Cost Reduction and Optimization of Advanced Impregnation Technologies with Nanotechnology

by

Xiaolin Cai
Research Scientist
Department Value-Added Products

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Abstract

This study selected acylate monomers/oligomers as the nanoparticle transportation chemicals to produce high value-added wood surface densification products. The effect of nanoparticles in the formulations on the Brinell surface hardness, impact resistance and abrasion resistance was evaluated in this project. It was found that the addition of nanoparticles showed significant effect on mechanical properties of surface densification wood products. Different ratio of monomer/oligomers formulation and their viscosities on the chemical retention and penetration properties were investigated. Lower viscosity formulation presented better penetration and higher chemical retention with same surface densification process.

Two optimized advanced surface densification processes were developed to improve the efficiency and lower the chemical retention thus to decrease the cost of final value-added surface densification wood products. The first optimized advanced densification process that prepared surface-densified wood product by replacing the traditional time-consuming pressurization stage with only a short vacuum process was investigated. Formulations with nanoparticles were successfully impregnated into maple and oak engineered wood flooring planks by using a vacuum time from 30 s to 10 min without further pressurizing during the impregnation process. The properties of these short vacuum process impregnated wood products were also comparable to or even superior to the conventional vacuum/pressure impregnated wood products. The Brinell surface hardness of impregnated maple wood were improved 205% with a 30s vacuum process and oak wood were improved 108% with 60s vacuum process. The second optimized advanced surface densification process contained three steps process. The 1st step consists on application of a layer of resin on the wood surface by roller or curtain coater; the 2nd step is using a 60s vacuum to penetrate the resin into the wood surface to a target depth 1-2 mm; the 3rd step is to cure the impregnated wood with UV/thermal dual 

Electron beam (EB) and UV/thermal dual cure process which was industrial viable online in situ polymerization process have been successfully developed to cure the surface densification wood products. The efficacy of EB and UV/thermal dual cure was validated by differential scanning calorimetry (DSC) and photo-DSC characterization. The results showed that EB cure is a powerful instant online polymerization method to cure the fully penetrated chemical surface densification wood products with a relative high capital investment on equipment. UV/thermal dual cure method is a cost-effective approach to polymerize the roller/coater resin application and vacuum penetration surface densified wood products.

In general, this study implied that reduce cost from surface densification process is possible through application of resin by roller/curtain coater followed with a short vacuum process to penetrate the resin into wood surface. This work also implied that in situ UV/thermal dual cure could replace the high cost EB cure surface densification products, which in turn, favour our industrial to adopt this technology cost-effectively.
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Table of Contents

Abstract ........................................................................................................................................................................ ii
Acknowledgements ........................................................................................................................................................ iii
List of Tables .................................................................................................................................................................. vi
List of Figures ............................................................................................................................................................. vi
1 Objectives ................................................................................................................................................................. 1
2 Introduction .............................................................................................................................................................. 1
3 Background ............................................................................................................................................................... 2
4 Staff ............................................................................................................................................................................. 3
5 Results and Discussion ............................................................................................................................................. 3
  5.1 Chapter 1 — Acrylate Wood Densification: Effects of Vacuum Time and Nanoparticles on Chemical
    Retention, Penetration and Resin Distribution ........................................................................................................... 3
    5.1.1 Abstract ............................................................................................................................................................ 3
    5.1.2 Introduction ................................................................................................................................................... 3
    5.1.3 Experimental and Materials ......................................................................................................................... 4
        5.1.3.1 Wood Species ........................................................................................................................................ 4
        5.1.3.2 Chemicals and Formulations ................................................................................................................ 5
        5.1.3.3 Impregnation Process ........................................................................................................................... 5
        5.1.3.4 Chemical Retention ............................................................................................................................. 5
        5.1.3.5 X-ray Vertical Density Profiles ......................................................................................................... 5
        5.1.3.6 SEM Characterization of Resin Distribution in the Wood Structure ................................................... 6
    5.1.4 Results and Discussion ................................................................................................................................... 6
        5.1.4.1 Chemical retention .................................................................................................................................. 6
        5.1.4.2 X-Ray Vertical Density Profile ............................................................................................................ 7
        5.1.4.3 Morphology of Impregnated Wood by Scanning Electron Microscopy (SEM) ..................................... 8
    5.1.5 Conclusions .................................................................................................................................................... 8
  5.2 Chapter 2 — Effect of Vacuum Time, Formulations and Nanoparticles on the Properties of Surface
    Densification Products ............................................................................................................................................. 17
    5.2.1 Abstract .......................................................................................................................................................... 17
    5.2.2 Introduction ................................................................................................................................................ 17
    5.2.3 Materials and Experimental ......................................................................................................................... 18
        5.2.3.1 Materials and impregnation process ....................................................................................................... 18
        5.2.3.2 Brinell surface hardness ...................................................................................................................... 19
        5.2.3.3 Impact resistance .................................................................................................................................. 19
        5.2.3.4 Abrasion resistance ............................................................................................................................ 19
        5.2.3.5 Experiment design and data analyses .................................................................................................. 19
    5.2.4 Results and Discussion .................................................................................................................................. 20
        5.2.4.1 Brinell Surface Hardness .................................................................................................................... 20
        5.2.4.2 Impact resistance .................................................................................................................................. 20
        5.2.4.3 Abrasion resistance ............................................................................................................................ 22
    5.2.5 Conclusions ................................................................................................................................................... 22
  5.3 Chapter 3 — An Investigation of Electron-Beam Curing of Acrylate/Nanoparticle Impregnated Wood .... 37
    5.3.1 Abstract ......................................................................................................................................................... 37
    5.3.2 Introduction ................................................................................................................................................ 37
    5.3.3 Materials and Experimental ......................................................................................................................... 39
        5.3.3.1 Materials and sample preparation ....................................................................................................... 39
        5.3.3.2 EB curing HDDA/TMPTA/nanoparticles impregnated engineered wood planks ................................ 39
        5.3.3.3 Validation characterization with DSC ................................................................................................... 39
        5.3.3.4 Scanning electron microscopy and surface hardness measurement of EB cure wood samples ....... 40
5.3.4 Results and Discussion..................................................................................................................40
5.3.4.1 EB curing HDDA/TMPTA/nanoparticles impregnated engineering wood planks..................40
5.3.4.2 Curing behaviour of EB polymerization acrylate/nanoparticles..............................................41
5.3.4.3 SEM characterization EB cured impregnated maple wood.......................................................42
5.3.4.4 Improvement of Brinell surface hardness and impact resistance..............................................42
5.3.5 Conclusions.......................................................................................................................................43
5.4 Chapter 4 — UV/thermal dual cure acrylate surface densified maple engineered wood planks by
roller/coater application resin with a vacuum penetration process......................................................52
5.4.1 Abstract........................................................................................................................................52
5.4.2 Introduction.....................................................................................................................................52
5.4.3 Materials and Experimental...........................................................................................................54
5.4.3.1 Materials and sample preparation...............................................................................................54
5.4.3.2 Application resin and penetration of resin into wood surface..................................................54
5.4.3.3 X-ray Vertical Density Profiles..................................................................................................54
5.4.3.4 UV/thermal dual cure the surface densification wood products photo-DSC characterization....55
5.4.3.5 Data reduction............................................................................................................................55
5.4.4 Results and Discussion....................................................................................................................56
5.4.4.1 Formulation viscosity and chemical retention...........................................................................56
5.4.4.2 X-Ray Vertical Density Profile....................................................................................................56
5.4.4.3 Curing behaviour of UV/thermal dual polymerization acrylate surface densified maple engineered planks 57
5.4.5 Conclusions.......................................................................................................................................58
5.5 Chapter 5 — Wood Densification through Roller/Coater Application with Different Viscosity Acrylate
Monomer/Oligomers through Vacuum Penetration Process and UV/Thermal Dual Cure........................70
5.5.1 Abstract........................................................................................................................................70
5.5.2 Introduction.....................................................................................................................................70
5.5.3 Materials and Experimental...........................................................................................................72
5.5.3.1 Materials and sample preparation...............................................................................................72
5.5.3.2 Application resin and penetration of resin into wood surface..................................................72
5.5.3.3 Brinell surface hardness................................................................................................................72
5.5.3.4 Impact resistance..........................................................................................................................72
5.5.3.5 Experiment design and data analyses.........................................................................................73
5.5.4 Results and Discussion....................................................................................................................73
5.5.4.1 Chemical retention.......................................................................................................................73
5.5.4.2 Brinell Surface Hardness...............................................................................................................73
5.5.4.3 Impact resistance..........................................................................................................................74
5.5.5 Conclusions.......................................................................................................................................75
6 Conclusions...........................................................................................................................................86
7 Recommendations...............................................................................................................................87
8 References.............................................................................................................................................87
Appendix I Concept Disclosure of Obstructive Wood Surface Densification Using a Nanotech Approach Cured
by EB, UV/Thermal Curing.....................................................................................................................88
Appendix II Flow Chart of Concept Disclosure of Obstructive Wood Surface Densification Using a Nanotech
Approach Cured by EB, UV/Thermal Curing.........................................................................................100
Cost Reduction and Optimization of Advanced Impregnation Technologies with Nanotechnology

List of Tables

Table 1 ANOVA results for chemical retention (CR) of impregnated maple and oak wood ........................................10
Table 2 Average density for maple and oak wood specimens treated through different vacuum times and formulations (with and without nanoparticles) ........................................................................................................10
Table 3 Density peak position from surface (from left to right) according to the vertical density profiles of maple and oak wood specimens impregnated with nanoparticles/formulations ........................................10
Table 4 Factorial experimental design used in this study .........................................................................................25
Table 5 Effect of dependent variable on Brinell surface hardness of impregnated maple and oak wood ........26
Table 6 ANOVA analysis of impact resistance on maple and oak wood .............................................................26
Table 7 Effect of dependent variable on impact resistance on impregnated maple and oak wood – indentation fracture depth with different impact strength ................................................................. 27
Table 8 Effect of dependent variable on impact resistance on impregnated maple and oak wood – indentation fracture diameter with different impact strength ..............................................................28
Table 9 DSC characterization results for pure acrylate resin, acrylate/nanoparticles, acrylate impregnated maple wood, acrylate/nanoparticle impregnated maple wood, EB cure impregnated wood, wood controls .......................................................................................................................................................45
Table 10 Impact resistance of EB cure impregnated sugar maple samples ..........................................................45
Table 11 Viscosity and components of different formulations .............................................................................60
Table 12 Output of the UV lamp used to polymerize the surface densified wood products † ..................................60
Table 13 Photo–DSC analysis results of different viscosity (results of Figure 5-9) .........................................................60
Table 14 Component ratio of formulations and their viscosity .............................................................................77
Table 15 Full factorial experimental design with 3 factors .....................................................................................77
Table 16 ANOVA analysis of CR – Chemical retention .........................................................................................77
Table 17 Effect of dependent variable on chemical retention ................................................................................78
Table 18 ANOVA analysis of Brinell surface hardness ..........................................................................................78
Table 19 Effect of dependent variable on Brinell surface hardness ........................................................................78
Table 20 ANOVA analysis of impact resistance – indentation fracture diameter with different impact strength ....79
Table 21 Effect of dependent variable on impact resistance – indentation fracture diameter with different impact strength ......................................................................................................................................................80

List of Figures

Figure 1 Specimen preparation for formulations involving different viscosities and micro/nanoparticles. Each treatment contains 15 specimens .........................................................................................................................11
Figure 2 Chemical retention of wood specimens for different vacuum times and formulations containing nanoparticles (WN) or no nanoparticles (NN) ................................................................................12
Figure 3 X-ray density profiles of maple specimens for different vacuum times and formulations containing nanoparticles (WN) or no nanoparticles (NN) ................................................................................13
Figure 4 X-ray density profiles of oak specimens for different vacuum times and formulations containing nanoparticles (WN) or no nanoparticles (NN) ................................................................................14
Figure 5 SEM photographs of maple wood specimens before and after treatment with 60-s vacuum impregnation time: (a) control specimen; (b) maple treated with HDDA/TMPTA and 1% nanoparticles (47.1 wt% chemicals including nanoparticles); (c) maple treated with HDDA/TMPTA (62.5 wt% chemicals). .................................................................15

Figure 6 SEM photographs of oak wood specimens before and after treatment (with 60-s vacuum impregnation time: (a) oak control specimen; (b) oak treated with HDDA/TMPTA and 1% nanoparticles (36.8 wt% chemical/nanoparticles); (c) oak treated with HDDA/TMPTA (47.3 wt% chemicals). .........................................................................................................16

Figure 7 Picture of impact resistance equipment (a) a falling ball can be placed at different height thus the indentation force varied due to the falling height; (b) The impact spot of indentation fractures was examined and determined in both diameter and depth of indentation ........................................29

Figure 8 Brinell surface hardness of maple wood and treated maple wood with neat resin or resin/nanoparticles with different vacuum process ..................................................................................30

Figure 9 Brinell surface hardness of oak wood and treated oak wood with neat resin or resin/nanoparticles with different vacuum process ..................................................................................30

Figure 10 Indentation fracture diameter of maple wood with low impact strength (a), low impact from 3”, (b) medium impact from 9”, (c) high impact from 18” .................................................................31

Figure 11 Indentation fracture depth of maple wood with low impact strength (a), low impact from 3”, (b) medium impact from 9”, (c) high impact from 18” .................................................................32

Figure 12 Indentation fracture diameter of oak wood with low impact strength (a) low impact from 3”, (b) medium impact from 9”, (c) high impact from 18” .................................................................33

Figure 13 Indentation fracture depth of maple wood with low impact strength (a), low impact from 3”, (b) medium impact from 9”, (c) high impact from 18” .................................................................34

Figure 14 Weight loss after different abrasion circles for maple wood (a) 100 cycles taber abrasion, (b) 300 cycles taber abrasion, (c) 500 cycles taber abrasion .................................................................35

Figure 15 Weight loss after different abrasion circles for oak wood (a) 100 cycles taber abrasion, (b) 300 cycles taber abrasion, (c) 500 cycles taber abrasion .................................................................36

Figure 16 (a) Electron Beam curing work mechanism: utilize highly energetic electrons at controlled energy levels to polymerize and cross-link polymeric materials, (b) RDI Dynamitron accelerator of E-Beam ........................................................................46

Figure 17 EB cure impregnated sugar maple samples, A-Control, B-10min vacuum, C-5min vacuum, D-15/15min vacuum/pressure ........................................................................................................46

Figure 18 Chemical retention and final density of HDDA/TMPTA impregnated maple wood with different vacuum impregnation time ........................................................................................................47

Figure 19 DSC analysis curing behaviour of Formulation 1 – HDDA/TMPTA (75/25 wt%) ........................................................................................................48

Figure 20 DSC analysis curing behaviour of maple engineered plank impregnated using acrylate monomer – HDDA/TMPTA (75/25 wt%), and acrylate monomer – HDDA/TMPTA (75/25 wt%) plus 1 wt% nanoparticles Claytone®APA ........................................................................48

Figure 21 Comparison of DSC characterization results of HDDA/TMPTA (75/25), HDDA/TMPTA(75/25) and 1 wt% nanoparticles, maple impregnated with HDDA/TMPTA, EB (electron beam) cured impregnated maple sample, pure maple sample without any treatment ........................................................................48

Figure 22 Scanning electron microscopy of cross section of (a) maple controls, (b) EB polymerized maple wood impregnated with HDDA/TMPTA and 1% nanoparticles, (c) EB polymerized maple wood impregnated with HDDA/TMPTA resin ........................................................................49

Figure 23 Brinell surface hardness of EB cured HDDA/TMPTA impregnated maple wood with different vacuum impregnation time ........................................................................................49
Figure 24  Chemical retention of different viscosity with different resin application methods, where V1 is CN2262/SR351 (100/0), V2 is CN2262/SR351 (75/25), V3 is CN2262/SR351 (50/50) and V4 is CN2262/SR351 (25/75). R – roller coating, C – curtain coating, x – 1 application of resin, s – multiple application of resin until the surface is saturated .................................................................61

Figure 25  Vertical X-ray density profile of formulations with different viscosities and application methods ..........63

Figure 26  Photo-DSC characterization of neat acrylate resin with different viscosity, where V1, V2, V3 and V4 contains different of ratio of acrylate monomer, multifunctional monomer and oligomers .................................64

Figure 27  Conversion of Photo-DSC characterization of neat acrylate resin with different viscosity, where V1, V2, V3 and V4 contains different of ratio of acrylate monomer, multifunctional monomer and oligomers ................................................................................................................................................65

Figure 28  Photo-DSC characterization of neat acrylate resin of V1, V1 impregnated wood, UV/thermal cured V1 surface densification products with roller and curtain applications ...............................................................66

Figure 29  Photo-DSC characterization of neat acrylate resin of V2, V2 impregnated wood, UV/thermal cured V2 surface densification products with roller and curtain applications ........................................................................67

Figure 30  Photo-DSC characterization of neat acrylate resin of V3, V3 impregnated wood, UV/thermal cured V3 surface densification products with roller and curtain applications ........................................................................68

Figure 31  Photo-DSC characterization of neat acrylate resin of V4, V4 impregnated wood, UV/thermal cured V4 surface densification products with roller and curtain applications ........................................................................69

Figure 32  Effect of resin application method, application time and viscosity on the chemical retention ........81

Figure 33  Effect of resin application method, application time and viscosity on the Brinell surface hardness ....82

Figure 34  Indentation fracture diameter of resin application method, application time and viscosity with low impact strength (the impact steel ball falling from 3”) .........................................................................................83

Figure 35  Indentation fracture diameter of resin application method, application time and viscosity with medium impact strength (the impact steel ball falling from 9”) ........................................................................84

Figure 36  Indentation fracture diameter of resin application method, application time and viscosity with high impact strength (the impact steel ball falling from 18”) ..............................................................................85
1 Objectives

The objective of this study was to investigate the feasibility to reduce the cost of wood surface densification process to produce high value-added wood products and optimize the chemical impregnation technologies with nanotechnology. More specifically, detailed objectives included selection of nanoparticles transport medium chemical, decrease the chemical consumption thus to lower the cost of surface densification wood products and development of online in situ polymerization process to cure the surface densification of wood products.

2 Introduction

Chemical impregnation methods to produce high-value wood products with high quality, densified surfaces have been around for decades. In spite of their performance attributes, applications of these products have been limited because of their large volumes of impregnation chemicals using, a consequence of high cost, slow curing methods and low efficient impregnation process needed to produce these products.

The market opportunities for surface densification wood have been addressed in numbers projects of FPInnovations previous work (Ayer et al. 2003, Wan 2004, Wan and Wang 2007). In general, surface densification wood can be used for interior and exterior applications, i.e. flooring, door, window, decking, siding, etc. The industry’s latest interest in wood surface densification technologies is driven by cost-effective approaches to produce these high value-added products with enhanced surface hardness, impact resistance and wear resistance. Consequently, FPInnovations’ member companies require economical technologies to densify wood thus to improve its performance.

Our previous work has demonstrated the potential of impregnating wood cells with nanoparticles (Cai et al. 2007a, b, 2008, 2010a, b). Surface densification of wood products seems possible at lower cost through these approaches. The main objectives of this project under the transformative technology (TT) program were to study the feasibility of optimizing advanced impregnation technologies, which could considerably reduce the cost and improve the efficiency of the conventional vacuum/pressure impregnation surface densification process. In parallel, a 3-minute vacuum step process was designed by the engineering firm Roche-Groupe conseil in the frame of the STCI 50 project for the chemical penetration. Some work was performed under contract for Lauzon International in parallel with TT project. The objective of Lauzon’s proprietary work was to identify a simplest way to make the material penetrate in wood and the objective was obtained. More specific objectives of this current project included the following steps:

1) Selection of suitable monomers/oligomers as the nanoparticles transport medium chemical.
2) Development of high efficient advanced impregnation process to lower the chemical consumption of surface densification process, thus to decrease the cost in consequence to produce high value-added surface densification wood products which can be used in interior or exterior, such as wood flooring, doors/windows, cabinets, furniture, sidings, decking, etc.
3) Development of industrial viable online in situ polymerization process to cure the surface densification wood products

The work done in this project is good science because the study of this project has generated 5 scientific peer reviewed articles in the results and discussion parts and a concept disclosure in Appendix I. The peer reviewed scientific articles in the Results and Discussion part included Chapter 1 — Acrylate wood densification: Effects of vacuum time and nanoparticles on chemical retention, penetration and resin distribution; Chapter 2 — Effect of vacuum time, formulations and nanoparticles on the properties of...
surface densification products; Chapter 3 — An investigation of electron-beam curing of acrylate/nanoparticle impregnated wood; Chapter 4 — UV/thermal dual cure acrylate surface densified maple engineered wood planks by roller/coater application resin with a vacuum penetration process; Chapter 5 — Wood densification through roller/coater application with different viscosity acrylate monomer/oligomers through vacuum penetration process and UV/thermal dual cure. Among of them, Chapter 1 (1st article) was submitted to peer reviewed journal Wood and Fiber Sci. and the reviewers comments were already feed back to us and it’s under review. Chapter 2 (2nd article) is ready to be submitted and the rest articles from Chapter 3 – Chapter 5 (3rd – 5th articles) are work related to the concept disclosure of this study and they are going to be submitted once the patent application process is completed.

In summary, this study implied that reduce cost from surface densification process is possible through application resin by roller/curtain coater followed with a short vacuum process to penetrate the resin into wood surface. This work also implied that in situ UV/thermal dual cure could replace the high cost EB cure surface densification products, which in turn, favour our industrial to adopt this technology in cost-effectively.

3 Background

Various methods have been proposed to treat wood to promote surface hardness and other properties, in general the prior art methods present numerous deficiencies (Beall et al. 1973, 1975, Fuller et al. 1997, US Patent.5609915, Mayer 1981, 1982, 1984, Schneider 1994, 2004). Applications of these products have been limited because of their high cost, a consequence of large volumes of impregnation chemicals, slow curing methods and low efficient impregnation process needed to produce these products. Thus, there exists a need for a practical and economical method of treating wood to improve its hardness that also permits treatment to become a cost-effective and online operational process.

Recent work of Xiaolin Cai at University Laval has demonstrated the potential of impregnating wood cells with nanoparticles (2007, Cai et al. 2007a, b, 2008, 2010a, b). Surface densification of wood products seems possible at lower cost through these approaches. This project will select monomers/prepolymers used as mediums for nanoparticle transportation, select micro and nanoparticles and develop a commercially viable system to densify wood through surface treatment.

The conventional vacuum/pressure impregnation process typically involves two steps: the application of a vacuum (a minimum 15 minutes to several hours) to remove the air from wood; followed by the application of pressure (a minimum 15 minutes to several hours) to force the chemicals into wood structure. The chemical retention (CR) achievable in a conventional vacuum/pressure impregnation process is quite high, up to 80-200% (wt) in some cases, which leads to extremely high costs (Beall et al. 1973, Brelid P. L. 2002, Rowell 1991, Wright and Mathias, 1993a,b, Wan 2004). As long as impregnation schedules require batch processing, production efficiency is quite low. Shorter processing time combined with reduced CR such as achievable through treatments focusing on wood surfaces, where high density is needed, would yield significant savings and added value. It has been observed that the use of breaks in vacuum application enhances chemical penetration into wood, and they are an essential element in the traditional vacuum/pressure impregnation process. Pressure steps maximize chemical penetration into wood void spaces, sometimes resulting in excessive CR levels. Elimination of the pressure step with introduction of a vacuum step seemed to offer potential for better control of penetration paths and chemical consumption.

Traditional methods of wood densification through thermal curing, i.e. steam or hot press need long cure time, and high energy consumption. Thermal cure methods also produce volatile toxic by-products, create residual stresses in the materials, and require expensive tooling capable of withstanding high autoclave
temperatures. Attempts to develop fast curing technologies to polymerize the chemical impregnated wood products were investigated in the early stage of this project. Radio frequency (RF), microwave radiation (MW), wafer drying with infrared (IR) quartz radiant heater and electron beam (EB) technologies were tested to cure the chemical impregnated wood samples. In these tests, the resulted impregnated wood samples presented unique properties. The results showed that EB cure is a powerful instant online polymerization method to cure the fully penetrated chemical surface densification wood products with a relative high capital investment on equipment.

4 Staff

- Xiaolin Cai Research Scientist/Project Leader
- Pierre Blanchet Research Scientist/Group Leader
- Hui Wan Research Scientist
- Tommy Martel Technologist
- Martin O’Connor Technologist
- Simon Paradis-Boies Technologist
- David Pagé Technologist

5 Results and Discussion

5.1 Chapter 1 — Acrylate Wood Densification: Effects of Vacuum Time and Nanoparticles on Chemical Retention, Penetration and Resin Distribution

5.1.1 Abstract

The feasibility of preparing a surface-densified wood product by replacing the traditional time-consuming pressurization stage with only a short vacuum process was investigated. Maple and oak wood specimens were successfully impregnated with low-viscosity resins of 1,6 hexanediol dimethacrylate (HDDA) and trimethylolpropane trimethacrylate (TMPTA), and layered silicate nanoparticles, using a vacuum time that ranged from 30 s to 10 min without further pressurization during the impregnation process. The chemical retention (CR) and vertical density profiles of the treated wood specimens were measured. The CRs obtained with the shortened vacuum impregnation process, even with a vacuum of 30 s or 60 s, proved comparable to those achieved by the traditional 30-min vacuum plus 30-min pressure process. With maple wood impregnated with neat resin, a CR of 52-63 wt% was observed, while the formulations containing nanoparticles achieved 44-55 wt% as the vacuum time was increased from 30 s to 10 min. Oak wood yielded lower CR values. The vertical density profiles indicated better treatability for maple than for oak. Examination of the resin and/or resin/nanoparticles penetration into the wood by scanning electron microscopy revealed successful wood impregnation with both nanoparticles and resin.

Keywords: Nanoparticles, surface densification, density profile, chemical retention, morphology

5.1.2 Introduction

Wood modification through chemical impregnation to produce high value-added wood products with high quality densification has been around for decades (Ellis et al. 1999, Gindl 2003a,b, Mahmoud et al. 2000, Moore 1983). In spite of the performance attributes of the resulting products, applications have been limited because of high costs due to large chemical retention levels, slow curing methods and the general low efficiency of the process. The conventional vacuum/pressure impregnation process typically involves
two steps: the application of a vacuum (a minimum 15 minutes to several hours) to remove the air from the wood; followed by the application of pressure (a minimum 15 minutes to several hours) to force the chemicals into the wood structure. The chemical retention (CR) achievable in a conventional vacuum/pressure impregnation process is quite high, up to 80-200% (wt) in some cases, which leads to extremely high costs (Beall et al. 1973, Brelid P. L. 2002, Rowell 1991, Wright and Mathias, 1993a,b, Wan 2004).

As long as impregnation schedules require batch processing, production efficiency is quite low. Shorter processing time combined with reduced CR such as achievable through treatments focusing on wood surfaces, where high density is needed, would yield significant savings and added value. It has been observed that the use of breaks in vacuum application enhances chemical penetration into wood, and they are an essential element in the traditional vacuum/pressure impregnation process. Pressure steps maximize chemical penetration into wood void spaces, sometimes resulting in excessive CR levels. Elimination of the pressure step with introduction of a vacuum step seemed to offer potential for better control of penetration paths and chemical consumption.

The aim of this work was to investigate the feasibility of preparing a densified wood surface. Specific objectives were to shorten the impregnation schedule by eliminating the pressure step and generally optimize the schedule. Success with this approach could strategically turn the conventional discontinuous impregnation process into a continuous industrial densification process.

Recent work by Cai et al. (2007a, b, 2008) has demonstrated that nanoparticles can penetrate into wood cell walls as part of a vacuum/pressure impregnation process, producing significantly improved mechanical/physical properties with additions of only 1% layered silicate nanoparticles in a low viscosity resin as transport medium. A combination of nanoparticles and a melamine-urea-formaldehyde (MUF) resin significantly improved the surface hardness, abrasion resistance and modulus of elasticity (MOE) of the impregnated wood specimens, while drastically enhancing their moisture resistance and dimensional stability.

In this work, engineered wood flooring surface components were impregnated with different formulations with and without nanoparticles. Two wood species, sugar maple (Acer saccharum) and red oak (Quercus rubra), were considered using only a vacuum step as impregnation process with four different vacuum times: 30 s, 60 s, 5 min and 10 min. Low viscosity resins, i.e.: 1,6 hexanediol dimethacrylate (HDDA) and trimethylolpropane trimethacrylate (TMPTA), were chosen as carriers for the nanoparticles. These are clear resins, easier to handle than the methyl methacrylate (MMA) associated with traditional impregnation processes (Schneider 2001, Wan 2004). The nanoparticles selected were nanoclay (Claytone® APA) at 1% loading, mixed with the HDDA/TMPTA (75/25 by mass) resin, blending being achieved with a high-speed mixer. The impregnation performance criterion was the chemical retention (CR). Nanoparticle distribution and penetration were investigated through chemical retention and vertical density profile analysis of the densified wood specimens. The morphology and the penetration of the resin and/or resin/nanoparticles into wood were observed and characterized by scanning electron microscopy (SEM).

5.1.3 Experimental and Materials

5.1.3.1 Wood Species

Sugar maple (SM), one of the two species used in this study is a diffuse-porous species while red oak (RO) is a porous species. Both are important hardwood species on the North American market. Specimen size was 72 cm in length × 10 cm in width × 0.32 cm in thickness. The specimens were cut so wide faces were in the longitudinal-tangential plane. As shown in Figure 1 the specimen preparation cutting pattern was selected to minimize property variations and optimize data comparisons in statistical analyses. They
were numbered by 1-1, 2-1, n-1, ..., 15-1; 1-2, 2-2, n-2, ..., 15-2; n-m; 1-9, 2-9, n-9, ..., 15-9, where the maximum number of n is 15, the total specimen number for each treatment; m represents different formulations/vacuum time treatment parameters. In total, there are 8 treatment combinations plus the control samples group, thus the maximum number of m is 9.

5.1.3.2 Chemicals and Formulations

The resins, 1,6 hexanediol dimethacrylate (HDDA) and trimethylolpropane trimethacrylate (TMPTA) were supplied by AkzoNobel (formerly Chemcraft International, Warwick, Canada) as the transportation medium for nanoparticles. The mass ratio of the formulation was 75/25 (HDDA/TMPTA). The viscosity of HDDA was 8 cps at 25°C and that of TMPTA was 106 cps. The Claytone® APA nanoparticles used in this work were provided by Southern Clay Products, Inc. (USA).

5.1.3.3 Impregnation Process

The engineered wood flooring surface components were oven-dried at 103°C for 24 hours, and their oven-dry mass was recorded. They were then placed into an impregnation container, care being taken to avoid any contact between specimens. The container was placed in a cylinder that was subjected to a 25 mm Hg vacuum, this vacuum being maintained for a given period of time. In this project, the vacuum was maintained for 30 s, 60 s, 5 min and 10 min, and then stopped to vacuum the cylinder by closing the vacuum valve of the cylinder. The chemicals were flushed into the container till the wood specimens were fully submerged. Right after that, the vacuum was released and the container holding the specimens was removed. The specimens were taken out of the container and any chemical residue was wiped off the wood surfaces with paper towels. The mass of the impregnated wood specimens was measured. Resin cure was achieved by electron beam (EB) radiation without any catalyst being added. EB curing utilizes highly energetic electrons at a controlled energy level to polymerize and cross-link polymeric materials. The detailed EB curing process and EB curing behaviour of the acrylate/nanofiller impregnated wood will be discussed in a further paper.

5.1.3.4 Chemical Retention

Chemical retention (CR) was defined as the mass of the impregnated specimens (\( M_1 \)) minus their oven-dry mass before impregnation (\( M_0 \)) over \( M_0 \) multiplied by 100. Chemical retention was thus calculated in (wt%) by Equation (1):

\[
CR = \frac{(M_1 - M_0)}{M_0} \times 100
\]  

(1)

5.1.3.5 X-ray Vertical Density Profiles

The specimens of untreated and treated maple and oak wood were cut into 5 cm x 5 cm sub-specimens for the measurement of density profiles. The specimens were conditioned at 65% RH (relative humidity) and 20°C for at least three weeks before testing. After proper conditioning, the exact dimensions and weight of all specimens were recorded in order to determine densities. Density values were then converted into specific gravity values at 12% moisture content using the following equation (Siau 1984):

\[
\rho_{12} = \frac{\rho}{\left(1 + \frac{MC}{100}\right) \times \rho_w}
\]  

(2)

where \( \rho_{12} \) is the wood specimen’s specific gravity at 12% moisture content, \( \rho \), its density, and \( \rho_w \) its density at different thickness positions, while MC is its moisture content.
The vertical density profiles of both impregnated and non-impregnated specimens were thus determined using an X-Ray density profilometer.

5.1.3.6 SEM Characterization of Resin Distribution in the Wood Structure

The resin distribution in the treated and untreated wood specimens and their morphology were characterized using a Jeol JSM-840A scanning electron microscope. The blocks of untreated maple and oak wood, and those treated with a chemical (or chemical/nanoparticles) were prepared with a microtome by carefully cutting one of the end-grain faces to a depth of about 3 mm. All blocks were desiccated with phosphorus pentoxide for two weeks. A gold/palladium alloy was sputtered onto the prepared surfaces prior to the investigation.

5.1.4 Results and Discussion

5.1.4.1 Chemical retention

Chemical retentions at different vacuum times were measured, calculated by Equation (1) and expressed in weight gain. The results obtained are illustrated in Figure 2. For SM impregnated with a formulation containing no nanoparticles, a mean CR of 56.5 wt% was obtained. Weight gains varied with the different vacuum times: 53.9 wt%, 62.5 wt%, 56.8 wt% and 52.7 wt% respectively for 30 s, 60 s, 5 min and 10 min, but vacuum time clearly had no major effect on chemical retention in maple wood impregnated with formulations containing no nanoparticles. This confirms the effect of the vacuum break. For SM impregnated with a formulation containing nanoparticles, weight gains averaged 49.5 wt%. With the nanoparticles/resin treated specimens, CR values of 51.7 wt%, 47.1 wt%, 54.9 wt% and 44.4 wt% were recorded respectively for the 30-s, 60-s, 5-min and 10-min vacuum times. It therefore appears that, with the maple specimens, impregnation with formulations containing nanoparticles yielded lower CR values (49.5 wt%) than formulations with no nanoparticles (56.5 wt%). This may be ascribed to the accumulation of nanoparticles in pores located near the surface as observed in our previous work (Cai et al. 2007a, b), and to the flow resistance caused by such nanoparticles, limiting resin penetration into the centre of the specimens, thus reducing CR.

For the oak wood specimens impregnated with neat formulations (no nanoparticles added), CR values averaged 39.5 wt%, much lower than for maple. With 30-s, 60-s, 5-min and 10-min vacuum times, CRs of 39.7 wt%, 47.3 wt%, 38.9 wt% and 32.3 wt% respectively were obtained. It may be worth noting that, for the oak specimens, the highest CR was obtained with a vacuum time of 60 s, which implies that vacuum of 30 s or a maximum 60 s would be enough to achieve considerable weight gains. With formulations containing nanoparticles, the oak specimens averaged a CR of 35.7 wt%, the results after 30-s, 60-s, 5-min and 10-min vacuum times being 35.9 wt%, 36.8 wt%, 38.0 wt% and 32.2 wt% respectively. The effect of vacuum time on the CR of the specimens impregnated with nanoparticle/resin formulations was not obvious; in fact it looks like the breaking of the vacuum is an important factor. As already observed with the maple specimens, the CR of oak specimens impregnated with formulations containing nanoparticles (35.7 wt%) was lower than for those impregnated with neat formulations (39.5 wt%).

A comparison between maple and oak shows that, under the same impregnation parameters (i.e. the same vacuum time and formulations applied), maple achieved higher CR values than oak. An ANOVA performed on CR values (Table 1) indicated that the differences between maple and oak were not statistically significantly different (α=0.01) in terms of vacuum time or the use of nanoparticles. The introduction of nanoparticles did have a significant effect on CR at lower level of comparison (α=0.05) in the case of maple wood. The interaction effect of the two factors (vacuum time × formula) on CR was not significantly different between the two wood species. In terms of wood species (i.e. maple and oak), CRs were highly statistically different (α=0.01). This may be ascribed to the different anatomy structures of
maple and oak wood. The first is a diffuse porous wood while the second is porous wood. Previous work on aspen showed that impregnation with melamine-urea-formaldehyde/nanoparticles by a traditional vacuum/pressure method with 30-min vacuum plus 30-min pressure yielded an average CR of 67.7 wt% (Cai et al. 2007a). Aspen is a diffuse porous wood with low density. For the high-density maple wood, a mean CR of 25-50 wt% was observed with methyl methacrylate (MMA) and a similar vacuum/pressure impregnation cycle (Wan 2004). A comparison with the CRs obtained in this study suggests that there is no major difference in chemical retention for the traditional long vacuum/pressure impregnation process and our shortened vacuum-only impregnation process, even with a vacuum time of less than 60 s.

5.1.4.2 X-Ray Vertical Density Profile

Figure 3 shows density profiles for the treated maple wood with different vacuum times and formulations (with and without nanoparticles). The average density of the untreated maple wood was 670kg/m³ (Table 2), while the densities of all treated maple specimens, at different vacuum times with formulations with or without nanoparticles, were above 1000kg/m³. With a 30-s vacuum, treatment with formulations containing no nanoparticles produced an average density of 1054kg/m³ and density distribution proved almost uniform. With formulations containing nanoparticles, a lower average density of 1007kg/m³ was obtained, and the density distribution decreased from the surface to the centre of the treated wood. Two small peaks were observed on both sides. The peak density was above 1100kg/m³, while the lowest density at the centre of the specimens was about 986kg/m³. Table 3 summarizes all peak positions in the treated wood with formulations containing nanoparticles. For the maple wood, all peaks dropped off within 0.22-0.38 mm from the surface. This was due to some nanoparticles accumulating in the pores near the surface, and resulting in a higher density in the top layer of the wood. The higher nanoparticle concentration and resulting higher density in the top layer are a benefit for the resulting wood products. Higher surface density yields an increase in surface hardness, a desirable attribute especially in wood flooring. Some other properties such as abrasion resistance may also be enhanced (Cai et al. 2007a). As nanoparticles accumulating in the wood surfaces reduce flow and penetration of the chemicals into the core of the wood, the overall chemical retention required to adequately densify product surfaces can be expected to be lower.

The average density of the treated maple specimens with 60-s vacuum time and formulations without nanoparticles was 1037kg/m³, as compared with 1001kg/m³ at the same vacuum time with formulations containing nanoparticles. As with maple, neat resin formulations yielded a slightly higher density and more uniform density distribution than those combining nanoparticles and a resin. With a 5-min vacuum time, the average density of maple wood treated with a neat resin formulation was 1047kg/m³, as compared to 1024kg/m³ with formulations containing nanoparticles. For the resin/nanoparticle formulation, the peak density was 1105kg/m³ near both faces, the lowest density being 1034kg/m³ at the centre part of the specimens. When a 10-min vacuum was used, density averaged 1042kg/m³ for the formulation without nanoparticles, and 978kg/m³ with the formulation containing nanoparticles.

The average density of the untreated oak specimens was 663kg/m³ and density distribution was relatively even (Figure 4). With a 30-s vacuum time, the average density of oak wood treated with a formulation containing no nanoparticle was 910kg/m³, and density distribution was even from the surfaces to the centre of the wood (Table 2). With formulations containing nanoparticles, a lower density (881kg/m³) was observed. With a 60-s vacuum, the density averaged 909kg/m³ with a pure resin formulation, and 915kg/m³ with a formulation containing a nanofiller. This was only a slight difference, but density peaks of about 1034kg/m³ were observed near the surface as compared to 912kg/m³ at the centre of the specimens. A similar pattern occurred with a 5-min vacuum, with 916kg/m³ for the neat resin, and 933kg/m³ for the nanoparticles/resin formulation. As vacuum time increased to 10 min, an average density of 901kg/m³ was obtained with the neat resin, but a lower density (863kg/m³) was observed with the formulation containing nanoparticles.
As it can be seen from the average density results, all treated oak specimens exhibited higher densities than the untreated control specimens. The nanoclay filler generally showed little impact on mean density, but its effect on density profiles was obvious, with density peaks occurring close to wood surfaces. Density distribution proved relatively even across wood sections when a neat formulation was used. The positions of density peaks in treated oak specimens are given in Table 3. Peaks occurred at a depth of 0.18 mm to 0.30 mm from the surface. With oak, some differences in density distribution were observed with the different vacuum times.

5.1.4.3 Morphology of Impregnated Wood by Scanning Electron Microscopy (SEM)

Figure 5 shows SEM photographs of maple wood specimens before and after treatment with 60-s vacuum impregnation: (a) control specimen, (b) maple treated with HDDA/TMPTA and 1% nanoparticles (47.1 wt% chemicals including nanoparticles), and (c) maple treated with HDDA/TMPTA (containing 62.5 wt% of chemicals) in a typical cross section. The good penetration and adhesion of the HDDA/TMPTA resin to the cell wall can clearly be observed in the treated maple wood. For the nanoparticles/HDDA/TMPTA treated maple, the chemical loading obtained was lower, and the impregnated materials seemed to be located in both cell walls and lumens (Figure 5 (b), (c)). A similar cross section morphology can be observed with the different impregnation parameters. The morphology of HDDA/TMPTA penetration into maple wood with the shorter vacuum times (30 s, 60 s, 5 min and 10 min) used in this work proved comparable to that obtained with the conventional impregnation process based on 15-45 min vacuum plus 15-45 min pressure (Cai et al. 2007b, 2008). The weight gains achieved were highest with the 60-s vacuum time treatment involving HDDA/TMPTA formulations without nanoparticles (62.5 wt%).

Figure 6 shows morphologies for typical cross sections of an untreated control oak specimen (Fig.6(a)) and a treated oak specimen (Figure 6(b), (c)) with a 60-s vacuum impregnation time. For the untreated oak, empty cell wall, the pit and parenchyma can easily be observed, while for the impregnated oak, the empty pores have been filled by HDDA/TMPTA or nanoparticles/HDDA/TMPTA. Some empty columns (mainly vessels and some cell lumens) could, however, still be observed.

5.1.5 Conclusions

The feasibility of preparing a surface-densified wood product by eliminating the traditional long impregnation pressure step with only a short vacuum step was investigated. Specimens of two wood species (maple and oak) were successfully impregnated with chemical formulations based on low viscosity resins, i.e., 1,6 hexanediol dimethacrylate (HDDA) and trimethylolpropane trimethacrylate (TMPTA), and clay nanoparticles, using a vacuum time of either 30 s, 60 s, 5 min or 10 min, without a further pressure step. The chemical retention (CR) and density profiles of the treated wood specimens were measured. The weight gains and density increases obtained with these short vacuum schedules (including vacuum times of 30 s to 60 s) proved comparable to those achieved with the traditional 30-min vacuum plus 30-min pressure impregnation process. With vacuum times ranging from 30 s to 10 min, chemical retentions of 52.7 wt% to 62.5 wt% were observed for the maple wood impregnated with a neat formulation of HDDA/TMPTA, the corresponding retentions being 44.4 wt% to 54.9 wt% for the formulations containing nanoparticles. Retentions were lower with the oak specimens for the same formulations and vacuum times. The density profile indicated that maple wood has better treatability than oak. The morphology and penetration of the resin with and without nanoparticles were observed and characterized by scanning electron microscopy. They indicated that both the nanoparticles and the resin successfully penetrated all the wood in both cell walls and lumens. Due to nanoparticle accumulations, density peaks were observed near wood surfaces at a depth of 0.2 - 0.4 mm for both maple and oak specimens when impregnated with formulations containing nanoparticles, which are considered to be a benefit for the resulting wood products for some specific applications such as flooring.
Acknowledgements
The authors acknowledge Mr. Tommy Martel and David Page for their laboratory work. This project was funded by Natural Resources Canada under the Transformative Technology program.

References
### Table 1 ANOVA results for chemical retention (CR) of impregnated maple and oak wood

<table>
<thead>
<tr>
<th>Source</th>
<th>Degree of Freedom</th>
<th>Type III Sum of squares</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Pr &gt;F</th>
</tr>
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<tr>
<td>ANOVA for impregnated maple wood</td>
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<td></td>
<td></td>
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<tr>
<td>Formula</td>
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<td>381.57</td>
<td>381.57</td>
<td>7.64</td>
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<td>Vacuum time</td>
<td>3</td>
<td>252.08</td>
<td>84.03</td>
<td>1.68</td>
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<td>Formula × vacuum time</td>
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<td>80.06</td>
<td>1.60</td>
<td>0.2146</td>
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<td>ANOVA for impregnated oak wood</td>
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<td></td>
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<td>ANOVA for maple and oak species comparison</td>
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<td>3794.56</td>
<td>54.35</td>
<td>&lt;.0001**</td>
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</table>

** significant difference at $\alpha=0.05$

### Table 2 Average density for maple and oak wood specimens treated through different vacuum times and formulations (with and without nanoparticles)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Average Density (kg/m$^3$)</th>
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</thead>
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<tr>
<td></td>
<td>Maple Wood</td>
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<tr>
<td></td>
<td>Average value</td>
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<tr>
<td>Control specimens</td>
<td>670</td>
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<tr>
<td>30s – NN</td>
<td>1054</td>
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<tr>
<td>30s – WN</td>
<td>1007</td>
</tr>
<tr>
<td>60s – NN</td>
<td>1037</td>
</tr>
<tr>
<td>60s – WN</td>
<td>1001</td>
</tr>
<tr>
<td>5min – NN</td>
<td>1047</td>
</tr>
<tr>
<td>5min – WN</td>
<td>1024</td>
</tr>
<tr>
<td>10min – NN</td>
<td>1042</td>
</tr>
<tr>
<td>10min – WN</td>
<td>987</td>
</tr>
</tbody>
</table>

### Table 3 Density peak position from surface (from left to right) according to the vertical density profiles of maple and oak wood specimens impregnated with nanoparticles/formulations

<table>
<thead>
<tr>
<th>Impregnation condition</th>
<th>Density peak position from the surface (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maple</td>
</tr>
<tr>
<td>30s-WN</td>
<td>0.22</td>
</tr>
<tr>
<td>60s-WN</td>
<td>0.22</td>
</tr>
<tr>
<td>5min-WN</td>
<td>0.34</td>
</tr>
<tr>
<td>10min-WN</td>
<td>0.38</td>
</tr>
</tbody>
</table>
(a) Chemical retention of maple wood impregnated with acrylate monomer and acrylate/nanoparticles

Figure 1  Specimen preparation for formulations involving different viscosities and micro/nanoparticles. Each treatment contains 15 specimens.
(b) Chemical retention of oak wood impregnated with acrylate monomer and acrylate/nanoparticles

Figure 2  Chemical retention of wood specimens for different vacuum times and formulations containing nanoparticles (WN) or no nanoparticles (NN).
Figure 3 X-ray density profiles of maple specimens for different vacuum times and formulations containing nanoparticles (WN) or no nanoparticles (NN)
Figure 4  X-ray density profiles of oak specimens for different vacuum times and formulations containing nanoparticles (WN) or no nanoparticles (NN)
Figure 5  SEM photographs of maple wood specimens before and after treatment with 60-s vacuum impregnation time: (a) control specimen; (b) maple treated with HDDA/TMPTA and 1% nanoparticles (47.1 wt% chemicals including nanoparticles); (c) maple treated with HDDA/TMPTA (62.5 wt% chemicals).
Figure 6  SEM photographs of oak wood specimens before and after treatment (with 60-s vacuum impregnation time: (a) oak control specimen; (b) oak treated with HDDA/TMPTA and 1% nanoparticles (36.8 wt% chemical/nanoparticles); (c) oak treated with HDDA/TMPTA (47.3 wt% chemicals).
5.2 Chapter 2 — Effect of Vacuum Time, Formulations and Nanoparticles on the Properties of Surface Densification Products

5.2.1 Abstract

Surface densified wood products were prepared by eliminating the traditional time-consuming pressurizing stage with only a short vacuum impregnation process. 1,6 hexanediol dimethacrylate (HDDA) and trimethylolpropane trimethacrylate (TMPTA) with low viscosity and layered silicate nanoparticles were successfully impregnated into engineered wood flooring planks by using a vacuum time from 30 s to 10 min without further pressurizing during the impregnation process. Two species including maple and oak wood were treated and the Brinell surface hardness, impact resistance and abrasion resistance of the treated wood samples were measured. The Brinell surface hardness was improved from 5.05 MPa to 15.42 MPa for maple wood, the highest improvement of 205% with 30s vacuum process. For the oak wood, the Brinell surface hardness was improved from 5.25 MPa to 11.05 MPa, the highest improvement of 108% with a 60s vacuum process. The impact resistance was tested through a falling ball method and the impact resistance was determined by measuring the diameter and depth of the indentation fracture. The indentation fracture diameter decreased from 4.96 mm to 2.84 mm, while the indentation fracture depth was decreased from 0.172 mm to 0.034 mm for maple wood impregnated through 60s vacuum process with nanoparticles formulations, which means the impact resistance of short vacuum process impregnated wood was improved drastically. The abrasion resistance property of the surface densified wood products by short vacuum impregnation process was evaluated for both maple and oak wood. The weight loss of the treated wood decreased with the treatment. A factorial experimental design was completed to study the effects of vacuum time, nanoparticles and wood species on the properties of impregnated wood products. The main effect of the individual factors and the interaction between factors on the properties of impregnated wood products were analyzed with the Statistical Analysis System (SAS).

Key Words: nanoparticles, vacuum process, surface densification, Brinell surface hardness, abrasion resistance, impact resistance

5.2.2 Introduction

Specific uses of wood require that the wood is treated in a certain way prior being put in service. Chemical impregnation of wood to enhance specific wood properties, such as dimensional stability, hardness and abrasion resistance have been around for decades (Moore et al. 1983, Rowell 1984, 1991, Schneider 1994, 2001, Singh et al. 1999). The implications of this technology have been limited due to large volume chemical consumption and low efficient impregnation process. The tradition vacuum/pressure chemical impregnation process involved minimum 15 minutes to hours vacuum to remove air from wood, followed by a 15 minutes to hours pressure process to help the chemical to penetrate into the wood structure. The chemical retention (CR) can go up to over 200 wt% for acetylation impregnated pine wood to improve its dimensional stability (Brelid P. L. 2002). 110 wt% CR for aspen wood, 77 wt% CR for maple and 43 wt% CR for oak wood impregnated with PMMA have been observed to improve the surface hardness (Beall et al. 1973), which leads to the cost going up to unreasonably high.

The conventional impregnation process need long vacuum/pressure time to penetrate the chemical into wood structure. It was observed that application of vacuum to remove air from wood cells, and the break of the vacuum to let the chemical penetrate into the wood are essential for the penetration of chemicals into wood cells during our practice of vacuum/pressure impregnation process. It might be interesting to accelerate the impregnation process by shorten the vacuum time and removed the pressurizing process meanwhile to decrease the cost of the impregnation process by lower the chemical retention. This work investigated the feasibility of preparing a surface densified wood product by eliminating the impregnation pressurizing process with only the vacuum process and at the same time to find out whether such a
conventional vacuum time could also be reduced. This could strategically turn the conventional discontinuous impregnation process to an industrial viable surface densification process.

Our previous work (2007a, b, 2008) has proved that nanoparticles can penetrate into wood cell walls with the vacuum/pressure impregnation process, which significantly improved mechanical/physical properties of the impregnated wood products by adding only 1% nanoparticles with the help of a low viscosity chemical as transport medium. With the addition of nanoparticles combined with a melamine-urea-formaldehyde (MUF) resin, the surface hardness, abrasion resistance, and modulus of elasticity (MOE) were significantly improved, at the same time the moisture resistance and dimensional stability of chemical impregnation treated wood samples were also improved drastically. Through combination of nanotechnology and the upgraded impregnation process, less cost in preparation of high performance and value-added surface densification wood products would be expected.

The objective of this work was to investigate the feasibility of preparing surface densification wood products with simplifier process and lower cost. Specific objectives were to shorten the impregnation process by eliminating the pressure step and generally optimize the impregnation process. Success with this approach could strategically turn the conventional slow impregnation process into a more efficient industrial densification process to produce high value-added wood products, which can be used in exterior and interior, such as wood flooring, doors and windows, siding, deck, furniture, cabinet, etc.

In this work, two different species wood engineering planks, maple and oak wood were impregnated with only a vacuum process in different vacuum time with low viscosity 1,6 hexanediol dimethacrylate (HDDA) and trimethylolpropane trimethacrylate (TMPTA). Layered silicate nanoparticles Claytone® APA from Southern Clay Products, Inc. was the nanoparticles used in this research. 1,6 hexanediol dimethacrylate (HDDA) and trimethylolpropane trimethacrylate (TMPTA) with a ratio of 75/25 (HDDA/TMPTA) were selected as the transportation medium resin for nanoparticles. The engineered wood planks were placed in a container and vacuumed to 25 mm Hg, maintaining this vacuum for different periods. Close the valve, a known amount of resin was flushed into the system until all samples were covered by chemicals. The vacuum was released and samples were taken out from the cylinder. The residue of chemicals on the wood surface was wiped off. Details and impregnation process with different vacuum time were described in our previous work (Cai and Blanchet, 2010). The HDDA/TMPTA with or without nanoparticles impregnated wood engineering planks were polymerized by electron beam radiation without adding any catalyst. Electron beam (EB) curing method utilizes highly energetic electrons at controlled energy level to polymerize and cross-link polymeric materials. The detailed EB curing process and EB curing behaviour of the acrylate/nanofiller impregnated wood was discussed in another paper separately.

5.2.3 Materials and Experimental

5.2.3.1 Materials and impregnation process

The wood materials using in this research include maple (Acer saccharum) and oak (Quercus velutina). Claytone® APA from Southern Clay Products, Inc. was the nanoparticles used in this research. 1,6 hexanediol dimethacrylate (HDDA) and trimethylolpropane trimethacrylate (TMPTA) with a ratio of 75/25 (HDDA/TMPTA) were selected as the transportation medium resin for nanoparticles. The engineered wood planks were placed in a container and vacuumed to 25 mm Hg, maintaining this vacuum for different periods. Close the valve, a known amount of resin was flushed into the system until all samples were covered by chemicals. The vacuum was released and samples were taken out from the cylinder. The residue of chemicals on the wood surface was wiped off. Details and impregnation process with different vacuum time were described in our previous work (Cai and Blanchet, 2010). The HDDA/TMPTA with or without nanoparticles impregnated wood engineering planks were polymerized by electron beam radiation without adding any catalyst. Electron beam (EB) curing method utilizes highly energetic electrons at controlled energy level to polymerize and cross-link polymeric materials. The detailed EB curing process and EB curing behaviour of the acrylate/nanofiller impregnated wood was discussed in another paper separately.
5.2.3.2 Brinell surface hardness

The Brinell surface hardness was measured according to the European Standard EN 1534, using Alliance RT/50 systems from MTS Systems Corporation (Eden Prairie, MN 55344-2290 USA). The hardness modulus was calculated as the slope of load vs. indentation within the 20% to 60% indentation range. Three points were tested for each sample and at least 9 samples were tested for each combination.

5.2.3.3 Impact resistance

The falling ball impact resistance test measures the ability of the impregnated wood boards to resist indentations due to impact by a large diameter ball. The test apparatus is free-falling ball test equipment which followed a standard of FPInnovations – Forintek interior practice method to measure the impact resistance of wood flooring, cabinets and furniture. The picture of the falling ball equipment is presented in Figure 7. (a) a falling ball can be placed at different height thus the indentation force varied due to the falling height. Three electromagnet falling height levels representing low (falling from a height of 3”), medium (falling from a height of 9”) and high (falling from a height of 18”) impact force was tested to evaluate the impact resistance of the impregnated wood boards. The impact spot of indentation fractures was examined and determined Figure 7 (b). The indentation depth and two diameters were examined on the impact fracture spot.

5.2.3.4 Abrasion resistance

The abrasion resistance of the treated and untreated samples was estimated according to ASTM D-4060-95 where an abrasive wheel was mounted on a test wood specimen and rotated for a specified number of cycles, e.g. at 100, 300 and 500 cycles. Weight losses of specimens after rotation were determined and compared. The weight loss ($WL$) after abrasion rotation was calculated as in Equation 1:

$$WL = \left(\frac{W_0 - W_f}{W_0}\right) \times 100$$

(1)

Where $WL$ is weight loss percentage, $W_0$ is mass of sample before taber abrasion, $W_f$ is mass of sample after taber abrasion.

5.2.3.5 Experiment design and data analyses

The factorial design used in this study is presented in Table 4. Factors considered were species (maple and oak), formulation with nanoparticles (WN) and formulation without nanoparticles (NN), and vacuum process time (30s, 60s, 5min, 10min). This led to 8 combinations with nanoparticles and vacuum process time for both maple and oak wood.

The effect of wood species, nanoparticles in the formulations and the vacuum time on Brinell surface hardness, abrasion resistance and impact resistance were analyzed with the Statistical Analysis System (SAS) software. The analysis of variance (ANOVA) of Brinell surface hardness was performed at 9 levels (8 levels of treatments and 1 level of control). The analysis of Duncan group of Brinell hardness was conducted. ANOVA analysis of impact resistance of both indentation fracture diameters and depths at different impact strength on maple and oak wood was performed at 16 levels. The analysis of Duncan group of abrasion resistance was also conducted.
5.2.4 Results and Discussion

5.2.4.1 Brinell Surface Hardness

The Brinell surface hardness of treated maple and oak wood and their controls were presented in Figure 8 and Figure 9, respectively. The Duncan group of Brinell surface hardness were marked in Figure 8 and 9, same letter indicated that the results belongs to the same group and no significant difference in the group. For maple planks, all treatment formulations, both HDDA/TMPTA resin alone and combinations of nanoparticles and different vacuum from 30s, 60s, 5min to 10min, displayed significant improvements in Brinell surface hardness compared with untreated engineering planks. The highest improvement of Brinell surface hardness was shown by HDDA/TMPTA formulation at vacuum time of 30s and 60s, where the surface hardness was improved from 5.05 (Duncan group D) to 15.42 (Duncan group A) and 15.29 (Duncan group A) MPa, respectively, three-fold improvement vs. untreated maple wood. The improvement of surface hardness of maple engineering planks impregnated by only vacuum process from 30s, 60s, 5min and 10min ranged from 125.5% to 202.4%. These improvements regarding surface hardness are similar with the conventional vacuum/pressure (15min/15min) impregnation process to treat aspen wood with MUF and MUF/nanoparticles, where the aspen surface hardness was improved from 1.09 to 3.25 MPa, almost three-fold improvements compared with the untreated aspen wood (Cai et al. 2007a). The surface hardness comparison of conventional vacuum/pressure impregnation process and one step vacuum impregnation process indicated that the elimination of the conventional pressurizing step from the traditional impregnation process was possible to obtain high quality surface densification products.

For oak engineering planks impregnated with HDDA/TMPTA either with or without nanoparticles at different vacuum time, the surface hardness was all improved when compared with untreated oak wood. The surface hardness was improved from 5.25 (Duncan group D) MPa from control oak to minimum 8.78 (Duncan group C) MPa up to maximum 11.05 (Duncan group A) MPa, ranged from 65.7% to 108.5%. The highest improvement was the combination of formulation HDDA/TMPTA with nanoparticles at 5 minutes vacuum time impregnation (Figure 3).

Statistical analyzed the effect of dependent variable and their interaction on Brinell surface hardness of impregnated maple and oak wood by short vacuum process. The statistical analysis results showed a significant effect of nanoparticle addition in the formulation and vacuum process time on the specific Brinell surface hardness at the 0.01 probability level (Table 5) for maple wood. No significant effect of nanoparticle and vacuum process time on the Brinell surface hardness at 0.01 level for oak wood (Table 5). The effect of the two factors interaction of nanoparticles and vacuum process time on the Brinell surface hardness for maple wood is not significant at 0.01 probability level for both maple and oak wood. This could be ascribed to the different anatomy structures of maple and oak wood. Maple is a diffuse porous wood while oak is porous wood, which means the penetration of nanoparticles and formulations have significant effect on diffuse porous structure wood species, thus resulting higher treatability and higher improvement of mechanical performance.

5.2.4.2 Impact resistance

Table 6 presents results of the analysis of variance (ANOVA) for impact resistance properties of maple and oak wood surface densified from short vacuum process and formulation with/without nanoparticles. The diameter and depth of impact indentation fracture from low, medium and high levels impact strength were measured and analyzed by SAS program, which shows a significant effect of surface densification process on the impact resistance from low impact to medium to high impact strength at 0.01 probability level. Figures 10 and 11 show the indentation fracture diameters and depth of treated maple wood and control samples from low, medium and high impacts. The diameter decreased from 4.96 mm to 2.84 mm, 74.6% percent decrease in diameter. The depth of the indentation fracture decreased from 0.172 mm to
0.027 mm, 537% decrease in depth for maple wood treated with 60 s vacuum process with formulation nanoparticles, when the impact strength is low, which indicated that the impact resistance of treated maple wood was improved drastically when the impact strength was low. The diameters of impact indentation fracture decreased from 6.49 mm to 4.10 mm, 58.3% decrease in diameter at medium impact force. The depth of the indentation fracture decreased from 0.302 mm to 0.059 mm, 411.9% decrease in depth for maple wood treated with a 30 s vacuum process and formulation without the addition of nanoparticles when impact strength is medium. When impact strength is high, the diameters of impact indentation fracture decreased from 7.72 mm to 4.62 mm, 67.1% decrease for maple wood treated with 10 min vacuum process and formulation without addition of nanoparticles. The depth decreased from 0.462 mm to 0.107 mm, 331.8% decrease for maple sample treated with 60s vacuum process and formulation without addition of nanoparticle.

Figures 12 and 13 show the indentation fracture diameters and depth of treated oak wood and control sample from different impact strength. At low impact level, the diameter decreased from 4.98 mm to 3.63 mm, 37.2% decrease for oak wood treated with 60s with formulation without addition of nanoparticles and 10min vacuum process with formulation added nanoparticles. The depth of the indentation fracture decreased from 0.145 mm to 0.054 mm, 168.5% decrease for oak wood treated with 60s vacuum process with formulation without addition of nanoparticles, when the impact strength is low. At medium impact level, the diameters of impact indentation fracture decreased from 6.58 mm to 4.84 mm, 36.0% decrease for oak treated with nanoparticles formulation at 10min vacuum process. The depth of the indentation fracture decreased from 0.337 mm to 0.140 mm, 140.7% decrease for oak wood treated with nanoparticles at 60s vacuum process when impact is medium. At high impact level, diameters of impact indentation fracture decreased from 7.60 mm to 6.23 mm, 22% decrease for oak wood treated with 30s vacuum process and formulation without addition of nanoparticles. The depth decreased from 0.472 mm to 0.223 mm, 111.7% decrease for oak sample treated with 5min vacuum process and formulation with addition of nanoparticle.

The effect of dependent variable on impact resistance on impregnated maple and oak wood –indentation fracture depth with different impact strength was presented in Table 7. For the impact indentation fracture depth, the individual factors of wood species time showed significant effect at 0.01 probability level for all impact strength. The vacuum process time showed significant effect on the indentation facture depth at 0.01 probability level when impact strength is low. The effect of vacuum process on indentation fracture depth was not significant at 0.01 probability level when impact strength in medium and high level. The two level interactions of wood species and nanoparticles showed no significant effect at 0.01 probability level on the indentation fracture depth when impact is low. The interactions of wood species and nanoparticles have significant effect on indentation fracture depth at 0.01 probability level when impact strength level is medium and high. The three level interactions of wood species, nanoparticles and vacuum process time showed significant effect at 0.01 probability level on indentation fracture depth when impact strength is in medium level. Considering the weight of F value of individual factor of wood species (F=289.85 at medium impact level, F=273.76 at high impact level) and nanoparticles, the wood species play a key role to determine the interaction which have significant effect for indentation fracture depth at the 0.01 probability level.

For the indentation fracture diameter, the individual factor of wood species and vacuum process time has significant effect at 0.01 probability level for low, medium and high impact strength (Table 8). The effect of addition nanoparticles on the indentation fracture diameter was not significant at 0.01 probability level. The interaction of wood species and vacuum process time, the interaction of nanoparticle and vacuum showed no significant effect on indentation diameter at 0.01 probability level when impact is low. The two factors interaction of wood species and nanoparticle, nanoparticle and vacuum time showed significant effect on indentation fracture diameter at 0.01 probability level when impact strength is at medium and high level. For the three factor interactions, wood species, nanoparticles and vacuum process
time, the effect of indentation diameter is significant at 0.01 probability level only for low impact level. In these two or three levels interactions, the F value of wood species plays a key role because of its high weight ($F = 255.33$ at medium impact level, $F = 396.0$ at high impact level). This could be accredited to the different anatomy structures of maple and oak wood. The nanoparticles plays more important role for diffuse porous structure maple wood than porous oak wood, thus resulting significant effect on impact resistance improvement for maple wood impregnated maple wood than oak wood. Also, the vacuum time is a key factor which related to the diffuse porous and porous structure.

5.2.4.3 Abrasion resistance

The abrasion resistance of treated maple wood and their controls were presented in Figure 14 (a) 100 cycles, (b) 300 cycles and (c) 500 cycles taber abrasion. The weigh loss percentage was presented. The Duncan group of weight loss after taber abrasion with different cycles were marked in Figure 8. The same letter indicated that results belong to the same group and no significant difference in the group. Figure 8 presents the average weight loss value of abrasion resistance test for maple and oak engineered planks treated with 1 step vacuum impregnation process at abrasion rotation cycles of 100, 300 and 500. The weight loss of control maple wood is 0.46%, 1.16% and 1.87% after 100, 300 and 500 cycles abrasion rotation, respectively. The lowest weight loss for treated maple wood is 0.38%, 0.98%, 1.65% at 100 cycles (Ducan group E), 300 cycles (Ducan group C) and 500 cycles (Ducan group D) rotation test, respectively, where the maple wood impregnated with no nanoparticle formulations and the impregnation process of vacuum time at 5 minutes (Figure 14). Maple impregnated with the same formulation at 60s vacuum time showed a little bit higher weight loss than 5 min vacuum time, but still belongs to low weight loss group, where Ducan group belongs to DE for 100 cycles taber rotation test, BC group for 300 cycles and CD group for 500 cycles, respectively. Maple impregnated with nanoparticles/formulations with 10 minutes vacuum time presented highest weight loss of 0.49% (Ducan group ABC), 1.29% (Ducan group A) and 2.08% (Ducan group A) for 100, 300 and 500 cycles taber rotation test, respectively, which presents similar results with control samples at the same taber rotation test. The weight loss of the taber rotation test of treated maple wood presented various group at different rotation cycles. The weight loss of abrasion resistance for first 100 cycles have 5 Ducan groups from A to E, the first 300 cycles have three different Ducan groups from A to C while after 500 cycles, the weight loss percentage of taber rotation test have 4 Ducan groups from A to D.

For the surface densified oak wood, the taber rotation test presented two different Ducan groups for 100, 300 and 500 cycles abrasion test (Figure 15). The weight loss of first 100 cycles taber for oak control samples was 0.68% (Ducan group A), 1.70% (Ducan group A) for 300 cycles and 2.46% (Ducan group A) for 500 cycles taber rotation test, respectively. The lowest weight loss after taber rotation test is the oak wood treated with 5 min vacuum process time and formulation with addition of nanoparticles. They are 0.46% (Ducan group B) after 100 cycles, 1.16% (Ducan group B) after 300 cycles and 1.86 (Ducan group B) after 500 cycles taber rotation test. All the weight loss of treated oak wood after taber rotation was classified to Ducan group B while the control samples are in group A, which indicated the treatment has significant effect for the weight loss of abrasion resistance test and the treatments factors have no significant effect on the weight loss parameters.

The weight loss of both surface densified maple wood and oak wood though short vacuum impregnation process was decreased at different level, which means the abrasion resistance of these treated wood products was improved by the short vacuum impregnation process.

5.2.5 Conclusions

Surface densified wood products were successfully prepared by impregnated into engineered wood flooring planks with low viscosity resin by using simplify vacuum process from 30 s to 10 min without further pressurizing process. The most widely used species of maple and oak in wood flooring industry
were treated with the short vacuum process and formulation with or without addition of nanoparticles. The Brinell surface hardness, impact resistance and abrasion resistance of the treated wood samples were measured. The highest improvement of Brinell surface hardness was improved by 205%, where the Brinell surface hardness increased from 5.05 MPa to 15.42 MPa for maple wood with 30s vacuum process. The Brinell surface hardness of treated oak wood was improved from 5.25 MPa to 10.38 MPa, the highest improvement of 98% with a 60s vacuum process. The impact resistance was tested through a falling ball method and the impact resistance was determined by measuring the diameter and depth of the indentation fracture. The indentation fracture diameter decreased from 4.96 mm to 2.84 mm, 74.6% decrease; while the indentation fracture depth was decreased from 0.172 mm to 0.027 mm, 537% decrease for maple wood impregnated through 60s vacuum process with nanoparticles formulations, which means the impact resistance of short vacuum process impregnated wood was improved drastically. The abrasion resistance property of the surface densified wood products by short vacuum impregnation process was improved for both maple and oak wood. The weight loss of the treated wood decreased with the treatment. A factorial experimental design was completed to study the effects of vacuum time, nanoparticles and wood species on the properties of impregnated wood products. The main effect of the individual factors and the interaction between factors on the properties of impregnated wood products were analyzed with the Statistical Analysis System (SAS).

Acknowledgement
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References

Table 4  Factorial experimental design used in this study

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### Table 5  Effect of dependent variable on Brinell surface hardness of impregnated maple and oak wood

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*significant at the 0.05 probability level, **significant at the 0.01 probability level, NS = not significant at the 0.05 probability level.

### Table 6  ANOVA analysis of impact resistance on maple and oak wood

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Table 7: Effect of dependent variable on impact resistance on impregnated maple and oak wood – indentation fracture depth with different impact strength

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Figure 7  Picture of impact resistance equipment (a) a falling ball can be placed at different height thus the indentation force varied due to the falling height; (b) The impact spot of indentation fractures was examined and determined in both diameter and depth of indentation
Figure 8  Brinell surface hardness of maple wood and treated maple wood with neat resin or resin/nanoparticles with different vacuum process

Figure 9  Brinell surface hardness of oak wood and treated oak wood with neat resin or resin/nanoparticles with different vacuum process
Figure 10  Indentation fracture diameter of maple wood with low impact strength (a), low impact from 3”, (b) medium impact from 9”, (c) high impact from 18”
Figure 11  Indentation fracture depth of maple wood with low impact strength (a), low impact from 3”, (b) medium impact from 9”, (c) high impact from 18”
Figure 12  Indentation fracture diameter of oak wood with low impact strength (a) low impact from 3”, (b) medium impact from 9”, (c) high impact from 18”
Figure 13  Indentation fracture depth of maple wood with low impact strength (a), low impact from 3”, (b) medium impact from 9”, (c) high impact from 18”
Figure 14  Weight loss after different abrasion circles for maple wood (a) 100 cycles taber abrasion, (b) 300 cycles taber abrasion, (c) 500 cycles taber abrasion
Figure 15  Weight loss after different abrasion circles for oak wood (a) 100 cycles taber abrasion, (b) 300 cycles taber abrasion, (c) 500 cycles taber abrasion
5.3 Chapter 3 — An Investigation of Electron-Beam Curing of Acrylate/Nanoparticle Impregnated Wood

5.3.1 Abstract

The feasibility of developing an online industrial viable curing method to cure chemical surface-densified wood products by replacing the traditional time-consuming thermal/pressurization curing with electron beam (EB) cure process was investigated. Traditional methods of wood densification through thermal curing need long cure time, and high energy consumption. Thermal cure methods also produce volatile toxic by-products, create residual stresses in the materials, and require expensive tooling capable of withstanding high autoclave temperatures. Engineered maple wood planks specimens were impregnated with low-viscosity resins of 1,6 hexanediol dimethacrylate (HDDA) and trimethylolpropane trimethacrylate (TMPTA), and layered silicate nanoparticles, using different impregnation processes with a 62 – 64 (wt)% chemical retention (CR). The impregnated wood samples were cured by electron beam (EB) irradiation. E-beam curing method utilizes highly energetic electrons at controlled energy level to polymerize and cross-link polymeric materials. The advantages of this technology over the conventional hot press curing and gamma ray processes include significantly reduced curing time leading to order-of-magnitude improvements in throughput, reduced volatile emissions, reduced energy consumption and no catalyst cost compared to thermal curing method. This research examines the validity of e-beam curing technology in polymerizing wood boards that are chemically impregnated by differential scanning calorimetric (DSC). Neat acylate monomers and the combination of nanoparticles, the acylate impregnated maple samples, EB cured acylate impregnated maples samples and control samples were characterized by DSC from 25°C to 200°C at a heating rate of 5°C/min. Polymerization exotherms were observed for the neat acrylate resin and formulations of acrylate/nanoparticles, impregnated maple samples. No polymerization exothermal peaks were observed for both EB cured impregnated maple and control maple samples. The DSC characterization curves of EB cured impregnated maple and control sample are almost overlapped when compared with neat resin and impregnated maple samples, which confirmed that EB irradiation is an efficient curing method to polymerization acylate impregnated wood surface densification products. The surface hardness and impact resistance properties of EB cured acylate/nanoparticles impregnated maple wood were investigated. The cross section of EB cured acylate/nanoparticles impregnated maple wood was characterized by scanning electron microscopy (SEM).

Key Words: Electron beam (EB), polymerization, differential scanning calorimetric (DSC), surface densification, curing behaviour

5.3.2 Introduction

Wood surface densification via chemical impregnation to improve specific wood properties with high quality wood products has been around for decades (Moore et al. 1983, Rowell 1984, 1991, Schneider 1994, 2001, Singh et al. 1999). Applications of this technology have been limited because of high cost due to large volume chemical consumption, low efficient impregnation process and slow curing process. In our previous work, the feasibility of developing a fast surface densification process, which could significantly decrease chemical consumption but maintain the same or even better properties improvement of the final surface densified wood products, has been investigated (Cai and Blanchet, 2010a, b). This research is to evaluate the feasibility of developing alternative fast curing process – electron beam (EB) irradiation to polymerize chemical impregnated wood products to replace conventional slow thermal cure process. Through combination of our previous developed high efficient surface densification process (Cai and Blanchet, 2010a) and the instant online curable EB technique, a cost–effective industrial viable surface densification–online curing process could be developed, thus to
benefit wood industrial applications such as wood flooring, siding, windows/doors, cabinets and furniture, etc.

Traditional methods of wood densification through thermal curing need long cure time from 30 minutes to hours, and high energy consumption (Cai et al. 2007a, b, 2010). Thermal cure methods also produce volatile toxic by-products, create residual stresses in the materials, and require expensive tooling capable of withstanding high autoclave temperatures. EB curing method utilizes highly energetic electrons at controlled energy level to polymerize and cross-link polymeric materials. The process utilizes ionizing radiation in the form of accelerated electrons which interact with matter by transferring energy to the electrons orbiting the atomic nuclei of target materials. These electrons may then be either released from atoms, yielding positively charged ions and free electrons, or moved to a higher-energy atomic orbital, yielding an excited atom or molecule (free radical) (Wilson 1974). These ions, electrons and excited species are the precursors of any chemical changes observed in irradiated material. At this point, crosslinking occurs in many materials. The amount of energy absorbed, also known as dose, is measured in units of kilogray (kGy), or megarad (MR or Mrad). One Mrad (10 kGy) is equal to 1,000,000 ergs per gram (Bly 1988)

The aim of this work was to investigate the feasibility of EB curing acylate impregnated wood surface densification products. Specific objectives were to develop an instant online polymerization process to cure chemical surface densified wood products to replace the conventional slow pressure thermal curing process. Success with this approach could strategically turn the conventional discontinuous curing process into a continuous industrial viable curing process to polymerize chemical densification wood products. EB radiation as an alternative to chemical initiation in polymerization is a well-known technique (Pusch and Van Herk, 2005, Wadhwa and Walsh, 1982, Crivello et al. 1996, Madani and Badawy, 2004, Janke et al., Minibiole and Yasenchak, 2007). Allaway et al. (1983, US patent 4378278) had successfully applied EB cure multi-functional acylate monomer to form a foaming polymer. Tran et al. (2000, US patent 6103316) reported a method of making electron beam polymerized emulsion-based acrylate pressure sensitive adhesive. In this patent, a one-step process using electron beam radiation to polymerize pressure sensitive adhesives on web from acrylate emulsions is disclosed. Both patents proved that acrylate resin can be polymerized under exposure to EB radiation.

In this work, the engineered maple and oak planks were impregnated with a formulation contains HDDA/TMPTA (75/25) plus 1% nanoparticles at different vacuum time. The impregnated wood planks with a chemical retention above 60 (wt%) were cured by EB radiation. The validation analysis of EB polymerization acrylate oligomers impregnated wood planks were characterized with different scanning calorimetric (DSC). Neat formulation of acrylate oligomers HDDA/TMPTA, HDDA/TMPTA plus 1% nanoparticles were scanned with DSC from 25°C temperature to 200°C with a heating rate of 5°C /min. Both formulations of HDDA/TMPTA with and without nanoparticles impregnated maple wood were characterized with DSC at same test parameters. The control maple wood sample and EB cured HDDA/TMPTA impregnated wood samples were scanned with DSC characterization. Polymerization exothermal peaks of neat acrylate resin, formulation of acrylate/nanoparticles and impregnated maple samples were compared. No polymerization exothermal peaks were observed for both EB cured impregnated maple and control maple samples. The characterization of DSC confirmed that EB cure is an efficient polymerization method to cure fully penetrated acrylate oligomers impregnated wood planks. The surface hardness of EB cured acrylate oligomers impregnated maple planks were improved up to 200% compared to the control maple wood. Scanning electron microscopy (SEM) characterization photos showed that the EB cured acrylate monomer impregnated wood penetrated into the wood voids space.
5.3.3 Materials and Experimental

5.3.3.1 Materials and sample preparation

The engineered wood planks used in this research included maple (*Acer saccharum*), with a dimension of 28.5” × 3.5” × 1/8”. 1,6 hexanediol dimethacrylate (HDDA) and trimethylolpropane trimethacrylate (TMPTA) with a ratio of 75/25 (HDDA/TMPTA) were selected as the transportation medium resin for nanoparticles, which was supplied by AkzoNobel (formerly Chemcraft International, Warwick, Canada). The Claytone® APA nanoparticles used in this work were provided by Southern Clay Products, Inc. (USA). The wood planks with a moisture content of 8% were impregnated with formulation of HDDA/TMPTA (75/25) either containing 1% nanoparticle or neat monomers. The details of impregnation process were described in our previous work (Cai et al. 2007a, Cai and Blanchet 2010). The chemical retention of the impregnation maple wood was calculated based on their mass change as follow:

\[
CR = \left( \frac{M_1 - M_0}{M_0} \right) \times 100
\]

where \(M_0\) is the mass before treatment and \(M_1\) the mass after impregnation.

5.3.3.2 EB curing HDDA/TMPTA/nanoparticles impregnated engineered wood planks

The process utilizes ionizing radiation in the form of accelerated electrons which interact with matter by transferring energy to the electrons orbiting the atomic nuclei of target materials. These electrons may then be either released from atoms, yielding positively charged ions and free electrons, or moved to a higher-energy atomic orbital, yielding an excited atom or molecule (free radical). These ions, electrons and excited species are the precursors of any chemical changes observed in irradiated material. The accelerated electrons can penetrate the curing substrate and the depth of the penetration depends on the dose of the EB generator. The mechanism of electrons penetration and thus cure the substrate is illustrated in Figure 16 (BNP-guide, 2006). The acrylate monomers impregnated wood planks were sent to EB Services Inc. for the curing. All samples were irradiated to 100kGy, using 4.5 MeV energy electrons. The accelerator used was a RDI Dynamitron. The dose provided increments of 25 kGy per pass. Samples were processed from one side. Temperature of samples was below 120°F upon completion of the irradiation. The time between passes was about 7 minutes when running at full speed. The polymerization reaction of HDDA and TMPTA was completed under the accelerated electrons radiation. Figure 17 shows the EB cured HDDA/TMPTA impregnated maple planks with different impregnation time. The mass of the EB cured impregnated wood samples were measured to calculate the density of the final surface modification wood products. The chemical retention of acrylate impregnated maple was above 60 wt% and the density of the EB cured final products are presented in Figure 3.

5.3.3.3 Validation characterization with DSC

All DSC measurements were made with a Mettler DSC 20 that was equipped with a Mettler TA400 thermal analysis system and STAR® software. The neat HDDA/TMPTA resins and the nanoclay/resin mixtures with 1% of thermal catalyst Vazo®67 were tested, by placing about 10 mg of each sample into a sample crucible. A high-pressure steel-sealed capsule that can withstand vapour pressure up to 10 MPa was used to prevent the components of the samples from evaporating at high temperature. Dynamic scans were made from 25°C to 200°C at heating rates of 5°C/min. Minimum 3 repetitions DSC characterization were carried out for each group of samples. Both neat resin and resin with 1% nanoparticles impregnated maple and oak wood was scanned with DSC, by placing about 10 mg of each sample into an aluminum gold-sealed capsule. EB cured impregnated maple and oak wood samples and control pure wood samples were scanned by placing about 10 mg of each sample into an aluminum capsule sealed with a gold film. The heating rate with 5°C/min of the dynamic scans were made from 25°C to 200°C. The apparent activation energy of the curing reaction of the HDDA/TMPTA resin along or a mixed nanofiller/HDDA/TMPTA sample was calculated on the basis of the variation of the peak reaction
temperature ($T_{max}$) as a function of the heating rate increase of the DSC scan, using Kissinger methods (1957). The integral of the exotherm peak was calculated and summarized.

5.3.3.4 Scanning electron microscopy and surface hardness measurement of EB cure wood samples

The cross section of EB cured HDDA/TMPTA impregnated wood samples were characterized using a Jeol JSM-840A scanning electron microscope. The blocks of untreated maple and oak wood, and those treated with a chemical (or chemical/nanoparticles) were prepared with a microtone by carefully cutting one of the end-grain faces to a depth of about 3 mm. All blocks were desiccated with phosphorus pentoxide for two weeks. A gold/palladium alloy was sputtered onto the prepared surfaces prior to the investigation. The Brinell surface hardness of acrylate impregnated maple wood cured by EB radiation were measured. The Brinell surface hardness was measured according to the European Standard EN 1534, using Alliance RT/50 systems from MTS Systems Corporation (Eden Prairie, MN 55344-2290 USA). The hardness modulus was calculated as the slope of load vs. indentation within 20% to 60% indentation range. Three points were tested for each sample and at least 9 samples were tested for each combination.

5.3.4 Results and Discussion

5.3.4.1 EB curing HDDA/TMPTA/nanoparticles impregnated engineering wood planks

Electron beam generators are commercially available from a variety of sources. For any given piece of equipment and irradiation sample location, the dosage delivered can be measured in accordance with ASTM E-1275 entitled “Practice for use of a radiochromic film dosimetry system.” Dose is the total amount of energy deposited per mass unit. It can be determined in accordance with the following equation:

$$Dose = \frac{CurrentDensity}{ExposureTime} \times C \quad (2)$$

wherein the current density is in milliamperes, the exposure time is the sample exposure time and $C$ is the processing machine constant, an inherent value depending upon the particular machine used. Exposure time is often expressed in line speed. Dose is commonly expressed in Megarads (Mrads) or kilograys (kGy). A Mrad is 10 kilograys. A rad is defined as the amount of radiation required to supply 100 ergs of energy per gram of mass, with a megarad comprising one million rads. A kilogray is defined as the amount of radiation required to supply 1 joule of energy per kilogram of mass. The total dose received by the precursor emulsion – acrylate resin impregnated into the wood primarily affects the extent to which monomer is converted to polymer and the extent to which the polymers are crosslinked. Total dosage depends on a number of processing parameters including voltage, beam current, residence time (total time the sample is irradiated), distance from the accelerated electron source, web speed, and number of passes. Dose can be regulated by controlling line speed (i.e., the speed at which the precursor emulsion target dose can be conveniently calculated by multiplying an experimentally measured coefficient (a machine constant) by the beam current and dividing by the web speed to determine the dose. The machine constant varies as a function of beam voltage. (Tran and Weiss, 1998; Allaway et al. 1981)

In order to provide enough penetration and polymerization of acrylate impregnated wood planks, it is preferable that the dosage should be greater than 25 kGy with 4 passes. A radiation polymerization step can be carried out in a broad range of temperatures, with the preferred range being from about 20°C to 30°C. At this range of ambient temperatures, the heating or cooling energy requirements of the process are minimized. The fully penetrated multifunctional acrylate monomer formulations or formulations mixed with nanoparticles impregnated engineering wood planks is then passed under the electron beam so as to polymerize the acrylate monomers to a polymer composites structure. The chemical retention of the acrylate impregnated wood planks is ranged from 62 – 64 (wt)% as shown in Figure 18. The density of
the EB cured acylate impregnated maple planks and the control maple wood was also indicated in Figure 18. Final EB cured acrylate impregnated wood products were presented in Figure 17, where sample A is the control sample, B is acrylate monomers impregnated maple planks with 10 min vacuum process, C is acrylate monomers impregnated maple planks with 5 min vacuum, D is acrylate monomers impregnated maple planks with conventional 15 min vacuum followed by a 15 min pressure process (Cai et al. 2007a, Cai and Blanchet, 2010). The EB cured acrylate monomers formulation or formulations with nanoparticles impregnated engineered wood planks have smooth surface and some polymerized acylate polymer on the side faces of the cured impregnated maple wood samples can be found.

5.3.4.2 Curing behaviour of EB polymerization acrylate/nanoparticles

The validation analysis of polymerization of EB irradiation is very important to develop an online applicable curing process to cure impregnated wood planks. To verify if the EB cure is an efficient polymerization method, further investigation via differential scanning calorimetric (DSC) characterization was using to validate the curing behaviour of EB cure acylate or acylate/nanoparticles impregnated wood samples. Neat HDDA/TMPTA acylate multifunction monomer, HDDA/TMPTA/nanoparticles plus 1% of thermal catalyst Vazo®67 were characterized by DSC from 25°C to 200°C with a heating rate of 5°C/min. A minimum of three experiments were repeated for each formulations. The DSC characterization analysis results are presented in Figure 4. Big exothermal peaks were observed for both neat acrylate monomers and acylate/nanoparticles. The peak temperature of neat acrylate monomer is 102.24°C and a little higher peak was observed with the addition of 1% nanoparticles into the acylate monomer formulations, where 105.15°C peak temperature was observed (Table 9). The onset temperature of the reaction ranged from 98°C to 101°C for neat acrylate monomers and addition of nanoparticles.

HDDA/TMPTA acylate impregnated maple wood, HDDA/TMPTA/nanoparticles acylate monomer impregnated maple wood were placed in an aluminum gold-sealed capsule. Same scanning parameters as neat acylate monomers or formulation plus nanoparticles were used to characterize the impregnated maple wood. The DSC characterization analysis results are presented in Figure 20. Exothermal peaks were observed for both neat acylate monomers and acylate/nanoparticles. Similar with neat acrylate resin and acylate/nanoparticles, lower peak temperature for neat acrylate impregnated maple wood was observed at 96°C while the acylate/nanoparticles impregnated wood peak was observed at 104°C (Table 9). The onset temperature of the reaction ranged from 85°C to 102°C, which indicated that the addition of nanoparticles shifted the polymerization onset temperature.

EB cured acrylate impregnated maple wood and control maple wood were characterized with DSC at the same test parameter as uncured impregnated maple wood. The analysis results are presented in Figure 21. No exothermal peaks were observed for both neat EB cured impregnated maple wood and the maple control wood. The comparison analysis results of DSC characterization for neat acrylate monomers, impregnated wood, EB cured impregnated wood and wood control samples are presented in Figure 21. It can be observed that either the neat acrylate monomer or acylate/nanoparticles have big exothermal peaks compare to acylate impregnated maple wood. The integral energy of the peaks (mJ) for neat acrylate monomers, acylate/nanoparticles, maple wood impregnated with acylate monomers and acylate/nanoparticles, the EB cured impregnated maple wood and the control maple wood were summarized in Table 9. The integral energy of the neat acrylate monomer peak is 4036.15 mJ while the acylate/nanoparticles is 4553.63 mJ, which is the highest peaks compare with the other groups. The integral energy of impregnated maple wood is 1934.23 mJ and 840.01 mJ for neat resin and acylate/nanoparticles impregnated maple wood, respectively. The integral energy of impregnated of EB cured impregnated maple wood and maple control wood has least value where only as least as negligible 45.73 mJ and 44.11 mJ compare with neat resin or uncured impregnated wood samples, respectively. No exothermal peaks were observed for both EB cured acylate impregnated maple wood and control maple wood samples, which meant no free monomer exists in the EB cured acylate impregnated wood and control wood samples. Furthermore, the DSC analysis of EB cured acylate impregnated maple wood and
the control maple wood samples are almost overlapped, which indicated that they had very similar reaction when analyzed with DSC characterization. Thus the comparison of curves in Figure 21 confirmed that the EB cure is an efficient curing method for acylate, acylate/nanoparticles impregnated engineered wood planks.

5.3.4.3 SEM characterization EB cured impregnated maple wood

The cross sections of the control maple wood samples, EB cured neat acylate monomer impregnated maple wood and acylate/nanoparticles impregnated maple wood samples were characterized by SEM to see the morphology of cured acylate in the wood structure. The SEM pictures were presented in Figure 22. Figure 22 (a) is the control maple wood, (b) is neat acylate impregnated maple wood cured by EB and (c) is the acylate/nanoparticle impregnated maple wood cured by EB irradiation. From (b) and (c), it can be observed that the void part of the maple cross section were filled with cured acylate polymers or cured acylate/nanoparticle polymers, thus to form a three dimensional polymer composites structure with wood.

5.3.4.4 Improvement of Brinell surface hardness and impact resistance

Surface hardness and impact resistance are two important properties for wood products, especially for some specific applications, for example, used as wood flooring products. The improvement of surface hardness and impact resistance via surface densification process are desirable properties that wood products industry are seeking for. Brinell surface hardness of maple control samples, neat HDDA/TMPTA resin impregnated maple wood cured by EB were measured according to standard EN1534 and the results are presented in Figure 23. For the control maple, the Brinell surface hardness is 5.2 MPa. The surface hardness is 15.4 MPa for the EB cured acrylate impregnated maple wood with 5 minutes vacuum process, 197% improvement compare to controls. The surface hardness of 10 minutes vacuum impregnation process and 15min vacuum plus 15 pressure impregnation process gives 14.8 MPa and 16.4 MPa surface hardness, respectively, where 185% and 215% improvement were achieved via EB cured acylate impregnated maple wood. The surface hardness of EB cured acylate impregnated maple wood was improved drastically.

The impact resistance were measured with a lab standard setup practiced at FPInnovations – Forintek eastern lab. A steel ball was falling down from different heights to hit the target wood surface. The impact resistance properties were indicated by measuring the diameters and depth of the indentation fracture by the hitting of the falling steel ball. The control maple wood samples, EB cured acylate impregnated maple wood with different impregnation process were tested. Three heights represent three level of impact (low, medium and high impact where 3”, 9” and 18” in height were measured). Minimum 5 samples were tested, 6 testing points for each samples, thus 30 test datas were collected for each parameters. Results were summarized in Table 10. Both indentation depth and diameters were measured for three different impact strengths. For the indentation depth, compared with the control maple samples with different impregnation process, depth was significantly lower than untreated control wood at different impact levels. The indentation depth is 0.187 mm, 0.332 mm and 0.485 mm for untreated control maple wood from different falling height of 3”, 9” and 18”, respectively. The same value for the EB cured acylate impregnated maple wood from 5 min vacuum process are 0.043 mm, 0.053 mm and 0.080 mm, for the steel ball falling from 3”, 9” and 18”, respectively. Similar results were observed for different impregnation processes. This indicated that the indentation depth of EB cured acylate impregnated maple wood was decreased significantly compared to the untreated maple samples. Similar results were observed for the diameters of the impact indention fracture. For the untreated maple wood samples, the diameters of indentation were 5.07 mm, 6.65 mm and 7.77 mm for the impact steel ball falling from different heights at 3”, 9” and 18”, respectively. These parameters were 3.48 mm, 4.06 mm, 4.96 mm for EB cured acylate impregnated maple wood with 5 min vacuum impregnation process, significantly lower than untreated maple wood. Both indentation depth and diameters were decreased significantly for EB
cured acrylate impregnated maple wood with different impregnation processes, which indicated that the impact resistance of the EB cured surface densification wood products are improved drastically.

5.3.5 Conclusions

This research investigated the feasibility of developing an online EB curing process to polymerize chemical surface-densified wood products by replacing the traditional slow thermal/pressurization curing process. Low viscosity HDDA/TMPTA impregnated maple wood with a chemical retention of 62-64 wt% was cured by EB irradiation. The EB cured acrylate impregnated maple wood, acrylate or acrylate/nanoparticles impregnated wood, neat acrylate resin and acrylate/nanoparticles were characterized by DSC to validate the polymerization reaction of the acrylate into the maple wood. Polymerization exothermal peaks were observed for neat acrylate resin, formulation of acrylate/nanoparticles, impregnated maple samples. No polymerization exothermal peaks were observed for both EB cured impregnated maple and control maple samples. The DSC characterization curves of EB cured impregnated maple and control samples are almost overlapped when compared with neat resin and impregnated maple samples, which confirmed that EB irradiation is an efficient curing method to polymerize acrylate impregnated wood surface densification products. The surface hardness and impact resistance properties of EB cured acrylate/nanoparticles impregnated maple wood were drastically improved compared to the untreated maple wood. The surface hardness was improved up to 200% compare to the untreated maple wood. The cross section of EB cured acrylate/nanoparticles impregnated maple wood was characterized by scanning electron microscopy (SEM) and it was confirmed that the EB cured acrylate polymer distributed into the void and lumen of the maple structure. This work proved that EB cure might be an efficient alternative instant curing process to cure chemical impregnated wood products.

Acknowledgements

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Reference

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Christopher J. Janke; George F. Dorsey; Stephen J. Havens; Vincent J. Lopata, ELECTRON BEAM CURING OF EPOXY RESINS BY CATIONIC POLYMERIZATION


Rowell 1984,


Singh et al. 1999


Table 9  DSC characterization results for pure acrylate resin, acrylate/nanoparticles, acylate impregnated maple wood, acylate/nanoparticle impregnated maple wood, EB cure impregnated wood, wood controls

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¹ acrylate – HDDA/TMPTA (75/25)
² M-acylate – HDDA/TMPTA (75/25) impregnated maple wood
³ EB cure M – EB cure impregnated maple wood

Table 10  Impact resistance of EB cure impregnated sugar maple samples

<table>
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<td>0.187 a</td>
<td>0.332 a</td>
</tr>
<tr>
<td>V-5 min</td>
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<td>0.053 b</td>
</tr>
<tr>
<td>V-10 min</td>
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<td>0.057 b</td>
</tr>
<tr>
<td>V/P-15/15min</td>
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<td>0.056 b</td>
</tr>
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</table>
Cost Reduction and Optimization of Advanced Impregnation Technologies with Nanotechnology

Figure 16  (a) Electron Beam curing work mechanism: utilize highly energetic electrons at controlled energy levels to polymerize and cross-link polymeric materials, (b) RDI Dynamitron accelerator of E-Beam

Figure 17  EB cure impregnated sugar maple samples, A-Control, B-10min vacuum, C-5min vacuum, D-15/15min vacuum/pressure
Figure 18  Chemical retention and final density of HDDA/TMPTA impregnated maple wood with different vacuum impregnation time.
Figure 19  DSC analysis curing behaviour of Formulation 1 – HDDA/TMPTA (75/25 wt%)

Figure 20  DSC analysis curing behaviour of maple engineered plank impregnated using acrylate monomer – HDDA/TMPTA (75/25 wt%), and acrylate monomer – HDDA/TMPTA (75/25 wt%) plus 1 wt% nanoparticles Claytone® APA
Figure 21  Comparison of DSC characterization results of HDDA/TMPTA (75/25), HDDA/TMPTA (75/25) and 1 wt% nanoparticles, maple impregnated with HDDA/TMPTA, EB (electron beam) cured impregnated maple sample, pure maple sample without any treatment
Figure 22  Scanning electron microscopy of cross section of (a) maple controls, (b) EB polymerized maple wood impregnated with HDDA/TMPTA and 1% nanoparticles, (c) EB polymerized maple wood impregnated with HDDA/TMPTA resin
Figure 23  Brinell surface hardness of EB cured HDDA/TMPTA impregnated maple wood with different vacuum impregnation time
5.4 Chapter 4 — UV/thermal dual cure acrylate surface densified maple engineered wood planks by roller/coater application resin with a vacuum penetration process

5.4.1 Abstract

This work investigated the feasibility of preparing surface-densification wood products with applying a layer of resin on the wood surface either by roller or coater coating. The resin applied wood samples were then vacuumed for 60s to penetrate the acrylate monomers/oligomers into the wood surface. Maple engineered wood planks were surface densified with acrylate monomers/oligomers at different viscosity. 4(wt)% photo initiator plus 1(wt)% thermal catalyst were added into the impregnation formulations. The chemical retention was measured. The treated maple engineered wood planks were cured by UV/thermal dual cure. The penetrated depth of maple surface densification products through application of resin on the surface followed by a vacuum process was investigated by vertical X-ray density profile. The chemical retention was much lower than the traditional fully penetrated chemical impregnated wood surface densification products. The chemical penetration depth of this approach is concentrated from the surface to a depth of 1 – 2 mm. The validity of UV/thermal dual cure to polymerize wood surface densification products was evaluated by photo-DSC characterization. Neat acrylate monomers with 4(wt)% photo initiator and 1(wt)% thermal catalyst, the acrylate surface densified maple samples, UV/thermal cured acrylate surface densified maple samples with different resin application methods were characterized by photo-DSC. Polymerization exotherms were observed for the neat acrylate resin and surface densified maple samples. No polymerization exothermal peaks were observed for both UV/thermal cured acrylate densified maple for different viscosity formulations. 4 different viscosities of acrylate monomer/oligomers formulations were evaluated, the polymerization exotherms peaks are decreased with the decrease of the viscosity. The photo-DSC characterization curves of UV/thermal dual cured acrylate densified maple are almost a flat line when compared with neat resin and impregnated maple samples. No polymerization exotherms peaks were observed for UV/thermal dual cure acrylate densified maple samples, which confirmed that UV/thermal approach is an efficient curing method to polymerization acrylate impregnated wood surface densification products.

Keywords: UV/thermal dual cure, roller/curtain coating, vacuum process, vertical X-ray density profile, photo-DSC, chemical penetration

5.4.2 Introduction

Traditional methods of wood surface densification through chemical impregnation can produce high value-added wood products. However, the applications of traditional vacuum/pressure impregnation technology to produce value-added surface densification wood products were limited. The main obstacle to apply this technology for wood products industry is due to the slow impregnation process, relatively high cost because of the large volume of chemical using, slow curing methods. The traditional vacuum/pressure impregnation process needs a minimum of half an hour to hours to complete the application and penetration chemicals into the wood structure. The high volume chemical consumption of this process might go up to 80-200 (wt)% and fully penetrate the wood from surface to the center of the treated sample, which cause the cost of the surface densification products unreasonably high (Beall et al. 1973, Brelid P. L. 2002, Rowell 1991, Wright and Mathias, 1993a, b, Wan 2004). The conventional thermal curing either by steam or hot press took long cure time from 30 minutes to hours to complete the polymerization of chemical impregnated wood samples. Thermal cure with steam or hot press need high energy consumption and require expensive tooling capable of withstanding high autoclave temperatures (Cai et al. 2007a, b, 2010). Thermal cure methods also produce volatile toxic by-products, create residual stresses in the materials and some impregnated chemical can be evaporated with the hot press process (Wan 2004).
As vacuum/pressure schedules require batch processing, the impregnation process is a discontinuous process and the production efficiency is quite low. This work investigated the feasibility of development a continuous impregnation process followed with an instant UV/thermal fast cure process to polymerize the free radical chemical densified wood products. The impregnation process contains two steps. The first step is the application of a layer of resin on the wood surface either by roller or curtain coater. The second step is to penetrate the resin into the wood structure with a 60s vacuum process. Our previous work (Cai and Blanchet 2010a) proved that the break of vacuum plays a key role for the penetration of chemicals into the wood structure. The last step of the surface densification process is the development of an instant cure process to polymerize the chemical surface densified wood products. Attempt of using electron beam irradiation to polymerize the chemical impregnated wood products was successfully developed in our previous work in this project (Cai and Blanchet 2010b). EB cure is an efficient and powerful instant online curing approach to polymerize the free radical chemical impregnated wood products. The main drawback of EB cure for our wood industry to deploy this technology is that the capital investment of EB generator was quite high. Alternative instant online curing approach with reasonable cost was seeking to benefit our wood industry.

Hoyle and Pojman (2009) developed a method for rapidly curing wood putty utilizing frontal polymerization. The reaction is initiated with UV light, and a reaction front propagates through the putty, completing the cure in seconds. A depth of cure of more than 1 cm deep of the wood putty is rapidly achieved. The mechanism of this UV/thermal dual cure used a combination of photoinitiator(s) and thermal initiator(s) in the system. Polymerization starts at the top layer as a result photoinitiation. The heat generated from photopolymerization causes thermal decomposition of thermal initiators, producing initiating radicals that initiate the polymerization; the polymerization front travels downwards from the surface to achieve a complete cure. Similar to conventional thermal frontal polymerization, the amount of heat produced is essential in increasing the temperature of the immediate, uncured layer to the decomposition temperature of thermal initiators and to maintain the traveling front.

The aim of this work was to develop a two step online surface densification process through application resin with roller/curtain coater and followed a fast vacuum penetration process. The feasibility of development of online UV/thermal dual cure process to polymerize the surface densification products was also investigated. A successful combination of the two steps impregnation process plus an instant UV/thermal dual cure process can strategically turn the conventional discontinuous curing process into a continuous industrial viable surface densification process. The new development surface densification process can efficiently replace the traditional discontinuous vacuum/pressure impregnation plus a slow thermal cure process, thus to benefit our wood industry, especially for wood flooring, siding, windows/doors, cabinets, furniture, decking, etc.

In this work, the feasibility of preparing surface-densification wood products with application of resin on the wood surface either by roller or curtain coater was investigated. A short vacuum process followed with 60s to help the resin penetrate into the wood surface. Maple engineered wood planks were surface densified with acylate monomers/oligomers at different viscosity. 4(wt)% photo initiator plus 1(wt)% thermal catalyst were added into the impregnation formulations. The chemical retention was measured and the chemical retention was much lower than the traditional fully penetrated chemical impregnated wood surface densification products. The treated maple engineereed wood planks were cured by UV/thermal dual cure. The penetrated depth of maple surface densification products through application of resin on the surface followed by a vacuum process was investigated by vertical X-ray density profile. The chemical penetration depth of this approach is concentrated from the surface to a depth of 2 mm. The validity of UV/thermal dual cure to polymerize wood surface densification products was evaluated by photo-DSC characterization. Neat acylate monomers with 4(wt)% photo initiator and 1(wt)% thermal catalyst, the acylate surface densified maple samples, UV/thermal cured acylate surface densified maples samples with different resin application methods were characterized by photo-DSC. Polymerization
exotherms were observed for the neat acrylate resin and surface densified maple samples. No polymerization exothermal peaks were observed for both UV/thermal cured acrylate densified maple for different viscosity formulations. 4 different viscosities of acrylate monomer/oligomers formulations were evaluated, the polymerization exotherms peaks are decreased with the decrease of the viscosity. The photo-DSC characterization curves of UV/thermal dual cured acrylate densified maple are almost a flat line when compared with neat resin and impregnated maple samples. No polymerization exotherms peaks were observed for UV/thermal dual cure acrylate densified maple samples, which confirmed that UV/thermal approach is an efficient curing method to polymerization acrylate impregnated wood surface densification products.

5.4.3 Materials and Experimental

5.4.3.1 Materials and sample preparation

The engineered wood planks used in this research included maple (Acer saccharum), with a dimension of 5'' × 3.5'' × 1/8'' (where 1/8” is the top layer thickness of the engineered surface). Polyester acrylate oligomer (PEAO) and trimethylolpropane triacrylate (TMPTA) were selected as free radical impregnation resin, which was supplied by Sartomer. 4 different viscosities (V1, V2, V3 and V4) with different ratio of PEAO and TMPTA were used as the surface densification formulations. The details of the ratio and their viscosities were measured and the results are presented in Table 11. Photo initiator ESACURE SM246 was added into the formulation with a ratio of 4 wt% and it was supplied by R.M. Ferguson & Company Inc. 1 (wt)% thermal catalyst of Vazo® 67 was added into the formulation, which was supplied by DuPont.

5.4.3.2 Application resin and penetration of resin into wood surface

Wood planks with a moisture content of 8% were roller or coater coated with a layer of acrylate monomers/oligomers resin with 4 formulations at different viscosity V1, V2, V3 and V4. The coated wood planks were then placed in a vacuum autoclave. For single resin application time, 1 time 60s vacuum process followed by the application of resin. For multiple resin application times (3 times), 60s vacuum process followed each resin application, totally 3 times of 60s vacuum process followed to help chemical penetration. The vacuum process parameter include vacuum to a pressure of 25 mm Hg, maintain this vacuum for 60s, then open the valve to release the vacuum. Remove the samples from the cylinder, the samples were wiped off for the residue of the chemicals. The mass of wood planks were measured before and after the application and penetration of the chemicals. Chemical retention was calculated through the equation as follows:

\[
\text{Chemical retention (g/m}^2\text{)} = \frac{(M_f-M_0)}{\text{surface area}} \tag{1}
\]

where \(M_f\) is the sample mass after treatment and \(M_0\) the sample mass before treatment.

5.4.3.3 X-ray Vertical Density Profiles

Specimens of untreated and treated maple engineered wood planks were cut into 5 cm × 5 cm sub-specimens for the measurement of density profiles. Specimens were conditioned at 65% RH (relative humidity) and 20°C for at least three weeks before testing. After proper conditioning, the exact dimensions and weight of all specimens were recorded in order to determine densities. Density values were then converted into specific gravity values at 12% moisture content using the following equation (Siau 1984):
\[
\rho_{12} = \frac{\rho}{(1 + \frac{MC}{100}) \times \rho_w}
\]  

(2)

where \(\rho_{12}\) is the wood specimen’s specific gravity at 12% moisture content, \(\rho\), its density, and \(\rho_w\) its density at different thickness positions, while \(MC\) is its moisture content.

The vertical density profiles of both impregnated and non-impregnated specimens were thus determined using an X-Ray density profilometer.

### 5.4.3.4 UV/thermal dual cure the surface densification wood products photo-DSC characterization

The validation of UV/thermal cure acrylate monomers/oligomers curing behavior was evaluated with a Photo-DSC (DSC822e from METTLER-Toledo). The UV source used is Lightningcure\textsuperscript{TM} L8333, which is a gallium lamp (240 nm to 400 nm) from Hamamatsu with a maximum absorption at 360 nm. Table 12 presents the output of the UV lamp used. Neat acylate monomer/oligomer with different viscosity samples prepared for these experiments were prepared at 2.0 ± 0.1 mg and they were cured at an intensity of 40 mW/cm\(^2\) at a thickness of 200 μm. Experiments were performed under airflow of 50 ml/min at 30°C. Heat of reaction and induction times are obtained from exotherms. Kinetic parameters of the different formulations like reaction orders and rate constant were determined.

### 5.4.3.5 Data reduction

Photo-DSC allows obtaining an exothermal reaction related to the UV radiation curing of the acylate monomer/oligomer coating and painting films (Landry \textit{et al.} 2008). There are two general kinetics models which include \(n\)th-order and autocatalytic models for thermosetting resins. The equation of \(n\)th-order could be expressed as follows:

\[
\frac{d\alpha}{dt} = k(1-\alpha)^n
\]  

(3)

where \(d\alpha/dt\) is the reaction rate given in sec\(^{-1}\), \(\alpha\) is conversion of the reaction or fraction content with time \(t\), \(k\) is the specific rate constant and \(n\) is the reaction order. The UV radiation curable coating/painting followed by an autocatalytic model, which was first introduced by Kamal (1973) as indicated in Equation (4) as follows:

\[
\frac{d\alpha}{dt} = (k_1 + k_2\alpha^n)(1-\alpha)^m
\]  

(4)

where \(k_1\) is the externally catalyzed rate constant and \(k_2\) is the autocatalyzed rate constant with Arrhenius temperature dependency. The reaction orders \(m\) and \(n\) represented the initiation and propagation step, respectively. If the initial rate of the reaction is negligible, eq. (3) can be reduced to:

\[
\frac{d\alpha}{dt} = k\alpha^n(1-\alpha)^m
\]  

(5)

For both \(n\)th-order and autocatalytic models, temperature dependence of the specific constant rate, \(k\), was assumed to follow the Arrhenius equation presented below:

\[
k = A \exp\left[-\frac{E}{RT}\right]
\]  

(6)
where $A$ is the frequency or the pre-exponential factor which is a constant, $E_a$ is the activation energy of the system, $R$ is the universal gas constant (8.31 J mol$^{-1}$K$^{-1}$) and $T$ the temperature. Parameters $d\alpha/dt$ and $\alpha$ can be both obtained from the DSC curves. The reaction rate, $d\alpha/dt$, is given by $(dH/dt)/\Delta H_p$ and $\alpha$, the extent of reaction, by $\Delta H_p/\Delta H_o$. $\Delta H_p$ is the curing enthalpy after time $t$ and $\Delta H_o$ is the maximum enthalpy, calculated from the area under the DSC curve.

5.4.4 Results and Discussion

5.4.4.1 Formulation viscosity and chemical retention

Table 11 presents the viscosities of different formulations. V1 contains 100% Polyester acrylate oligomer (PEAO) and the viscosity is 584.1 cps at room temperature. V2 contains PEOA and trimethylolpropane triacrylate (TMPTA) with a ratio of 75% to 25%, the viscosity is 295.4 cps. The component PEOA/TMPTA ratio of V3 is 50% to 50% and their viscosity is 167.7 cps. The ratio of PEOA/TMPTA of V4 is 25% to 75% and the viscosity is 97.4 cps. The formulation viscosity decreased drastically with the addition of TMPTA.

The mass before and after surface densified wood products through roller/coater applied technology under single or multiple applied times with different formulation viscosities were measured. The chemical retentions of surface densified products was calculated by Equation (1) and expressed as weight gain per square meter (g/m$^2$). The results obtained are illustrated in Figure 24. By comparing the effect of application technology and application time on the chemical retention, it can be found that roller coating with 1 application showed lowest CR from 95g/m$^2$ to 124g/m$^2$. Multiple application of roller coating showed higher chemical retention from 227g/m$^2$ to 473g/m$^2$ than single roller coating application of resin; the wood surface varied from 168g/m$^2$ to 207g/m$^2$. Single coater coating application of resin on the wood surface presented higher chemical retention from 131g/m$^2$ to 332g/m$^2$ than single roller application of resin on the wood surface. When comparing the effect of viscosity on the CR, it can be found that the chemical retention improved from V1 to V4, which means the CR increased with the decrease of formulation viscosity, which means lower viscosity formulation have better permeability than high viscosity formulations.

5.4.4.2 X-Ray Vertical Density Profile

Figure 25 shows density profiles for the treated maple wood with different vacuum times and formulations (with and without nanoparticles) from the surface to a depth of 2 mm. Figure 25(a) is the formulation V1 with different resin application technologies and different application times (single/multiple application times). Figure 25(b), (c) and (d) are the vertical density profile of formulation V2, V3 and V4, respectively. All formulations from V1-V4 showed a density peaks. For formulation V1, peaks depth ranged from 0.14 mm – 0.20 mm and the highest peak density is 1016kg/m$^3$ compare with controls’ peak at 0.10 mm with 872kg/m$^3$. The peaks depth located from 0.12 mm – 0.22 mm with a highest peak density of 943kg/m$^3$ compare with controls’ peak at 0.12 mm with 787kg/m$^3$. For formulation V2, the peaks depth ranged from 0.08 mm – 0.14 mm and the highest peak density is 1070kg/m$^3$ compare with controls’ peak at 0.08 mm with density of 880kg/m$^3$. The peaks depth located from 0.18 mm – 0.24 mm and the highest peak density is 980kg/m$^3$ compared with the controls’ peak at 0.12 mm with density of 735kg/m$^3$.

Chemical penetration depth can be found clearly from Figure 25 (a-d). The penetration depth increased with the decrease of formulation viscosity from V1 to V4. For formulations V1, V2 and V3, the density of treated samples with different resin application technologies and different application time reached the highest from the peak and then decreased from a depth of 0.60 mm to 1 mm to overlap with the control samples. However, for formulation V4, this density reached highest in the peak and decrease to a constant density until the depth of 2 mm, especially for multiple roller and coater resin application. One time
coater coating application treated samples reached the same density with controls at the depth of 1.70 mm. Figure 25(d) indicated that the formulation V4 presented highest penetration depth over the 4 groups of formulations. This is a desirable character for our targeting purpose to penetrate the chemical in a certain depth (1-2 mm) from the surface.

5.4.4.3 Curing behaviour of UV/thermal dual polymerization acrylate surface densified maple engineered planks

The validation analysis of polymerization whether UV/thermal dual system that could efficiently cure the acrylate monomers/oligomers surface densified wood surface products is crucial to determine the successful development of online curing process. The cure mechanism used a combination of photoinitiator(s) and thermal initiator in this UV/thermal dual cure system. The UV radiation polymerization reaction from the top layer generated amount of heat, which causes thermal decomposition of thermal initiators and produces initiating radicals that initiates the polymerization. The polymerization front travels downwards from the surface to achieve a complete cure to a depth of 1 cm. This photo-initiator kicking off polymerization similar to conventional thermal frontal polymerization, the amount of heat produced is essential in increasing the temperature of the immediate, uncured layer to the decomposition temperature of thermal initiators and to maintain the traveling front. To verify if the UV/thermal cure is an efficient polymerization method, further investigation via photo–DSC (differential scanning calorimetric) characterization was using to validate the curing behaviour of UV/thermal cure acrylate impregnated wood samples.

Table 12 presents the output of the UV lamp used to polymerize the surface densified wood products. Figure 26 presents the photo-DSC characterization of neat acrylate monomers/oligomers resin with different viscosities, where V1 is 100% Polyester acrylate oligomer (PEAO) with highest viscosity of 584.1 cps at room temperature. V2 is the formulation of 75% PEAO with 25% trimethylolpropane triacrylate (TMPTA) and the viscosity of formulation is 295.4 cps. V3 contains 50% PEAO and 50% TMPTA with a viscosity of 167.7 cps and V4 contains 25% PEAO and 75% TMPTA with a viscosity of 97.4 cps. All neat acrylate monomers/oligomers resin showed a big exothermal peak with the photo-DSC characterization. The height of the exothermal peak decreased with the decrease of viscosities. The peak height of V1 is 187.67 mW and is located at 122.02 s. The peak height of V2 is at 164.97 mW and presents at 122.5s. For V3 and V4, the peak height lowered at 109.66 mW and 101.95 mW at 122.54 s and 122.72 s, respectively. The integral energy of the neat acrylate monomers/oligomers peak decreased from 635.26 mW, 584.49 mW, 507.28 mW to 453.36 mW from V1 to V2 with the decrease of viscosity. Autocatalytic model data fit of conversion of neat resin is presented in Figure 27.

Figures 8 to 31 presents the photo-DSC characterization results of neat V1, V2, V3, V4, the uncured surface densified wood samples with V1, V2, V3, V4, the UV/thermal dual cured surface densified wood samples with these formulations and their untreated wood control samples. Neat acrylate monomers/oligomers formulations and the uncured acrylate surface densified wood samples with these formulations presented very similar exothermal peaks. The peak height and integral energy of neat acrylate monomers/oligomers formulation and uncured surface densified wood samples by these formulations are very similar except formulation V4. Their value were summarized and compared in Table 13. For formulation V1, the peak height for neat formulation and V1 surface densified wood are 187.67mW and 172.18mW, respectively, the peak appeared time is very close in 0.04s (122.02s for neat V1 acrylate resin and 121.98s for V1 surface densified wood, Figure 28). Similar results can be found in formulation V2, V3, V4 and their uncured surface densified wood products. The UV/thermal dual cured surface densified wood samples with V1, V2, V3 and V4 were characterized with photo-DSC and their results were presented in Figures 28, 29, 30 and 31. No exothermal peaks were found for these UV/thermal cured surface densified wood samples, which indicated the UV/thermal dual cure has polymerized the acrylate monomers/oligomers surface densified wood planks. When comparing these UV/thermal cure acrylate densified wood samples with the untreated wood control samples, the curve of
photo-DSC are almost overlapped. Thus the comparison curves further confirmed that the UV/thermal dual cure method is an efficient approach to cure the surface densified wood planks through roller/coater application technology with a vacuum process.

5.4.5 Conclusions

This work investigated the possibility of development of three steps surface densification process: 1st step is to apply a layer of acrylate monomers/oligomers on the wood surface by roller/coater coating; 2nd step is to penetrate the resin into the wood to a depth from the surface to 1-2 mm with a 60s vacuum process; 3rd step is to cure the surface densified wood products with an online instant UV/thermal dual cure method. The chemical retention and chemical penetration depth were investigated. The chemical retention was decreased drastically compared to the conventional vacuum/pressure impregnation process. The chemical penetration reached to our target depth 1-2 mm for formulation V4. The UV/thermal cure methods were validated by photo-DSC characterization. The photo-DSC characterization curves of UV/thermal dual cured acylate densified maple were almost a flat line when compared with neat resin and impregnated maple samples. No polymerization exotherms peaks were observed for UV/thermal dual cure acylate densified maple samples, which confirmed that UV/thermal approach is an efficient curing method to polymerization acylate impregnated wood surface densification products.

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Charles E. Hoyle John A. Pojman, Rapid curing wood putty based on frontal polymerization,  
http://www.faqs.org/patents/app/20090155485

Table 11  
**Viscosity and components of different formulations**

<table>
<thead>
<tr>
<th>Samples</th>
<th>chemical component (oligomer/TMPTA)</th>
<th>Viscosity (cps)</th>
<th>Test speed (rpm)</th>
<th>Test temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1</td>
<td>100/0</td>
<td>584.1</td>
<td>50</td>
<td>21.7</td>
</tr>
<tr>
<td>V2</td>
<td>75/25</td>
<td>295.4</td>
<td>100</td>
<td>22.4</td>
</tr>
<tr>
<td>V3</td>
<td>50/50</td>
<td>167.7</td>
<td>20</td>
<td>21.8</td>
</tr>
<tr>
<td>V4</td>
<td>25/75</td>
<td>97.4</td>
<td>50</td>
<td>21.7</td>
</tr>
</tbody>
</table>

Table 12  
**Output of the UV lamp used to polymerize the surface densified wood products**

<table>
<thead>
<tr>
<th>Gaullium Lamps</th>
<th>mJ/cm²</th>
<th>mW/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>UVA</td>
<td>1350.768</td>
<td>2337.882</td>
</tr>
<tr>
<td>UVB</td>
<td>1304.789</td>
<td>2427.965</td>
</tr>
<tr>
<td>UVC</td>
<td>272.289</td>
<td>518.012</td>
</tr>
<tr>
<td>UVV</td>
<td>1445.254</td>
<td>2353.440</td>
</tr>
</tbody>
</table>

1 the conveyor speed is 1m/18 second, which equal to 10m/min.

Table 13  
**Photo–DSC analysis results of different viscosity (results of Figure 5-9)**

<table>
<thead>
<tr>
<th>Species</th>
<th>Integral (mJ)</th>
<th>Peak height (mW)</th>
<th>Extra plot peak (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1 neat resin</td>
<td>635.26</td>
<td>187.67</td>
<td>122.02</td>
</tr>
<tr>
<td>V1-impregnated wood</td>
<td>565.02</td>
<td>172.18</td>
<td>121.98</td>
</tr>
<tr>
<td>UV/thermal cured V1-R</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>UV/thermal cured V1-C</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>V2 neat resin</td>
<td>584.49</td>
<td>164.97</td>
<td>122.5</td>
</tr>
<tr>
<td>V2-impregnated wood</td>
<td>621.20</td>
<td>162.88</td>
<td>122.48</td>
</tr>
<tr>
<td>UV/thermal cured V2-R</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>UV/thermal cured V2-C</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>V3 neat resin</td>
<td>507.28</td>
<td>109.66</td>
<td>122.81</td>
</tr>
<tr>
<td>V3-impregnated wood</td>
<td>513.53</td>
<td>114.25</td>
<td>122.54</td>
</tr>
<tr>
<td>UV/thermal cured V3-R</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>UV/thermal cured V3-C</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>V4 neat resin</td>
<td>453.36</td>
<td>101.95</td>
<td>122.6</td>
</tr>
<tr>
<td>V4-impregnated wood</td>
<td>337.76</td>
<td>63.06</td>
<td>122.72</td>
</tr>
<tr>
<td>UV/thermal cured V4-R</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>UV/thermal cured V4-C</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
Figure 24  Chemical retention of different viscosity with different resin application methods, where V1 is CN2262/SR351 (100/0), V2 is CN2262/SR351 (75/25), V3 is CN2262/SR351 (50/50) and V4 is CN2262/SR351 (25/75). R – roller coating, C – curtain coating, x – 1 application of resin, s – multiple application of resin until the surface is saturated.
V1 - Comparison of resin applications approach

(a) Formulation of V1

Viscosity 2 - comparison of different application method

(b) Formulation of V2
Figure 25  Vertical X-ray density profile of formulations with different viscosities and application methods
Figure 26  Photo-DSC characterization of neat acrylate resin with different viscosity, where $V_1$, $V_2$, $V_3$ and $V_4$ contains different ratio of acrylate monomer, multifunctional monomer and oligomers
Figure 27 Conversion of Photo-DSC characterization of neat acrylate resin with different viscosity, where V1, V2, V3 and V4 contains different ratio of acrylate monomer, multifunctional monomer and oligomers
Figure 28  Photo-DSC characterization of neat acrylate resin of V1, V1 impregnated wood, UV/thermal cured V1 surface densification products with roller and curtain applications.
**Figure 29**  Photo-DSC characterization of neat acrylate resin of V2, V2 impregnated wood, UV/thermal cured V2 surface densification products with roller and curtain applications
Figure 30  Photo-DSC characterization of neat acrylate resin of V3, V3 impregnated wood, UV/thermal cured V3 surface densification products with roller and curtain applications
Figure 31  Photo-DSC characterization of neat acrylate resin of V4, V4 impregnated wood, UV/thermal cured V4 surface densification products with roller and curtain applications
5.5 Chapter 5 — Wood Densification through Roller/Coater Application with Different Viscosity Acrylate Monomer/Oligomers through Vacuum Penetration Process and UV/Thermal Dual Cure

5.5.1 Abstract

This work investigated the feasibility of preparing surface densification wood products with three steps process to lower the chemical consumption and penetration depth of traditional vacuum/pressure impregnation process, to decrease the cost of surface densification process to produce high value-added wood products. A layer of low viscosity acrylate monomer/oligomer was applied on wood surface by roller or coater, followed with a 60s vacuum process to penetrate the acrylate resin to a depth between 1-2 mm from the surface. Samples were then polymerized by UV/thermal curing process. Surface densified maple engineered wood planks were prepared through the three steps procedure with 4 different viscosities of acrylate monomer/oligomers formulations with 4 (wt) % photo initiator and 1 (wt)% thermal catalyst. The properties of chemical retention (CR), Brinell surface hardness and impact resistance of surface densified maple engineered wood were evaluated. The CR varied from 95g/m² to 473g/m² with different resin application technologies, single or multiple resin application times and formulation viscosities. The Brinell surface hardness was improved up to 22% from 4.5MPa to 5.50MPa. The impact indentation fracture diameter decreased from 5.2 mm to 4.7 mm, while the indentation fracture depth decrease from 0.17 mm to 0.12 mm, which means that the impact resistance of the surface densified wood by roller/coater followed with a vacuum process was improved. A factorial experimental design was completed to study the effects of formulation viscosities, resin application technologies and resin application times on the properties of impregnated wood products. The main effect of the individual factors of viscosity, resin application technology and application times, and the interaction between factors on the properties of impregnated wood products were analyzed with the Statistical Analysis System (SAS).

Keywords: roller/coater coating, vacuum process, formulation viscosities, chemical retention, Brinell surface hardness, impact resistance

5.5.2 Introduction

The applications of traditional vacuum/pressure impregnation technology to produce high value-added surface densification wood products were limited due to low efficient impregnation process, relatively high cost because of the large volume of chemical using and slow thermal curing methods (Ayer et al. 2004, Cai et al. 2007a,b). Conventional vacuum/pressure chemical impregnation process is slow and un-continuous process due to up to hours vacuum and pressure time to remove the air from wood structure and force the chemical into wood structure (Cai et al. 2008, Schneider 2001, Wright and Mathias 1993a,b). The traditional impregnated wood was fully penetrated by chemicals under vacuum/pressure condition (Cai et al. 2007a). Thus high volume of chemical consumption was needed to fully penetrate the wood structure and resulted high cost to produce these value-added densified wood products. The traditional vacuum/pressure impregnation is not cost-effective approach to improve the wood properties, especially for applications require only surface properties, such as surface hardness, abrasion resistance and surface impact resistance.

Attempts to remove the pressure step from the traditional two steps of vacuum/pressure impregnation process thus to strategically turn the slow efficient impregnation process to a faster process have been made in our previous work (Cai and Blanchet 2010 a, b). The work proved the concept that breaking vacuum plays a key role for the penetration of chemicals into the wood structure. However, the chemical retention of one step vacuum impregnation is still high, up to 52-63 wt% of CR for maple wood and 44-55 wt% of CR for oak wood, thus the cost of this approach to produce surface densification products is
still relatively high (Cai and Blanchet 2010a). The surface densified maple and oak wood with only vacuum impregnation were fully penetrated by the chemicals from sample surface to the center. Attempt of using electron beam (EB) irradiation to instant cure the chemical impregnated wood products was successfully developed in our previous work (Cai and Blanchet 2010c). EB cure is an efficient and powerful technology to polymerize the free radical chemical impregnated wood products. The main obstacle of EB cure for our wood industry to deploy this technology is that the capital investment of EB generator was expensive. Alternative instant online curing approach with reasonable cost was seeking to benefit our wood industry.

The objectives of this work were to develop a three steps online surface densification process through application of a layer of resin with roller/coater on the wood surface, followed by a 60s vacuum to penetrate the acrylate resin into wood from the surface to a depth of 1-2 mm. The acrylate penetrated wood samples were polymerized with UV/thermal dual cure process. The resin application by roller/coater technologies and 60s vacuum penetration process can control the chemical consumption and penetration, thus to control the cost of produce value-added wood surface densification products. A successful combination of the two steps impregnation process plus an instant UV/thermal dual cure process can strategically turn the conventional slow steam or hot press thermal curing process into industrial viable surface densification process, meanwhile to decrease the cost of surface densification process to a practical range, which can be easily adopted by our wood industry. The slow traditional discontinuous vacuum/pressure impregnation process and the slow thermal cure process to produce high cost value-added products can be easily replaced by the new developed cost-effective surface densification process, thus to benefit our wood industry, especially for wood flooring, siding, windows/doors, cabinets, furniture, decking, etc.

The surface densified wood products with application of a layer of resin on the wood surface through roller/coater, followed with a 60s vacuum process to penetrate the acrylate monomers/oligomers into the wood surface to a depth of 1-2 mm were prepared. The acrylate monomers/oligomers penetrated wood surface was then polymerized by a UV/thermal dual cure methods with a UV lamps. The specific objectives of this project investigated 4 different viscosities formulations of acylate monomers/oligomers contains 4 (wt) % photo initiator and 1 (wt)% thermal catalyst that were applied on the wood surface by roller or coater coating. Single or multiple application of resin on the wood surface followed vacuum process until the wood surface saturated were applied to prepare surface densification maple engineered planks. The penetrated wood samples were then polymerized by UV/thermal dual cure technology. The development of online UV/thermal dual cure process to polymerize the surface densification products was investigated in a separated article (Cai and Blanchet 2010d).

The properties of chemical retention (CR), Brinell surface hardness and impact resistance of surface densified maple engineered wood were investigated. The CR varied from 95g/m² to 473g/m² with different resin application technologies, single/multiple resin application and viscosities. The Brinell surface hardness was improved up to 22% from 4.5MPa to 5.50MPa. The impact indentation fracture diameter decreased from 5.2 mm to 4.7 mm, while the indentation fracture depth decrease from 0.17 mm to 0.12 mm, which means that the impact resistance of the surface densified wood by roller/coater followed with a vacuum process was improved. A factorial experimental design was completed to study the effects of formulation viscosity, resin application method and resin application times on the properties of impregnated wood products. The main effect of the individual factors of viscosity, resin application technology and application times, and the interaction between factors on the properties of impregnated wood products were analyzed with the Statistical Analysis System (SAS).
5.5.3 Materials and Experimental

5.5.3.1 Materials and sample preparation

Maple (*Acer saccharum*) engineered wood planks with a dimension of 5” × 3.5” were used in this research. Polyester acrylate oligomer (PEAO) and trimethylolpropane triacrylate (TMPTA) were selected as free radical impregnation resin, which was supplied by Sartomer. 4 different viscosities (V1, V2, V3 and V4) with different ratio of PEAO and TMPTA were used as the surface densification formulations. The ratio of PEAO/TMPTA for V1, V2, V3 and V4 are 100/0, 75/25, 50/50 and 25/75, respectively. The details of the ratio and their viscosities were measured and the results were presented in Table 1. Photo initiator ESACURE SM246 was added into the formulation with a ratio of 4 wt% and it was supplied by R.M. Ferguson & Company Inc. 1 (wt)% thermal catalyst of Vazo® 67 was added into the formulation, which was supplied by DuPont.

5.5.3.2 Application resin and penetration of resin into wood surface

Wood planks with a moisture content of 8% were roller or coater coated with a layer of acylate monomers/oligomers resin with 4 formulations at different viscosity V1, V2, V3 and V4. The coated wood planks were then placed in a vacuum autoclave (Table 14). For single resin application time, 1 time 60s vacuum process followed after the application of resin. For multiple resin application times (3 times), 60s vacuum process followed after each resin application, totally 3 times of 60s vacuum process followed to help the chemical penetration. The vacuum process parameter include vacuum to a pressure of 25 mm Hg, maintain this vacuum for 60s, then open the valve to release the vacuum. Remove the samples from the cylinder, and wiped off residue of the chemicals from samples. The mass of wood planks were measured before and after the application and penetration of the chemicals. The chemical retention was calculated through the equation as follows:

\[
\text{Chemical retention (g/m}^2\text{) = (M}_1\text{-M}_0\text{)/surface area} \quad (1)
\]

Where \(M_1\) is the sample mass after treatment and \(M_0\) is the sample mass before treatment.

5.5.3.3 Brinell surface hardness

The Brinell surface hardness was measured according to the European Standard EN 1534, using Alliance RT/50 systems from MTS Systems Corporation (Eden Prairie, MN 55344-2290 USA). The hardness modulus was calculated as the slope of load vs. indentation within 20% to 60% indentation range. Three points were tested for each sample and at least 9 samples were tested for each combination.

5.5.3.4 Impact resistance

The falling ball impact resistance test measures the ability of the impregnated wood boards to resist indentations due to impact by a large diameter ball. The test apparatus is free-falling ball test equipment which followed a standard of FPInnovations interior practice method to measure the impact resistance of wood flooring, cabinets and furniture. Detailed procedure of the falling ball equipment to evaluate the impact resistance were described in our previous work (Cai et al. 2010b). Three electromagnet falling height levels representing low (falling from a height of 3”), medium (falling from a height of 9”) and high (falling from a height of 18”) impact forces were tested to evaluate the impact resistance of the impregnated wood boards. The impact spot of indentation fractures was examined and determined. The indentation depth and two diameters were examined on the impact fracture spot. The indentation fracture diameter and depth of treated sample was smaller than control samples. This means the impact resistance of treated sample was improved.
5.5.3.5 Experiment design and data analyses

The factorial design used in this study is presented in Table 15. The factors considered were resin application technologies (roller and coater), resin application times (single – 1 times and multiple application to saturated wood surface – 3 times application for maple wood surface to achieve the saturated point), and formulation viscosity with different acylate monomers/oligomers ratio (V1, V2, V3 and V4). This led to 16 combinations with resin application technologies, application times and different viscosities.

The effect of resin application technologies, single or multiple application of resin and the formulation viscosities on chemical retention, Brinell surface hardness, and impact resistance was analyzed with the Statistical Analysis System (SAS) software. The analysis of variance (ANOVA) of chemical retention (CR) and Brinell surface hardness was performed at 16 levels. ANOVA analysis of impact resistance of both indentation fracture diameters and depths at different impact strength on maple engineered wood planks was performed at 16 levels.

5.5.4 Results and Discussion

5.5.4.1 Chemical retention

Table 16 presents the results of the analysis of variance (ANOVA) for chemical retention of maple engineered wood planks surface densified from roller/coater application resin with single or multiple applications at different viscosities. The CR values were analyzed by SAS program, which shows a significant effect of different resin application technologies on the CR from different application times and different viscosities at the 0.01 probability level. The results of chemical retention by different resin application technologies, application time and different viscosities were presented in Figure 32. The single application of resin with roller showed lowest chemical retention for different viscosities varied from 95.28g/m² to 124.31g/m². Multiple (3 times) application of resin with roller showed higher CR than single roller application of resin varied from 168.46g to 206.59g for V1 to V4. Single application of resin with coater presented a good chemical retention varied from 131.34g/m² to 331.88g/m² for different viscosities. Multiple application of resin with coater presented the highest CR varied from 240.19g/m² to 473.16g/m². The chemical retention (CR) is much lower than the conventional vacuum/pressure impregnation process (up to 100wt% to the treated samples).

The effect of dependent variable on CR of surface densified maple engineered wood planks was presented in Table 17. The individual factors of resin application technologies showed significant effect at the 0.01 probability level on the CR. The resin applications time (pass) showed significant effect at the 0.01 probability level for the CR. The viscosities of formulations also showed significant effect at the 0.01 probability level for chemical retention. The two factors interaction of resin application technologies and application times (pass) showed no significant effect at the 0.01 probability level on CR. The interactions of resin application technologies and formulation viscosities showed significant effect at the 0.01 probability level on chemical retention. The three factors interaction of resin application technologies, resin application time and formulation viscosities showed no significant effect at the 0.01 probability level for chemical retention.

5.5.4.2 Brinell Surface Hardness

Table 18 presents the results of the analysis of variance (ANOVA) for Brinell surface hardness of maple engineered wood planks surface densified from roller/coater application resin with single or multiple applications at different viscosities. The CR values were analyzed by SAS program, which shows a significant effect of different resin application technologies on the CR from different application times and different viscosities at 0.05 probability level. The Brinell surface hardness of treated maple
engineered wood planks and their controls were presented in Figure 33. For maple planks, all treatment with different resin application technologies, single and multiple resin applications, and different formulation viscosities from V1, V2, V3 to V4 (the viscosity decreased from V1-V4), displayed improvements in Brinell surface hardness compared with untreated engineering planks. The highest improvement of Brinell surface hardness was shown by single roller and coater coating with formulation of V4. The Brinell surface hardness was improved from 4.5 MPa to 5.3-5.5 MPa, 22% improvement was obtained for engineered planks treated with single roller applications of V4.

The effect of dependent variable on Brinell surface hardness of surface densified maple engineered wood planks was presented in Table 19. The individual factors of resin application technologies and resin applications time (pass) showed no significant effect at the 0.01 probability level on the Brinell surface hardness. The viscosities of formulations showed significant effect at the 0.01 probability level for Brinell surface hardness. The two level interactions of resin application technologies and application times (pass), resin application technologies and formulation viscosities, resin application times and formulation viscosities showed no significant effect at the 0.01 probability level on Brinell surface hardness. The three factors interaction of resin application technologies, resin application time and formulation viscosities showed no significant effect at the 0.01 probability level for Brinell surface hardness.

### 5.5.4.3 Impact resistance

Table 20 presents the results of the analysis of variance (ANOVA) for impact resistance properties of maple engineered wood planks densified from different resin application technologies, resin application time and formulations with different viscosities. The diameter of impact indentation fracture from low, medium and high levels impact strength were measured and analyzed by SAS program, which shows a significant effect of surface densification process on the impact resistance from low impact at the 0.01 probability level. The impact indentation fracture diameter showed significant effect at the 0.05 probability level when impact strength is in medium and high level. All indentation diameters were decreased for different treatments and their combinations. The biggest decrease of indentation fracture diameter was 5.2 mm to 4.44 mm when engineered maple planks were treated with 3 times roller coating of formulation V3 when impact strength is low (Figure 34). When impact strength was in medium level, the indentation fracture diameters were decreased with different treatment combinations. It was decreased from 6.9 mm for the control samples to 6.20 mm when maple engineered planks treated with 1 times roller coating for formulation V4 (Figure 35). The indentation fracture diameter was decreased for all groups when impact strength is high. The highest decrease was from 8.20 mm to 7.35 mm (Figure 36).

The effect of dependent variable on impact resistance of surface densified maple engineered wood planks–indentation fracture diameters with different impact strength was presented in Table 21. For the impact indentation fracture diameter, the individual factors of acrylate monomers/oligomers formulation viscosities showed significant effect at the 0.01 probability level for all impact strength level from low, medium to high. The other two individual factors of resin application technologies, resin application times showed no significant effect on indentation fracture diameter at the 0.01 probability level from impact strength level. The two factors interaction of resin application technologies and application times, resin application technologies and formulation viscosities, the resin application times and formulations viscosities showed no significant effect at the 0.01 probability level on indentation fracture diameter at different impact strength level. The three factors interaction did not show significant effect on indentation fracture diameter at different impact strength level at the 0.01 probability level. The effect of dependent variable on impact resistance of surface densified maple engineered wood planks–indentation fracture depth with different impact strength was analyzed by SAS program too. No significant effect at the 0.01 probability level on indentation fracture depth was founded either for single individual factors or their combinations.
5.5.5 Conclusions

The feasibility of preparing surface densification wood products with three steps process to lower the chemical consumption and penetration depth of traditional vacuum/pressure impregnation process was investigated in this work. A layer of low viscosity acrylate monomer/oligomer was applied on the wood surface by roller or coater, followed with a 60s vacuum process to penetrate the acrylate resin to a depth between 1-2 mm from the surface (Cai and Blanchet 2010d). The impregnated wood samples were then polymerized by UV/thermal dual curing process. The properties of chemical retention (CR), vertical density profile, Brinell surface hardness and impact resistance of surface densified maple engineered wood were evaluated. The CR varied from 95g/m² to 473g/m² with different resin application technologies and viscosities, which is much lower than the chemical retention might be up to 100 wt% of treated samples by traditional vacuum/pressure impregnated wood. The cost to produce value-added surface densification products was decreased drastically compare to the traditional vacuum/pressure impregnation approach. The Brinell surface hardness was improved up to 22% from 4.5MPa to 5.50MPa. The impact indentation fracture diameter decreased from 5.2 mm to 4.7 mm, while the indentation fracture depth decrease from 0.17 mm to 0.12 mm, which means that the impact resistance of the surface densified wood by roller/coater followed with a vacuum process was improved. The Statistical Analysis System (SAS) analysis results showed that the formulation viscosity had significant effect on the improvement of Brinell surface hardness and impact resistance.

Acknowledgement

The authors acknowledge Mr. Tommy Martel and Mr. Simon-Paradis Bois for their laboratory work. This project was funded by Natural Resources Canada under the Transformative Technology program.

Reference


Table 14  Component ratio of formulations and their viscosity

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<th>chemical component (PEAO /TMPTA)</th>
<th>Viscosity (cps)</th>
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<tr>
<td>V1</td>
<td>100/0</td>
<td>584.1</td>
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<tr>
<td>V2</td>
<td>75/25</td>
<td>295.4</td>
</tr>
<tr>
<td>V3</td>
<td>50/50</td>
<td>167.7</td>
</tr>
<tr>
<td>V4</td>
<td>25/75</td>
<td>97.4</td>
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Table 15  Full factorial experimental design with 3 factors

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<th>Sample code</th>
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<th>Pass (Single application 1 or Saturated application 3)</th>
<th>Formulations with different viscosity</th>
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<td>R1-V1</td>
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<td>V1</td>
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<td>V2</td>
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<td>R1-V3</td>
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<tr>
<td>R3-V3</td>
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<td>V4</td>
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<td>C1-V1</td>
<td>Coater</td>
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Table 16  ANOVA analysis of CR – Chemical retention

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<tr>
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<th>F Value</th>
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<td>Model</td>
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** significant difference at the 0.01 probability level
Table 17  Effect of dependent variable on chemical retention

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<td>2</td>
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</tr>
<tr>
<td>Viscosities</td>
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<td>0.7578NS</td>
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** significant difference at the 0.01 probability level
NS not significant difference at the 0.01 probability level

Table 18  ANOVA analysis of Brinell surface hardness

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<th>Source</th>
<th>Degree of Freedom</th>
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<td>1.47</td>
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* significant difference at the 0.05 probability level

Table 19  Effect of dependent variable on Brinell surface hardness

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** significant difference at the 0.01 probability level
### Table 20  ANOVA analysis of impact resistance – indentation fracture diameter with different impact strength

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### Table 21  Effect of dependent variable on impact resistance – indentation fracture diameter with different impact strength

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** significant difference at the 0.01 probability level
Figure 32  Effect of resin application method, application time and viscosity on the chemical retention
Figure 33  Effect of resin application method, application time and viscosity on the Brinell surface hardness
Figure 34  Indentation fracture diameter of resin application method, application time and viscosity with low impact strength (the impact steel ball falling from 3”)

Impact indentation diameter with low impact (mm)

Resin application methods
Figure 35  Indentation fracture diameter of resin application method, application time and viscosity with medium impact strength (the impact steel ball falling from 9")
Figure 36  Indentation fracture diameter of resin application method, application time and viscosity with high impact strength (the impact steel ball falling from 18”)

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6 Conclusions

Attempts to develop high efficiency impregnation process to lower the chemical consumption thus to decrease the cost of producing high value-added surface densification products have been evaluated in this project. Instant industrial viable online *in situ* polymerization methods to cure chemical impregnated wood products have been investigated in this study. The main findings can be summarized as follows:

1. Acylate monomers/oligomers were selected as the nanoparticle transportation chemicals to produce high value-added wood surface densification products. The effect of nanoparticles in the formulations on the Brinell surface hardness, impact resistance and abrasion resistance was evaluated. The addition of nanoparticles showed significant effect on mechanical properties of surface densification wood products. Different ratio of monomer/oligomers formulation and their viscosities on the chemical retention and penetration properties were investigated. Lower viscosity formulation presented better penetration and higher chemical retention with same surface densification process.

2. Two different surface densification processes were developed to improve the efficiency and lower the chemical retention thus to decrease the cost of final value-added surface densification wood products. The first densification process that prepared surface-densified wood product by replacing the traditional time-consuming pressurization stage with only a short vacuum process was investigated. Formulations with nanoparticles were successfully impregnated into maple and oak engineered wood flooring planks by using a vacuum time from 30 s to 10 min without further pressurizing during the impregnation process. The properties of these short vacuum process impregnated wood products were also comparable to or even superior to the conventional vacuum/pressure impregnated wood products. The Brinell surface hardness of impregnated maple wood were improved 205% with a 30s vacuum process and oak wood were improved 108% with 60s vacuum process.

3. The second surface densification process contained three steps process. The 1st step is application of a layer of resin on the wood surface by roller or curtain coater; the 2nd step is using a 60s vacuum to penetrate the resin into the wood surface to a target depth of 1-2 mm; the 3rd step is to cure the impregnated wood with UV/thermal dual *in situ* polymerization process. Chemical retention decreased drastically with this approach compare to conventional vacuum/pressure impregnation process. 22% improvement of the Brinell surface hardness was found through this low cost approach.

4. Electron beam (EB) and UV/thermal dual cure process which was industrial viable online *in situ* polymerization process have been successfully developed to cure the surface densification wood products. The efficacy of EB and UV/thermal dual cure was validated by differential scanning calorimetry (DSC) and photo-DSC characterization. Results showed that EB cure is a powerful instant online polymerization method to cure the fully penetrated chemical surface densification wood products with a relative high capital investment on equipment.

5. UV/thermal dual cure method is a cost-effective approach to polymerize the roller/coater resin application and vacuum penetration surface of densified wood products.

In general, this study implied that reduce cost from surface densification process is possible through application of resin by roller/curtain coater followed with a short vacuum process to penetrate the resin into wood surface. This work also implied that *in situ* UV/thermal dual cure could replace the high cost EB cure surface densification products, which in turn, favour our industrial to adopt this technology cost-effectively.
7 Recommendations

Industrial implementation of a surface densification process based on the findings from this TT project is recommended. Full pilot plant scale surface densification process and UV/thermal dual cure in situ polymerization were recommended.

8 References

Appendix I

Concept Disclosure of Obstructive Wood Surface Densification Using a Nanotech Approach Cured by EB, UV/Thermal Curing
CONCEPT DISCLOSURE REDUCED TO PRACTICE

An electronic version and a paper copy, with original signatures, are to be sent to Merle Roy in the Patents & Licensing Department. A copy is to be sent to your Supervisor, Program Manager and Chris Kanters.

Concept Disclosure Number: Internal Form 2

Related to Project No(s): 201000354
Manager(s): Gérald Beaulieu
Date of Concept: November 8, 2008
Date Revised: January 25, 2010
Cross Reference: Enter concept number, patent application number etc.

Title of Invention: Obstructive Wood Surface Densification Using a Nanotech Approach Cured by EB, UV/thermal Curing

Alternative Title: No

Assignee(s): FPInnovations-Forintek Division (Xiaolin Cai, Pierre Blanchet)

Inventor: Xiaolin Cai
Address: Value-added
FPInnovations-Forintek Division
319, rue Franquet
Québec, QC
G1P 4R4

Employer: FPInnovations- Forintek Division

Inventor: Pierre Blanchet
Address: Value-added
FPInnovations-Forintek Division
319, rue Franquet
Québec, QC
G1P 4R4

Employer: FPInnovations- Forintek Division

REPEAT FOR EACH INVENTOR

Keywords: obstructive surface densification process, instant polymerization process, UV/thermal polymerization, electron beam polymerization, nanoparticles, acrylate monomers

Suggested Reviewers: Bob Knudson, Véronic Landry
Library Search: Dec. 10, 2009 Conducted by: Odile Fleury
ABSTRACT

An obstructive surface densification process with chemical quantitative control to lower the cost of the final hardening wood products is disclosed, wherein the obstructive surface densified wood product is made from an acrylate resin combined with nanoparticles, which penetrated from the surface to 1-2 mm in depth with a density gradient. A known amount of low viscosity formulations were applied to the wood surface either by rollering/curtaining followed with a vacuum penetration process to help the chemical penetrate into the wood structure, or the formulation was spraying into the wood surface with pressure spraying booth. An instant online polymerization process with electron beam radiation or UV/thermal initiator to cure the chemical penetrated into the wood is developed and also disclosed, which is specifically related to industrial viable online curable process to produce surface densification products. The surface densification products produced via obstructive surface densification process have the following characteristics:

1) Low chemical consumption with chemical retention (CR): 100g/m² – 500g/m².
2) A high density gradient from the surface to a depth of 0.2 mm – 2 mm.
3) Improvement of surface hardness: 30% – 75%.
4) Improvement of impact resistance: 15-30%.

These surface densification products have a broad use either interior or exterior such as wood flooring, siding, windows, doors, cabinets, and furniture etc.

BACKGROUND OF THE INVENTION

i) Field of the Invention

This invention relates to an obstructive wood surface densification process with chemical quantitative control to lower the cost of the final hardening wood products. More specifically, it relates to a process for making an obstructive surface densified wood product through a nanotech approach via application of a resin/nanoparticles mix that penetrates to the surface layer of the wood, followed by an electron beam (EB) cure or UV/thermal cure of the impregnated resin. In another aspect, this invention relates to a novel EB cure or UV kicking off thermal cure process specifically developed to polymerize the chemical penetrated into the wood, which is directly related to industrial viable online curable process to produce surface densification products for a broad use i.e. in exterior, such as specialty siding, decking, and patio furniture; and in interior applications such as flooring, mouldings, doors and windows, etc.

ii) Description of the Prior Art

Wood modification can be mainly classified into two categories: thermal based and chemical based. The former includes thermal modification, thermal compress, and heat oil treatment; and the latter contains chemical treatment and chemical impregnation modification. Surface modification wood can be used in a range of outdoor applications such as siding, decking, and patio furniture, and in interior applications such as flooring, mouldings, windows and doors. Surface modification allows lower-cost species to compete with naturally durable and higher-cost species, such as cedar and oak. Surface modification can improve the physical properties, such as surface hardness, abrasion resistance, etc. of high-cost species.

From a manufacturing process standpoint, thermal modification heated wood at temperatures of 180-240°C under controlled conditions for several hours/days. Chemical treatment substituted water binding sites in the wood cell wall and chemical impregnation technologies filled the voids in wood. From the modification principle standpoint, thermal and chemical treatments modify wood at the molecular level and impregnation technologies modify the wood structure at the microscopic level. From a performance standpoint, wood modifications improve mechanical
properties – strength and hardness; reduce cupping, checking, opening of joints and premature failure of coatings; improve durability – achieve a 60 years service life; improve aesthetics.

Wood modifications through chemical impregnation to produce highly value-added wood products have been around for decades. A conventional vacuum / pressure impregnation process followed by a radiation curing process is described in the U.S. Pat. No. 3663261. In this patent, it discloses a method for preparing plastic impregnated wood, in which dry wood with moisture content below 10 percent is impregnated with a liquid resin material in a process that (1) the wood is put into a vacuum impregnation vessel, (2) the air is evacuated, (3) the vessel flushed with nitrogen, (4) the liquid resin is introduced in the vessel until the wood is immersed, (5) an atmospheric nitrogen pressure or an overpressure of 1 to 8 atmospheres gauge is applied, (6) the wood is transferred into bags or containers filled with nitrogen, then hermetically sealed, and (7) the impregnated wood is cured utilizing radioactive radiation optionally in the presence of chemical catalyst addition. The resin utilized for the wood impregnation contains commercial unsaturated polyester between 35 and 95 percent and styrene and/or methyl methacrylate. The amount of radiation is between 0.5 and 1.5 Mrad in the case of gamma radiation and between 1 and 5 Mrad if high energy electron radiation is used. As an organic peroxide catalyst is used, the curing is carried out at a temperature between 40°C and 60°C. It tooks hours to days to complete all procedures from impregnation to curing steps. The surface densification and curing process was not a continuous online process.

The closest known prior art in wood modification through chemical impregnation is described in the U.S. Pat. No 6673395, wherein similar vacuum/pressure impregnation process is applied. The chemical formulations used for the wood impregnation consisted of styrene, methystyrene and tertiary butyistyrene monomers. The impregnation process takes from 0.5 hour to hours and the cure time is from about 2 h to about 12 h with catalysts being used. In addition, up to 50% of monomers are used to penetrate into the wood.

The implications of these prior arts in wood modification through chemical impregnation have been limited due to three problems. First, a typical scenario of conventional vacuum/pressure impregnation process contained a minimum 15 minutes to hours vacuum to remove air from wood, followed by a minimum 15 minutes to hours pressure process to help the chemical penetrate into the wood structure. This traditional vacuum/pressure impregnation process is not a continuous process and the production efficiency is low. Second, the chemical retention of conventional vacuum/pressure impregnation process is quite high, for example, sometimes might go up to 80-90 (wt%). The impregnated wood samples are fully penetrated by chemicals, leading the cost to go up to unreasonably high. Third, traditional methods of wood densification through thermal curing need long cure time, and large energy consumption. Thermal cure methods also produce volatile toxic by-products, create residual stresses in the materials, and require expensive tooling capable of withstanding high autoclave temperatures.

It would be desirable in the art to provide a process that is capable of making novel wood polymer composites that are just surface densified, and at the same time, such a process will not take too long time either in chemical impregnation or curing, and can be better in an online process so as to efficiently control the cost of the final products. This invention is concerned with such a process.

Appendices I to III provide a patent search report from NERAC, a key summary of the related patents that highlight their key differences to the invention and other related patents.
Deficiencies in prior art that the invention overcomes

In comparison with the traditional process technologies used for producing surface densification wood products, this invention eliminates the massive usage of the chemical(s) that fully penetrated wood, and substantially decreases the cost of raw materials in producing surface densification wood products. The hardness and strength of wood products are the primary properties for structural and industrial applications, which are closely related to their density. The obstructive surface densification technique is to fill the voids of the wood surface layer in a certain depth with a monomers/oligomers formulation as transporting medium that mixed with microparticles and nanoparticles, thus to form a high density surface layer which contributes to a high mechanical performance.

The obstructive surface densification process applied either with pressure spraying; or application of resin on the wood surface then using vacuum alone in a very short time (30-60 seconds) to allow a predetermined amount of chemicals to penetrate just into the wood surface layer. The penetrated wood planks were polymerized by a EB curing or a UV/thermal instant curing process, which strategically turn the conventional discontinuous impregnation process to an industrial viable online surface densification process.

EB curing method utilizes highly energetic electrons at controlled energy level to polymerize and crosslink polymeric materials. The advantages of this technology over the conventional hot press curing and gamma ray processes include significantly reduced curing time leading to order-of-magnitude improvements in throughput, reduced volatile emissions, reduced energy consumption and no catalyst cost compare to thermal curing method. Significant market interest has been developed in both military and aerospace industries, indicating that the process and performance of EB cured composites offer significant benefits as compared to other traditional curing technologies. (Berejka and Eberle; Saunders et al.).

Besides thermally activated reactions, many polyadditions and radical polymerizations can also be started by irradiation with sufficiently high energy. The main advantages of light (normally UV-) curing systems are their fast reaction – within a few seconds at low isothermal temperature. A combination of thermal and light curing reaction can be applied to dual cure adhesives or paints/coating (Patent: 20090155485).

Comparing to the traditional gamma radiation process, which is technically complex and requires a license from Atomic Energy of Canada Limited (AECL) in Canada, the main drawback of the radiation method is the safety and environment concerns. The cost of transportation of various wood products to and from the irradiation site would be prohibitive (Meyer 1965). The curing technique involved in the invention uses a technology developed for packaging and printing, and aerospace industries – an electron beam curing technology or an UV/thermal curing technology. When these techniques are applied to non-traditional wood products, the polymerization is very constant and complete. Further, EB curing and UV/thermal cure techniques are more environmentally friendly as compared to the conventional radiation curing process.

In comparison with conventional thermal curing technique, EB cure needs no initiator and catalyst agents (for the thermal curing chemical impregnation wood products, in-situ polymerization with heating method needs various types of catalysts, depending on the impregnation chemicals) and substantially decreases the cost of the formulations. UV/thermal cure needs a few seconds to kick off the curing reaction and complete the polymerization, while thermal curing techniques involve long time polymerization time.

In short, the new obstructive surface densification wood product is made from acrylate monomers/oligomers mixed with a predetermined amount of nanoparticles, which penetrate to the
surface layer of the modified wood products. Compared with conventional chemical impregnated wood products, the product made from this invention is low in chemical retention and has lower cost since the chemical penetrated only from the surface to a certain depth of the product. Moreover, unlike convention chemical surface densification wood products which utilized formaldehyde contained products or methyl methacrylate (MMA), the product made from this invention is “green” and environmentally friendly. The EB or UV/thermal polymerization of the surface modification wood products are online processes and industrial viable compared to traditional thermal polymerization, and no catalyst is needed for the EB cure, which lowers the cost of the formulations drastically. The performance of the product can be further improved via increasing the amount of the chemical formulation, or the addition of nanoparticles, or their combination. The invented surface hardening products can be widely used in a variety of appearance wood products either interior or exterior such as wood flooring, sidings, doors, windows, cabinets, and furniture etc.

References cited


SUMMARY OF THE INVENTION

In many applications, the failure of utilization of wood materials is associated with the surface hardness. It is more obvious in the wood floor finishing system. The surface hardness is a key factor for the application of wood flooring, especially in the high loading commercial place. The traditional chemical impregnation uses large quantity of polymer because the penetration is deep to the center (the final cost is $25/pi^2). The typical conventional impregnation chemical MMA, which is a volatile monomer, causes occupational hygiene problems. The surface treatment involved takes hours to days from low efficiency vacuum/pressure impregnation process to thermal curing process.

This invention creates a new concept of an obstructive surface densification process from control of chemical consumption, penetration depth, industrial viable resin application and penetration process, online polymerization, to produce strong and uniform surface densification wood products, which combines the merits of impregnation wood products with lower cost and high efficiency. In the present invention, the acrylate monomers are used as a transportation medium to carry microparticles and nanoparticles and fill the voids of the wood surface. After polymerization, acrylate crosslinks the wood substrate, microparticles and nanoparticles to form a composites-structure that exhibits superior improvement in the wood properties in all ways such as density, surface hardness, and impact resistance, etc.

The invention demonstrates that pressure spraying or application of resin with roller/curtain followed by a 30-60 seconds vacuum penetration process is able to compete with the traditional 15-30 minutes vacuum followed with a 15-30 minutes pressure impregnation process. The EB curing or UV/thermal curing are efficient and industrial viable online curing processes. The typical properties of obstructive surface densification were summarized as follow.

1) Low chemical consumption compares with conventional vacuum/pressure impregnation process where chemical retention (CR) is about 50-90 wt%. The chemical retention (CR) via obstructive surface densification process was about 100g/m² – 500g/m².
2) A high density gradient from the surface to a depth of 0.2 mm – 2 mm. The penetration is about 1.5-2 mm, while the conventional vacuum/impregnation process can penetrate the resin to the center of the treated wood samples (2cm plus).
3) The improvement of surface hardness via obstructive is about 30% – 75%.
4) The improvement of impact resistance is about 15-30%.

DESCRIPTION OF THE DRAWINGS

The process is described in two process flow charts (Figures 1 2 and 3) which are included in a separate file. Figure 1 is the principle of operation of surface densification – process in three stages. The first stage is application of resin on the wood surface, the second stage is penetration of resin into wood, the third stage is the curing of surface densification products.

Figure 2 is the flow chart of approaches to apply resin and penetrate resin into wood surface. Three approaches were utilized to apply and penetrate the resin. The first approach is single or multiple application of resin on wood surface with roller coating followed by a 30s-60s vacuum
Cost Reduction and Optimization of Advanced Impregnation Technologies with Nanotechnology

process to help the resin penetrate into the wood structure. The second approach is single or multiple application of resin with curtain coating on the wood surface followed by a 30s-60s vacuum process to penetrate the resin into wood structure. The third approach utilized a pressure spraying booth to apply and penetrate the resin into the wood structure. Single or multiple applications of spraying can be used at different pressure level to control the consumption of chemicals.

Figure 3 is the flow chart of approaches of online curing methods. Two approaches successfully cured the surface densification products. The first approach is EB curing, where no thermal catalyst neither photo initiators were needed for the curing. The second approach is UV/thermal curing, 4% photo initiator and 1% thermal catalyst were used into the formulations. Figure 4 explicated the curing mechanism of EB polymerization and UV polymerization.

DETAILED DESCRIPTION OF THE INVENTION

This invention comprises a method to produce obstructive surface densified wood products. Figure 1 shows the principle of obstructive surface densification process, which contains three stages. First, application of resin, this is a deposited resin process, which can be done either by roller coating, curtain coating or pressure spraying booth. The second, penetration of the resin, this can be done at the break of a vacuum, and finally polymerization of the impregnated resin through EB curing or UV/thermal curing.

Stages 1 and 2 — Application and Penetration of Resin

In a traditional process, an impregnation time of 15-30 minutes vacuum followed by a 15-30 minutes pressure to remove the air from wood is used, thus application of the resin and penetration of the chemicals into the wood substrate are accomplished in a quite slow process, where a full penetration of the resin is observed, which cause a large volume of chemical use. In this invention, three approaches have been tested to apply and penetrate the resin onto the wood surface. Figure 2 shows the process flow chart of the resin application and penetration of the obstructive surface densification process. The viscosity of the resin affects the penetration of both the resin and nanoparticles into the wood.

Approach I utilized a roller coating to deposit a predetermined amount of resin on the wood surface. Wood samples were put into a vacuum system for 30 to 60 seconds. Succeeded in breaking the vacuum, the deposited resin penetrated into the top layer of the surface, and the micro/nanoparticle filled the void parts of the wood surface layer with the resin as transportation medium. One or multiple applications of resin followed by a vacuum process can be repeated to achieve an ideal chemical retention amount.

Approach II utilized a curtain coating to deposit a predetermined amount of resin on the wood surface, which followed by a vacuum for 30-60s. Succeeding to break the vacuum, the samples were penetrated by the flushing of resin. The application and penetration can be repeated to achieve maximum chemical retention on the surface.

Approach III, using a pressure spraying booth to apply a predetermined amount of resin and let the resin penetrate to the surface layer of the wood. The quantity of the resin can be controlled either by adjusting the spraying pressure or by adding more spraying guns.

Stage 3 – Polymerization of the resin

The traditional thermal curing process for impregnated wood products may take hours to days, and thermal cure produces volatile toxic by-products. In some cases, such as MMA impregnated
Cost Reduction and Optimization of Advanced Impregnation Technologies with Nanotechnology

wood products, the polymerization process may evaporate up to 49% penetrated chemical to the production line, which cause occupational hygiene problem. The hot press process creates residual stresses in the materials, and requires expensive tooling capable of withstanding high autoclave temperatures. The traditional radiation cure such as gamma radiation requires a license from AECL in Canada and involves complex technology. This invention uses a technology well established for packaging and printing industry – the electron beam cure process and UV/thermal cure process. E-beam curing method utilizes highly energetic electrons at controlled energy level to polymerize and cross-link polymeric materials (Figure 4). The advantages of this EB cure technology over the conventional hot press curing and gamma ray processes include significantly reduced curing time leading to order-of-magnitude improvements in throughput, reduced volatiles emissions, reduced energy consumption and no catalyst cost compare to thermal curing method. More importantly, the polymerization is constant and complete with conveyor. In this disclosure, all of the samples were irradiated to 100 kGy, using 4.5 MeV energy electrons. The fully penetrated impregnated wood boards were completely cured. The EB cured impregnated wood samples were analyzed by differential scanning calorimetric (DSC) to valid the fully polymerization.

Besides developing highly efficient EB online curing method to cure surface densification wood products, another industrial viable online polymerization process of UV/thermal curing was developed in this disclosure. Many polyadditions and radical polymerizations can be started by irradiation with sufficiently high energy besides thermally activated reactions. The main advantages of light (normally UV-) curing systems are their fast reaction – within a few seconds at low isothermal temperature. A combination of thermal and light curing reaction can be applied to dual cure adhesives or paints/coating (Patent: 20090155485). 4% photo initiator was added into the formulation plus 1% of thermal catalyst. The UV/thermal curing surface densification wood products were analyzed by photo-DSC to valid the polymerization.

**Example 1**
Solid maple wood flooring samples with dimension 3.5” in width and 28” in length were deposited with a predetermined amount of resin by a roller coater. For comparison, 15 samples were deposited resin once, and another 15 samples were deposited resin until the surface was saturated. The coated samples were then put in a cylinder. A vacuum with 25 mm Hg pressure was used, maintaining this vacuum for 30 – 60 seconds. Remove the samples and cure it with electron beam radiation with a dosage of 100 kGy, using 4.5 MeV energy electrons. Samples were cured completely. Mechanical properties including surface hardness and impact resistance were measured.

**Example 2**
Solid maple wood flooring samples with dimension 3.5” in width and 28” in length were deposited with a predetermined amount of resin by a curtain coating. For comparison, 15 samples were deposited resin once, and another 15 samples were curtain coated resin until the surface was saturated. The coated samples were then put in a vacuum system. A vacuum with 25 mm Hg pressure was used, maintaining this vacuum for 30 – 60 seconds. The formulation contains 1% nanoparticles with 4% photo initiator and 1% thermal catalyst. The densification surface of treated samples passed under a gallium lamp of UV radiation equipment with a conveyor speed of 1.8m/min.

**Example 3**
Engineering maple, oak and cherry wood flooring samples with dimensional of 4” in width and 28” in length were deposited and penetrated with a predetermined amount of resin by pressure spraying booth. 8 samples for each species have been sprayed one time, and another 8 samples for
each species have been sprayed twice under the same pressure of 500 psi. The chemical retention of both treatments was recorded and calculated. Samples were cured by electron beam at the same condition of Example 1.

Example 4
Solid maple wood flooring samples with dimension 3.5" in width and 28" in length were deposited with a predetermined amount of resin by a roller coater. For comparison, 15 samples were deposited resin once, and another 15 samples were deposited resin until the surface was saturated. The coated samples were then put in a cylinder. A vacuum with 25 mm Hg pressure was used, maintaining this vacuum for 30 – 60 seconds. Remove the samples and cure it with UV/thermal cure. The formulations and curing condition is the same as Example 2.
CLAIMS

What is claimed is:

1) A method for preparing obstructive surface densified wood products by application and penetration a wood material and/or wood-based material, comprising the steps of: providing wood material having a moisture content of from about 8% based on the weight of said wood material; application and penetration resin said wood material with a composition comprising at least one polymerizable monomer and/or oligomer selected from the group consisting of acrylate monomers and/or oligomers that are to be polymerized in the wood; micro- and nanoparticles selected from aluminum oxide and nanoclay, and the polymerization being initiated with EB curing or UV/thermal curing process.

2) The method of claim 1, wherein the wood material is deposited resin either by roller coating, curtain coating or pressure spraying.

3) The method of claim 2, wherein the penetration of resin either deposited by roller coating of curtain coating were vacuumed to penetrate the resin into the wood structure.

4) The method of claim 1, wherein the impregnation resin is an acrylate with viscosity ranged from 20 cps to 500 cps.

5) The method of claim 1, wherein the micro- and nanoparticles are selected from nanoclay or aluminum oxide.

6) The method according to claim 1, wherein said wood samples moisture content is about 8%.

7) The method according to claim 1, wherein the time of vacuum is from about 30 to about 60 seconds.

8) The method of claim 1, wherein the obstructive densification wood is EB cured with a dosage of 100 kGy, using 4.5 MeV energy electrons.

9) The method of claim 8, wherein the formulation contains no thermal catalyst, nor photo initiator.

10) The method according to claim 8, wherein time of curing is less than 10 seconds.

11) The method according to claim 8, wherein the conveyor speed is 10m/min.

12) The method according to claim 8, wherein the curing time is instant.

13) The method according to claim 8, wherein said curing occurs in a room temperature.

14) The method of claim 1, wherein the formulation of UV/thermal curing contain 4% photo initiator and 1% thermal catalyst.

15) The method according to claim 14, wherein time of curing is within a few seconds.

16) The method according to claim 14, wherein the conveyor speed is 1.8 m/min.

17) The method according to claim 14, wherein the surface curing time is instant to kick off the thermal curing under the surface.

18) The method according to claim 14, wherein the samples were passed 4 times under UV radiation equipment.

19) The method according to claim 14, wherein gallium lamps were used.
20) The method according to claim 1, wherein the chemical penetrates in the surface layer of the wood.

21) The method according to claim 1, wherein the depth of the wood densified layer is in the range of 1-2 mm from the surface.

Enclose this Footer at the end of the last page of the Concept Disclosure.

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Appendix II

Flow Chart of Concept Disclosure of Obstructive Wood Surface Densification Using a Nanotech Approach Cured by EB, UV/Thermal Curing
Figure 1 Flow Chart of Principle of operation - Process in three stages

Applications and Penetration of Resin

I) Roller coating 1 or multi-applications on the surface of planks
   Vacuum 30-60s to penetrate the resin

II) Curtain coating 1 or multi-applications on the surface
   Vacuum 30-60s to penetrate the resin

III) Pressure spraying 1 or 2 applications of resin under different pressure

Figure 2 Flow Chart of Approaches – Application and Penetration of Resin
Figure 3 Approaches of Industrial Viable Online Curing Process

1) Electron Beam Curing

2) UV/Thermal Curing
Figure 4 Electron beam penetration mechanism