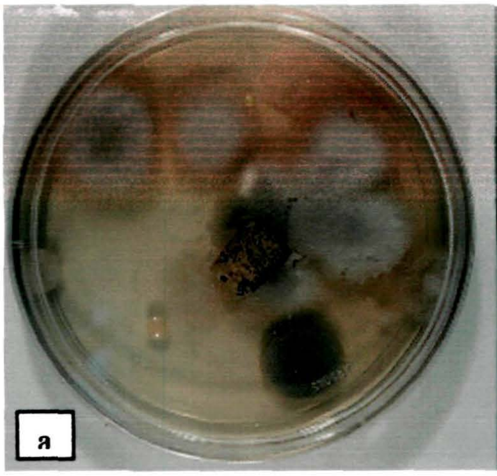


Fig. 4.1.7. SEM photographs of (a) untreated, (b) Styrene treated, (c) styrene-GMA (5:1) treated and (d) Styrene-GMA (1:1) treated rubber wood samples.

4.1.2.13. Biodegradation study

In the biodegradation test fungal colonization of chemically modified and untreated wood samples were found to differ. The surfaces of all reference samples were colonized within one weak of exposure. In comparison, colonization of modified samples took place more slowly. Fig. 4.1.8. shows the photographs of biodegradation test samples for untreated (a), styrene treated (b), styrene-GMA (c-d) and GMA treated samples.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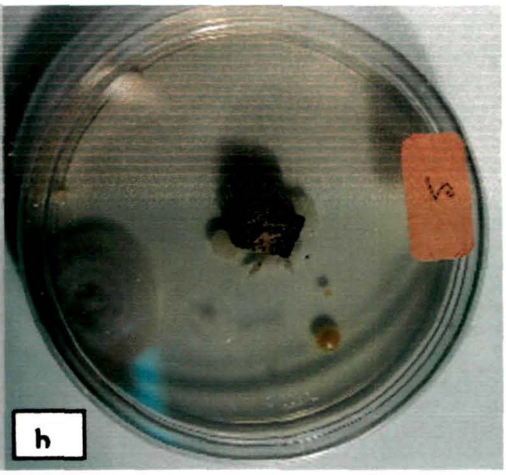
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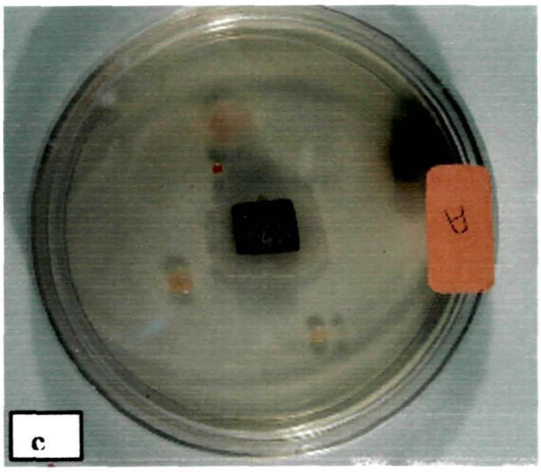
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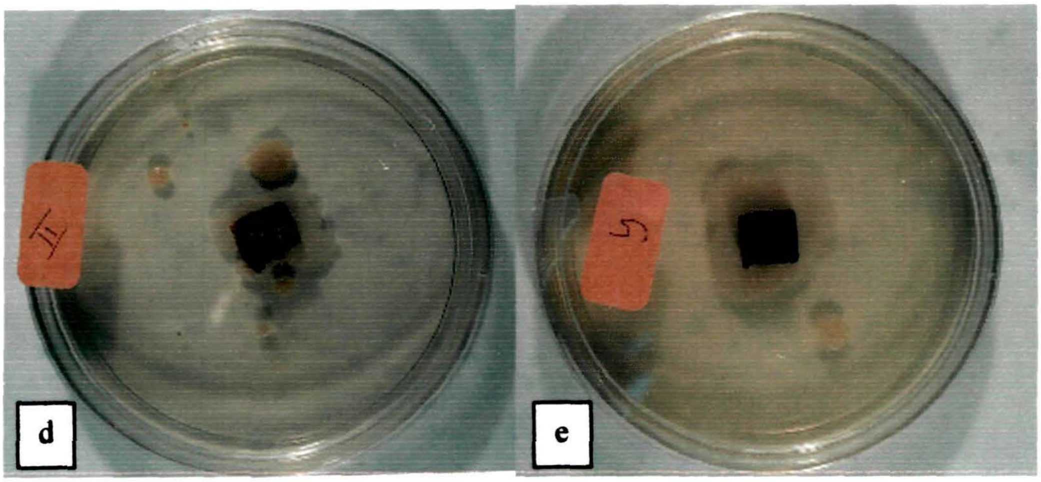


Fig. 4.1.8. Comparison of biodegradation of (a) untreated, (b) styrene treated, (c) styrene-GMA (5:1) treated, (d) styrene-GMA (1:1) treated and (e) GMA treated rubber wood samples.

4.2. Modification of pine wood with impregnation of styrene as the monomer and GMA as the crosslinking monomer using AIBN catalyst

Introduction

Numerous investigations have been performed to improve the various properties of pine wood. Modification by treatment with polymers is widely used by different industries. This part covers the studies on effect of impregnation of monomer and crosslinker on different properties of wood. Treated samples of more or less similar polymer loading were considered for conducting different tests and each result presented in the figure or table was the mean of five samples.

4.2.1. Results

4.2.1.1. Properties of pine wood

The density and void volume of pine wood was determined and given in table 4.2.1. The measurement of each property was done in triplicate and the reported result was the average value.

4.2.1.2. Standardization of Impregnation conditions

In order to optimize the impregnation conditions, a series of experiments were conducted at room temperature by varying level of initiator, time, vacuum and monomer concentration. The best condition which produced maximum improvement in properties was 5” Hg vacuum, 2% AIBN, 1:1 styrene-GMA monomer concentration and 4h of impregnation time.

Table 4.2.1. Properties of pine wood

Properties	values
Density (g/cm^3)	0.43
Void volume	0.71

Table 4.2.2. Effect of variation of initiator (AIBN) concentration on polymer loading (WPG) (%) of pinewood: [AIBN: 0.2-5% (by weight), Styrene: GMA= 100:20, Time: 4h, Temperature: 30± 1° C, Vacuum: 5" Hg]

Initiator Concentration (%)	0.2	0.5	2	5
WPG (%)	18.3	22.1	31.0	25.8
Volume increase After curing (%)	0.1	0.17	1.21	0.6
Water uptake (%)	26.9	20.8	15.5	21.3
Swelling in water (%)	10.5	10.0	7.6	9.9
Hardness	51.3	44.4	52.7	46.3

4.2.1.3. Effect of variation of initiator concentration

Table 4.2.2. shows the results of variation of initiator concentration on polymer loading (WPG) using styrene-GMA system. The maximum polymer loading of 31% was found with 2% AIBN catalyst concentration (by weight), which showed maximum improvement in properties.Water absorption (%) and swelling (%) in water after 24h immersion in distilled water were 15.5 and 7.6 respectively.. Hardness value increased to 52.7% for 2% AIBN concentration compared to 51.3, 44.4 and 46.3 for 0.2, 0.5 and 5% AIBN concentration.

4.2.1.4. Effect of variation of monomer concentration

Pine wood samples showed negligible change in volume on impregnation with styrene. But significant change in volume (%) of wood samples was noticed when GMA was introduced (table 4.2.3.). The higher the percentage of GMA, the higher was the % volume change. At 1:1 styrene: GMA concentration the highest improvements in the properties were obtained. Water uptake capacity decreased to 15.3% over 38.7% for untreated, 17.5% for styrene treated, 17.0% for styrene: GMA (5:1) treated and 16.1% for styrene: GMA (2:1) treated wood samples. Improvement in hardness values (54.5 for styrene: GMA (1:1) treated samples) was also observed with increase in the percentage of GMA.

Table 4.2.3. Effect of variation of monomer concentration on polymer loading WPG (%) and other properties: [Styrene-GMA= 100:0 to 100: 100, AIBN: 2% (by weight), Time: 4h, Temperature: 30±1°C, Vacuum: 5" Hg]

Samples particulars		WPG (%)	Volume (%) increase after curing	Water uptake (%)	Swelling in water (%)	Hardness (Shore D)
Untreated		-	-	38.7	10.0	45.4
Treated with						
Styrene	GMA					
100	0	24.9	0.1	17.5	8.2	50.0
100	20	30.9	1.2	17.0	7.6	51.3
100	50	30.3	7.3	16.1	6.3	53.0
100	100	20.6	11.5	15.3	5.2	54.5

Table 4.2.4. Effect of variation of vacuum on loading and other properties: [Styrene-GMA= 100:50, Vacuum: 1-15"Hg, AIBN: 2% (by weight), Time: 4h, Temperature: 30±1°C]

Vacuum applied (Inches of Hg)	WPG (%)	Volume increase(%) after curing	Water uptake (%)	Swelling in water (%)
1	10.0	0.1	38.5	15.6
5	30.3	7.3	16.2	7.3
10	35.7	2.9	15.6	11.6
15	29.9	0.2	25.4	12.3

Table 4.2.5. Effect of variation of time on loading and other properties: [Styrene: GMA= 100:50, AIBN: 2 %(by weight), Time: 2-20h, Vacuum: 5"Hg, Temperature: 30±1°C]

Time (h)	WPG (%)	Volume increase(%) after curing	Water uptake (%)	Swelling (%) in water	Hardness
2	21.1	5.2	32.1	7.8	47.8
4	30.0	7.3	16.1	6.3	53
6	32.3	6.3	20.2	5.9	46.9
8	35.8	6.1	20.5	3.7	48.0
20	40.3	4.2	16.9	3.9	55.4

4.2.1.5. Effect of variation of vacuum

Vacuum during impregnation was varied from 1" Hg to 15" Hg keeping the others parameters constant. When effect of variation of vacuum (1" – 15"Hg) on impregnation was studied it was found that with increasing vacuum, polymer loading increased first and then it decreased (table 4.2.4.). Maximum improvements in the properties were obtained at 5" Hg with 30.3% polymer loading.

4.2.1.6. Effect of variation of time

The results showing the effect of variation of impregnation time on polymer loading are presented in table 4.2.5. Loading was found to be increased throughout the time period studied (upto 20h). Both water uptake and swelling in water decreased with increase in polymer loading. Overall improvements in properties were obtained when impregnation was done for 4h.

4.2.2. Characterization

4.2.2.1. Water Uptake Test

The water uptake (%) or water absorption (%) was calculated using the relation given in experimental section.

The results of water uptake for treated and untreated samples were shown in fig 4.2.1 and table 4.2.6. In both treated and untreated samples upto the time period studied water absorption increased with the increase in time and untreated samples absorbed more water compared to treated samples. Styrene-GMA (1:1) treated samples showed least water uptake throughout the time period studied. After 168 h, untreated wood absorbed 95.4% water, while on treatment with styrene water absorption decreased to 48.5%. The value decreased to 48.5, 39.9 and 36.5% for styrene-GMA (5:1), styrene-GMA (2:1) and styrene-GMA (1:1) samples. The higher the percentage of GMA, the lower was the water absorption.

4.2.2.2. Water repellent effectiveness

Water repellent effectiveness values of the treated samples in water at room temperature (30^0C) were calculated according to the relation given in experimental section and the results are presented in table 4.2.7. An improvement was observed in WRE values on treatment. Styrene-GMA (1:1) treated samples showed highest value of WRE (61.7%) after 168h, compared to 58.2% for (2:1) styrene-GMA or 49.2% for both (5:1) styrene-GMA and styrene-GMA (1:0) treated samples.

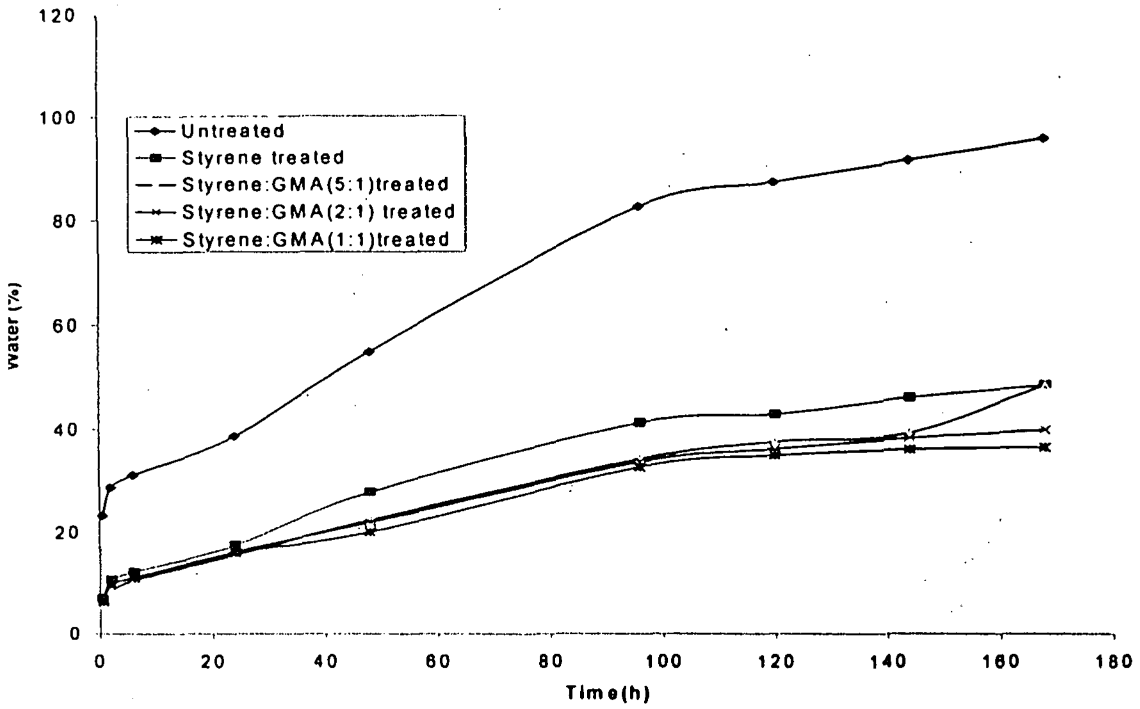


Fig. 4.2.1. Weight gain (%) of WPC in water at 30^0C

Table 4.2.6. Weight gain in water at 30^{0}C

Time (h)	0.5	2	6	24	48	96	120	144	168
Untreated	23.3	28.8	31.2	38.7	55.1	82.5	87.1	91.3	95.4
Treated with									
Styrene-GMA (1:0)	6.9	10.6	12.2	17.5	27.9	41.3	42.9	46.1	48.5
Styrene-GMA (5:1)	5.5	8.4	10.5	15.5	22.5	34.3	37.6	39.3	48.5
Styrene-GMA (2:1)	6.2	9.6	11.1	16.2	22.0	33.7	36.2	38.3	39.9
Styrene-GMA (1:1)	6.3	9.9	11.0	15.9	20.1	32.7	35.0	36.1	36.5

Table 4.2.7. Water repellent effectiveness (WRE)

Time (h)	0.5	2	6	24	48	96	120	144	168
Treated with									
Styrene-GMA (1:0)	70.4	63.2	60.9	54.8	49.4	49.9	50.7	49.5	49.2
Styrene-GMA (5:1)	76.4	70.8	66.3	59.9	59.2	58.4	56.8	56.9	49.2
Styrene-GMA (2:1)	73.4	66.7	64.4	58.1	60.1	59.2	58.4	58.1	58.2
Styrene-GMA (1:1)	72.8	65.6	64.7	58.9	63.5	60.4	59.8	60.5	61.7

4.2.2.3. Water vapour exclusion

The water vapour exclusion (%) of the untreated and treated wood samples was calculated from the relation given in experimental section. The results are summarized in table 4.2.8. and fig. 4.2.2.

In a series of water vapour exclusion study in 90% RH and at 30^0C for various time periods, treated samples absorbed less water vapour than untreated samples. The absorption of water vapour followed the trend: untreated> styrene treated > styrene-GMA (5:1) treated>styrene-GMA (2:1) treated>styrene-GMA (1:1) treated samples. After 168h untreated wood absorbed 12.9% water vapour. Water vapour absorption (%) value of treated samples of styrene-GMA (1:0), styrene-GMA (5:1), styrene-GMA (2:1) and styrene: GMA (1:1) were 10.8, 10.8 10.6 and 9.1 respectively.

Table 4.2.8. Weight gain in moisture (90% RH)

Time (h)	0.5	2	4	8	24	48	96	120	144	168
Untreated	3.0	3.2	4.0	4.9	8.9	10.9	12.5	12.6	12.6	12.9
Treated with										
Styrene-GMA (1:0)	2.6	2.7	3.6	3.9	7.0	9.5	10.5	10.6	10.6	10.8
Styrene-GMA (5:1)	2.6	2.6	3.9	4.2	6.9	9.4	10.0	10.3	10.4	10.8
Styrene-GMA (2:1)	2.5	5.6	3.5	4.1	6.2	9.0	10.4	10.6	10.6	10.6
Styrene-GMA (1:1)	2.5	2.5	3.4	4.1	6.2	8.6	9.3	9.5	9.0	9.1

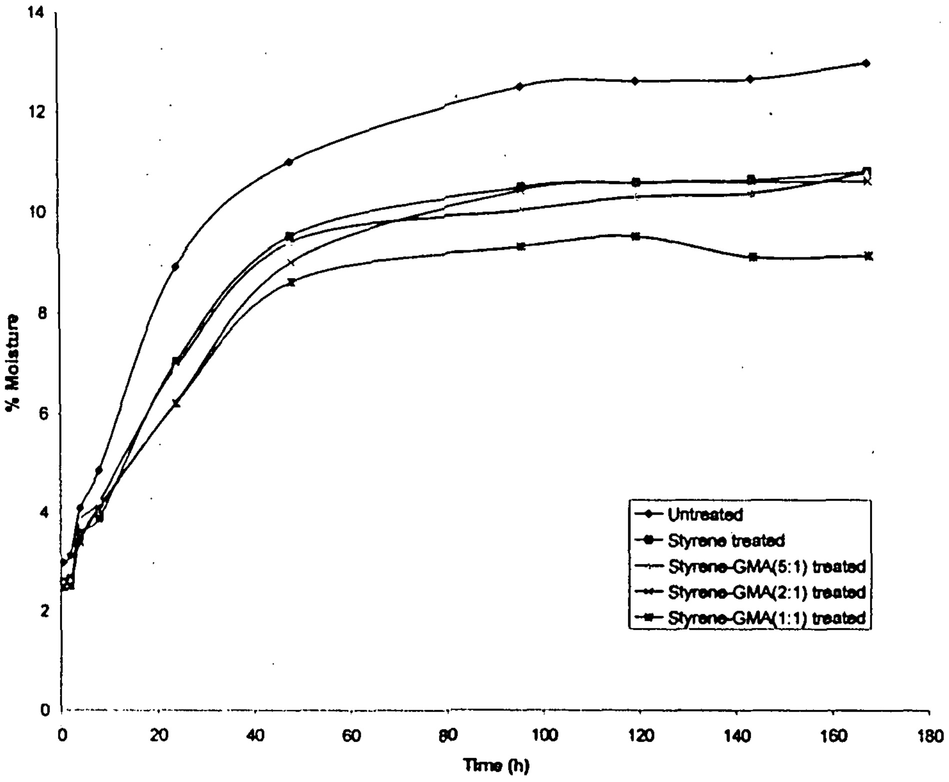


Fig. 4.2.2. Weight gain of WPC in water vapour at 90% RH and 30^0C

4.2.2.4. Dimensional Stability Tests

Dimensional stability test at room temperature (30^0C) was done in terms of volumetric swelling in liquid water and water vapour at 90% RH and calculated according to the formula given in experimental section.

The results of swelling in liquid water are presented in table 4.2.9. and in fig 4.2.3. From the results it was observed that on treatment swelling (%) in water decreased. After 168h of treatment in distilled water, swelling (%) for styrene-GMA (1:1) was found to be 4.6%, while for untreated it was 11.1%.

The results showing the effect of swelling in water vapour at 90% RH and room temperature (30^0C) upto 168 h are presented in table 4.2.10. and fig. 4.2.4. As expected treated samples particularly those where GMA was incorporated showed more reduction in swelling. After 168 h treatment in water vapour untreated samples swelled upto 7.9%, compared to 6.0% for styrene treated samples. Swelling (%) decreased with increase in the concentration of incorporated GMA.

Table 4.2.9. Volumetric swelling in liquid water at room temperature (30^0C)

Time (h)	0.5	2	6	24	48	96	120	144	168
Untreated	6.1	7.6	8.3	10.0	10.2	10.4	10.9	11.1	11.1
<u>Treated with</u>									
Styrene-GMA (1:0)	5.4	5.8	6.5	8.2	8.4	8.6	8.8	8.9	9.1
Styrene-GMA (5:1)	1.5	3.5	4.5	7.6	8.6	9.8	9.9	10.4	10.4
Styrene-GMA (2:1)	2.1	2.7	3.9	6.2	7.4	7.5	7.5	7.5	7.6
Styrene-GMA (1:1)	1.8	2.0	2.5	4.1	4.3	4.5	4.7	4.8	4.6

Table 4.2.10. Volumetric swelling in 90% RH at room temperature (30^0C)

Time (h)	0.5	2	4	8	24	48	96	120	144	168
Untreated	0.5	0.9	1.2	2.0	5.2	5.5	7.7	7.7	7.8	7.9
<u>Treated with</u>										
Styrene-GMA (1:0)	0.3	0.6	0.7	0.8	4.0	4.6	5.3	5.4	5.4	6.0
Styrene-GMA (5:1)	0.4	0.6	0.6	0.7	3.8	4.2	4.6	4.7	4.7	5.0
Styrene-GMA (2:1)	0.3	0.4	0.6	0.7	3.0	3.2	3.8	3.9	4.0	4.5
Styrene-GMA (1:1)	0.3	0.4	0.6	0.7	2.9	3.0	3.2	3.4	3.9	4.0

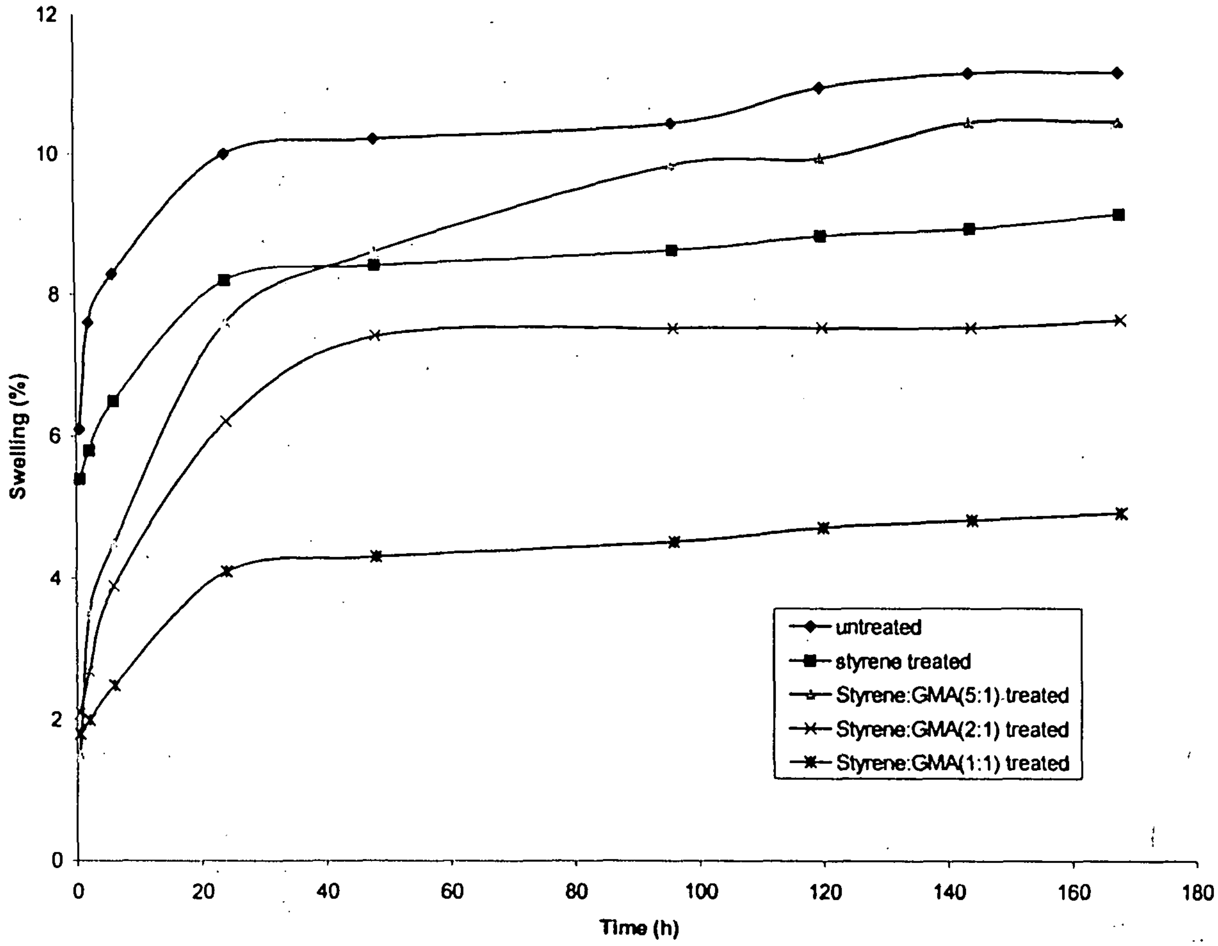


Fig. 4.2.3. Volumetric swelling of WPC in water

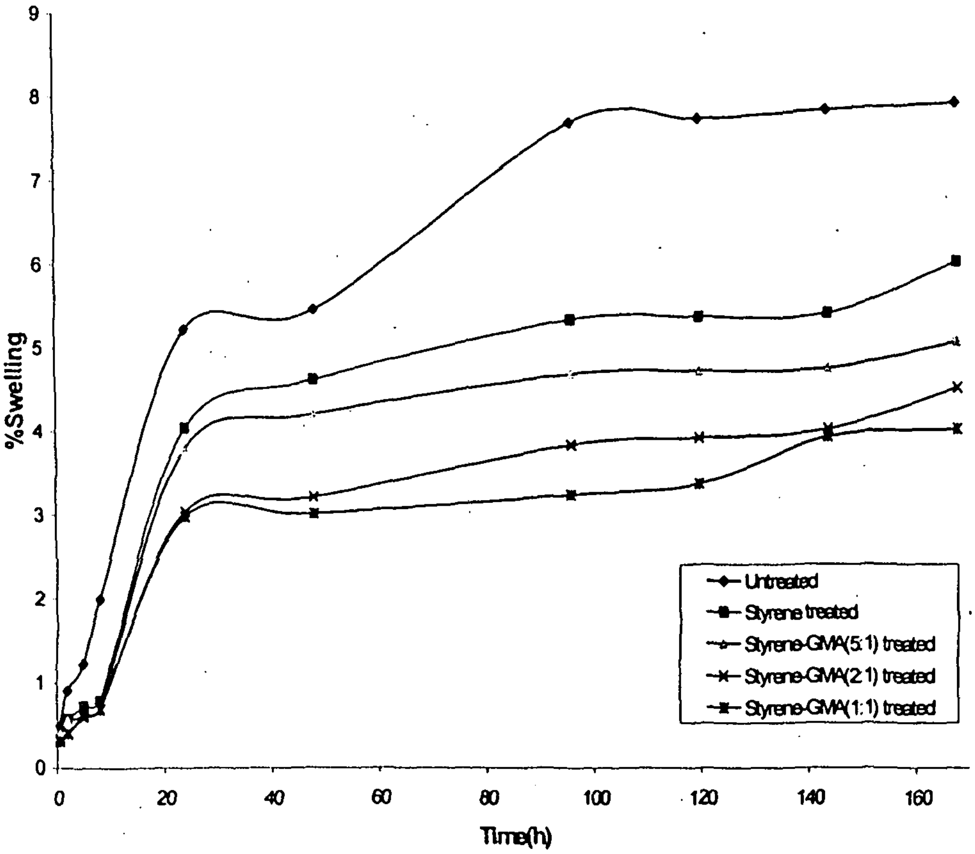


Fig. 4.2.4. Swelling of WPC conditioned at 90% RH and at 30^0C

4.2.2.5. Anti swell efficiency (ASE) study

Table 4.2.11. summarizes the results of anti-swell efficiency (ASE) values for the wood polymer composites. ASE values obtained were based on the changes in longitudinal, tangential and radial dimensions measured by using a vernier caliper and expressed to the nearest 0.01 cm. For styrene: GMA (1:1) treated samples, an ASE value of 55.9 was obtained after 168 h immersion in distilled water compared to 17.4 for styrene treated, 6.3 for styrene-GMA (5:1) treated, 31.5 for styrene-GMA (2:1) treated samples.

4.2.2.6. Hardness study

Hardness values of the untreated and treated wood samples were measured using a Durometer (Shore D) and the values are summarized in table 4.2.12. There was an increase in the hardness values of the wood samples after treatment with either styrene or styrene-GMA. Untreated samples showed a hardness value of 45.4 while on treatment with styrene-GMA (1:1), it increased to 54.5.

Table 4.2.11. Anti-swell efficiencies of the wood polymer composites

Time (h)	0.5	2	6	24	48	96	120	144	168
Treated with									
Styrene-GMA (1:0)	24.1	23.7	22.6	20.1	19.8	18.9	18.4	17.8	17.4
Styrene-GMA (5:1)	75.4	53.9	46.0	24.0	15.7	5.8	9.2	6.3	6.3
Styrene-GMA (2:1)	65.6	54.5	53.2	38.0	27.5	27.9	31.2	32.4	31.5
Styrene-GMA (1:1)	74.5	73.6	70.6	62.6	57.8	57.0	56.7	56.2	55.9

Table 4.2.12. Hardness values of the treated and untreated wood samples

Sample particulars	WPG (%)	Hardness (Shore D)
Untreated	-	45.4
Treated with		
Styrene: GMA (1:0)	24.9	50.0
Styrene: GMA (5:1)	30.9	51.3
Styrene: GMA (2:1)	30.3	53.0
Styrene: GMA (1:1)	20.6	54.5

4.2.2.7. Compressive strength Test

The results of compressive strengths of treated and untreated samples are shown in table 4.2.13. Wood samples on treatment with polymers (either styrene or styrene/GMA) showed an improvement in compression strength when tested in both parallel and perpendicular to fibre direction. Compressive strength was found to 103.5 Kg cm^{-2} for styrene-GMA (1:1) treated samples in perpendicular direction compared to 60.9 Kg cm^{-2}for untreated samples when measured in perpendicular direction. In parallel direction the value of compressive strength was also found highest for styrene-GMA (1:1) treated samples.

4.2.2.8. Bending Strength Test results

MOE and MOR of the untreated and treated samples were measured and calculated according to ASTMD790 method and the relation given in experimental section.

Table 4.2.14. showed the results of the MOE and MOR of the untreated and treated wood samples. The results showed that both MOE and MOR values increased on treatment and was highest for styrene-GMA (1:1) treated samples. MOE value of styrene treated samples was more compared to either 5:1 or 2:1 styrene-GMA treated samples.

Table 4.2.13. Compressive strengths of untreated and polymer treated wood samples in perpendicular and parallel to fibre directions

Sample particulars	WPG (%)	Compressive strength perpendicular to fibre direction (Kg cm-^{2})	Compressive strength parallel to fibre direction (Kg cm-^{2})
Untreated	-	60.9	376.6
Treated with			
Styrene-GMA (1:0)	30.1	74.2	453.8
Styrene-GMA (5:1)	29.3	80.1	467.4
Styrene-GMA (2:1)	28.2	85.7	472.7
Styrene-GMA (1:1)	25.6	103.5	521.1

Table 4.2.14. Modulus of rupture (MOR) and modulus of elasticity (MOE) data for untreated and polymer treated wood samples

Sample particulars	WPG (%)	MOR (MPa)	MOE (MPa)
Untreated	-	102.8	4732.1
Treated with			
Styrene-GMA (1:0)	20.1	131.6	7036.4
Styrene-GMA (5:1)	20.8	134.5	6131.4
Styrene-GMA(2:1)	21.0	121.4	6615.4
Styrene-GMA (1:1)	20.5	158.1	8144.3

4.2.2.9. FT-IR spectroscopy study

The FT-IR spectra of treated and untreated wood samples are presented in fig. 4.2.5.(I-V). From the FT-IR spectra it was found that the peak at 1736 cm^{-1}, which was due to carbonyl stretching vibration, became more pronounced on treatment with styrene-GMA. The position of the peak at 3395.02 cm^{-1} (O-H stretching) for untreated wood remained almost unchanged by the incorporation of styrene, but shifted to higher wave number on incorporation of GMA with styrene. The intensity of C- O stretching vibration (1058.41 cm^{-1}) also increased on treatment.

4.2.2.10. Scanning Electron Microscopy Study

The fine structures of wood and the compatibility between wood and the polymers were investigated by Scanning Electron Microscopy (SEM). The photographs were taken from the fracture surfaces of some selected samples. Fig 4.2.6.(a), (b) and (c) represent SEM photographs of untreated, styrene treated and styrene-GMA (1:1) treated samples respectively. The cells swelled more (arrow marked) due to treatment.

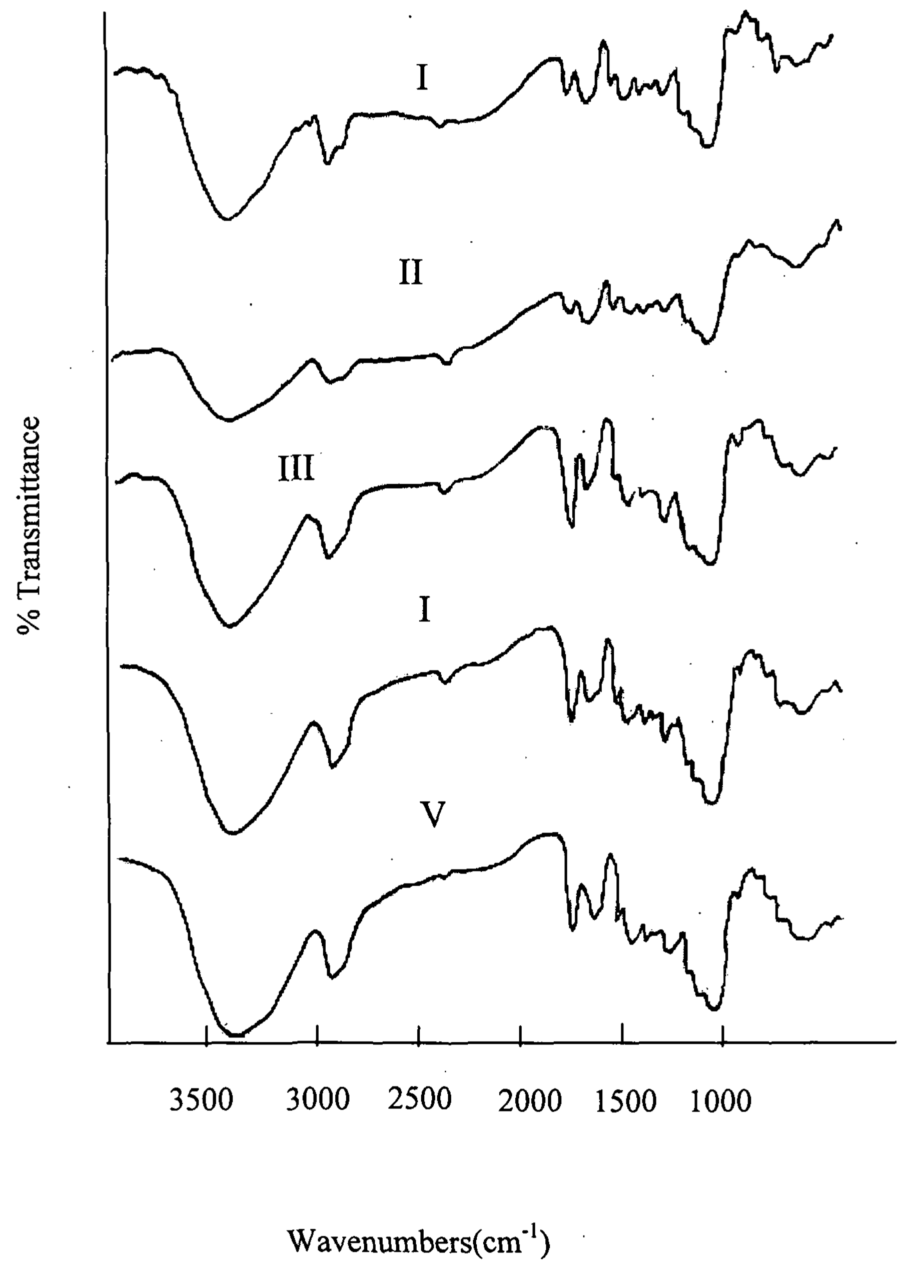


Fig. 4.2.5. FT-IR spectra of (I) styrene treated, (II) untreated, (III) GMA treated, (IV) styrene-GMA (1:1) treated and (V) styrene-GMA (2:1) treated pine wood

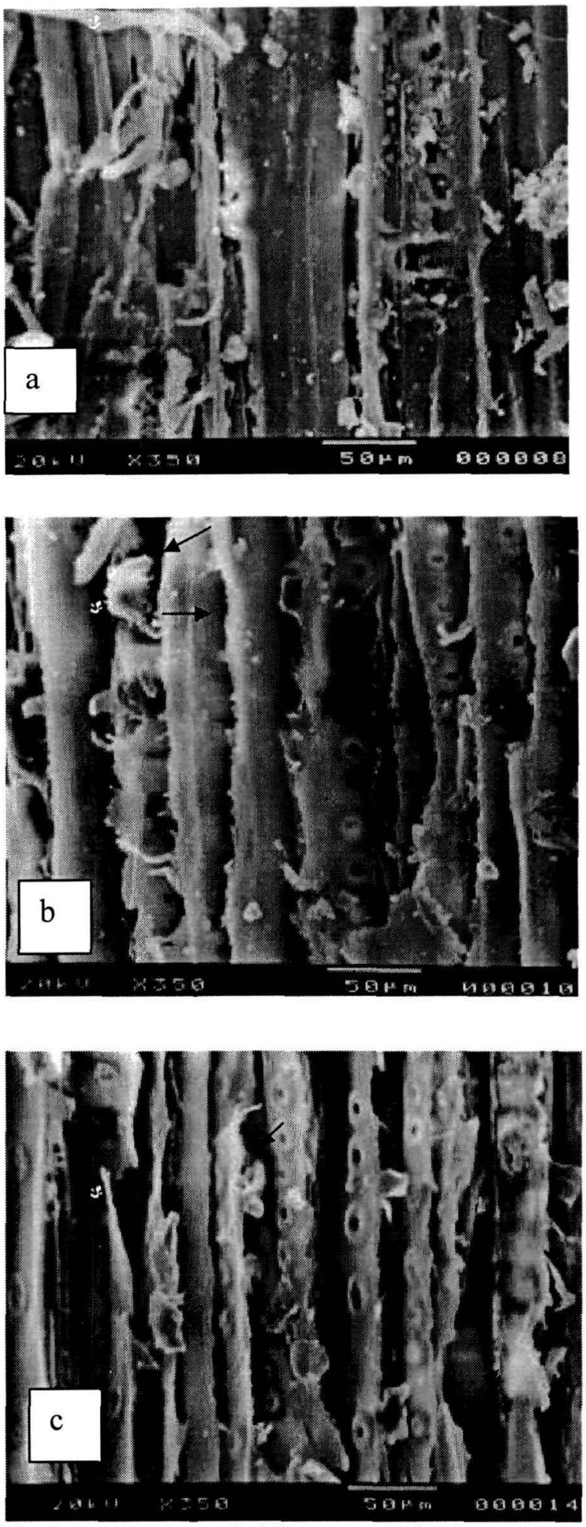


Fig. 4.2.6. SEM photographs of (a) untreated, (b) styrene treated and (c) styrene-GMA (1:1) treated pinewood.

4.2.2.11. Thermal study

Table 4.2.15. shows the initial decomposition temperature (T_i), maximum pyrolysis temperature (T_m) and residual weight (%) (RW) for untreated and polymer treated wood samples. T_i and T_m values for both the stages of pyrolysis in treated samples were higher than untreated samples. RW (%) value was observed higher in the case of untreated wood samples compared to those of treated ones.

Table 4.2.16. shows the temperature of decomposition (%) (T_D) at different weight loss (%) of untreated and treated wood samples. It was observed that $T_D$values of treated samples were higher compared to untreated sample upto 50% decomposition, beyond that the value decreased.

Table 4.2.15. Thermal analytical data for untreated and polymer treated wood samples

Sample particulars	T_i (^{0}C)	Tm_i^a (^{0}C)	Tm_{ii}^b (^{0}C)	RW (%)
Untreated	277	309	347	38.3
Treated with				
Styrene-GMA (1:0)	280	342	410	17.8
Styrene-GMA (5:1)	281	340	396	-
Styrene- GMA (2:1)	283	342	394	-
Styrene-GMA (1:1)	288	347	392	21.45

a : T_m value for the first step b: T_m value for the second step

Table 4.2.16. Temperature of decomposition (T_D) at different weight losses (%) of untreated and treated wood samples

Sample particulars	% Weight losses					
	20	30	40	50	60	70
Untreated	302	324	342	353	440	-
Treated with						
Styrene-GMA (1:0)	300	320	335	350	358	395
Styrene- GMA (5:1)	308	330	345	358	398	-
Styrene- GMA (2:1)	307	329	344	357	382	395
Styrene-GMA (1:1)	307	328	345	356	370	395

4.2.2.7. Differential scanning calorimetric (DSC) study

Fig. 4.2.7. shows the DSC results of untreated and treated wood samples. Untreated wood (curve I) showed a single peak at 380^0C. Physical mixture of styrene-GMA and styrene or styrene-GMA treated wood samples showed one endothermic peak in the range 379-384^0C and another endothermic peak in the range 430-460^0C (curve II-V).

4.2.2.12. Biodegradation study

In order to study the biodegradation resistance, the treated and untreated wood samples were placed in an agar medium for 30 days to access the growth of microorganisms. The treated samples showed either little/or low production of *Bacillus spp.* bacteria while untreated sample showed more production of bacteria.

Fig. 4.2.8. shows the photographs of biodegradation test samples for untreated (a), styrene treated (b) and styrene-GMA treated (c-e) pine wood samples.

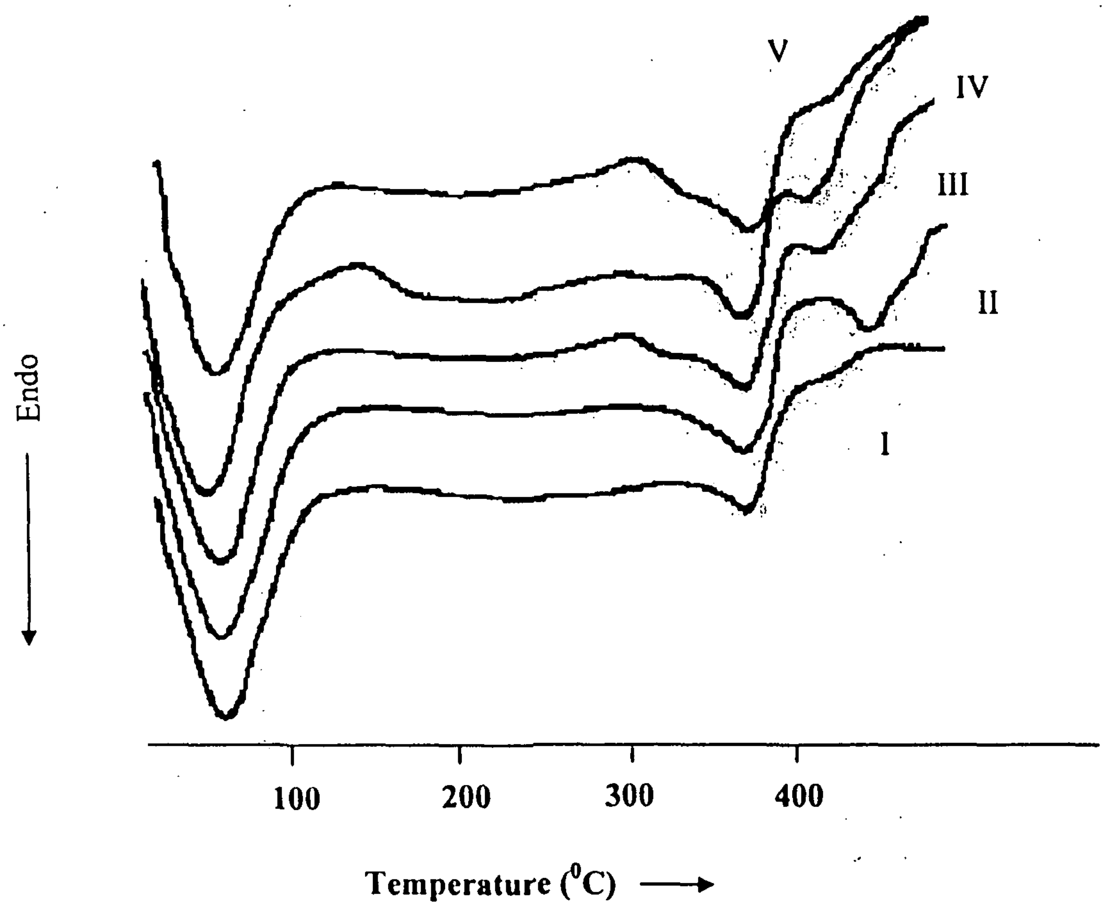
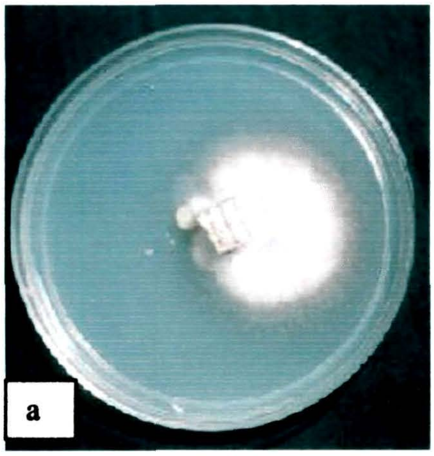


Fig. 4.2.7. DSC thermograms of untreated (I), styrene treated (II), styrene-GMA (5:1) treated (III), physical mixture of styrene-GMA (5:1) treated (IV) and styrene-GMA (1:1) treated (V) pine wood samples.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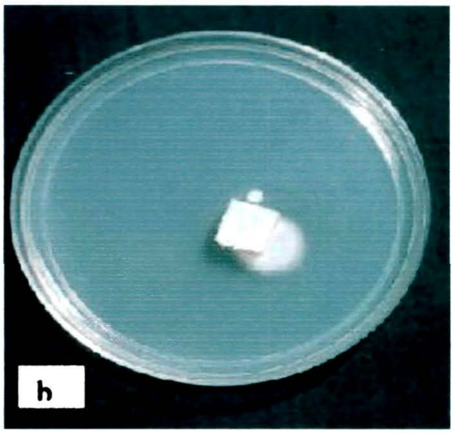
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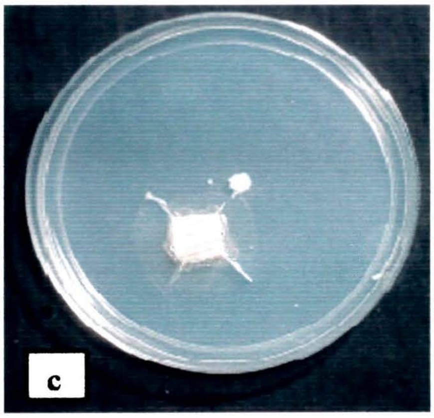
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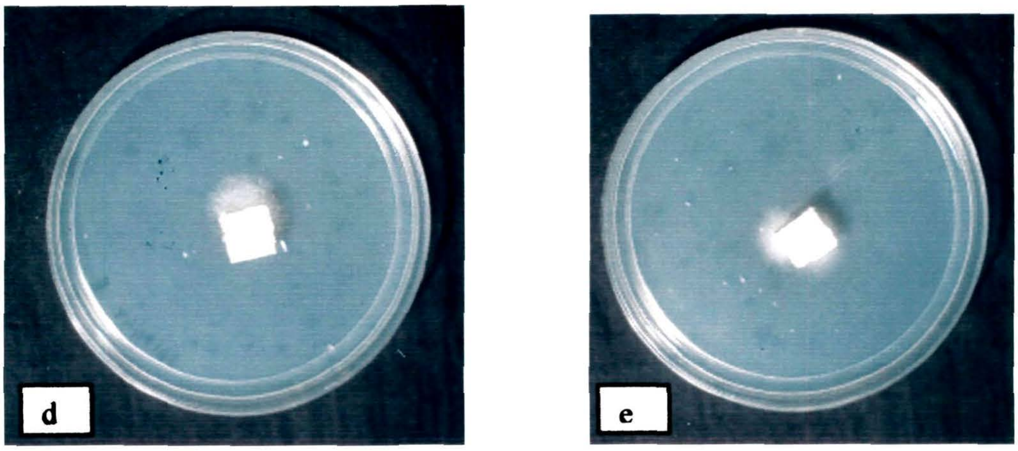

Fig. 4.2.8. Comparison of biodegradation of (a) untreated, (b) styrene treated, (c) styrene-GMA (5:1), (d) styrene-GMA (2:1) and (e) styrene-GMA (1:1) treated pine wood samples.

4.3. Discussions

Standardization of the impregnation conditions

Attempts were made by many researchers to optimize the impregnation conditions in various woods by varying different parameters [1, 2]. The main aim behind this was to get the optimum level of weight percent gain (WPG) which would produce maximum overall improvement in properties. The best conditions of impregnation for both rubber and pine wood were optimized.

Effect of variation of initiator concentration

In both rubber and pine wood, WPG showed an increasing trend initially followed by a decreasing trend later with the increase in initiator concentration. Similar trend was reported in the literature, while impregnating methyl methacrylate into bass wood samples using AIBN [3, 4]. At higher initiator concentration, the heat from the exothermic polymerization reaction increased the chance of eliminating monomer mixture from the wood cell. This monomer mixture may polymerize at the intersurface of wood leading to decrease in WPG (%). The probability of bleeding out of monomer mixture was less at lower initiator concentration. The above explanation could be the probable cause for observing trend.

Effect of variation of monomer concentration

A noticeable change in volume and WPG were observed in rubber and pine wood samples, when GMA was incorporated along with styrene. Again on impregnation with styrene-GMA, samples of rubber and pine wood swelled less in water compared to styrene treated or untreated samples. These improvements in properties might be attributed to the interaction of GMA with wood and styrene through its epoxy group and terminal double bond. GMA could penetrate into the cell wall more easily compared to styrene due to its advantageous molecular structure [5]. Styrene on the other hand instead of reacting fully with wood could able to bulk the cell wall.

Effect of variation of vacuum

The trend of WPG shown with variation of vacuum could be explained as follows: the evacuation of capillaries might take place efficiently at a certain applied vacuum. The increasing trend could be due to the more penetration of monomer mixture into the void spaces of wood. The decreasing trend might be probably due to the decrease in evacuation efficiency at higher application of vacuum. Lower loading at higher vacuum was reported in literature during impregnation of glycidyl methacrylate and diallyl phthalate into rubber wood [5].

Effect of variation of time of impregnation

WPG or polymer loading was found to increase with the increase in impregnation time for both rubber and pine wood samples. With increasing time, the capillaries and void spaces were getting more time to become filled up with monomer mixture, which in turn would lead to increase the polymer loading.

Water uptake capacity

In case of treated rubber wood and pinewood, water absorption decreased due to confinement of polymer into wood. The results obtained in water uptake test could be explained as follows: with the increase in time the capillaries and void spaces were getting more time to become filled up with water which in turn leads to increase the water uptake. In treated samples the decrease in spaces, available to hold water due to filling up of the same by polymer, was responsible for lowering in water absorption. The water absorption decreased further due to the crosslinking formed by the interaction of glycidyl group and double bond of GMA with hydroxyl group of wood and styrene respectively.

Water repellent effectiveness (WRE)

In both the wood polymer composites, highest and lowest WRE value was obtained with styrene-GMA (1:1) monomer concentration and styrene respectively. These results indicated that styrene only bulked the cell wall and did not interact fully with wood. The interaction of GMA with wood and styrene through its epoxy group and terminal double bond might be responsible for increase in WRE values. There was good agreement between these results and those in the literature for wood polymer composites [6, 7].

Water vapour exclusion

The reason for the trend observed in the absorption of water vapour by both the untreated and treated rubber and pine wood samples could be explained as earlier.

Dimensional stability and antiswell Efficiency (ASE)

Styrene-GMA (1:1) treated samples of both rubber and pine wood showed least swelling compared to either untreated or other treated samples. The reduction in the rate of swelling could be explained with the help of combined effect of crosslinking by GMA and filling of the void space by polymers. Similarly ASE values were observed more in both the cases at the same styrene-GMA ratio. An increase in the ASE values for wood-polymer composites was reported by [8]. Improvement in dimensional stability of WPC was reported in the literature [5, 9, 10].

Hardness

In both rubber wood and pine wood composites hardness increased to maximum value for styrene-GMA (1:1) treatment. The reason was similar to that of explanation given earlier. The results obtained are supported by some previous research on wood polymer composites [11, 12, 13].

Bending Strength Test

MOE and MOR

Styrene-GMA (1:1) treated samples showed highest MOE values compared to either styrene treated or untreated ones. MOR value was also significantly improved for both the wood polymer composites. This might be due to the fact that GMA could penetrate into the cell wall of the wood easily and interacted in a better way with styrene and wood. The increase in MOE (45-60%) and MOR value of rubber wood on treatment with MMA and DAP was observed and reported by Rozman et al., [12].

Compressive Strength

Both rubber and pine wood samples on treatment with polymers (either styrene or styrene/GMA) showed an improvement in compressive strength when tested in both parallel and perpendicular to fibre direction. In all the cases, higher values were observed in parallel directions compared to perpendicular direction. Similar type of observation was reported by Solpan and Guven [13]. Untreated wood sample showed less compression due to buckling of relatively thin cell wall [5]. In treated wood, polymer in the cell lumen might help to restrain the cell wall from buckling under compression. The addition of polymer placed a coating on the cell walls, which thickened and thus greatly increased their lateral stability [5]. This restraining effect might further increase due to interaction of GMA with hydroxyl group of wood and double bond of styrene through its epoxy linkage and terminal double bond.

FT-IR spectroscopy study

The FT-IR spectra of the treated wood samples showed the required bands for the chemicals used in the modification [2, 14]. FT-IR spectroscopy of wood polymer composites of geronggang, a light tropical hardwood, prepared by impregnation with methyl methacrylate (MMA), MMA-co-acrylonitrile (1:1MAN) and styrene-co-acrylonitrile (3:2 STAN) were studied and reported by Yap et al., [15]. In both rubber and pine wood treated samples, the shifting or increase in intensity of the bands for OH stretching, carbonyl stretching and C-O stretching indicated the interaction between wood, styrene and GMA.

Thermal Study

Thermo gravimetric analysis (TGA)

The weight loss prior to 100^{0}C was attributed to the evaporation of moisture. It was reported in literature [16,17] that pyrolysis took place between 150 and 200^{0}C, with the hemicellulose starting to decompose at about 200^{0}C, followed by lignin at about 220^{0}C, and subsequently by cellulose at 250^{0}C. At temperature higher than 250^{0}C, rapid weight loss was observed due to the volatilization of the wood components. Pyrolysis could be considered to be complete at around 360^{0}C. The next phase of weight loss around 400^{0}C could be attributed to the oxidative combustion of the non-volatile pyrolysis products. Complete decomposition was achieved at around 480^{0}C [16,17]

The increasing trend in T_D values might be due to the decreasing chance of elimination of small molecules like CO and CO_2 etc. with the formation of crosslinking, verified experimentally by swelling, which act as an infusible support and provided thermal resistance to the wood fibres. The decreasing trend might be due to the earlier decomposition of polystyrene chain at higher temperature compared to wood fibres. Again a decreasing trend in T_D values was observed in the treated samples when GMA was added. The higher the percentage of GMA, the lower was the T_D value. The higher decomposition rate of GMA polymer at higher temperature might be responsible for the lower stability of wood treated with styrene-GMA combination.

Differential Scanning Calorimetric (DSC) study

DSC results for both the cases of rubber and pine wood indicated that some chemical interaction might occured between wood, polystyrene and polyGMA. These results also supported a low compatibility in thermal properties in relation to wood and styrene polymer.

Scanning electron microscopy (SEM) Study

The interaction between wood and the polymers was investigated with the help of scanning electron microscopy by Solpan and Guven [13]. They used allyl alcohol, acrylonitrile and methyl methacrylate to impregnate beech and spruce wood and observed that almost all the wood cell lumens were filled by impregnation. The SEM micrographs indicated the existence of a powerful interaction between wood and the polymers.

In the present experiments also, the adherence/ reactions of chemicals were well evidenced from the SEM photographs. The white patches that were seen in the micrographs were nothing but the chemicals adhered/absorbed to the cell walls of the wood substrate. The photographs also showed interaction between wood and polymers. These photographs indicated the presence of polymers in the cell lumen and in cell wall.

Biodegradation test

From analysis of the samples of the untreated wood samples, much production of *Bacillus spp.* bacteria and fungal colonization was observed but no or little production of these were seen on polymer treated wood samples.

The lower biodegradation of the both the rubber and pine wood, treated samples might have been due to the decrease in the water uptake capacity of the treated wood. Similar types of observations were also reported in literature [13, 18].

4.4. Modification of rubber wood with impregnation of styrene as the monomer and diethyl allyl phosphate (DEAP) as the comonomer to improve the thermal stability of WPC

Introduction

Flame retardancy are generally imparted to woods by impregnating phosphorous or chlorine containing polymers, or copolymerization products of these with more flammable polymers like polymethylmethacrylate, acrylonitrile and polystyrene into wood.

In this part of work, attempt was made to impregnate rubber wood with styrene as the impregnating monomer and Diethyl allyl phosphate (DEAP) as the flame retardant monomer. For this, DEAP was synthesized, characterized and then impregnated into wood.

Preparation and characterization of diethyl allyl phosphate monomer

Diethyl allyl phosphate (DEAP) was synthesized and characterized according to the procedure described by Sundarrajan et al., [19].

The method of synthesis was given in experimental section.

The synthesized DEAP was characterized by FT-IR and ^{1}H NMR spectroscopy.

4.4.1. Results and discussion

4.4.1.1 Standardization of impregnation conditions

The optimum condition for impregnation was kept partly similar to those of the conditions used for impregnating styrene/GMA into rubber wood. DEAP as such was not compatible with styrene. The optimum ratio (V/V) of styrene and THF (a solvent for both styrene and DEAP) to form a miscible mixture with DEAP was 4:1. The final optimized impregnating condition was

Impregnating conditions

Vacuum	5 inch Hg
Time of impregnation:	4h
AIBN (by weight)	5%
Styrene:	88ml
Tetrahydrofuran (THF)	22ml
DEAP	0.5-5.0ml

4.4.2. Characterization

4.4.2.1. Effect of variation of DEAP concentration of DEAP concentration on WPG (%)

Effect of variation of DEAP concentration of DEAP concentration on WPG (%) and other other properties is shown in table 4.4.1 other properties. Weight gain in water and other properties were calculated according to the relation given in experimental section. Polymer loading (WPG %) was found to increase with the increase in DEAP concentration. With the increase in the concentration of DEAP, an increase in the volume (%) was observed. Both water uptake (%) and swelling in water decreased first and then leveled off. Hardness showed a rising trend initially followed by a decreasing trend latter. Improvement in hardness for MMA and silane treated radiata pine (softwood) and black butt (hardwood) was reported in the literature [20].

The improvement in properties might be due to the deposition of polymer into the void spaces and capillaries of wood along with crosslinking by DEAP with wood and styrene through its alkoxy linkage and double bond.

Table 4.4.1. Effect of variation of DEAP concentration on polymer loading (WPG %) and other properties [Styrene-THF (v/v) = 88:22; AIBN = 0.5% (by weight); Time = 4h; vacuum = 5" Hg; Temperature= 30 ±1^{0}C]

DEAP (ml)	WPG (%)	Volume increase (%)	Weight gain in water (%)	Swelling in water (%)	Hardness (Shore D)
0.5	8.1	5.1	64.9	7.1	54.5
1.0	8.4	5.6	60.0	7.3	57.6
1.5	9.0	7.1	43.8	3.4	62.5
3.0	10.8	10.4	44.7	4.2	58.1
5.0	12.9	10.3	44.9	4.4	57.8

4.4.2.2. Comparison of styrene-DEAP treated WPC with styrene treated WPC

Table 4.4.2 represents the results for comparison of different properties of WPC with and without DEAP (1.5ml) and untreated wood. From the results it was observed that on treatment properties of wood improved. The improvement was more on introduction of DEAP, which may be attributed to the improved adhesion caused by the crosslinking effect of DEAP with that of wood and styrene. Similar types of results were reported in literature for silane coupling agents [20]. Improved dimensional stability and hardness of WPC over wood was due to deposition of polymer into the void spaces of wood which prevented the cell walls from shrinking in response to water absorption. The DEAP treatment minimized the gaps between polymer strands and the cell wall of the wood, resulting in further reduction in water absorption.

4.4.2.3. Bending Test

MOE and MOR values of DEAP-styrene-THF treated WPC was evaluated using the relation given in experimental section and compared with untreated or styrene-THF treated WPC. From table 4.4.3 it was observed that MOE value increased on incorporation of DEAP, while MOR values decreased. The increment in MOE was due to increased interaction of DEAP with styrene and wood

Table 4.4.2. Comparison of properties of WPC with or without DEAP

Samples	WPG (%)	Volume (%) increase after impregnation	Water absorption (%) after 24h	Swelling in water (%) after 24h	Hardness (Shore D)
Untreated	-	-	104.4	3.9	46.6
Treated with					
Styrene-THF (88:22)	11.0	negligible	42.8	5.6	58.0
DEAP-styrene-THF (88:22:1.5)	9.0	7.1	43.8	3.4	62.5

Table 4.4.3. MOE and MOR for Styrene-DEAP rubber wood composites

Samples	MOE (MPa)	MOR (MPa)
Untreated	3680.5	53.5
Treated with		
Styrene-THF	4589.0	61.2
Styrene-THF-DEAP (1.5ml)	4790.8	50.5

4.4.2.4. FT-IR study

a) FT-IR spectrum of DEAP

The FT-IR spectrum of DEAP is presented in fig 4.4.1. The peak observed at ~1033.42 cm^{-1} was due to P-O-C (aliph) stretching vibration. The peak at 1166cm^{-1} , 1690.02 cm-1 and 2987.46 cm^{-1} were is due to the P=O (aliph), C=C stretching and aliphatic C-C *stretching vibration* [27].

b) FT-IR spectra of polymer impregnated wood

The FT-IR spectra of styrene-DEAP treated and DEAP treated rubber wood is presented in fig 4.4.2. The spectrum of untreated wood is shown in figure 4.1.5 (I). The peak at 3395.02 cm^{-1} of untreated wood shifted in the region 3422-3427 cm^{-1} when either DEAP or styrene-DEAP was incorporated into wood. The peak observed in the spectrum of untreated wood at 1058.41 cm^{-1} [fig 4.1.5 (I)] was due to C-O stretching vibration. The peak appeared in DEAP spectrum at 1033.42 cm^{-1} (fig 4.4.1) was due to P-O-C aliphatic stretching vibration. The peak at 1058.41 cm^{-1} of untreated wood was found to shift towards P-O-C aliphatic stretching vibration when wood was treated with DEAP. The peak appeared at 3000 cm^{-1} in the wood-styrene-DEAP treated sample was due to aromatic C-H stretching vibration. These results confirmed that interaction improved between styrene and wood due to incorporation of DEAP.

4.4.2.5. NMR study

The ^{1}H NMR spectrum of DEAP in $CDCl_3$ is presented in fig 4.4.3. Among the vinylic protons, the CH proton showed a multiplet between δ 5.7 and 6.1 ppm while the CH_2 protons showed a signal in the range δ 5.1-5.5 ppm. The O-CH_2 resonance of the ethoxy groups was centered in the region δ 4.0-4.7 ppm and the CH_3 group appears at δ 1.2-1.5 ppm.

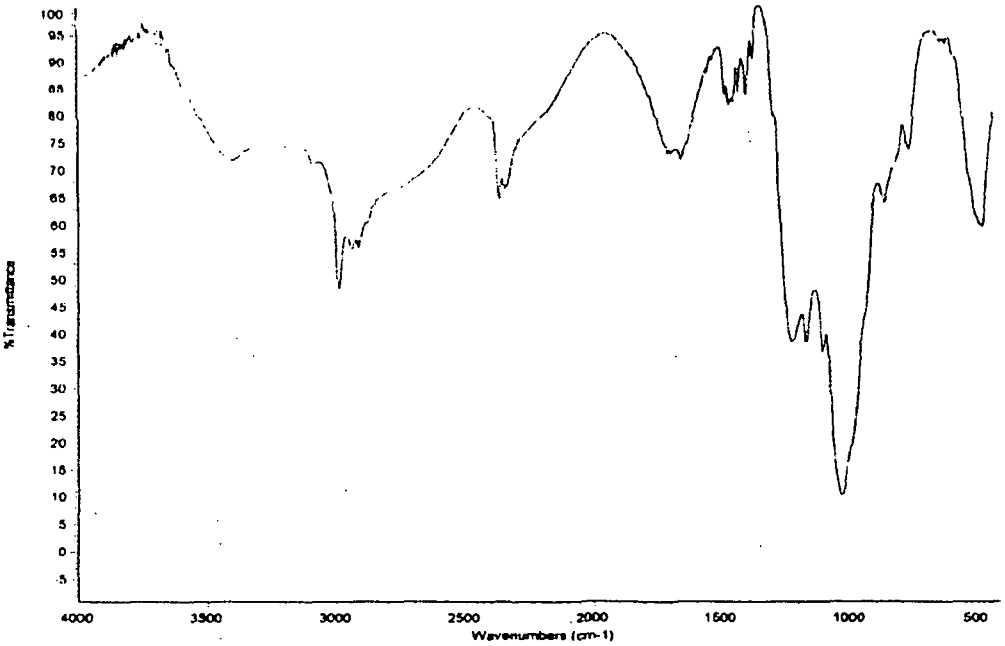

Fig. 4.4.1. FT-IR spectrum of DEAP

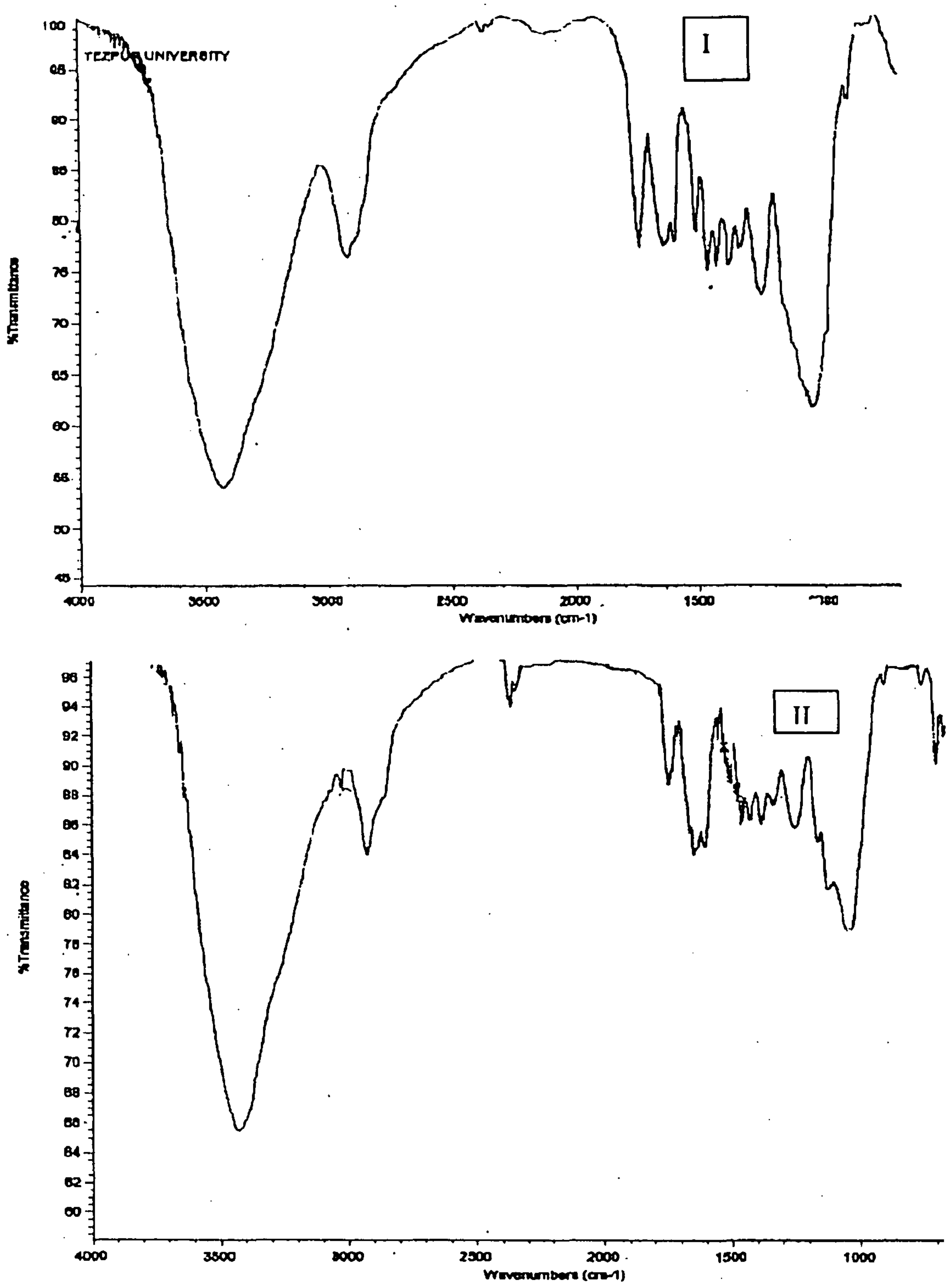

Fig. 4.4.2. FT-IR spectra of DEAP-THF treated (I) and Styrene-DEAP-THF treated (II) wood samples

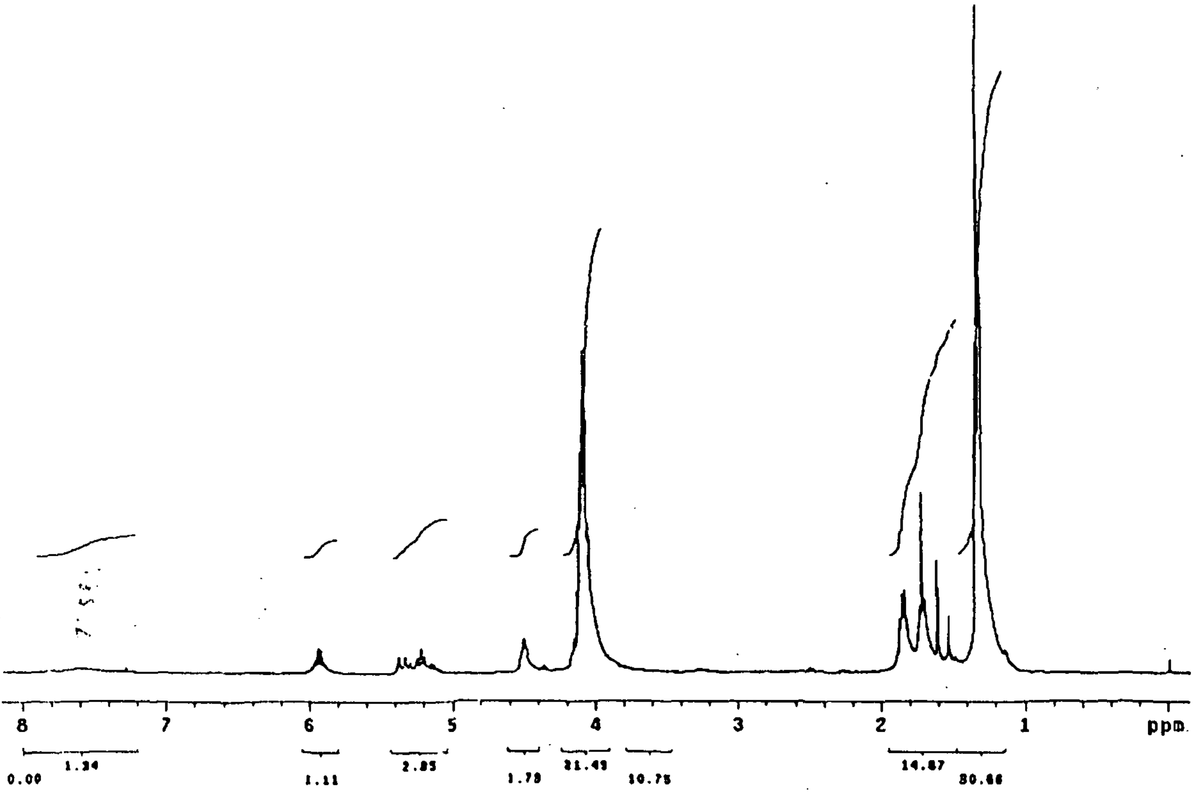

Fig. 4.4.3. ^{1}H NMR spectrum of DEAP

4.4.2.6. Thermogravimetric analysis

The TG and DTG curves of the rubber wood-polymer composites are presented in fig 4.4.4-4.4.8. The results are shown in table 4.4.4 and table 4.4.5. Three particular aspects of these curves were examined: (1) the initial temperature of decomposition at 5% weight loss; (2) the temperatures of the first and second exothermic peak and (3) the char yield. The effectiveness of a flame retardant was often measured in terms of its ability to lower the decomposition temperature of the treated wood specimen. It was reported that if the onset of thermal decomposition took place at lower temperature, then a lower percent of flammable volatile products would be formed, leading ultimately to a high char yield [21]. This seems to be the mode of operation of inorganic salts [22].

Table 4.4.4 shows the values of initial temperature of decomposition, temperatures of the first and second exothermic peaks and the char yield. Table 4.4.5 represents temperatures of decompositions at different weight loss percentages. The initial temperature of decomposition, T_i of untreated and treated wood samples in this work was chosen on the criterion of 5% weight loss. It was observed that on incorporation of DEAP with styrene T_i value decreased. The higher the percentage of DEAP, lower was the T_i value.

Char yield (%) was also increased with the increase in the concentration of DEAP. Char yield was calculated, at two temperatures namely 450^0C and 600^0C. Styrene treated wood produced char yield similar to that of untreated wood at both the temperatures. Char value increased with the incorporation of DEAP. The highest char yield of 34% (at 450^0C) and 27% (at 600^0C) was obtained with DEAP concentration of 3.0ml.

The temperature of the first endothermic peak increased due to treatment with either styrene or styrene-DEAP mixture. The position of second exothermic peak shifted to higher temperature (425^0C) in case of styrene treated sample. The second peak appeared in shoulder form for styrene-DEAP system as revealed by the DTG curves (fig 4.4.6- 4.3.8).

Based on these observations, it was concluded that DEAP could be used as a flame retardant monomer because of its ability to lower the temperature of initial decomposition temperature as well as to maintain a high char yield. PDEAP could to be used as a potent fire retardant additive when used either with polystyrene or methyl methacrylate [19]. It was reported in literature that polyphosphate polymers generally produce the char through the formation of phosphoric acid [23]. Phosphoric acid alters the pyrolytic decomposition reactions of the wood components, resulting in a higher carbonaceous char yield [21, 24]. Similar types of results were also reported by Chan et al., [25].

Table 4.4.4. Thermal Analytical data for untreated and polymer treated wood samples

Sample particulars	Ti (^{0}C) at 5% weight loss	Tm$_i$^{a} (^{0}C)	Tm$_{ii}$^{b} (^{0}C)	RW (%)	
				450 (^{0}C)	600 (^{0}C)
Untreated	90	309	360	22	6
Treated with					
Styrene-THF	90	360	425	22	7
Styrene-DEAP (0.5)	70	349.2	-	25	10
Styrene-DEAP (1.5)	70	350	-	28	12
Styrene-DEAP (3.0)	65	352.4	-	34	27

a : T_m value for the first step b: T_m value for the second step

Table 4.4.5. Temperature of decomposition (T_D) at different weight losses (%) of untreated and treated wood samples

Sample	Temperature of decomposition (T_D) in ^{0}C at different weight loss (%)								
particulars	10	20	30	40	50	60	70	80	90
Untreated	255	302	318	338	357	370	397	475	550
<u>Treated with</u>									
Styrene-THF	260	305	320	340	352	368	410	465	560
Styrene-DEAP (0.5)	145	300	320	340	360	370	428	520	645
Styrene-DEAP (1.5)	250	294	320	342	355	370	425	530	645
Styrene-DEAP (3.0)	250	310	320	340	355	385	530	680	-

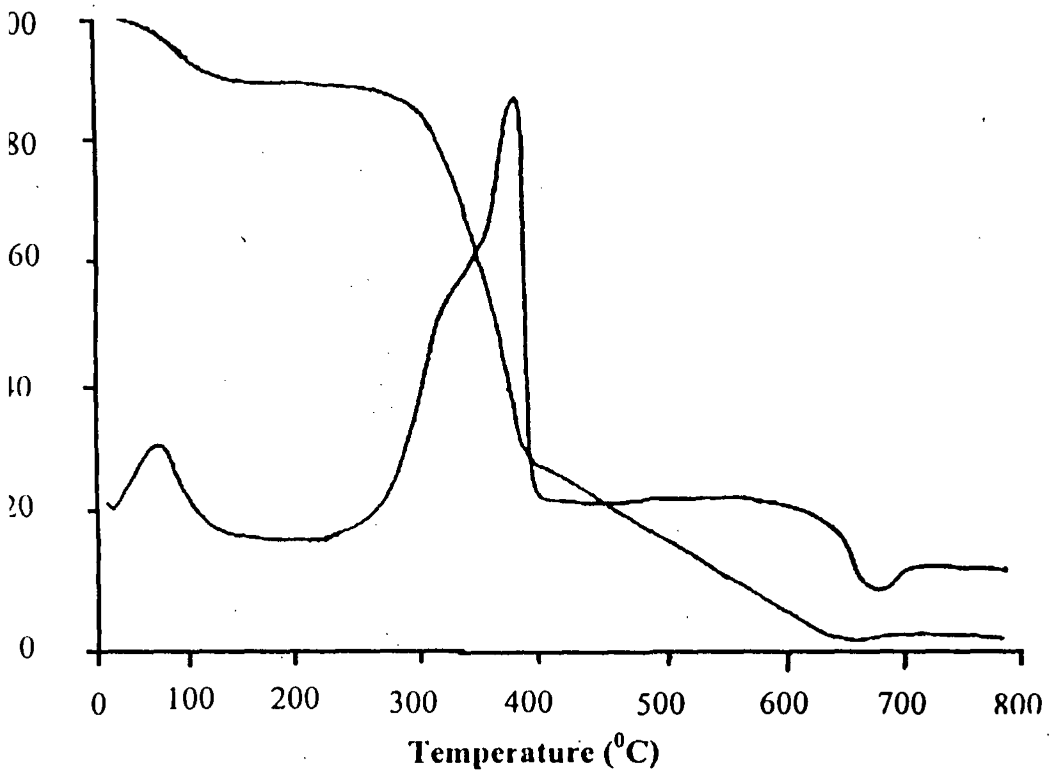

Fig. 4.4.4. TG and DTG curve for untreated wood sample

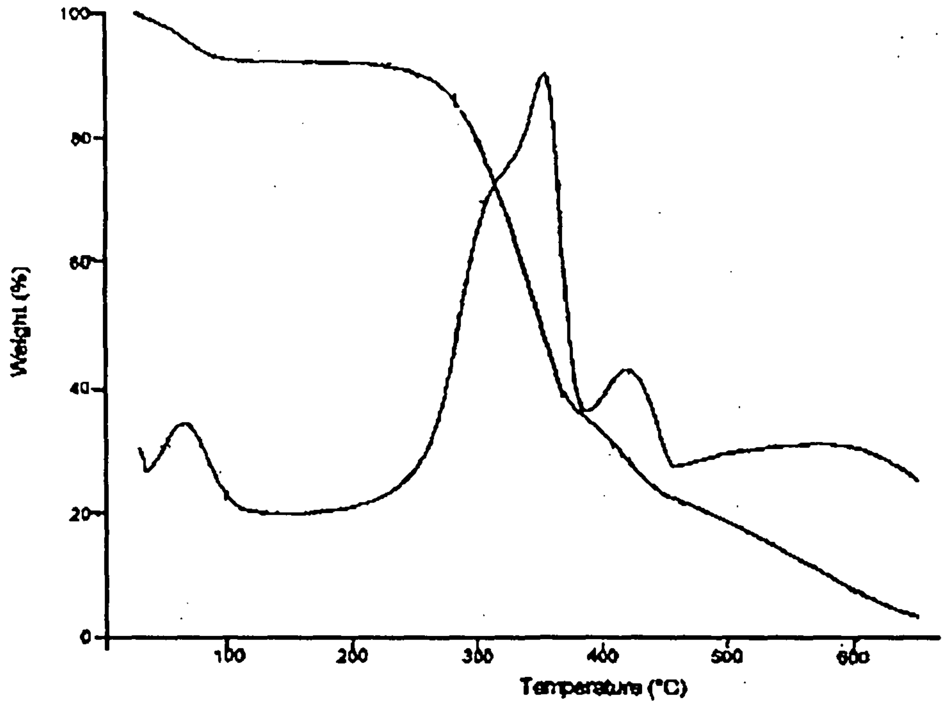

Fig. 4.4.5. TG and DTG curve for styrene-THF treated wood sample

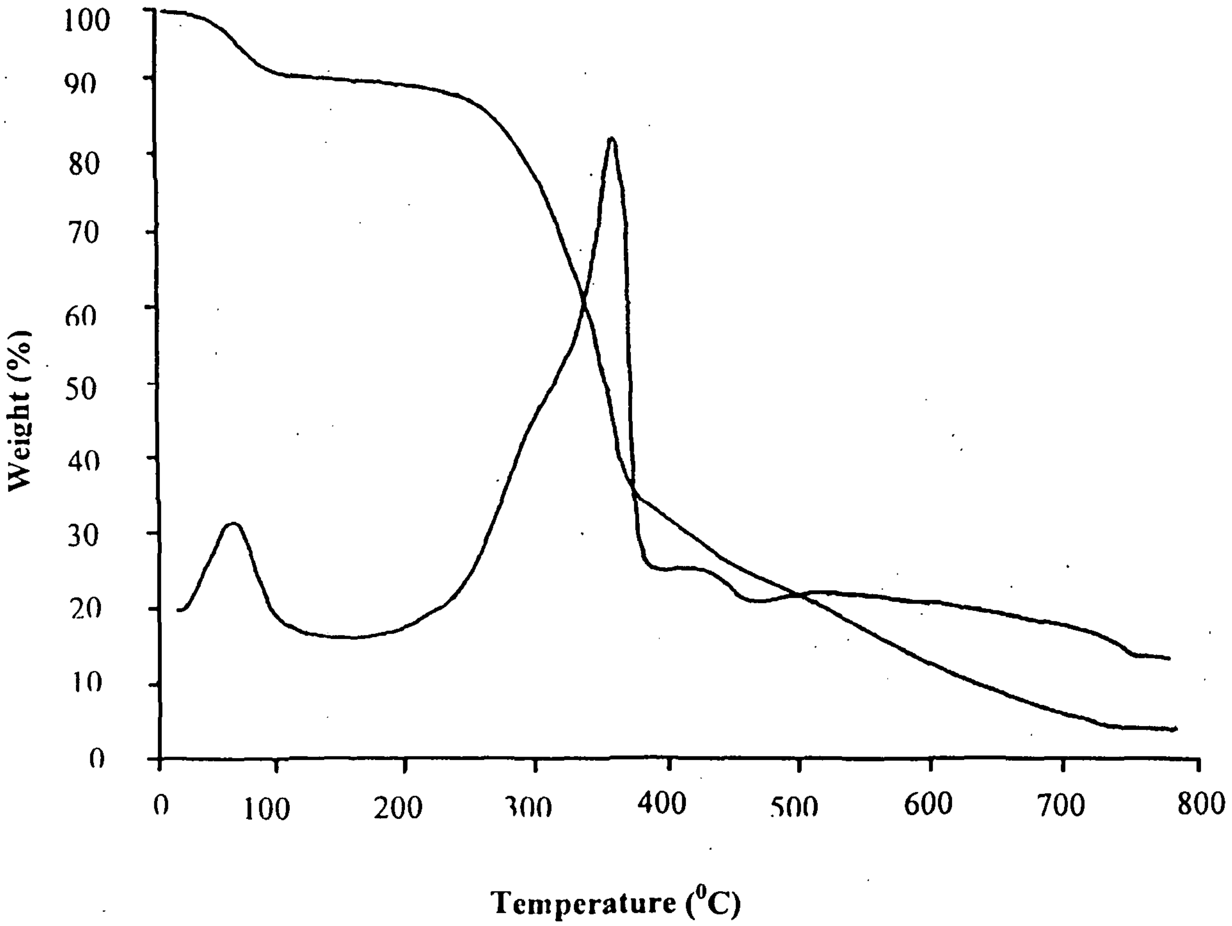

Fig. 4.4.6. TG and DTG curve of Styrene-DEAP (0.5) treated wood sample

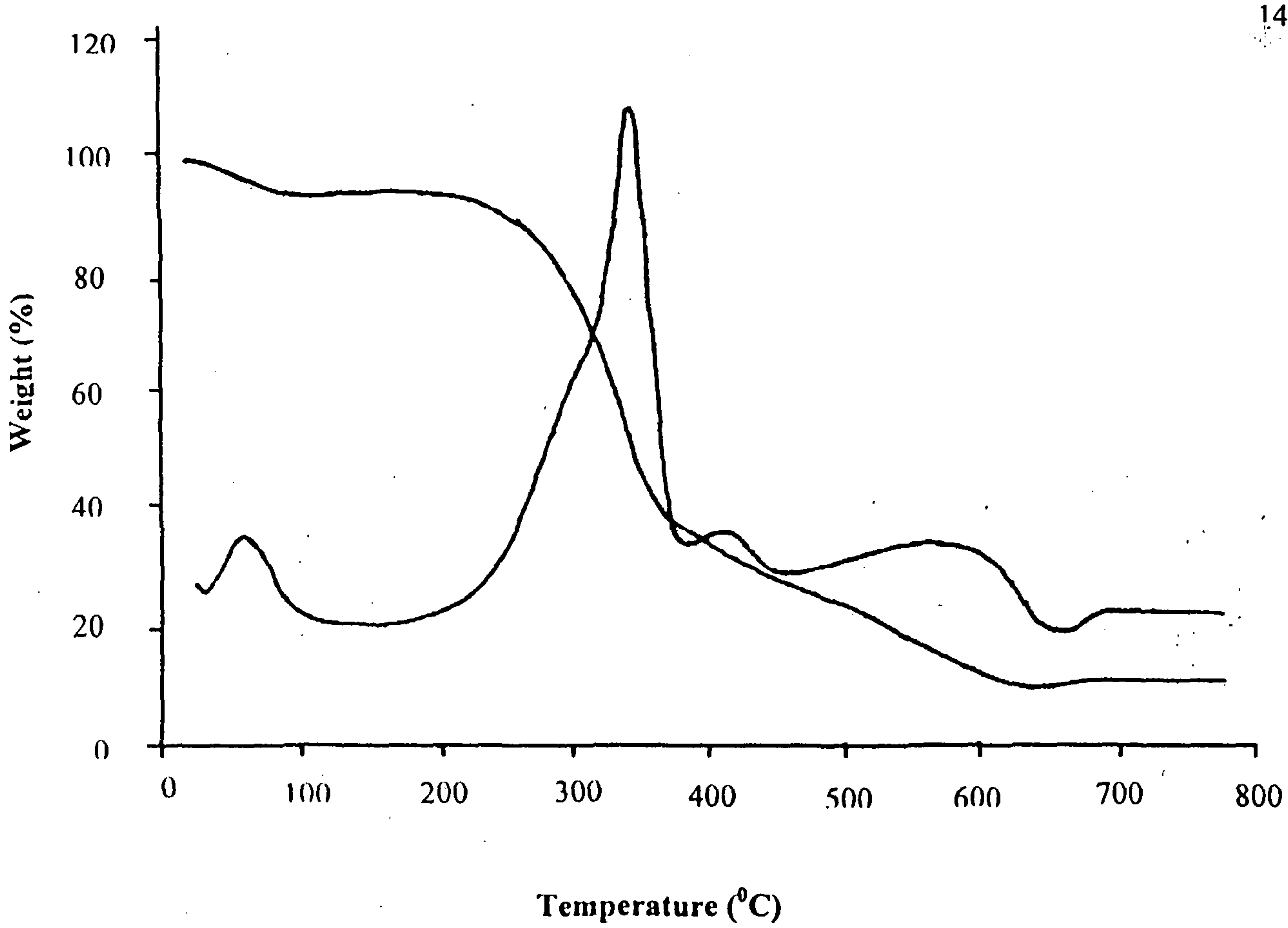

Fig. 4.4.7. TG and DTG curve of styrene-DEAP (1.5) treated wood sample

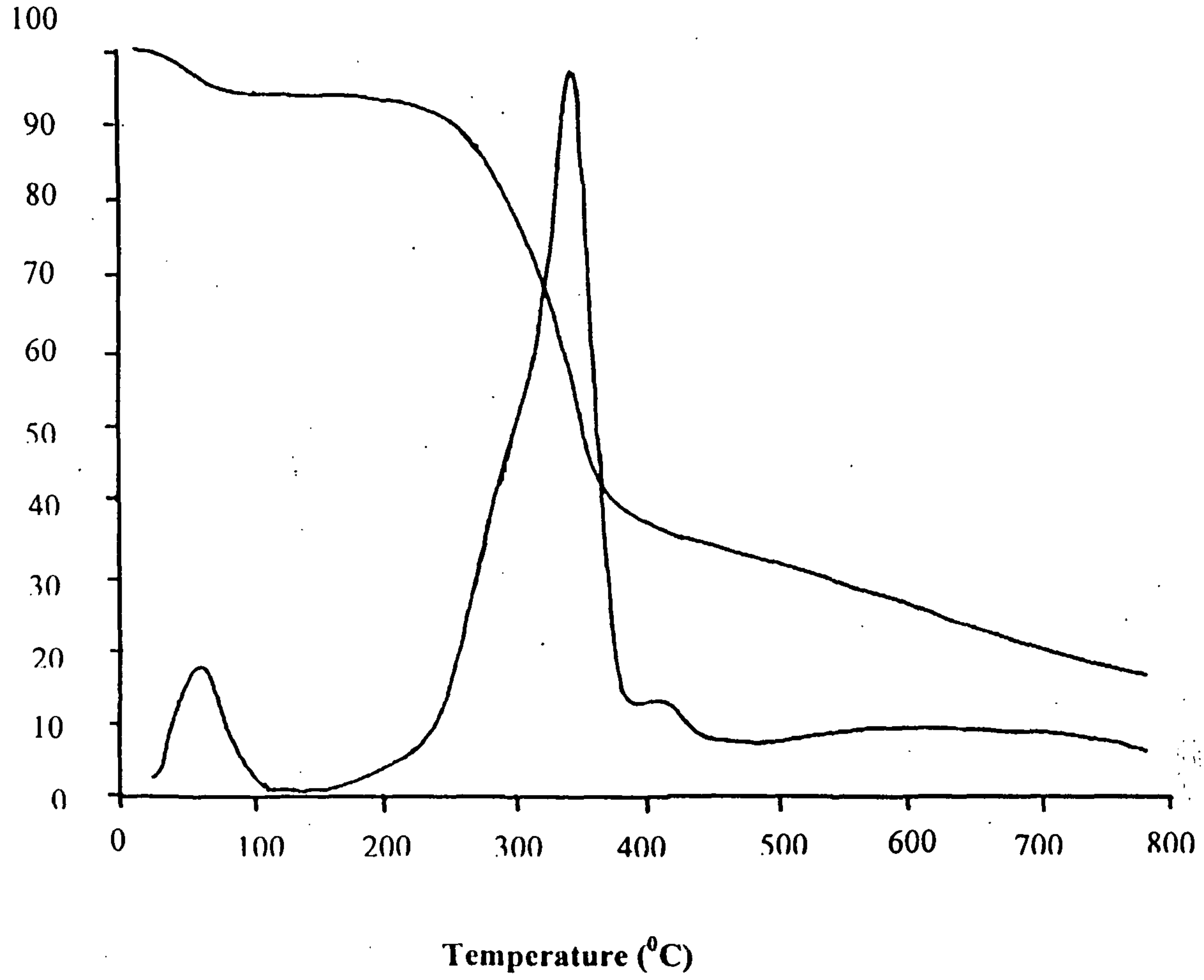

Fig. 4.4.8 TG and DTG curve of Styrene-DEAP (3.0) treated wood sample

4.4.2.7. Limiting Oxygen Index

The results of LOI measurements are presented in table 4.4.6. The measurement and calculation of LOI was as per the procedure and relation given in experimental section. The LOI test assumes that inherently less flammable materials require greater oxygen concentrations to produce the heat necessary for the continued production of flammable volatiles and flame propagation. Rubber wood treated with styrene-DEAP system exhibited improved flame retardancy as evident from higher LOI value. Effective flame retardancy was associated with localized flame, minimal smoke or fume generation, high char yield etc. It was known that decomposition of the cellulose fraction and solid state oxidation of lignin fraction was primarily responsible for the flaming combustion and glowing reactions [24]. Table 4.4.6 showed that wood treated with styrene-DEAP produced small smoke, localized flame and high char yield leading to improved flame retardancy. Similar types of results were also reported [25, 26].

4.3.2.7. Scanning electron microscopy Study

Scanning electron microscopy (SEM) was used to examine the interaction of the polymer with the cell walls of the wood. Figure 4.4.9 shows the void spaces in untreated rubber wood. Figure 4.4.10 and 4.4.11 shows the micrograph of WPC treated with styrene, THF and styrene-DEAP respectively. From the figures 4.4.10 and 4.4.11 it was be observed that there was swelling of the cell wall. The adhesion between wood and polymer increased when DEAP was introduced (Fig 4.4.11). Elvy and coworkers [20] observed and reported that the gaps between the polymer strand and the cell decreased due to increased adhesion caused by silane coupling agent [20].

Table 4.4.6. Limiting Oxygen Indices and flaming characteristics

Samples	WPG (%)	LOI (%)	Flame description	Smoke and fumes	Char
Untreated	-	26	Candle like, localized	-	Little
<u>Treated with</u>					
Styrene-THF	11.4	27	Strong flame	Tall stream of smoke	Little
Styrene-DEAP(1.5)-THF	10.2	30	Small localized flame	Small and black smoke	Higher

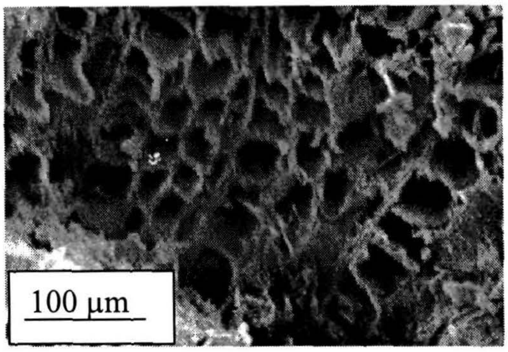

Fig. 4.4.9. SEM micrograph of untreated rubber wood (Magnification ×230)

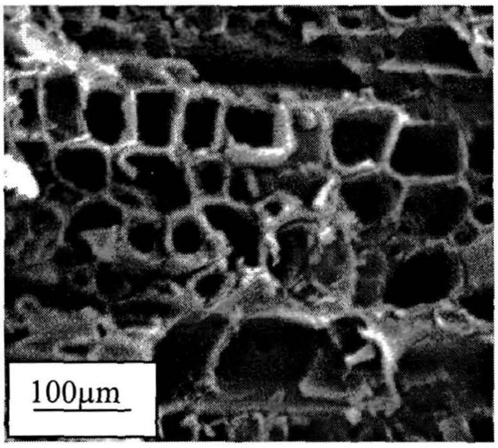

Fig. 4.4.10. SEM micrograph of styrene-THF treated rubber wood (Magnification ×330)

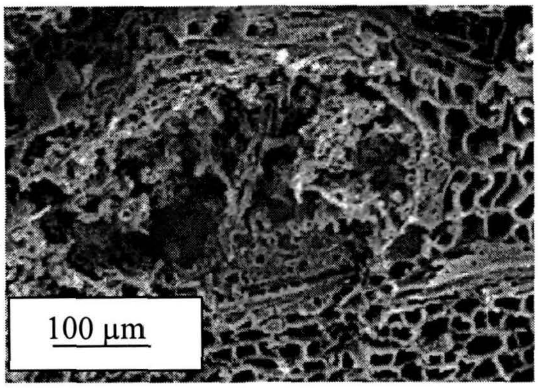

Fig. 4.3.11. SEM micrograph of DEAP-styrene-THF treated rubber wood (Magnification ×140)

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CHAPTER V

SUMMARY AND CONCLUSION

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SUMMARY AND CONCLUSION

5.1. Summary and conclusion

In the present experimental work, it was found that the maximum improvement in the properties of WPC took place at 1:1 styrene-GMA concentration, 5" Hg vacuum and 4h of impregnation time. Optimum concentration of AIBN required for rubber and pine wood composites were 0.5% and 2% respectively. These were the optimum conditions at which maximum overall improvement in properties were found. For DEAP-styrene system, the maximum improvement in the properties in rubber wood was obtained at styrene- DEAP concentration of 88:1.5 (v/v) at an AIBN concentration of 0.5% (by weight).

Maximum volume increase was noticed at 1:1 styrene-GMA combination. That volume increase took place for rubber and pinewood at 61 weight percent gain (WPG) (%) and 21 WPG (%) respectively.

Wood shrinks when it is dried and swells when it absorbs moisture. Once the wood cell walls are bulked with chemicals, these will neither expand nor contract further in contact with water molecules. At 61% and 21% WPG (for rubber and pine wood composites, respectively), highest bulking coefficients also resulted in highest moisture and water exclusion capacity, indicating the blockage of reactive sites of the wood cell wall components by the chemical and thus preventing the wood components to absorb water molecules. Swelling in water and water vapour decreased significantly. Again highest WRE value was obtained at (1:1) styrene-GMA concentration. The interaction of

GMA with wood and styrene through its epoxy group and terminal double bond might be responsible for increase in WRE values. ASE values of styrene-GMA treated samples were found to be highest over the styrene treated samples. Thus styrene: GMA (1:1) samples showed the highest dimensional stability.

The hardness for styrene-GMA (1:1) treated samples increased by 50% and 20% for rubber and pine wood respectively. Rubber wood treated with styrene-DEAP (v/v) (88:1.5) produced an increase in hardness by 34% over untreated samples. The water uptake capacity (%) and swelling in water (%) decreased by 58% and 13% compared to untreated sample. The same ratio of styrene-DEAP showed an increase in volume by 7% compared to negligible for styrene treated samples. The ratio of styrene-DEAP (V/V) (88:1.5) produced lowest water absorption, swelling and highest improvement in hardness.

FT-IR and ^1H NMR spectroscopy confirmed the synthesis of DEAP. FT-IR spectroscopy proved that there was interaction between wood, styrene and GMA. The interaction possibly took place between hydroxyl groups of wood and glycidyl group of GMA and double bond of GMA to that of styrene. It was also evident from improvement in dimensional stability, mechanical property, thermal properties and biodegradability. The FT-IR spectroscopic study also confirmed the interaction between wood, styrene and DEAP. The interaction could possibly take place between hydroxyl group of wood and alkoxy group of DEAP, and double bond of DEAP to that of styrene. SEM study proved the existence of polymers in the wood cells.

Styrene-GMA (1:1) treatment led to harder WPC compared to styrene treated or untreated samples. The highest MOE and MOR values for both the wood composites were obtained for styrene-GMA (1:1) system compared to either styrene treated or untreated samples. Styrene-DEAP (V/V) (88:1.5) treated rubber wood produced maximum MOE value compared to either styrene treated or untreated wood sample. Compressive strengths for treated rubber and pine wood increased both in the parallel and perpendicular to fibre direction, in which, highest improvement was obtained for styrene-GMA (1:1) treatment.

Fungal colonization and bacterial growth took place more slowly for treated samples in comparison to the untreated ones for both rubber and pine wood composites after one-month exposure to nutrient agar medium. In this case also, highest improvement was obtained with styrene-GMA (1:1) combination.

DSC results indicated that there may be some chemical interaction between wood, polystyrene and polyGMA. The analysis also suggested a low compatibility in thermal properties in the relation between wood and styrene polymer.

Incorporation of GMA improved the thermal stability of both rubber and pine wood. The treated rubber and pine wood samples were thermally stable upto 60 and 50% decomposition respectively.

The highest thermal stability was obtained when DEAP was introduced in place of GMA. With the increase in DEAP concentration, the temperature of initiation decreased, and decomposition temperature and residual weight (RW) (%) increased, which showed an evidence for increased thermal stability. The effectiveness of DEAP as a flame retardant could be seen in its ability to lower the initial decomposition temperature and to maintain a high char yield (%). Limiting oxygen index test indicated that DEAP incorporation could improved the flame retardancy behaviour of rubber wood.

On the basis of void volume pine wood should produce more polymer loading compared to rubber wood. This was contrary to what was assumed from the measured void volume. It was reported that polymer loading was more in sapwood compared to heartwood although both had approximately same void volume [1]. The polymer loading of wood was governed not only by the permeability of wood species but also on the particular piece of wood being treated. Variation of polymer loading might also depend on the wood species from location to location.

Nevertheless an improvement in overall properties was observed by using the present system. Table 5.1 shows at a glance the optimum conditions of impregnation producing maximum overall improvement in properties.

Table 5.1 Optimum conditions versus properties of impregnated rubber and pine wood composites

Chemicals					Conditions			Properties						
Type of wood	Styrene (ml)	GMA (ml)	DEAP (ml)	THF (ml)	Vacuum (inches of Hg)	Initiator conc. (%)	Impregnation time (h)	WPG (%)	Water uptake (%) after 24h	Swelling in water (%) after 24h	Compressive strength (Kg/cm^2)		MOE (MPa)	MOR (MPa)
											Parallel to grain	Perpendicular to grain		
Rubber	-	-	-	-	-	-	-	-	104.4	3.9	260.2	90.1	3031.2	64.6
Rubber	100	100	-	-	5	0.5	4	61.4	10.9	0.6	329.0	152.2	12,341.5	138.6
Rubber	88	-	1.5	22	5	0.5	4	9.0	43.8	3.4	-	-	4790.8	50.5
Pine	-	-	-	-	-	-	-	-	38.7	10.0	376.6	60.9	4732.1	102.8
Pine	100	100	-	-	5	2	4	20.6	15.3	5.2	521.1	103.5	8144.3	158.1

5.2 Future Scope

From the present investigation, it is seen that the physical, mechanical, thermal and biodegradation properties of the two kinds of softwood, namely rubber and pine could be improved to a certain extent by using styrene-GMA or styrene-DEAP system. Further work using DEAP and other monomers can be tried. It may provide more valuable information regarding flame retardancy, strength and dimensional stability. However, the present investigation is restricted to laboratory scale only. Further works on a large scale have to be carried out to investigate commercial utilization of the products.

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7. "Studies of properties of rubber wood-Diethyl allyl phosphate-styrene composite" Rashmi R. Devi and T.K.Maji.

Studies on Dimensional Stability and Thermal Properties of Rubber Wood Chemically Modified with Styrene and Glycidyl Methacrylate

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ABSTRACT: Rubber wood (*Hevea brasiliensis*) was impregnated with styrene and glycidyl methacrylate (GMA) as the crosslinking monomer. After impregnation, the polymerization was accomplished by catalyst heat treatment. Water uptake (%) and water vapor exclusion (%) of the rubber wood were found to be improved on treatment. Dimensional stability expressed in terms of volumetric swelling in water vapor (90% relative humidity) as well as in liquid water and water repellent effectiveness (WRE) of the treated samples were determined and also found to be improved. The wood–polymer interaction was confirmed by FTIR spectroscopy. Thermal properties of untreated and treated wood samples were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetery (DSC) and an improvement in thermal stability was observed for the wood–polymer composites. The improvement in properties observed as more with styrene–GMA (1:1) combination. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1938–1945, 2004

Key words: wood–polymer composite; dimensional stability; crosslinker; glycidyl methacrylate; thermal properties

INTRODUCTION

Wood has been used as an engineering material for centuries. Wood is a heterogeneous material that is made up of two major components, carbohydrate and lignin, and two subcomponents that are organic extractives and inorganic minerals. Impregnating wood with polymerizable monomer formulation and then polymerizing it in place produces a wood–polymer composite (WPC). WPC could be more useful for more products, and have a longer life, because it is less susceptible to moisture-induced swelling, shrinking, and biodeterioration and has a harder surface.

Over the years, researchers have impregnated wood with a variety of chemicals to produce WPC. A few of these have found commercial applications, some for a limited time. There are many potential applications for the material. The preservation of wood can best be achieved by proper selection of consolident materials. The crucial point is, therefore, selecting a monomer that can protect and consolidate the wood. In principle, the consolident action can be effectively obtained if a polymer is fully compatible with the chemical constituents of the wood.[1]

Chemical modification of wood to improve its dimensional stability and to decrease its flammability depends on adequate distribution of reacted chemicals in the water-accessible regions of the cell wall. The chemicals used for modifying wood to facilitate penetration must react with the cell wall polymer hydroxyl groups under neutral or mild alkaline conditions at temperatures below 120°C.

Wood–plastic composites were prepared for the first time as a result of experimental work done at the University of West Virginia in 1962.[2] Wood treated with vinyl monomers followed by curing (radiation or catalyst) significantly improves the moisture resistance, hardness, etc.[3] WPC made with combinations of hexanediol diacrylate, hydroxyethyl methacrylate, hexamethylene diisocyanate, and maleic anhydride has reduced the rate of swelling in water as well as in water vapor.[4] Chemical modification of rubber wood with glycidyl methacrylate (GMA) and diallyl phthalate (DAP) has enhanced the properties of rubber wood significantly.[5,6] Impregnation of wood with vinyl or acrylic monomers shows less dimensional stability in the presence of moisture. This may be due to the confinement of monomer in cell lumen instead of cell wall.[7] Crosslinking of material in wood samples provides better dimensional stability to the wood–polymer composite.[8] The problem of limited adhesion

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was extensively addressed in numerous reports on the effects of compatibilizers and coupling agents on the mechanical properties of composites.[9-13] Wood treated with styrene and GMA as the crosslinking monomer has shown improvement in properties.[14,15] The glycidyl group of GMA is capable of reacting with groups containing active hydrogens such as amino, hydroxyl, and carbonyl group.[16] The glycidyl group and terminal double bond of GMA can be exploited for reaction with hydroxyl groups of cellulose in wood and for copolymerization with vinyl or acrylic monomers.

Encouraged by our earlier study,[14] the present investigation was carried out to determine the effect of impregnation with styrene in the presence of a difunctional crosslinking monomer, GMA, on the water absorption, dimensional stability, and thermal properties of softwood.

EXPERIMENTAL

Materials

Rubber wood (*Hevea brasiliensis*) was collected from a local forest in Assam, India. Styrene, obtained from Merck (Mumbai, India), was purified by following standard procedure.[17] GMA and 2,2'-azobisisobutyronitrile (AIBN) obtained from Merck were used as received. All other chemicals used were of analytical grade and used directly.

Sample preparation

The wood samples used for the study were prepared from clear, defect-free wood cut into blocks of 2.5 × 1 × 2.5 cm^3 for water uptake, water vapor exclusion, water-repellent effectiveness, and dimensional stability test.

Impregnation procedure

All samples were oven dried at 105°C to constant weight before treatment and the dimensions and weights were measured. The samples were then placed in an impregnation chamber followed by application of load over each sample to prevent them from floating during the addition of monomers. Vacuum was applied for a specified time period to remove the air from the pores of the wood before addition of monomers. Now sufficient mixture of styrene, GMA, and initiator, or mixture of styrene and initiator, or that of GMA and initiator was added from a dropping funnel to completely immerse the wood samples. The samples were then kept in the chamber at room temperature for another 4 h after attaining atmospheric pressure. This was the minimum time to get a polymer loading, which showed maximum improvement in properties. The condition of impregnation was varied by changing different parameters such as monomer concentration, initiator concentration, level of vacuum, and time. After impregnation samples were taken out of the chamber and excess chemicals were wiped from wood surfaces, the samples were then wrapped in aluminum foil and cured at 90°C for 24 h in an oven. This was followed by drying at 105°C for 24 h. The cured samples were then Soxhlet extracted to remove homopolymers, if any, formed during impregnation. Finally, the samples were dried and the dimensions were measured by using a slide caliper and weights were taken.

Measurements

Water uptake test

Both untreated and treated wood samples were immersed in distilled water at room temperature (30°C) and weights were taken after 0.5,2,6,24,48,96,120, 144, and 168 h, expressed as

$$\text{water uptake (\%)} = \left[\frac{W_t - W_d}{W_d}\right] \times 100 \quad (1)$$

where W_d is the oven dry weight; and W_t is the weight after immersion in distilled water for a specified time period.

Water vapor exclusion test

Oven-dried samples were conditioned at 30°C and 30% relative humidity (RH) and weighed. Samples were then placed in a chamber where temperature and RH were maintained at 30°C and 90%, respectively, and weights were measured after 0.5, 2, 4, 8, 24, 48, 96, 120, and 168 h. It is expressed as a percentage of moisture absorbed based on oven dry weight.[4]

Water repellent effectiveness (WRE)

WRE was measured for different soaking periods. Resistance to water uptake is expressed as WRE and calculated as

$$\text{WRE} = \left[\frac{(D_0 - D_t)}{D_0}\right] \times 100 \quad (2)$$

where D_0 is the water uptake of untreated samples immersed for 0.5, 2,6, 24, 48, 96, 120, 144, and 168 h; and D_t is the water uptake of treated wood samples immersed for the same periods.

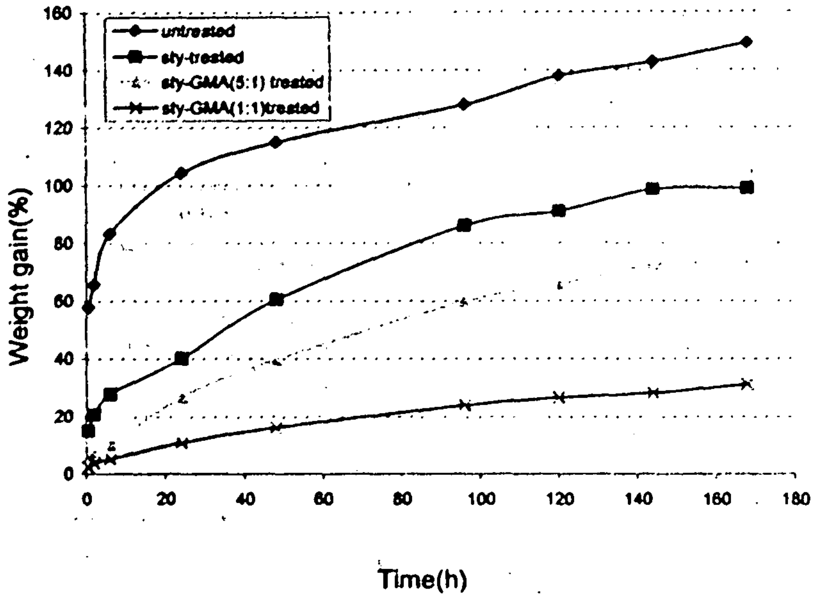

Figure 1 Weight gain of WPC in water at 30°C.

Dimensional stability test

Dimensional stability test was performed by using a procedure described elsewhere.[4]

Swelling in water vapor. Samples were first dried at 105°C followed by measuring the dimensions in radial as well as tangential directions. Samples were then conditioned at 30°C and 30% RH. Finally, the samples were placed in a chamber where RH and temperature were maintained at 90% and 30°C, respectively. The dimensions were remeasured after 0.5, 2,4, 8, 24, 48, 96, 120, and 168 h.

Swelling in water. Dimensions of the oven-dried samples were measured and conditioned at room temperature (30°C) and 30% RH. Final placement of the samples as done in distilled water and then dimensions were remeasured after 0.5, 2, 6, 24, 48, 96, 120, 144, and 168 h.

In both the cases, swelling was considered as a change in volume and expressed as the percentage of volume increase compared to oven-dried samples,

$$\% \text{ Swelling} = \left[\frac{V_{t,u}-V_0}{V_0}\right]\times 100 \qquad (3)$$

where $V_{t,u}$ is the volume of the untreated or treated wood after water absorption; and V_0 is the volume of the untreated or treated wood before water absorption.

FTIR study

The treated and untreated samples were grounded and FTIR spectra were recorded by using a KBr pellet in a Nicolet Impact 410 spectrophotometer.

Thermal study

Thermal properties of the untreated and treated wood samples were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC study was carried out in a differential scanning calorimeter (model Metler TA 4000) at a heating rate of 10°C/min up to 500°C. TGA was carried out by using a thermogravimetric analyzer (model Metler TA 4000) at a heating rate of 20°C/min up to 500°C.

RESULTS AND DISCUSSION

For the water uptake, water vapor exclusion, and dimensional stability measurements, the treated samples chosen were more or less of similar polymer loading and each result presented in figures or tables was taken from the average of five samples.

Water uptake test

The results of water uptake for treated and untreated samples were shown in Figure 1. In both treated and untreated samples up to the time period studied, water absorption increased with an increase in time and untreated samples absorbed more water compared to treated samples. Styrene–GMA (1 : 1) treated samples showed the least water uptake throughout the time period studied. With an increase in time, the capillaries and void spaces were getting more time to become filled up with water, which in turn leads to an increase in the water uptake. In treated samples, the decrease in spaces, available to hold water due to filling up of the same by

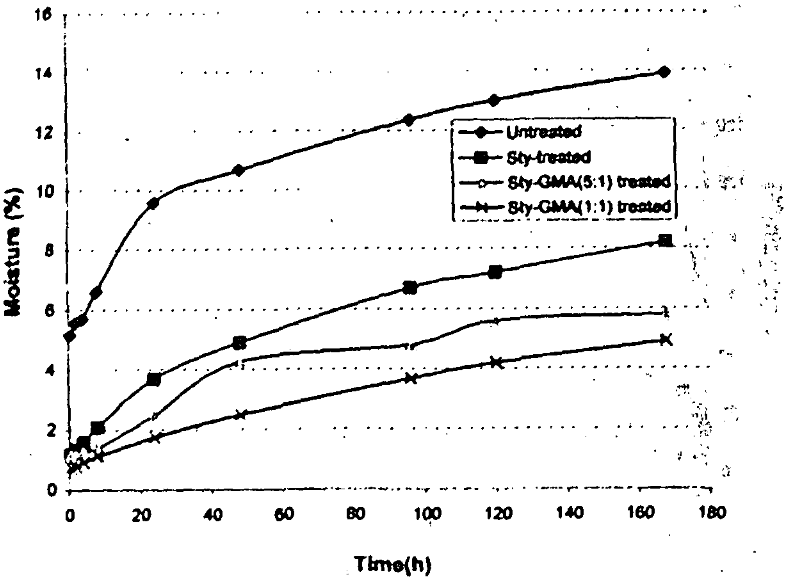

Figure 2 Weight gain of WPC in water vapor at 90% RH and 30°C.

polymer, was responsible for lowering in water absorption. The water absorption decreased further because of the crosslinking formed by the interaction of glycidyl group and double bond of GMA with hydroxyl group of wood and styrene, respectively.

Water vapor exclusion

In a series of water vapor exclusion study in 90% RH and at 30°C for various time periods, treated samples absorbed less water vapor than untreated samples (Fig. 2). The absorption of water vapor followed the trend untreated > styrene treated > styrene–GMA (5 : 1) treated > styrene–GMA (1 : 1) treated samples. The reason for this trend could be explained as earlier.

Water repellent effectiveness

Table I showed the results of the WRE values for treated and untreated wood samples in water at room temperature (30°C). An improvement in WRE values was observed for treated samples, particularly on incorporation of GMA. In all the cases, water repellency decreased initially at a faster rate and finally at a slower rate.[7] A similar type of observation was reported in the literature.[8,18] The improvement in WRE could be explained by the same reason as stated earlier.

Dimensional stability

Swelling in water vapor

The results showing the effect of swelling in water vapor at 90% RH and room temperature (30°C) up to 168 h were presented in Figure 3. As expected, treated samples, particularly those where GMA was incorporated, showed more reduction in swelling.

Swelling in liquid water

The effect of swelling in liquid water at room temperature (30°C) for untreated and treated wood samples

TABLE I
Water Repellent Effectiveness (WRE) (%) of Wood Polymer Composites

Time (h)	Styrene-treated wood	Styrene–GMA (5 : 1) treated wood	Styrene–GMA (1 : 1) treated wood
0.5	73.9	90.15	95.68
2	68.3	89.05	94.07
6	66.5	87.88	93.76
24	61.5	74.3	89.5
48	47.4	65.4	85.9
96	32.7	53.12	81.3
144	30.9	49.25	80.26
168	33.6	50.77	79.03

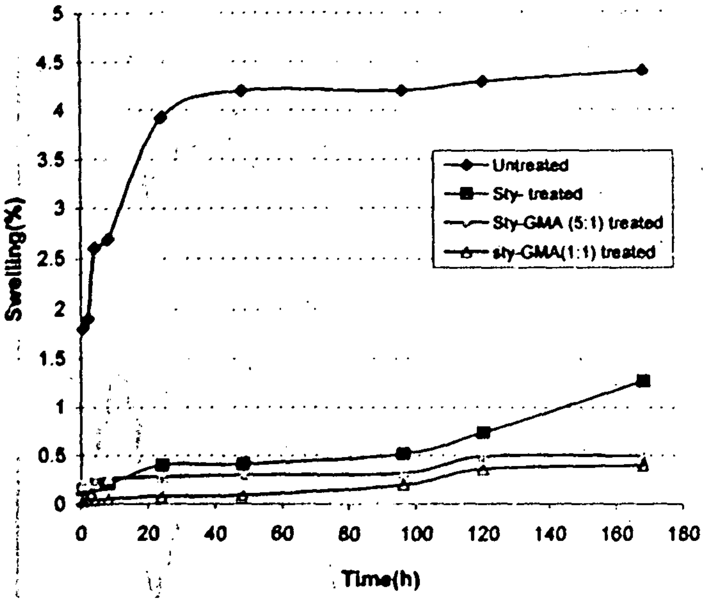

Figure 3 Swelling of WPC conditioned at 90% RH and at 30°C.

for different time periods was shown in Figure 4. Samples treated with styrene–GMA (1:1) combination showed the least swelling compared to either untreated or other treated samples. Samples treated with styrene or styrene–GMA (5 : 1) showed less swelling than the untreated samples up to a certain time (105–120 h); beyond that swelling increases. The reason for this was not clear. Overall, due to treatment, the reduction in swelling was noticed.

The reduction in rate of swelling in the above cases could be explained with the help of the combined effect of crosslinking by GMA and filling of void space by polymers.

FTIR study

The FTIR spectra of untreated and treated wood samples were presented in Figure 5I–III. From the FTIR spectra, it

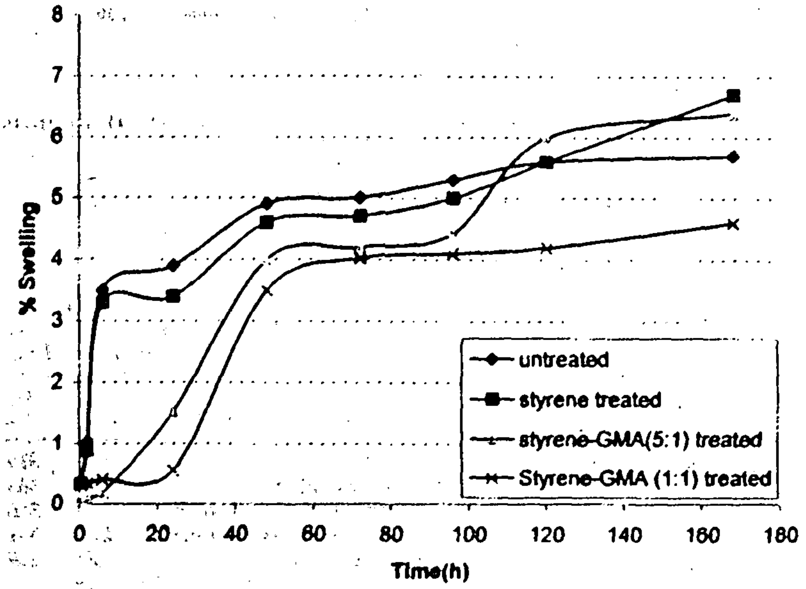

Figure 4 Volumetric swelling of WPC in water.

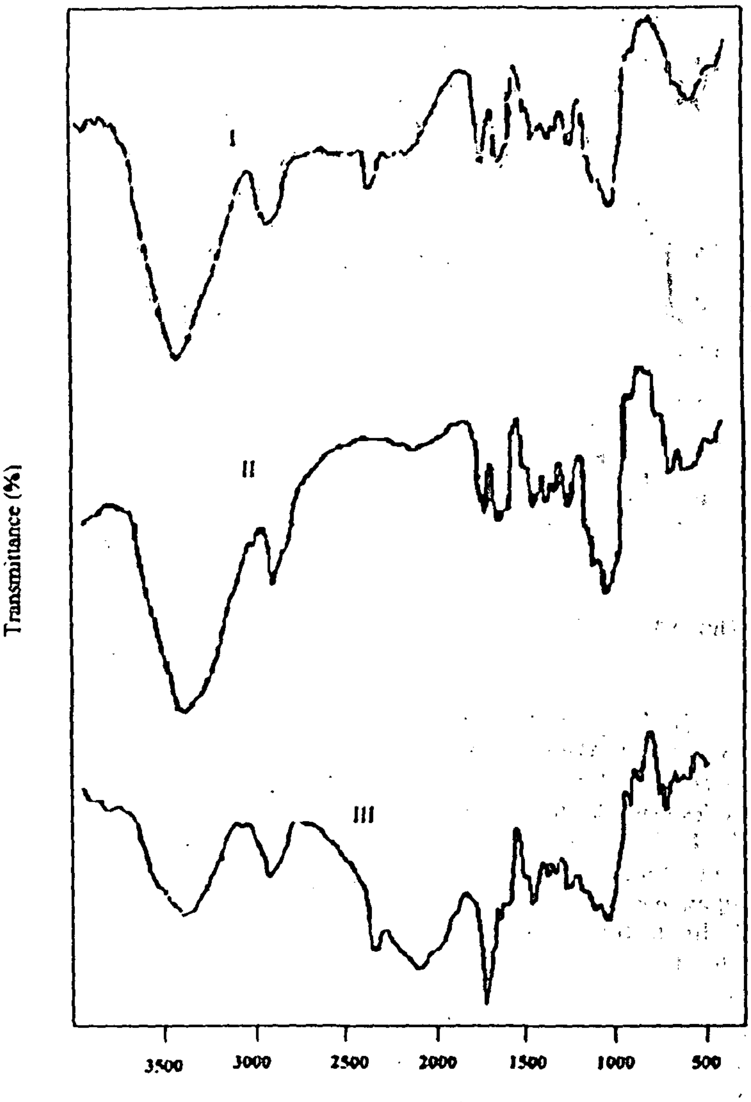

Figure 5 FTIR spectra of untreated (I), styrene-treated (II), and styrene–GMA-treated (1 : 1) (III) rubber wood samples.

was found that the peak at 1733 cm^{-1}, which was due to carbonyl stretching vibration, became more pronounced on treatment with styrene–GMA. The position of the peak at 3428.38 cm^{-1} (OH stretching) for untreated wood remained unchanged by incorporation of styrene. The peak shifted to 3432.39 cm^{-1} for styrene–GMA (1 : 1). The intensity of C—O stretching vibration (1113.56 cm^{-1}) of untreated wood was also found to increase on treatment with styrene and GMA. All these, as stated above, confirmed the interaction between wood, styrene, and GMA.[6,14,15,19,20]

Thermal properties

For the study of thermal properties, treated samples chosen were of approximately similar polymer loading.

TABLE II
Thermal Analytical Data for Untreated Wood and Polymer-Treated Wood Samples

Sample particulars	T_i (°C)	Tm_I[a] (°C)	Tm_{II}[b] (°C)	RW (%)
Untreated	270	315	368	31.55
Styrene treated	272	363	433	27.39
Styrene–GMA (5 : 1) treated	280	356.3	414.7	28.05
Styrene–GMA (1 : 1) treated	295	341.3	384.7	23.84
GMA treated	289	349	418	16.83

[a] T_m value for first step.
[b] T_m value for second step.

TABLE III
Temperature of Decomposition (T_D) at Different Weight Losses of Untreated and Treated Wood Samples

Sample particulars	Temperature of decomposition (T_D) in °C at different weight loss (%)						
	20	30	40	50	60	65	70
Untreated	302	326	350	363	380	430	—
Styrene treated	*303*	*330*	*352*	*370*	*417*	*432*	*455*
Styrene–GMA (5 : 1) treated	308	328	350	364	405	420	440
Styrene–GMA (1 : 1) treated	310	330	348	369	390	396	414
GMA treated	310	328	344	350	372	389	400

TGA study

Table II shows the initial decomposition temperature (T_i), maximum pyrolysis temperature (T_m), and residual weight (RW) for untreated and polymer-treated wood samples. T_i and T_m values for both stages of pyrolysis in treated samples were higher than untreated samples. RW value is observed higher in the case of untreated wood samples compared to those of treated ones.

Table III shows the T_D values at different weight losses for different samples. It was observed that T_D values of treated wood samples were higher than the untreated samples, up to 60% decomposition; beyond that, the value decreased. The increasing trend might be due to the decreasing chance of elimination of small molecules such as CO and CO_2, etc., with the formation of crosslinking, verified experimentally by swelling, which act as an infusible support and provided thermal resistance to the wood fibers. The decreasing trend might be due to the earlier decomposition of polystyrene chain at higher temperature compared to wood fibers. Again, a decreasing trend in T_D values were observed in the treated samples when GMA was added. The higher the percentage of GMA, the lower was the T_D value. The higher decomposition rate of GMA polymer at higher temperature might be responsible for the lower stability of wood treated with styrene–GMA combination.

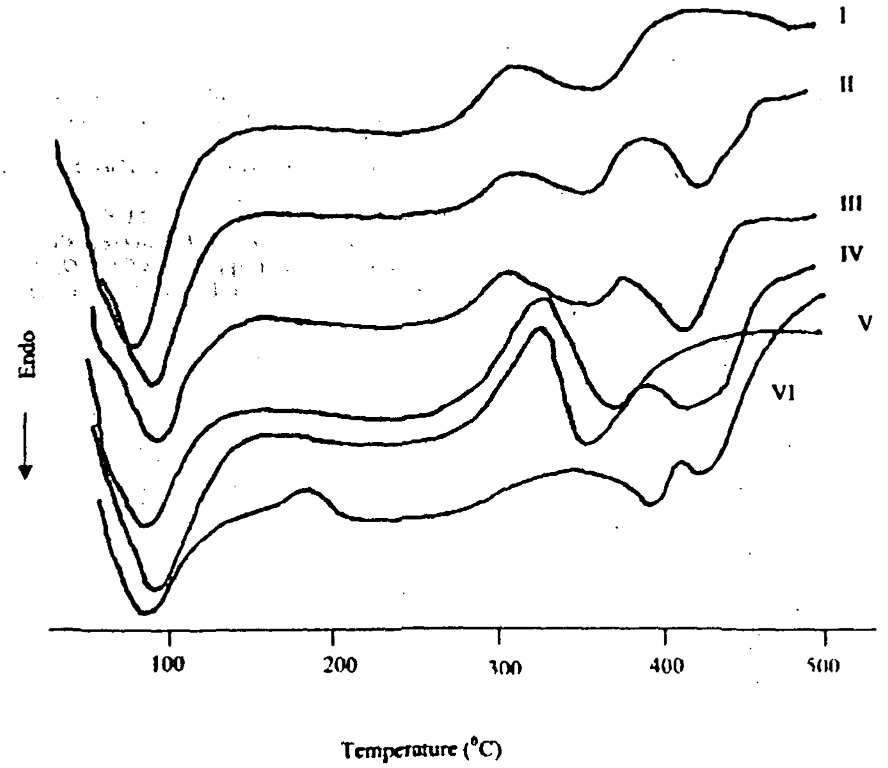

Figure 6 DSC thermograms of untreated (I), styrene treated (II), styrene–GMA (5 : 1) (III) treated, styrene–GMA (1 : 1) (IV) treated, and GMA (V) treated and physical mixture of styrene–GMA (5 : 1) (VI) treated rubber wood samples.

DSC study

Figure 6 I–VI shows the DSC results of untreated and treated wood samples. Untreated wood (curve I) shows a single endothermic peak at 360°C, which was due to the thermal decomposition of wood fibers. Wood treated with GMA (curve V) also showed one endothermic peak at around 351°C. Styrene and styrene–GMA impregnated wood samples (curves II–IV) showed one endothermic peak in the range 354–370°C and another endothermic peak in the range 416–432°C. The double endothermic peaks exhibited in DSC thermograms were due to the thermal decomposition of wood fibers and filled polystyrene in the wood. The position of one peak, which was due to the decomposition of wood fibers, remains almost unchanged with the exception of styrene–GMA (1 : 1) impregnated samples (curve IV), where it shifted to higher temperature. The other peak, which was due to the decomposition of filled polystyrene, shifted to lower temperature. Curve VI showed the thermograms of a physical mixture of wood, polystyrene, and poly(GMA). Polystyrene and poly(GMA) were mixed in a ratio of 5 : 1 and mixed with wood flour similar to that of polymer loading in sample (curve III) to prepare the physical mixture. These DSC results indicated that there may be some chemical interaction between wood, polystyrene, and poly(GMA). These results also support a low compatibility in thermal properties in relation to wood and styrene polymer.

CONCLUSION

From the study, it was found that incorporation of glycidyl methacrylate, a crosslinker, into wood improves more the various properties such as water absorption, water vapor exclusion, dimensional stability in water, as well as in water vapor compared to those of either untreated or styrene-incorporated wood samples. Further, the improvement observed is more in (1 : 1) styrene–GMA combination samples. FTIR spectra confirm the interaction between wood, styrene, and GMA. Impregnation with styrene and GMA also improves thermal stability, as revealed by thermal analysis.

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Chemical modification of rubber wood with styrene in combination with a crosslinker: effect on dimensional stability and strength property

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Abstract

Chemical modification of rubber wood (*Hevea Brasiliensis*) was carried out by impregnating the wood with styrene and in combination with a crosslinker Glycidyl Methacrylate (GMA). Polymerization was carried out by catalyst heat treatment. The dimensional stability in terms of % volumetric swelling and anti-shrink efficiency was determined and found to be improved on treatment. Water absorption was also found to be decreased considerably for treated wood samples. Mechanical strength of the treated samples in terms of modulus of rupture and modulus of elasticity were also found to be improved. The wood polymer interaction was confirmed by FT-IR spectroscopy. Biodegradability of the wood/polymer composites was determined and found to be improved on treatment with styrene/styrene-GMA.

Keywords: Wood composite; Crosslinker; Glycidyl methacrylate; Dimensional stability; Anti-shrink efficiency; Modulus of rupture; Modulus of elasticity; Biodegradation

1. Introduction

Wood, a natural cellulose composite material of botanical origin, possesses unique structural and chemical characteristics that render it desirable for a broad variety of end uses. The level of suitability for a given end use (i.e. wood quality) is frequently determined by the wood response to imposed physical and chemical treatments. From the chemical perspective, wood tissue (including cells and intercellular substance) is a composite material constructed from a variety of organic polymers, namely cellulose, hemicellulose and lignin. Wood, despite its many useful properties, also possesses some disadvantages like variation of properties, liability to distortion from absorption of moisture and to damage by attack with fungi and insects etc.

Woods can be classified as softwood and hard wood. Softwoods are poor in strength, dimensional stability etc. which restricts their uses as structural materials. Therefore they mostly find their uses in fuel purposes. But these softwoods can have value added by being made into wood suitable for different applications like furniture, office equipment and in construction through proper treatment such as chemical modification. Considerable work has been done on the modification of wood by impregnation with suitable polymers depending upon the end uses (Rowell, 1983). Treatment with vinyl type monomer followed by curing (radiation or catalyst) significantly improved the moisture resistance, hardness etc of wood (Meyer, 1981). Wood of different types impregnated with a polymer mixture containing an macromonomer and styrene had improved water repelleney, compression and bending strength (Baki et al., 1993). Use of glycidyl methacrylate (GMA) with diallyl phthalate (DAP) improved the dimensional stability, moisture resistance and mechanical properties of the wood more significantly than did GMA or DAP alone (Rozman et al., 1998; Rozman et al., 1997). The impregnation of wood with acrylic or vinyl type monomer showed less dimensional stability in the presence of moisture. This was due to the confinement of the

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monomer in the cell lumen instead of the cell wall (Rowell and Ellis, 1978).

Both double bond and glycidyl group are present in GMA. The glycidyl group was capable of reacting with groups containing active hydrogen such as amino, hydroxyl and carbonyl group (Kakiuchi, 1964). The glycidyl group and terminal double bond in GMA could be exploited for reaction with hydroxyl group of cellulose present in wood and for co-polymerization with vinyl or acrylic type monomers, respectively. Keeping the above in view, the present work was undertaken.

The present investigation was carried out to determine the effect of impregnation with styrene in the presence of a difunctional crosslinking monomer (GMA) on the dimensional stability and mechanical properties of a soft wood and also to see the effect on biodegradation of the treated wood.

2. Methods

2.1. Materials

Rubber wood (*Hevea brasiliensis*) was collected from a local forest in Assam, India. Styrene, obtained from Merck (Mumbai, India) was purified by following standard procedure (Sundarrajan et al., 2001). GMA and 2,2′-azobis-(isobutyronitrile) (AIBN) from Merck, India, were used as received. All other chemicals used were of analytical grade and were used directly.

2.2. Preparation of the wood samples

Wood samples were cut into 2.5 × 1 × 2.5 cm and 1 × 1 × 10 cm for measurements of dimensional stability, chemical resistance, hardness and bending. All the samples were oven dried at 105 °C to constant weight before treatment and the dimensions and weights were measured. The samples were then placed in a chamber followed by application of load over each sample in order to prevent them from floatation during addition of monomers. Vacuum was applied for a specified time period for removing the air from the pores of the wood before addition of monomers. Now a sufficient mixture of styrene, GMA and initiator/or mixture of styrene and initiator was added from a dropping funnel to completely immerse the wood samples. The samples were then kept in the chamber at room temperature for another 4 h after attaining atmospheric pressure. This was the minimum time to get a polymer loading, which showed maximum improvement in properties. The condition of impregnation was varied by changing different parameters such as monomer concentration, initiator concentration and level of vacuum. After impregnation, samples were taken out and excess chemicals were wiped from the wood surfaces. The samples were then wrapped in aluminum foil and cured at 90 °C for 24 h in an oven. This was followed by drying at 105 °C for 24 h. The cured wood samples were soxhlet extracted to remove homopolymers, if any, formed during impregnation. Finally the samples were dried and dimension was measured using a slide caliper, and weights were taken.

2.3. Evaluation of properties of the treated and untreated wood

The dimensional stabilities of the treated and untreated wood samples were determined by measuring volumetric swelling in distilled water, anti-shrink efficiency (ASE) and swelling in water vapour at 90% relative humidity (RH) for different times (Rozman et al., 1998; Ellis and O'Dell, 1999). Percent of swelling was also measured in acetic acid (glacial) and 4% NaOH after 24 h dipping in order to evaluate the chemical resistance of the treated wood samples. The hardness of the wood samples was determined and expressed as durometer hardness (Shore-D) according to the ASTM D 2240 method. The modulus of rupture (MOR) and modulus of elasticity (MOE) were calculated according to ASTM D 790 method.

The treated wood samples were ground and FT-IR spectra were recorded using KBr pellet in a Nicole Impact 410 Spectrophotometer in order to confirm the interaction between the wood and the polymer.

The wood samples showing improved dimensiona stability, improved strength properties were subjected to biodegradation tests using a procedure described elsewhere (Solpan and Guven, 1998).

3. Results and discussion

The conditions of impregnation to get the highes level of polymer loading were optimized by varying vacuum, monomer and initiator concentration respectively. The best condition for highest polymer loading was found with 5″ Hg vacuum at 5:1 (Styrene: GMA monomer concentration and with 0.5% of AIBN. All the measurements were carried out using styrene-GMA treated wood and styrene-treated wood samples of more or less similar polymer loading. The results given below are the average data of three samples in each case.

In a volumetric swelling study the styrene-GMA (0.58%) treated wood samples showed less swelling than untreated (0.66%) and styrene (0.62%) treated samples up to 96 h in water vapour (90% RH). After that swelling of the treated or untreated wood samples became almost similar. Similarly the rates of the volumetric swelling of the treated samples were found to be less than the untreated samples, in water for several hours. The reduction in the rate of swelling of wood-polymer composites corresponded to the moisture excluding capacity of the treatment. ASE of the styrene treated and styrene-GMA-treated samples was evaluated. In general, styrene-GMA-treated wood samples showed higher ASE than styrene-treated samples. An ASE value of 53% was obtained for styrene-GMA-treated wood samples compared to 23% for styrene-treated wood samples, upon soaking for 24 h. ASE values decreased for all the samples for 96 h soaking. Chemical resistance of the treated samples was also improved over the untreated one. Swelling in acetic acid was 6.07%, 12.97% and 3.38% for untreated, styrene-treated and styrene-GMA-treated samples respectively. Again with 4% NaOH swelling was 8.45%, 15.7%, 4.35% for untreated, styrene-treated and styrene-GMA-treated samples, respectively.

In a series of water absorption studies with varying time period, the styrene-GMA-treated wood samples absorbed less water than the styrene-treated or untreated ones. Water absorption was decreased from 142.86% (untreated) to 98.64% (styrene treated), and up to 72.5% for styrene-GMA-treated wood samples, after 6 days in distilled water at room temperature. These results indicated that styrene only bulked the cell wall and did not react fully with the wood whereas the presence of GMA could increase the interaction between styrene and wood through its epoxy linkage and terminal double bond. Because of that the improvement in volumetric swelling, chemical resistance and reduction in water absorption was noticed.

Hardness (Shore D) was higher for styrene (61.98) and styrene-GMA (61.5)—treated samples than that of untreated samples (46.57). When the treated wood samples were tested for strength, it was found that MOR values were increased on treatment with styrene and styrene-GMA. The values of MOR were 64.69, 127.2, 120.03 MPa for untreated, styrene treated and styrene-GMA-treated samples respectively. An increase of MOE was also observed in the treated samples. The values of MOE were 3038.18, 6718.41 and 7283.91 MPa for untreated, styrene treated and styrene-GMA-treated samples respectively. The MOR and MOE results for the treated wood samples showed improved mechanical properties of the rubber wood on polymer treatment. The increase in MOE value for the styrene–GMA treated samples may be attributed as before to the presence of crosslinker GMA which penetrates into the cell of the wood and provides better interaction between the styrene and wood.

Interaction between wood, styrene and GMA was confirmed by FT-IR spectroscopy (Rozman et al., 1997; Pandey, 1999), which showed an enhanced peak at 1733 cm^{-1} in the carbonyl region after the reaction with GMA. And this peak also shifted towards lower wave number, while a new peak appeared at 1610 cm^{-1} on treatment with styrene which became more pronounced on reaction with GMA and shifted to 1603 cm^{-1}, possibly due to aromatic skeletal vibration and carbonyl stretching. There was no shifting of the broad peak at 3428.38 cm^{-1} (O–H stretching) of untreated wood with styrene treatment but on incorporation of GMA this peak shifted to 3438.58 cm^{-1} and also broadened, which gave evidence of the reaction of wood hydroxyl groups with glycidyl groups of GMA. These results confirmed that GMA gave better interaction between the wood and styrene.

Lastly the polymer-treated wood samples were subjected to a biodegradation test and compared with the untreated wood samples. The untreated and treated wood samples were stored in an agar for 30 days to access the growth of microorganisms. In the untreated wood samples much production of *Bacillus* spp. bacteria and abundant growth of fungi was observed, but no or little production of these was seen in the polymer-treated wood samples. The smaller biodegradation of the treated wood samples might have been due to the decrease in the water uptake capacity of the treated wood. Similar observations for biodegradation were reported by Solpan and Guven (1998) for wood-polymer composites.

From the present study, it might be concluded that the presence of GMA as the crosslinking monomer improved the properties of wood-polymer composites prepared with styrene as the monomer. Volumetric swelling in water vapour as well as in water for the styrene-GMA-treated samples showed better results over the styrene treated and untreated samples. An ASE value of 53% was obtained for styrene-GMA treated samples compared to that of 23% for styrene treated wood samples, for 24 h in water. Polymer treatment improved the chemical resistance of the wood samples, resulting in less swelling in CH_3COOH and 4% NaOH. In this case also the styrene-GMA combination showed better results than the styrene treated samples. Hardness was almost the same for the styrene treated and styrene-GMA-treated samples and was increased by 33% over that of the untreated samples. MOE and MOR values showed an improvement over the untreated wood samples. FT-IR spectroscopy proved the interaction between wood, styrene and GMA. All the samples showed an improvement in biodegradation on treatment.

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Studies of properties of rubber wood with impregnation of polymer

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Abstract. Impregnation of rubber wood has been carried out under different conditions by using styrene as grafting monomer and glycidyl methacrylate (GMA) as crosslinker. Properties such as dimensional stability, water absorption, hardness, tensile strength, flexural strength, etc of the impregnated wood have been checked and found to be improved by incorporation of GMA as the crosslinker with styrene. The polymer-impregnated wood has also been characterized by FTIR spectroscopy and DSC.

Keywords. Wood; composite; crosslinker; polymers; styrene–glycidyl methacrylate.

1. Introduction

Wood, a renewable resource and naturally occurring material abundantly available has a wide range of applications as construction material, pulp, paper, fireboard products as well as source of energy and as raw materials for various industrially important chemicals. Two types of woods viz. hard and soft, are available. Softwood trees are lacking in strength, dimensional stability etc which restrict their uses. The softwood trees are generally used for fuel purposes. These softwoods can be converted into value added primary wood suitable for furniture, office equipment etc through impregnation with polymer in the capillaries, cavities, and void spaces of the wood cell.

Considerable work has been done on the modification of wood (Rowell 1983). Meyer (1981) reported that wood treated with vinyl type monomer followed by curing (radiation or catalyst) significantly improves the moisture resistance, hardness etc. Baki *et al* (1993) has shown that different types of wood impregnated with a polymer mixture containing macroionomer and styrene improves water repellency, compression and bending strength. Rozman *et al* (1998) reported that the use of glycidyl methacrylate as crosslinker with diallyl phthalate improves the dimensional stability compared to those based on diallyl phthalate alone. The composite prepared by wood and acrylic, vinyl type monomers show low dimensional stability in water. This may be due to the confinement of monomer in the cell lumen instead of cell wall (Rowell and Ellis 1998). Therefore, a system is sought which consists of a monomer that has the ability to penetrate into the cell wall and copolymerize with other monomers that can provide reaction sites for crosslinking. Rozman *et al* (1997) have observed an improvement in moisture resistance, mechanical properties etc of the wood when treated with glycidyl methacrylate and polymerized with diallyl phthalate.

GMA is a difunctional monomer, containing a terminal C=C and an epoxy group. It is able to react with wood hydroxyl group through its epoxy end. It may also be able to react with styrene through its double bond. It is assumed that styrene can react with GMA through its double bond. This present study reports the results of rubberwood treated with styrene with GMA as the crosslinker.

2. Experimental

2.1 *Materials*

Rubber wood was supplied locally. Styrene was used after purification and glycidyl methacrylate (GMA) was supplied by MERCK. The initiator used 2,2′-azobis-2(-methylbutyronitrile) (AIBN) was obtained from the National Chemical Co. (India). All other chemicals and solvents used in this study were of analytical grade.

2.2 *Methods*

2.2a *Sample preparation*: The wood specimen used for testing were prepared from clear defect free rubber wood cut into blocks of 2·5 × 2·5 × 0·5 cm for dimensional stability, water absorption, hardness and chemical resistance tests.

For tensile strength measurements samples were prepared in several steps. The blocks were cut into 11·5 × 20 × 0·7 cm using the standard method (Schneider *et al* 1990). Half of the samples were shaped into a 'dog-bone' shape with a 8 × 4 mm centre portion of 50 mm long, 25 mm of which would be the extensiometer gauge length. The other half of the samples was treated with polymer and then shaped. After that each sample was filled in the gauge length region (30 mm at specimen centre) with a fine, flat file to ensure an uniform rectangular cross section in the gauge length. Sample widths and thickness were

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measured at three places in the gauge length of each specimen and the values averaged to obtain cross-sectional area. Bending test samples were cut into blocks of 10 × 1 × 1 cm.

2.2b *Impregnation procedure*: All samples were oven dried to constant weight of 105°C and the dimensions and weights were then measured. Samples were then placed into an impregnation chamber, which was evacuated to two ranges of vacuums 5″ Hg and 10″ Hg, respectively for five min. Some loads were applied on the samples before impregnation so that no flotation occurs. The appropriate monomer system was then introduced through a dropping funnel and the specimens were left immersed while atmospheric pressure was reached and then allowed for 4 h at room temperature for further impregnation. The samples were then taken out from the chamber and excess chemicals were wiped out from the surfaces. Specimens were then wrapped in Al foils and cured at 90°C for 24 h. The samples were again oven dried at 105°C for 24 h. The treated samples were then extracted with benzene to remove the homo polymers. The specimens were then dried and measured to determine polymer loading.

3. Measurements

3.1 *Dimensional stability and water absorption tests*

Dimensional stability of the samples were measured by measuring the volumetric swelling of the samples after placing in a water bath for 24 h at room temperature and chemical resistance test of the samples by the same procedure in 4% NaOH and CH_3COOH (glacial), respectively.

Water absorption test was measured by measuring the weights increased after 24 h dipping in a water bath.

Volumetric swelling was considered as change in volume expressed as percentage of the volume of the dry heated specimen.

3.2 *Mechanical properties*

3.2a *Hardness*: Hardness was measured in a Durometer (Hiroshima) measured according to ASTM D2240 method expressed as ShoreD hardness.

3.2b *Tensile strength*: Tensile strength was measured in Zwick Testing machine (Z010 model) with a crosshead speed of 2 mm/min.

3.2c *Bending test*: Bending test was performed in Zwick Testing machine (Z010 model) according to ASTM D790 with a crosshead speed of 2 mm/min.

3.2d *FTIR*: IR study was performed using a Nicolet FTIR spectrophotometer (Impact 410) using KBr pellets.

3.2e *DSC*: DSC study was carried out by using a DSC analyser with Mettler Toledo Star system under N_2 atmosphere at initial scan from 50°C to 150°C to remove the thermal history effects, then cooled to 50°C and the data collected at 10°C/min to 225°C. Typical sample size was 6·5 mg.

4. Results and discussion

4.1 *Effect of variation of vacuum*

The percentage of polymer loading was checked at two levels of vacuum i.e. 5″ Hg and 10″ Hg (table 1). Polymer loading was found better at 5″ Hg. Therefore, all the successive experiments were performed at that level of vacuum.

4.2 *Variation of catalyst concentration and concentration of monomers*

Table 2 shows the results of variation of monomer concentration and catalyst concentration. Wood–styrene–GMA combination showed better results (higher polymer loading) compared to wood–styrene system, while wood–GMA system showed highest loading. This might be due to increased interaction of GMA with styrene and wood

Table 1. Effect of variation of vacuum on polymer loading (%) (catalyst (AIBN) with 0·5% concentration) on rubber wood.

Sample particulars (ratio)		Vacuum* (Hg)	
Styrene	GMA	5″	10″
100	20	49·82	35·0
100	0	33·28	–
0	100	93·0	–

*All the data were taken from average of five samples.

Table 2. Variation of styrene/GMA and catalyst concentration on polymer loading (%) (vacuum: 5″ Hg).

Sample particulars			Catalyst concentration* (by weight)		
Wood	Styrene	GMA	0·5	2	5
	100	0	33·28	–	–
	100	20	49·82	15·33	21·22
	0	100	93·0	–	–

*All values were taken from average of five samples.

Table 3. Effect of polymer loading on various properties of rubber wood.

Properties	Untreated	Treated with styrene (0·5% cat)	Treated with styrene–GMA (% catalyst) 0·5%	2%	3%
Loading	–	33·28	49·82	15·86	21·15
Hardness	46·57	61·98	61·5	60·34	65·98
% Volume increase after dipping in water (24 h)	10·65	6·13	7·83	–	10·33
Water absorbed (after 24 h dipping)	66·67	37·28	20·0	53·13	40·48
% Swelling (after 24 h dipping) in					
I. Acetic acid (glacial)	6·07	12·97	3·38	8·86	13·48
II. 4% NaOH	8·45	15·73	4·35	5·34	8·08

Table 4. Mechanical properties of treated rubber wood.

Sample parameters	Nature of test	*E*-modulus (MPa)	F_{max} (MPa)	Deflection at F_{max} (%)	RB (MPa)	Break load (MPa)	Tensile stress (MPa)
Untreated	Bending	2816·43	60·13	1·57	–	60·13	–
Styrene	"	6718·49	97·91	1·32	–	97·91	–
Styrene–GMA	"	7140·93	104·01	1·48	–	104·01	–
Untreated	Tensile	2252·59	57·12	–	57·12	–	57·12

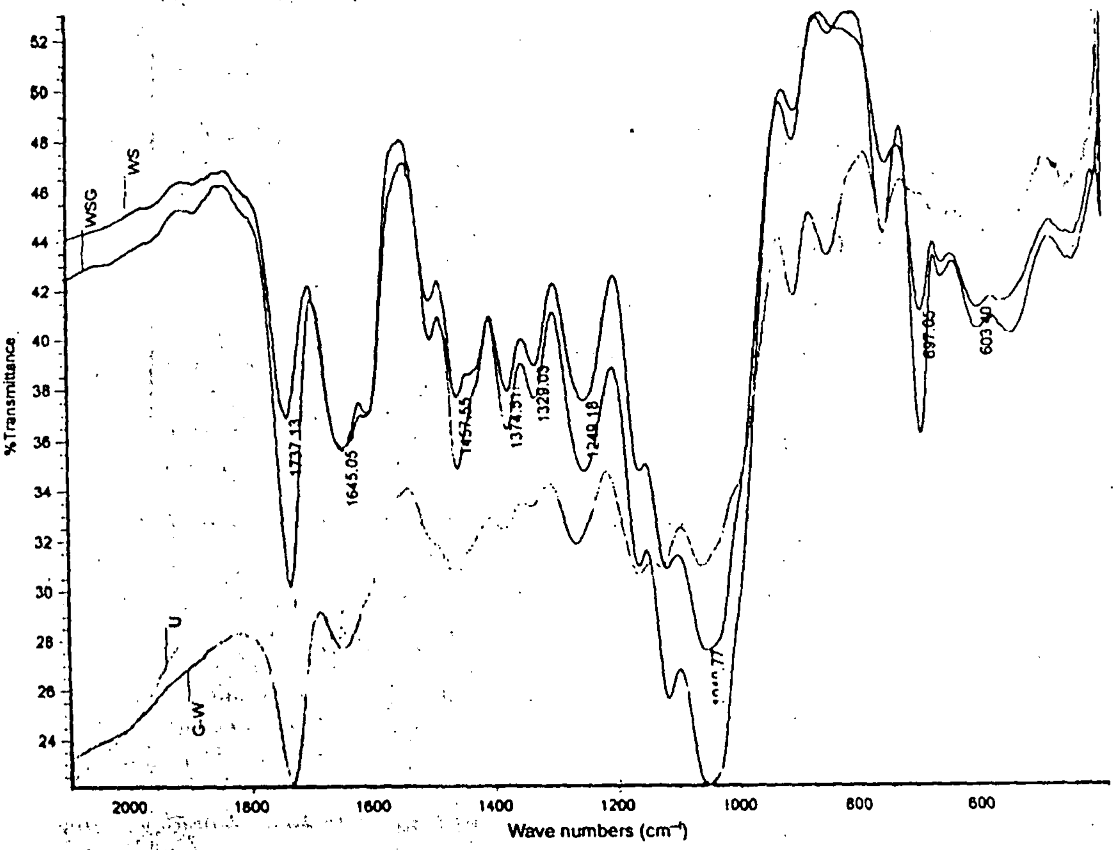

Figure 1. IR spectra of U, untreated; GW, GMA treated; WSG, styrene–GMA treated and WS, styrene treated rubber wood.

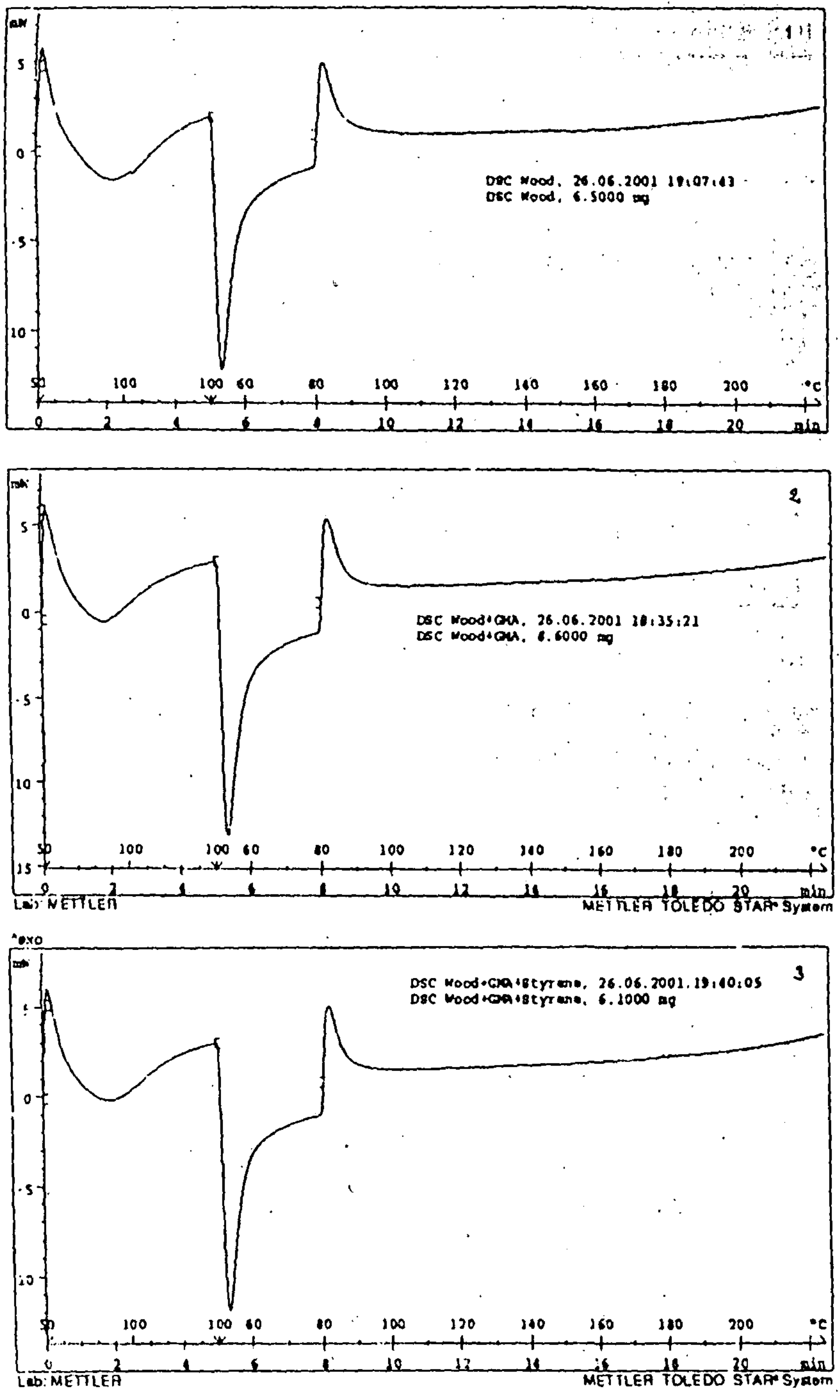

Figure 2. The DSC results of the 1. untreated, 2. GMA treated and 3. styrene–GMA treated wood.

through the epoxy group and the double bond. Loading was found to be decreased initially on increasing catalyst concentration, but again increased on further increase of catalyst concentration.

4.3 *Effect of polymer loading on various properties of rubber wood*

Different physical parameters of some of the selected polymer loaded samples are shown in table 3. All the samples were found to be more or less better compared to those of either untreated wood or styrene treated wood. Water absorption was found to be decreased remarkably for wood–styrene–GMA system. The results showed that styrene alone was not able to penetrate properly into the cell wall. But in combination with GMA it was able to penetrate into the cell wall more as compared to styrene due to the advantageous molecular size (Rozman *et al* 1995).

4.4 *Mechanical properties*

Table 4 shows the mechanical properties of rubber wood (untreated and treated ones). The properties were found to be improved after impregnation. Modulus of elasticity, F_{max}, was found to be increased for styrene–GMA treated one compared to untreated or styrene treated one (bending strength). Tensile strength of the untreated samples is shown in table 4.

4.5 *IR study*

Figure 1 shows the results of the IR-analysis of treated and untreated wood. Interaction between wood–styrene–GMA was also confirmed by FTIR spectroscopy (Rozman *et al* 1997; Pandey 1999) which showed an enhanced peak at 1733 cm^{-1} in the carbonyl region after the reaction with GMA. The peak (around 1457 cm^{-1}) which may be due to C–H deformation (methyl and methylene) was found to increase in the case of styrene–GMA treated samples compared to untreated or styrene treated samples. But the peak at 1429 cm^{-1} which is due to C–H plane deformation with aromatic ring stretching was found to decrease as one passes from untreated wood to styrene treated one and further decreased to styrene–GMA treated wood. The peak around 1610 cm^{-1}, which is due to aromatic skeletal vibration and carbonyl stretching, was found to be more pronounced in the case of styrene–GMA treated samples and styrene treated one compared to that of untreated one.

4.6 *DSC study*

Figure 2 shows the DSC results of the treated and untreated wood. DSC results showed no distinct phase change of the treated samples. If there were chemical bonding, some phase change may occur, which however, cannot on the basis of these data, conclude that there is no chemical bonding between wood–styrene–GMA. Similar findings were reported by Simonsen *et al*.

5. Conclusion

From the results it can be concluded that wood–styrene–GMA combination shows better performance in terms of mechanical and other properties compared to those of either untreated or wood–styrene combination. Although DSC results did not give any significant results, but the interaction between wood, GMA and styrene was confirmed by the IR results. Further investigation will reveal the picture clearly.

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4. In determination of LOI (N_2+ O_2), 300cc is the total volume of (N_2+ O_2) applied where volume of nitrogen was kept at a maximum value and volume of oxygen kept at minimum value.

5. In page 62, table 4.1.1. Void volume= 0.64 is the fractional void volume calculated according to the formula given in the paragraph 3.3 (Page No 53). It is expressed in percentage.

6. In page 63, paragraph 6.1.1.3, last line, hardness and..... 61.5(Shore D).

7. Vaccum was applied from 1-15 inches of Hg which is equivalent to 25.4- 381 mm of Hg.

8. As suggested in table 4.1.6 a value for styrene-GMA (0:1) cannot be put, as GMA was incorporated as a crosslinking monomer with styrene and the concentration of styrene-GMA was varied from 1:0 to 1:1. Some initial impregnation was carried out to see the effect of only GMA on wood. WPG was found to be 93%. Water absorption decreased to 5.0% after 24h immersion in distilled water and hardness increased to 73 (ShoreD). These observations showed the increasing trend of improvement in wood polymer composites. Similarly FT-IR and DSC study were done to see the interaction Moreover, GMA is costlier than styrene and was used as crosslinking monomer and so successive experiments were not performed by using GMA only.

9. As suggested in page no 98, Fig 4.2.1, only GMA treated results could not be incorporated. The reason is similar as given in the above (answer no 8).

31.03.2016

Corrigendum

1. Chapter I : References are to be inserted in text as follows

Page No.	Line	Reference
1	3, ……uses.	[1]
2	2, …….(fig 1.2.1).	[2]
2	22, ……(fig1.2.2.).	[2]
4	7, ……hardwood.	[2]
7	4, ……transport.	[2]
10	8, ……lignin.	[3-6]
15	4, …….solid	[4]
15	18, ……strength etc.	[7-9]
17	5, …… New Zealand.	[2,10,11]

2. In page 52, line 4 under para 3.2.5, "Vacuum (25.4-381 mm Hg) was applied".

3. Void volume Vv = 1- $S_0/1.50$ *

Where Solid volume= $S_0/1.50$

Specific gravity of the oven dry species= Density of the wood/ Density of water= S_0

Specific gravity of oven dry wood substance, i.e the maximum density of a completely solid wood specimen devoid of pores = 1.50.

Void volume is expressed as percentage.

* As per the calculation given in Wood Moisture Calculations by C.A.Eckelman (http// www.ces.purdue.edu/extmedia/FNR/FNR-156.html)

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