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Md Rezaur Rahman

# Wood Polymer Nanocomposites

Chemical Modifications, Properties  
and Sustainable Applications

 Springer

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Chemical Modifications, Properties  
and Sustainable Applications

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# Preface

Recently, nanoclay-dispersed polymeric materials exhibit better utilization in diverse applications. The nanoclay as inorganic fillers consequences from the exfoliation or the dispersion at nanoscale into polymeric matrices, which enhance the improvement of nanocomposites properties by adding slight amounts of clay due to the high specific area. Current studies reported about Wood Polymer Nanocomposites-Chemical Modifications, Properties, and Sustainable Applications, which demonstrated better mechanical and thermal properties as compared to nanoclay-reinforced polymer composites. The proposed book is focused on chemically dispersed nanoclay-impregnated wood polymer nanocomposites properties and applications. It will also include the introduction and reinforcing potential various clay and monomers dispersed wood nanocomposites. The readers will find complete information about preparation and characterizations of various clay and monomers dispersed wood nanocomposites, combined styrene/mma/nanoclay crosslinker effect, oxidation of wood species by phenyl hydrazine, *N,N*-dimethylacetamid impregnation, urea formaldehyde impregnation, epoxy/nanoclay impregnation, nanoclay/phenol formaldehyde resin impregnation, clay-dispersed styrene-co-glycidyl methacrylate impregnation, styrene-co-ethylene glycol dimethacrylate impregnation, styrene-co-3-(trimethoxysilyl)propyl methacrylate with clay impregnation, acrylonitrile/butyl methacrylate/halloysite nanoclay impregnation, furfuryl alcohol-co-glycidyl methacrylate/nanoclay impregnation, furfuryl alcohol-co-ethyl methacrylate-impregnated wood polymer nanocomposites, and sustainable application of various monomer/clay-dispersed wood polymer nanocomposites. I am thankful to all co-authors who contributed book chapters and provided their valuable ideas and knowledge to this edited book. I attempt to gather all the information of co-authors from same fields in chemically modified nanoclay-dispersed nanocomposites and finally produce this project that will hopefully become a success. I impressively appreciate co-authors' support to formulating ours idea in reality. I thank Springer International Publishing AG, Gewerbestrasse 11, 6330 Cham, Switzerland, team for their substantial cooperation at every stage of the book production.

Kota Samarahan, Malaysia

Md Rezaur Rahman

# Contents

<b>Introduction to Reinforcing Potential of Various Clay and Monomers Dispersed Wood Nanocomposites'</b> .....	1
M.R. Rahman and J.C.H. Lai	
1 Introduction .....	1
2 Problem Statement .....	3
3 Literature Review .....	4
3.1 Enhancement of Wood Quality .....	4
3.2 Modern Policies to Growth Wood Quality .....	5
3.3 Chemical Modification of Wood .....	6
3.4 Wood Modifications by Impregnation Technique .....	12
3.5 Wood Impregnated by Inorganic Substance .....	19
4 Summary .....	29
References .....	30
<b>Preparation and Characterizations of Various Clay- and Monomers-Dispersed Wood Nanocomposites</b> .....	37
M.R. Rahman and S. Hamdan	
1 Overview .....	37
2 Methods Related for Wood Polymer Nanocomposites (WPNC) .....	38
2.1 Curing Methods for Wood Polymer Nanocomposites (WPNC) Preparation .....	38
2.2 Wood-Hardening Process .....	39
2.3 Monomer and Polymer Treatments .....	40
2.4 Other Treatments .....	43
2.5 Combination of Two or Three Monomers .....	43
2.6 Chemical Impregnation and Compression of Wood .....	43
2.7 Summary of Wood Quality Improvement Methods and Technologies .....	44

3	Methods . . . . .	45
3.1	Flowchart of Project . . . . .	47
3.2	Preparation of WPNCs . . . . .	47
3.3	Characterization of Wood Polymer Nanocomposites (WPNC) . . . . .	48
4	Summary . . . . .	64
	References . . . . .	65
	<b>Combined Styrene/MMA/Nanoclay Crosslinker Effect on Wood Polymer Nanocomposites (WPNCs)</b> . . . . .	69
	M.R. Rahman and J.C.H. Lai	
1	Introduction . . . . .	69
2	Experimental . . . . .	70
2.1	Materials . . . . .	70
2.2	Preparation of Monomers . . . . .	71
2.3	Impregnation of Wood Specimens/Co-polymerization Reaction with Cellulose in Wood Cell . . . . .	71
2.4	Microstructural Characterizations . . . . .	72
3	Results and Discussion . . . . .	73
3.1	Weight Percent Gain (WPG %) . . . . .	73
3.2	Fourier Transform Infrared Spectroscopy (FT-IR) . . . . .	74
3.3	Mechanical Properties Test . . . . .	74
3.4	Thermogravimetric Analysis (TGA) . . . . .	76
3.5	Scanning Electron Microscopy (SEM) Analysis . . . . .	77
4	Conclusion . . . . .	78
	References . . . . .	79
	<b>Oxidation of Wood Species by Sodium Metaperiodate and Impregnation with Phenyl Hydrazine</b> . . . . .	81
	M.R. Rahman	
1	Introduction . . . . .	81
2	Experimental . . . . .	83
2.1	Materials . . . . .	83
2.2	Specimen Preparation . . . . .	83
2.3	Microstructural Characterizations . . . . .	83
3	Results and Discussion . . . . .	87
3.1	Fourier Transform Infrared Spectroscopy (FT-IR) . . . . .	87
3.2	Storage Modulus ( $\log E'$ ) and Loss Tangent ( $\tan \delta$ ) of Raw Wood, WPNC, and PTWPNC . . . . .	88
3.3	Dynamic Young's Modulus of Raw Wood, WPNC, and PTWPNC . . . . .	90
3.4	MOE and MOR Measurement . . . . .	92
3.5	Static Young's Modulus ( $E$ ) Measurement . . . . .	95
3.6	Fungal Decay Resistance Test . . . . .	95



3.7 Water Uptake . . . . . 97  
 3.8 Scanning Electron Microscopy (SEM) Analysis . . . . . 98  
 4 Conclusion . . . . . 99  
 References . . . . . 101

**Characterization of *N,N*-Dimethylacetamide Impregnated Wood Polymer Nanocomposites (WPNCs)** . . . . . 103

M.R. Rahman  
 1 Introduction . . . . . 103  
 2 Materials and Methods . . . . . 104  
     2.1 Materials . . . . . 104  
     2.2 Manufacturing of Wood Polymer Nanocomposites . . . . . 104  
     2.3 Microstructural Characterizations . . . . . 105  
 3 Results and Discussion . . . . . 108  
     3.1 Fourier Transform Infrared Spectroscopy (FT-IR) . . . . . 108  
     3.2 Thermogravimetric Analysis (TGA) . . . . . 109  
     3.3 Differential Scanning Calorimetry (DSC) . . . . . 111  
     3.4 Dynamic Young’s Modulus . . . . . 114  
     3.5 MOE and MOR Measurement . . . . . 115  
     3.6 Static Young’s Modulus (*E*) . . . . . 117  
     3.7 X-ray Diffraction (XRD) . . . . . 117  
     3.8 Scanning Electron Microscopy (SEM) . . . . . 119  
 4 Conclusion . . . . . 120  
 References . . . . . 120

**Mechanical and Thermal Characterization of Urea-Formaldehyde Impregnated Wood Polymer Nanocomposites (WPNCs)** . . . . . 123

M.R. Rahman  
 1 Introduction . . . . . 123  
 2 Materials and Methods . . . . . 124  
     2.1 Materials . . . . . 124  
     2.2 Manufacturing of Wood Polymer Nanocomposites . . . . . 125  
     2.3 Microstructural Characterizations . . . . . 125  
 3 Result and Discussion . . . . . 125  
     3.1 FT-IR . . . . . 125  
     3.2 TGA . . . . . 126  
     3.3 DSC . . . . . 127  
     3.4 Dynamic Young’s Modulus Measurement . . . . . 130  
     3.5 MOE and MOR Measurement . . . . . 130  
     3.6 Static Young’s Modulus (*E*) Measurement . . . . . 133  
     3.7 XRD Analysis . . . . . 134  
     3.8 SEM . . . . . 134  
 4 Conclusion . . . . . 135  
 References . . . . . 136

<b>Characterization of Epoxy/Nanoclay Wood Polymer Nanocomposites (WPNCs)</b> .....	137
M.R. Rahman	
1 Introduction .....	137
2 Materials and Methods .....	138
2.1 Materials .....	138
2.2 Preparation of Solution Through Impregnation .....	139
2.3 Manufacturing of Wood Polymer Nanocomposites .....	139
3 Result and Discussion .....	139
3.1 Fourier Transform Infrared Spectroscopy (FT-IR) Analysis .....	139
3.2 Thermogravimetric Analysis (TGA) .....	141
3.3 Dynamic Young's Modulus Measurement .....	141
3.4 Modulus of Elasticity (MOE) and Modulus of Rupture (MOR) Measurement .....	143
3.5 Static Young's Modulus ( <i>E</i> ) Measurement .....	146
3.6 X-ray Diffraction (XRD) Analysis .....	146
3.7 Scanning Electron Microscopy (SEM) Analysis .....	147
4 Conclusion .....	148
References .....	149
<b>Influence of Nanoclay/Phenol Formaldehyde Resin on Wood Polymer Nanocomposites</b> .....	151
M.R. Rahman	
1 Introduction .....	151
2 Materials and Methods .....	152
2.1 Materials .....	152
2.2 Impregnation Solutions Preparation .....	152
2.3 Fabrication of Wood Polymer Nanocomposites (WPNCs) .....	153
3 Result and Discussion .....	153
3.1 Fourier Transform Infrared Spectroscopy Analysis .....	153
3.2 Thermogravimetric Analysis .....	155
3.3 Dynamic Young's Modulus Measurement .....	156
3.4 Modulus of Elasticity and Modulus of Rupture Measurement .....	157
3.5 Static Young's Modulus Measurement .....	159
3.6 X-ray Diffraction Analysis .....	160
3.7 Scanning Electron Microscopy Analysis .....	162
4 Conclusion .....	162
References .....	163
<b>Clay Dispersed Styrene-<i>co</i>-glycidyl Methacrylate Impregnated Kumpang Wood Polymer Nanocomposites: Impact on Mechanical and Morphological Properties</b> .....	165
M.R. Rahman, S. Hamdan and J.C.H. Lai	
1 Introduction .....	165
2 Experimental .....	168

- 2.1 Materials . . . . . 168
- 2.2 Specimen Preparation . . . . . 168
- 2.3 Preparation of Wood Polymer Nanocomposites (WPNCs) . . . . . 168
- 2.4 Microstructural Characterizations . . . . . 169
- 3 Results and Discussion. . . . . 170
  - 3.1 Fourier Transform Infrared Spectroscopy (FT-IR). . . . . 170
  - 3.2 Modulus of Rupture (MOR), Modulus of Elasticity (MOE) and Dynamic Young’s Modulus ( $E_d$ ) Measurements . . . . . 172
  - 3.3 Weight Percentage Gain (WPG) and Water Uptake (WU) . . . . . 173
  - 3.4 Scanning Electron Microscopy (SEM) . . . . . 174
- 4 Conclusion . . . . . 175
- References . . . . . 176

**Physico-mechanical, Morphological, and Thermal Properties of Clay Dispersed Styrene-co-Maleic Acid Impregnated Wood Polymer Nanocomposites. . . . . 179**

M.R. Rahman, S. Hamdan and J.C.H. Lai

- 1 Introduction . . . . . 179
- 2 Experimental . . . . . 181
  - 2.1 Materials . . . . . 181
  - 2.2 Specimen Preparation . . . . . 181
  - 2.3 Preparation of Wood Polymer Nanocomposites (WPNCs) . . . . . 182
  - 2.4 Microstructural Characterizations . . . . . 182
- 3 Results and Discussion. . . . . 185
  - 3.1 FT-IR . . . . . 185
  - 3.2 Scanning Electron Microscopy (SEM) . . . . . 187
  - 3.3 MOR, MOE, and  $E_d$ . . . . . 188
  - 3.4 Weight Percentage Gain (WPG) and Water Uptake (WU) . . . . . 190
  - 3.5 Thermogravimetric Analysis (TGA) . . . . . 191
  - 3.6 Differential Scanning Calorimetry (DSC) . . . . . 193
- 4 Conclusion . . . . . 194
- References . . . . . 194

**Preparation and Characterizations of Clay-Dispersed Styrene-co-Ethylene Glycol Dimethacrylate-Impregnated Wood Polymer Nanocomposites. . . . . 199**

M.R. Rahman, S. Hamdan and J.C.H. Lai

- 1 Introduction . . . . . 200
- 2 Experimental . . . . . 201
  - 2.1 Materials . . . . . 201
  - 2.2 Specimen Preparation . . . . . 202
  - 2.3 Preparation of Wood Polymer Nanocomposites (WPNCs) . . . . . 202
  - 2.4 Microstructural Characterizations . . . . . 202

3	Results and Discussion . . . . .	205
3.1	FT-IR . . . . .	205
3.2	X-Ray Diffraction (XRD) Analysis . . . . .	206
3.3	Scanning Electron Microscopy (SEM) . . . . .	207
3.4	Modulus of Rupture (MOR), Modulus of Elasticity (MOE), and Dynamic Young's Modulus ( $E_d$ ) Measurements . . . . .	209
3.5	Weight Percentage Gain (WPG) and Water Uptake (WU) . . . . .	210
3.6	Thermogravimetric Analysis (TGA) . . . . .	211
3.7	Differential Scanning Calorimetry (DSC) . . . . .	213
4	Conclusion . . . . .	214
	References . . . . .	215

**Physico-Mechanical, Thermal, and Morphological Properties of  
Styrene-co-3-(Trimethoxysilyl)Propyl Methacrylate with Clay**

	<b>Impregnated Wood Polymer Nanocomposites . . . . .</b>	<b>219</b>
--	--	------------

M.R. Rahman, S. Hamdan and J.C.H. Lai

1	Introduction . . . . .	219
2	Experimental . . . . .	221
2.1	Materials . . . . .	221
2.2	Specimen Preparation . . . . .	221
2.3	Preparation of Wood Polymer Nanocomposites . . . . .	222
2.4	Characterizations . . . . .	222
3	Results and Discussion . . . . .	225
3.1	Fourier Transform Infrared Spectroscopy (FT-IR) Analysis . . . . .	225
3.2	X-ray Diffraction (XRD) Analysis . . . . .	225
3.3	Scanning Electron Microscopy (SEM) . . . . .	228
3.4	MOR, MOE, and Ed. . . . .	229
3.5	Weight Percentage Gain (WPG) and Water Uptake (WU) . . . . .	230
3.6	Thermogravimetric Analysis (TGA) . . . . .	230
4	Conclusion . . . . .	233
	References . . . . .	234

**Acrylonitrile/Butyl Methacrylate/Halloysite Nanoclay Impregnated  
Sindora Wood Polymer Nanocomposites (WPNCs): Physico-  
mechanical, Morphological and Thermal Properties**

	<b>. . . . .</b>	<b>237</b>
--	------------------	------------

M.R. Rahman, J.C.H. Lai and S. Hamdan

1	Introduction . . . . .	238
2	Experimental . . . . .	239
2.1	Materials . . . . .	239
2.2	Preparation of Acrylonitrile/Butyl Methacrylate/Halloysite Nanoclay Wood Polymer Nanocomposites (AN-co-BMA-HNC WPNCs) . . . . .	239
2.3	Impregnation of AN-co-BMA-HNC WPNCs . . . . .	240
2.4	Microstructural Characterizations . . . . .	240

3	Results and Discussion . . . . .	243
3.1	Weight Percent Gain (WPG %) . . . . .	243
3.2	Fourier Transform Infrared Spectroscopy (FT-IR) . . . . .	243
3.3	Scanning Electron Microscopy (SEM) Analysis . . . . .	245
3.4	Three-Point Flexural Test . . . . .	246
3.5	Dynamic Mechanical Thermal Analysis (DMTA) . . . . .	246
3.6	Thermogravimetric Analysis (TGA) . . . . .	249
3.7	Differential Scanning Calorimetry (DSC) Analysis . . . . .	252
3.8	Moisture Absorption Analysis . . . . .	252
4	Conclusion . . . . .	253
	References . . . . .	254

**Studies on the Physical, Mechanical, Thermal and Morphological Properties of Impregnated Furfuryl Alcohol-co-Glycidyl Methacrylate/Nanoclay Wood Polymer Nanocomposites** . . . . .

M.R. Rahman, J.C.H. Lai and S. Hamdan . . . . . 257

1	Introduction . . . . .	258
2	Experimental . . . . .	259
2.1	Materials . . . . .	259
2.2	Preparation of Furfuryl Alcohol/Glycidyl Methacrylate/ Halloysite Nanoclay Wood Nanocomposites (WPNCs) (FA-co-GMA-HNC WPNCs) . . . . .	259
2.3	Impregnation of FA-co-GMA-HNC WPNCs . . . . .	260
2.4	Microstructural Characterizations . . . . .	260
3	Results and Discussion . . . . .	262
3.1	Weight Percent Gain (WPG %) . . . . .	262
3.2	Fourier Transform Infrared Spectroscopy (FT-IR) . . . . .	263
3.3	Scanning Electron Microscopy (SEM) Analysis . . . . .	263
3.4	Three-Point Flexural Test . . . . .	264
3.5	Dynamic Mechanical Thermal Analysis (DMTA) . . . . .	267
3.6	Thermogravimetric Analysis (TGA) . . . . .	269
3.7	Differential Scanning Calorimetry (DSC) Analysis . . . . .	270
3.8	Moisture Absorption Analysis . . . . .	272
4	Conclusion . . . . .	273
	References . . . . .	273

**Nanoclay Dispersed Furfuryl Alcohol-co-Ethyl Methacrylate Wood Polymer Nanocomposites: The Enhancement on Physico-mechanical and Thermal Properties** . . . . .

M.R. Rahman, J.C.H. Lai and S. Hamdan . . . . . 275

1	Introduction . . . . .	276
2	Experimental . . . . .	277
2.1	Materials . . . . .	277
2.2	Methods . . . . .	277
2.3	Microstructural Characterizations . . . . .	278

3	Results and Discussion . . . . .	280
3.1	Weight Percent Gain (WPG %) . . . . .	280
3.2	Fourier Transform Infrared Spectroscopy (FT-IR) . . . . .	280
3.3	Scanning Electron Microscopy (SEM) Analysis . . . . .	282
3.4	Three-Point Flexural Test . . . . .	284
3.5	Dynamic Mechanical Thermal Analysis (DMTA) . . . . .	285
3.6	Thermogravimetric Analysis (TGA) . . . . .	287
3.7	Differential Scanning Calorimetry (DSC) Analysis . . . . .	288
3.8	Moisture Absorption Analysis . . . . .	290
4	Conclusion . . . . .	291
	References . . . . .	291
	<b>Sustainable Application of Various Monomer/Clay Dispersed Wood Polymer Nanocomposites . . . . .</b>	<b>295</b>
	M.R. Rahman, S. Hamdan and J.C.H. Lai	
1	Introduction . . . . .	295
2	Experimental . . . . .	298
2.1	Materials . . . . .	298
2.2	Preparation of ST- <i>co</i> -MMM-Nanoclay . . . . .	299
2.3	Impregnation of Wood Specimens with ST- <i>co</i> -MMM-Nanoclay . . . . .	300
2.4	Specimen Preparation . . . . .	300
2.5	Preparation of Different WPNCs and WPCs . . . . .	301
2.6	Decay Tests for Wood Specimens with ST- <i>co</i> -MMM-Nanoclay . . . . .	301
2.7	Laboratory Fungal Decay Resistance Test for WPCs and WPNC . . . . .	301
3	Results and Discussion . . . . .	303
3.1	Decay Test for Wood Specimens with ST- <i>co</i> -MMM-Nanoclay . . . . .	303
3.2	Decay Resistance of Styrene- <i>co</i> -3-(Trimethoxysilyl) Propyl Methacrylate with Clay Impregnated Wood Polymer Nanocomposites . . . . .	305
3.3	Investigation of Decay Resistance Properties of Clay Dispersed Styrene- <i>co</i> -Ethylene Glycol Dimethacrylate Impregnated Wood Polymer Nanocomposites . . . . .	307
3.4	Clay Dispersed Styrene- <i>co</i> -Maleic Acid Impregnated Wood Polymer Nanocomposites: Impact on Decay Resistance Properties . . . . .	308
3.5	Clay Dispersed Styrene- <i>co</i> -Glycidyl Ethacrylate Impregnated Wood Polymer Nanocomposites: Impact on Decay Resistance Properties . . . . .	309

3.6	Decay Resistance Characterization of Wood Polymer Composites Impregnated by 4-Methyl Catechol at Various pH Levels . . . . .	310
4	Conclusion . . . . .	311
	References . . . . .	311

# Introduction to Reinforcing Potential of Various Clay and Monomers Dispersed Wood Nanocomposites'

M.R. Rahman and J.C.H. Lai

**Abstract** In this chapter, various clay and monomer were introduce to produce high strength wood polymer nanocomposites and discussed how they play important role on nonocomposites to enhance their properties. Low-quality wood can be modified through suitable chemical treatments to improve the physical, mechanical, and thermal properties to meet specific end-use requirements. The in situ polymerization is one of the most popular technique to modified and produce wood polymer nanocomposites. Some common chemical treatments have proven to be effective in improving wood hardness, dimensional stability, stiffness, fire resistance, UV resistance, biological resistance, and aesthetic appeal. Due the further improvement, dual monomer mixture along with reinforcing filler was significant improve the physical, mechanical, thermal, hardness, dimensional stability, stiffness, fire resistance, UV resistance, and biological resistance. The various monomers were used, namely styrene, methyl methacrylate, phenol formaldehyde, phenolic resins, urea formaldehyde, and melamine formaldehyde. However, monomer impregnation and chemical modification were also investigated using new chemical formulations in the present study.

**Keywords** Mechanical properties · Stability · Chemical treatment · Wood polymer nanocomposites

## 1 Introduction

Wood is a natural resource and one of the most attractive materials because of its multidimensional assembly and its extensive exhibition on globe. Wood is made up of cellulose, hemicellulose, and lignin to make their multifaceted structures which are biologically originated (Bowyer et al. 2007). The chemically modified or monomer incorporation of three cell wall polymer can be changed the

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physico-mechanical, thermal, and chemical properties of wood (Rowell 2005). The performance of the modified wood would be changed due to the modification or monomer incorporation in the wood cell wall. The main objective of chemical modification or monomer impregnation of wood is to revolute its properties and to increase its performance.

Wood has a diversity of completion uses such as construction, furniture, and tools due to its gorgeous features. Solid wood is the greatest desired one for the building and construction material due to its high-physical strength, low-processing cost, and attractive desirability. Researchers are motivated and produced to hunt for substitute resources, such as softwood and some low-density hardwoods, for value-added application due to a deficiency of high-quality hardwoods. In Malaysia, especially Borneo Island has abundantly available softwood and low-density hardwood. To accomplish this objective, appropriate technologies are desired to enhance the wood quality such as mechanical properties, thermal properties, durability, decay resistance, and hardness, and to satisfy specific end-use necessities.

The biodegradability and high-moisture uptake have negative impact on the wood materials if handled incorrectly. Various defects could be ascribed the chemical assembly and some functional features in wood (Rowell et al. 1982). Besides, the main drawback and limitation of the wood is deteriorated by environmental variation which impacts on its physical and mechanical properties (Galperin et al. 1995; Hill 2006). Chemically, wood contains plentiful reactive sites. The most common responsive sites are the hydroxyl groups, which are abundantly available in the three major chemical components of wood, i.e., cellulose, hemicellulose, and lignin. These OH groups absorb humidity from humid environments, which then fluctuate the physical properties of wood. Dynamic humidity conditions effect in alternate swelling and in physical degradation of wood. The moisture absorption easily changes the mechanical properties of wood due to its hydrogen bonding (Kumar 1994). On the other hand, wood is an amorphous material. The porosity of both cell voids and micro pores in the cell walls occurs due its structure. The main paths for the moisture movement in wood are cell cavities. (Schneider 1994). The chemical modification and monomer impregnation were enhanced mechanical, thermal as well as biodegradation properties and to resist the changes in moisture content. The reactive chemicals and polymer could be the blockage of these reactive sites or plugging the pores of wood cell wall.

Many scientists have made boundless efforts to strengthen solid wood with single monomer, dual monomer, and polymers in the past decades. Both thermoplastic and thermosetting polymer systems have been introducing to strengthen the solid wood (Ayer et al. 2003; Schneider 1994). It is obvious that the production of wood polymer composites (WPC) is a favorable approach to improved wood properties. Impregnation method or technique is the most collective and cheap technique to prepare wood polymer composites with a polymeric monomer or prepolymer. This technique easily can fill the empty lumens in the wood by polymers or monomer. This leads to a mixture of two materials of the wood and polymer rather than a true composite.

Wood polymer composites have the capability to transmit energy efficiently from the polymer matrix to the inflexible cellulose constituent. Polymer and the wood cell wall interaction and chemical bonding that will improve polymers performing an active role in the composite. The strong interaction of wood cell wall and polymer resulted in mechanical strength, thermal stability, and resistance to decay, and degradation of wood. It has been observed that wood impregnated with thermosetting resins such as water-soluble phenolic resin, urea formaldehyde, and melamine formaldehyde prepolymers, increases its compressive strength and moisture related behaviors. The thermosetting resins impregnation polymerizes bulks of the cell wall and reacts with hydroxyl groups of wood constituents to prevent the shrinkage of the wood upon drying. But in most cases, the resulting wood polymer composites are quite stiff of the original wood due to the thermosetting polymer impregnation (Deka and Saikia 2000).

Organophilic layered silicates introduce in situ nanoreinforcement technique to manufacturing the nanocomposite. The various thermoplastic and thermoset nanocomposites at small silicate content have been enhanced the physical properties, flexural modulus and strength, static Young's modulus, and thermal stability (Ray and Okamoto 2003). Polymer-clay nanocomposites were first reported in the literature as early as 1961 (Blumstein 1961). Polymer/layered silicate nanocomposites were first used in industrial materials by researchers from Toyota based on the thermoplastic polyamide 6 (Usuki et al. 1993a, b). Since then, a great deal of research has been carried out in the field of polymer nanocomposites with various thermoplastic and thermoset polymers over the past decade (Ray and Okamoto 2003).

In this study, conventional and nanotechnology have been introduced on the selective tropical wood species. According to the literature finding, there was no work on tropical wood species with selective chemicals. Taking into account of all these observations and to overcome the above-mentioned problems, the nanotechnology technique and several kinds of chemicals modification have been considered in this study.

## 2 Problem Statement

Wood has many necessary features for a diversity of end uses such as furniture, building materials, and tools. A lack of high-quality hardwoods has driven researchers and manufactures to search for substitute resources, such as softwood and some low-density hardwood, for significant application. In addition, the dwindling supplies and rising costs of the heavy hardwoods have made attention in the consumption of lower quality woods such as tropical light hardwoods, whose usage can be prolonged by transforming into wood polymer composites. Low-quality wood can be treated through appropriate chemical treatments to improve their properties such as

physical, mechanical, and thermal properties to meet specific end-use requirements. In addition, low quality of wood properties will be better than hardwoods after the chemical modification of them.

The wood hardness, durability, dimensional stability, and mechanical properties will be improved by chemical treatments. However, it has been established that most of the chemicals or monomer does not react or bond with wood even though only filled the empty lumens in the wood, which leads to a mixture of two monomers rather than a single monomer. Therefore, the resulting products were still subject to physical and mechanical properties changes with environmental variations. Poor chemical and physical interfacial interactions between the wood surface and chemical are two of the most important mechanisms of bond failure.

### 3 Literature Review

#### 3.1 *Enhancement of Wood Quality*

The presence of abundant hydroxyl groups and various cavities in wood components have greatly been attributed to the changes of dimensional and biological degradation (Ghosh et al. 2008; Papadopoulos 2006; Singha and Thakur 2009; Tunc et al. 2010). These hydroxyl groups are considered to be reactive sites and the cell cavities are main paths for moisture movement in wood. The quality of wood will be changed if these reactive sites could be substituted by some suitable monomer or chemicals and the pores in the wood were also blocked by the polymer. The dimensional stability and physical and biodegradation properties have been improved by blockage of these reactive sites with some reactive chemicals or monomer. The pores have been plugging with a polymer will make the wood more resistant. Wood has been modified by different methods such as chemical, thermal, or enzymatic modification.

The idea of chemical modification of wood has been developed primarily to improve the dimensional stability of wood when subjected to change of moisture. Monomers or prepolymers for in situ polymerization or chemical treatments range have been introduced for the chemical composition of wood by chemical reactions which made product for sustainable application. The necessary requirements of chemical modifications are that the reacting chemicals must be penetrated into the wood cell wall and react with the available hydroxyl groups of the cell wall polymer with neutral or mild alkaline conditions at 120 °C temperatures (Ghosh et al. 2008; Papadopoulos 2006; Singha and Thakur 2009; Tunc et al. 2010). The thermoplastics and thermosets polymer are used to improve the quality product.

### 3.2 *Modern Policies to Growth Wood Quality*

Wood contains numerous hydroxyl groups and various cavities which create some unfavorable features such as high-moisture uptake, biodegradation, and dimensional instability that were permitted to modification of wood through various chemical treatments, single or dual monomer impregnation. (Hill 2011; Rowell 2005; Singha and Thakur 2009; Tunc et al. 2010). These hydroxyl groups are considered to be reactive sites and the cell cavities are main paths for moisture movement in wood. These reactive sites will be substituted by suitable or monomers to block the pores and react with hydroxyl and it changed their properties to improve the quality of wood product. Due the chemicals modification or polymer impregnation, the reactive sites blocked by reactive chemicals or the pores have been plugging by the polymer which enhanced the moisture-resistant content and improve its dimensional stability, physical, and biodegradation properties.

A number of studies have been engaged at improving numerous wood attributes through chemical modification or monomer impregnation. The chemical modification or polymer impregnation concept of wood was developed to improve their properties to become stability of wood product when exposed to change of moisture. The in situ polymerization is the most powerful technique to produce wood polymer composites using different chemicals reactions or monomers dispersion. The suitable chemicals or monomers are that the reacting chemicals which have been penetrated into the cell wall and react with the hydroxyl groups in alkaline conditions at 120 °C temperatures (Hill 2006; Papadopoulos 2006).

There are two types of polymers that used in improvement the quality of wood product. Thermoset polymers are the most widely used matrix in composite materials. The various types of thermoset polymer matrices are used for making reinforced composites such as Bis-Maleimids (BMI), Epoxy (Epoxide), Phenolic (PF), Polyester (UP), Polyimide, Polyurethane (PUR), Silicone, Polyetheretherketone (PEEK), and Cyanate ester (Salah and Raman 2014). A thermoplastic is a plastic polymer material, which can be flexible or moldable above a specific temperature and concentrate upon cooling. Thermoplastics become soft when heat is applied and have a smooth, hard finish when cooled. Thermoplastic polymer changed properties when heated and cooled. The different types of thermoplastic polymer matrix used to produce reinforced composites are Polyethylene (PE) (low and high density), Polypropylene (PP) (low and high density), Polystyrene (PS), Polybutylene (PB), Poly (vinyl fluoride) (PVF), Poly (vinyl chloride) (PVC), Poly (vinyl acetate) (PVAC), Poly (vinyl butyral) (PVB), and Nylon (Valente et al. 2011). In the case of thermoplastics, above a certain temperature, all polymers become softer and are able to melt. When the temperature increased the plastics frequently melt in the range of 100–250 °C. The polymers have liquid like order (they are shapeless and in the melting state). The density of polymer will enhance and specific volume decreases when reducing the temperature (Koutsos 2009).

In the past decay, most of the people are used expensive wood but durable hard wood species such as cheshnut or tropical hardwoods were the simplest solution to create strong wood products. As the availability of naturally durable species has declined, the industry has turned to softwoods plantations because of the first-growing species. Softwood species need to perform treatments modification or polymer impregnation in order to achieve satisfactory longevity under services conditions. Several approaches are introduced to increase wood properties for soft non-durable species. There are four important techniques to develop the wood product, namely chemical modifications, impregnation modifications, thermal modifications, and surface modifications.

Chemical modifications can be defined as the reaction of a chemical component with hydroxyls group from the cell wall of wood. They involve the formation of covalent bonds with OH groups from cellulose, hemicellulose, or lignin. The chemical composition of wood will be changed which confer to enhance the properties of wood species. Impregnation modifications define as solid specimens have been impregnated with various types of monomer or polymer to give biological resistance or in filling cell voids by polymers (bulk effect) to give dimensional stability. Thermal modification is one of the modifications that the heat is applied to the wood specimens that results in degradation associated with chemical composition in the wood material. If carefully controlled, the property changes on wood due to thermal modification can be interesting for certain applications. Surface modifications are applied to change the wood surface involving chemical modifications, biological modifications using enzymes, or physical processes such as plasma modifications. The main focusing areas of interest are modifications have been improved bonding between wood surfaces with monomer directly or between wood surfaces and coatings or to improve the weathering performance of wood. These wood treatments are proposed to increase at least one of the properties of wood. However, the chemical modifications or impregnations have an impact on the other wood properties as well, sometimes it will be positive while sometimes negative depend on the nature of the chemicals or monomers. For instance, the metal salts with reinforcing filler impregnation have improved light resistance against fungi decay, on the other hand, it brings the positive impact on the dimensional stability. Equally, thermal treatment has a negative impact on the mechanical properties while they increase the dimensional stability of wood. The next paragraphs present a short description of the past technologies to improve the characteristics of non-durable wood and detailed the new technologies that are applied in industry or are under current investigation in research laboratories.

### ***3.3 Chemical Modification of Wood***

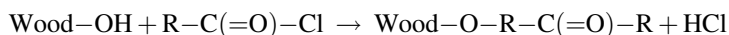
The alcoholic function group can create by the hydroxyl groups of the wood macromolecules. The most of the wood modification has been conducted by acylation reactions with hydroxyl groups of the wood. Due to the acylation reactions,

the functionalization of the OH groups and the natural hydrophilicity of wood are reduced. In addition, the dimensional stability and the biological resistance have been improved which reported in most cases (Militz et al. 1997). This modification increase of properties is due to covalent bonding and is therefore durable and not subject to leaching by water. Depending on the aim of this study, various properties of the chemically modified wood might be reported but they are not often comprehensively determined. They are laboratory biological tests to determine the decay and termite insect resistances, dimensional stability, mechanical properties, water repellency, and more rarely fire resistance and photodegradation.

The following paragraphs present the most frequency reported chemical reactions which enhanced the wood properties. The basic technical processes for wood quality improvement can be classified into the following, namely (Ayer et al. 2003; Fry 1976; Georgieva et al. 2008) the impregnation of wood with reactive chemicals, second is the compression of wood, and third is the chemical impregnation and compression of wood. Only few of them have the potential to be conducted in an industrial scale.

### 3.3.1 Reaction with Acid Chlorides

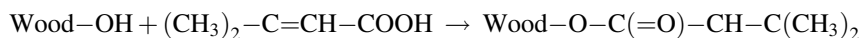
Wood has been acylated using acid halides. Hydrogen chloride is released as a by-product leading to degradation of the wood fibers if a base such as pyridine is not used. Therefore, the use of this technique is limited when treating lumber because of the necessity to remove the by-products present in wood after treatment.



It has been reported that reaction of wood with palmitoyl chloride permits to obtain a treated wood presenting an anti-swelling efficiency (ASE) of 48% for a weight percentage gain (WPG) of 21% (Prakash et al. 2006).

### 3.3.2 Esterification of Wood by Carboxylic Acids

The esterification of wood by carboxylic acids in presence of a catalyst is very effective. An in situ carboxylic acid chemical reagent is often used to convert cellulose esterification. The cellulose esterification is more reactive entity compare to anhydride or an acid chloride. The formation of anhydrides is effectively achieved with trifluoroacetic anhydride or with *N,N*-dicyclohexylcarbodiimide.

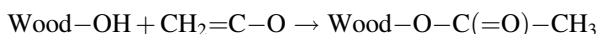


An in situ method was used to increase the oven-dry specimen's volume without a change in color or a decrease in either crystallinity or moisture content which

cause by unsaturated carboxylic acids esterification (Nakagami and Yokota 1975; Rowell 2005). Reaction with  $\alpha$ -methylcrotonic acid gave a higher degree of substitution which enough to make the reacted wood soluble in acetone and chloroform to the extent of 30% (Nakagami et al. 1976).

### 3.3.3 Wood Modification by Ketene

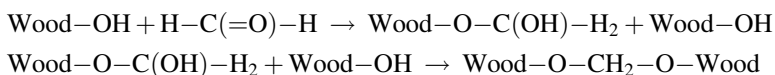
Ketenes are very toxic and reactive chemicals which penetrating in the wood cell and its tendency to polymerize. The particular case of ketene has been used to acetylate wood. This reaction does not create any by-product provided that the wood contains no moisture.



Ketene modification of wood has been established to increase dimensional stability but it is not as actual at improving this property as acetic anhydride. Oven-dry aspen and southern pine wood flakes react with ethenone at 50–60 °C leading to WPG of the order of 20% after 10–15 h of reaction. Furthermore, wood acetylation with ketene is not highly resistant to decay at a WPG of 17% (Rowell et al. 1986).

### 3.3.4 Wood Modification by Aldehydes

A hemiacetal is produced by the addition of an aldehyde to a hydroxyl group. The hemiacetal was further reacted with another OH group of the cell wall polymers producing an acetal crosslinking bond. This bonding is vulnerable to do the hydrolysis.

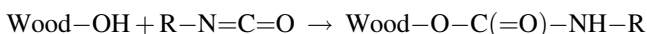


Formaldehyde is a very popular aldehydes compound which frequently used and it's reported in literature (Stevens et al. 1979). Due to the formaldehyde modification, the mechanical properties of such modified wood are poor and severe embrittlement because of the rigidity induced by the crosslinking and the acidic conditions of the modification. Formaldehyde treatment has been carryout under vapor phase in the presence of SO<sub>2</sub> as a catalyst with a minimal loss of strength compared to other treatments in liquid phases. The equilibrium moisture content (EMC) of wood product has been significant reduce even low levels of formaldehyde introduce in the wood specimens. Yasuda et al. (1995) found that a WPG level of only 3.5% resulted in a 50% reduction of the EMC compared to unmodified

wood. Decay resistance of formaldehyde treated with wood showed better results at only 2% of weight gain. It was reported that strong resistance showed against by white rot fungi while poor resistance show against by brown rot fungi (Minato et al. 1992). Glyoxal, glutaraldehyde, and other aldehydes have also been investigated as reagents for wood modification. It was concluded that none of them formed stable crosslinks in the wood cell wall.

### 3.3.5 Wood Modification by Isocyanates

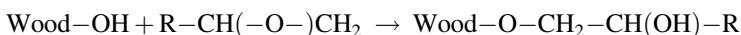
Isocyanates and thio-isocyanates rapidly react with wood hydroxyl groups to produce wood-urethane bonds (Deka and Saikia 2000).



4,4'-diphenylmethane diisocyanate (MDI) has been frequently used wood modification. Isocyanates swell wood and react with it at 100 to 120 °C without catalyst or with a mild alkaline catalyst such as trimethylamine (Gao and Gu 2007). The resulting urethane bond is very stable to acid and base hydrolysis. There are no by-products produced from the chemical reaction of isocyanate with dry wood. However, isocyanates react rapidly with water to yield a di-substituted urea. For this reason, it is significant that moisture is thoroughly omitted during reaction. Wood modified with butyl isocyanate shows a threshold for decay protection at around 15% of WPG with all the tested fungi. There is no major change in performance related to the chain length of isocyanate (Cardias and Hale 1999). Unlike mono-isocyanates, a reaction of wood with di- and poly-isocyanates can result in homopolymerization and subsequently in bulking effect.

### 3.3.6 Wood Modification by Epoxides

The epoxides modification occurred in the reaction between wood cell wall and epoxide to formation of an ether linkage with OH group. Therefore, graft-polymerization reactions are possible (Cetin and Hill 1999; Kumar 1994).

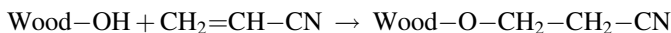


Several epoxides have been used in the past decades for wood modification purposes. They include ethylene oxide, propylene oxide, and butylene oxide (Norimoto et al. 1992). Usually, the reaction is catalyzed under mild basic conditions. In most experiments, trimethylamine is used as a catalyst. Wood modified with propylene oxide was ineffective toward *G. trabeum* decay resistance whereas butylene oxide modification proved to be effective at 23% WPG (Ibach et al. 2001).



### 3.3.7 Wood Modification by Cyanoethylation

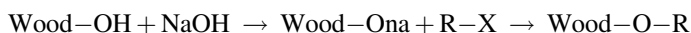
Wood cell wall and OH group react with Acrylonitrile in the presence of alkaline catalyst. NaOH modified treated wood get higher WPG up to 30% which has been reported giving ASE in the region of 60% (Stamm and Baechler 1960).



Biological resistance due to bulking, rather than toxicity, of such treated wood have also been reported. Cyanoethylated wood in ground contact at 15% of WPG has an average life of almost 8 years, compared with 4 years for untreated samples (Stamm and Baechler 1960).

### 3.3.8 Wood Modification with Alkyl Halide

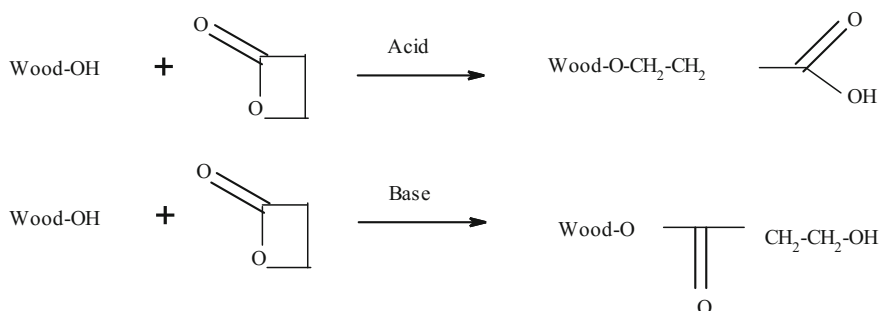
Wood has been etherificated by the alkyl halides in the presence of a strong base



Reactions of wood with crotyl chloride, methyl iodide, and butyl chloride have led to an improvement in dimensional stability. Decay resistance has also been investigated for wood treated with fatty dialkyldimethylammonium chlorides and bromides. Modified wood exhibited better resistance against brown rot fungi (Hill 2006).

### 3.3.9 Wood Modification by $\beta$ -Propiolactone

The wood OH group react with  $\beta$ -propiolactone in presence of acids or bases catalyst to yield two different products as shown in Fig. 1.



**Fig. 1** Schematic chemical reaction with  $\beta$ -propiolactone

The modified wood in acidic environments with 30% WPG resulted in better decay resistance and ASE of 60%. However, a strong degradation of wood has been protected by the  $\beta$ -propiolactone (Goldstein et al. 1959).

### 3.3.10 Wood Modification by Cyclic Anhydride

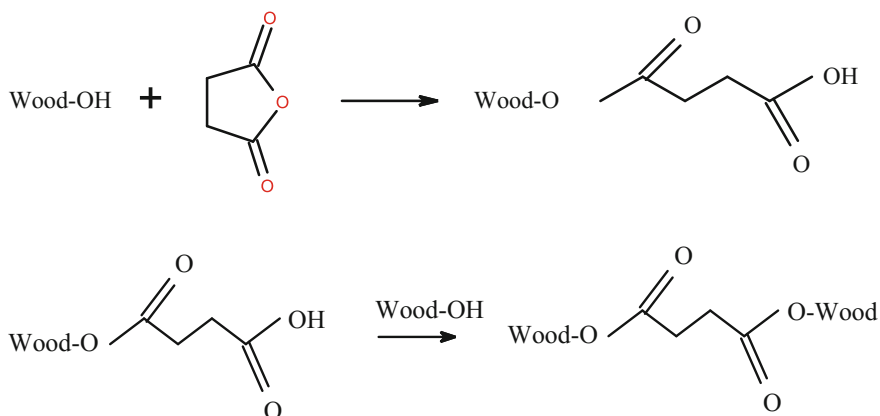
The hydroxyl groups of wood react with cyclic anhydrides do not yield a by-product. The anhydride covalently bonded on wood by an ester function yields a free carboxylic group at its end as shown in Fig. 2. The free carboxylic group undergoes with another OH group to crosslink the cell wall polymers of wood (Matsuda 1987).

Cyclic anhydrides have been used as chemical reagents for wood modification for example phthalic anhydride, maleic anhydride, glutaric anhydride, succinic anhydride, and alkenyl succinic anhydride (ASA) (Chauhan et al. 2001; Morard et al. 2007). Scots pine modified samples with petrochemical octenyl succinic anhydrides (ASAs) dissolved in pyridine. The succinic anhydrides modification did not present enough resistance against fungi decay but increased dimensional stability (Chauhan et al. 2001).

### 3.3.11 Wood Modification by Acrylic Anhydride

The acetic anhydrides react with the wood cell wall OH groups to produce an ester and acetic acid as a by-product. The following reaction is conducted at 70 °C without catalyst (Bongers and Beckers 2003) which shown in Fig. 3.

It is known that the rate of reaction is promoted by wood-swelling agents such as pyridine that can be used only at laboratory scale. The improved dimensional



**Fig. 2** Schematic chemical reaction with cyclic anhydride

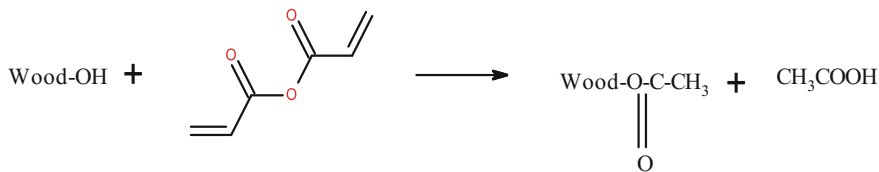


Fig. 3 Schematic chemical reaction with acrylic anhydride

stability of wood as a result of anhydride modification has been found to be a function of WPG only, regardless of the anhydride used for modification.

### 3.3.12 Oxidation of Wood

Wood has been oxidized using oxidizing agent with acidic catalyst as shown in Fig. 4. Oxidation reactions applied to cellulose in wood for chemical modifications (Hon and Shiraishi 2001). Oxidation reactions occur on cellulose selectively at particular position. The reaction of sodium metaperiodate with cellulose in wood fiber in the presence of sulfuric acid catalyst at 120 °C and 85 kPa pressure yielded the oxidized product. Sodium metaperiodate reacts with hydroxyl groups of cellulose and produces 2,3-dialdehyde cellulose which improved the mechanical and biological properties of wood (Rahman et al. 2010).

## 3.4 Wood Modifications by Impregnation Technique

Wood impregnation by various type of chemicals or polymer has been used to improve wood hardness, durability, dimensional stability, and mechanical properties (Ayer et al. 2003; Schneider 1994). The wood impregnation process

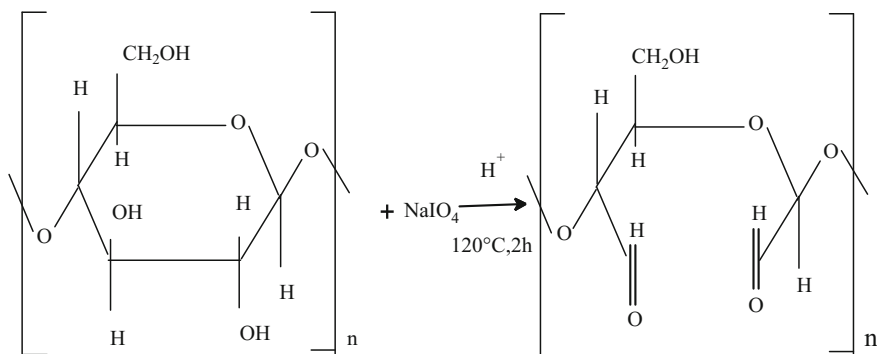


Fig. 4 Schematic chemical of oxidation

significantly depends on diffusion of the gas or liquid into the wood and the permeability of the wood cell wall. The specimens must be free from air, moisture, and water before chemical impregnation because it make the space for the treating chemicals to fill the pore. Treating chemical or monomer or polymer is required to be low viscosity, which normally corresponds to low or medium molecular weight. The treating chemicals are forced into the wood by vacuum and pressure. Vinyl monomers such as styrene and methyl methacrylate (MMA) are the examples of low viscosity monomer often used in wood polymer composites preparation through the impregnation technique. Some mechanical properties such as hardness of wood can be greatly enhanced by filling the empty spaces in the cell tissue with various type of chemicals or monomer or polymer. The filling process is done by impregnating the wood specimens in a closed chamber with a suitable chemical or monomer or polymer that can be hardened inside the wood. To penetrate the chemical or monomer or polymer evenly into the cell tissue of the wood is a stimulating problem due to the fact that the permeability of most species is poor and varies significantly in various sections of the wood (e.g., heartwood vs. sapwood). Another problem is how to polymerize the impregnated substances inside the wood without causing splits or burning of the treated wood or reducing its machinability. The wood structure and density, the properties of the treating chemicals, viscosity, and concentration of the treating solution, temperature, and pressure are all significant issues that affect the outcome of wood impregnation. Many chemicals have been used for wood impregnation, as briefly labeled in the following.

### **3.4.1 Wood Impregnated by Monomer and Prepolymer**

The monomer and prepolymer are subsequently polymerized with the cell lumens of wood and filled their void and block the hydroxyl group in wood cell wall which resulting wood polymer material normally retains most of the required characteristics of wood and shows various improved properties. Most wood species can be readily impregnated with vinyl monomers or prepolymers by using equipment and techniques similar to those used in the conventional wood preservation in industry (Chao and Lee 2003; Meyer 1981). There is a big difference of viscosity among monomer and prepolymers.

### **3.4.2 Enhancement of Wood Properties by Polymers Impregnation**

The thermoplastic and thermosetting polymers are used to produce wood-polymer composites. The well-known thermoplastic polymer is a poly vinyl chloride or similar monomers or modified vinyl monomers and polar monomers. Vinyl polymers have a large range of properties from soft rubber to hard. The brittleness of vinyl polymers depending upon the groups attached to the carbon-carbon backbone. Some examples of vinyl monomers are as follows: vinyl chloride, vinyl acetate, acrylonitrile, ethylene oxide, acrylates (especially methyl methacrylate), *t*-

butyl styrene, styrene, and chlorostyrene (Meyer 1981; Georgieva et al. 2008). The vinyl monomers are non-polar and poor interaction with wood hydroxyl groups.

In general, vinyl monomers fill the capillaries, vessels, and other void spaces in the wood structure (Georgieva et al. 2008). Polar monomers can swell cell wall to provide high-chemical resistance and dimensional stability in water. Thermosetting polymer is a type of polymers which include phenol formaldehyde, urea formaldehyde, melamine formaldehyde, polyurethanes, epoxides, silicones, and unsaturated polyesters (Ghosh et al. 2008). Phenol-formaldehyde resin is plasticized the cell wall of wood and yields dimensionally stability of the wood polymer composites (Tunc et al. 2010).

### **3.4.3 Wood Impregnated by Vinyl Monomers**

The vinyl monomer impregnated wood polymer composites significantly improve their moisture resistance, thermal properties, mechanical properties, hardness, and other qualities of wood. The vinyl monomers are polymerized in presence of catalysts or radiation techniques (Siau et al. 1965). It is required to have the vinyl polymer successfully stabilize the wood by bulking the cell wall, but with the exception of acrylonitrile, vinyl monomers are generally poor swelling agents for wood (Ellwood et al. 1972; Loos and Robinson 1968; Siau 1969). Loos et al. investigated the dimensional stabilization of wood with vinyl monomers. Their work showed that without additional swelling agent vinyl monomers penetrate in the cell walls only to a limited extend. They are not predictable to impart any substantial dimensional stabilization to wood. The impregnation of wood with acrylic or vinyl type monomers showed less-dimensional stability in the presence of moisture. This was due to the detention of the monomer in the cell lumen instead of the cell wall. MMA and styrene impregnated wood polymer composites showed better dimensional stability compared to other vinyl monomer impregnated wood polymer composites (Brebner et al. 1988; Chao and Lee 2003; Khan et al. 1992a; Langwig et al. 1968; Raff et al. 1965).

### **3.4.4 Wood Impregnated by Methyl Methacrylate (MMA)**

Methyl methacrylate (MMA) is the most commonly used vinyl monomers to produce wood polymer composites (WPCs). It is one of the least expensive and most readily available monomers that are used alone or in combination with other monomers to produce the crosslink the polymer system. MMA impregnated wood polymer composites showed fewer swells compared to other vinyl monomers (Loos and Robinson 1968). MMA monomer filled cell lumens but unchanged cell walls which showed in WPC. This type of WPC has time-dependent dimensional stability improvement on the other hand, and it might not be sustainable for long term. Over the years, MMA has been extensively used monomer for production of WPC (Duran and Meyer 1972; Langwig et al. 1968, 1969; Noah and Foudjet 1988; Siau

and Meyer 1966; Siau et al. 1978; Yalinkilic et al. 1998, 1999a, b). The use of a crosslinker rapidly increased the initial viscosity of the system and an auto-acceleration of the polymerization was observed for the crosslinker, trimethyl propane trimethacrylate (TMPTMA), reduced the time to the exothermic peak and dramatically increased the exothermic peak temperature. The effect of the crosslinking agent on the mechanical properties of wood polymer composites was uncertain (Islam et al. 2011). Siau and Meyer (1966) compared the properties of MMA impregnated wood polymer composites cured by heat and radiation, respectively. There is no significant change in yellow birch-polymethyl methacrylate combinations which were found between heat and radiation when tested for compression parallel to the grain direction, shear strength, permeability, diffusion coefficient, and anti-shrink efficiency. The material polymerized by radiation was about 25% better than that of the material polymerized by heat; this is due to the superior evaporation of monomer from near the surface during heat-induced polymerization which increases the surface hardness. The dimensional distortion and volumetric changes were observed if the wood impregnated by MMA and polymerized by heat (Siau 1969). The distortion of basswood was much more severe than that of maple wood. Siau (1969) also investigated the swelling behavior of basswood impregnated with MMA and styrene. Anti-shrink efficiency of up to 40% indicated the entry of monomer into the cell wall before polymerization. The rate of swelling by monomers improved with temperature and moisture content of the wood. The amount of swelling at steadiness usually reduced with temperature. Other studies report a large difference in swelling properties between wood species. Beall et al. (1966) investigated the polymerization of basswood impregnated with MMA containing a peroxide initiator by direct heat and radio-frequency radiation. Three types and two concentrations of organic peroxides were used for the initiation of the polymerization of MMA. Heating the wood-monomer composite by radio-frequency energy which temperature between 90 and 98 °C caused a rate of free radical generation satisfactory to overcome the inhibitor concentration and to stimulate the achievement of polymerization in about 20% of the time required for direct heating. The radio-frequency heating polymer retention was approximately 80% compared to direct heating. The radio-frequency treatment techniques were used to handle the accounted of monomer loss. The heat catalyst method applies for polymerization and impregnations of MMA monomer to heartwood and sapwood before and after which compare their properties (Young and Meyer 1968). Vazo free radical catalyst was used to polymerize the MMA in wood cell wall. Eight species of wood including yellow birch and red maple were investigated. After treatment, the sapwood exhibited greater increase in compressive strength perpendicular to the grain direction, tangential hardness and density than did the heartwood. Sapwood also showed a greater reduction in permeability and it had higher polymer retention. Beall et al. (1973) compared the hardness of WPC of red oak, aspen, and hard maple that were impregnated with MMA. They found that the hardness of untreated wood was mainly related to density. Schneider (1995) proposed a method to prepare cell wall and cell lumen wood polymer composites by using two monomers, one of which can swell the cell wall. Furfuryl alcohol-based