UNIVERSIDADE FEDERAL DE PELOTAS

Centro de Desenvolvimento Tecnológico

Programa de Pós-Graduação em Ciência e Engenharia de Materiais

Dissertação de mestrado

COMPÓSITOS MADEIRA-POLÍMERO PRODUZIDOS POR POLIMERIZAÇÃO *in situ* NOS LENHOS JUVENIL E ADULTO DE PINUS

ANDREY PEREIRA ACOSTA

Pelotas, 2020

Andrey Pereira Acosta

COMPÓSITOS MADEIRA-POLÍMERO PRODUZIDOS POR POLIMERIZAÇÃO *in situ* NOS LENHOS JUVENIL E ADULTO DE PINUS

Dissertação apresentada ao Programa de Pós-Graduação em Ciência e Engenharia de Materiais do Centro de Desenvolvimento Tecnológico da Universidade Federal de Pelotas, como requisito parcial para obtenção do título de Mestre em Ciência e Engenharia de Materiais

Orientador: Darci Alberto Gatto

Coorientador: Rafael de Ávila Delucis

Universidade Federal de Pelotas / Sistema de Bibliotecas Catalogação na Publicação

A185c Acosta, Andrey Pereira

Compósitos madeira-polímero produzidos por polimerização in situ nos lenhos juvenil e adulto de pinus / Andrey Pereira Acosta ; Darci Alberto Gatto, orientador ; Rafael de Ávila Delucis, coorientador. — Pelotas, 2020.

71 f. : il.

Dissertação (Mestrado) — Programa de Pós-Graduação em Ciência e Engenharia de Materiais, Centro de Desenvolvimento Tecnológico, Universidade Federal de Pelotas, 2020.

1. Preenchimento da madeira. 2. Impregnação. 3. Resistência mecânica. 4. Polímeros. 5. Qualidade da madeira. I. Gatto, Darci Alberto, orient. II. Delucis, Rafael de Ávila, coorient. III. Título.

CDD : 674

Elaborada por Aline Herbstrith Batista CRB: 10/1737

À minha família, em especial, aos meus pais: Celvanir e Jorge...

...dedico este trabalho.

“Você não consegue ligar os pontos olhando para frente; você só consegue ligá-los olhando para trás”

Steve Jobs

AGRADECIMENTOS

Agradeço em primeiro lugar a Deus, pois ele me possibilitou viver este momento.

Ao meu pai Jorge Everaldo Acosta, sem dúvidas, o exemplo que sigo de caráter, amizade e companheirismo. Sempre se mostrou presente em minha vida, me apoiando em todos os momentos.

À minha mãe, Celvanir Pereira Acosta, uma rainha, batalhadora, que apesar de todos os problemas sempre me apoiou em todos os momentos difíceis da minha vida, sendo sempre a minha primeira opção de conselhos e, além disto, quem mais me incentivou a fazer a graduação e agora iremos colher os frutos juntos. Por isto, dedico esta conquista, em especial, a ela e agradeço também a sorte que tive de ser seu filho.

Às minhas irmãs Denisi Pereira Acosta Silva e Deisi Mary Pereira Acosta, minhas segundas mães, minhas amigas e a quem devo muito. Agradeço também por ter permitido a entrada dos meus cunhados Cristiano Teixeira Correa e Patrick Nunes Silva, os quais se tornaram muito importantes. Grandes amigos que levarei para o resto da vida.

À minha sobrinha Alice Acosta Correa, praticamente minha terceira irmã, a qual sempre está ao meu lado me apoiando sempre e ajudando a alegrar minha vida.

À minha namorada Bruna Muller Rosenthal e sua família pelo apoio incondicional prestado nesse período tão importante da minha vida.

A todos meus amigos que de uma forma ou outra sempre se mostraram presentes nessa etapa.

Aos professores Darci Alberto Gatto (Orientador), Rafael Beltrame, Rafael de Ávila Delucis (Coorientador), exemplos a serem seguidos, tanto profissional, como pessoal.

Ao corpo técnico do Centro de Engenharias (Ricardo Ripoll de Medeiros e Faili Tonsem). Excelentes profissionais, sempre presentes e prestando total apoio.

Banca Examinadora

Prof. Dr. Darci Alberto Gatto (Orientador)

Doutor em Engenharia Florestal pela Universidade Federal de Santa Maria

Prof. Dr. Rafael de Ávila Delucis (Coorientador)

Doutor em Engenharia de Minas, Metalúrgica e de Materiais pela Universidade Federal do Rio Grande do Sul

Prof. Dr. Sandro Campos Amico (Banca 1)

Doutor em Engenharia Mecânica e Materiais pela University of Surrey

Prof. Dr. Pedro Henrique Gonzalez de Cademartori (Banca 2)

Doutor em Engenharia Florestal pela Universidade Federal do Paraná

ACOSTA, A, P. **COMPÓSITOS MADEIRA-POLÍMERO PRODUZIDOS POR POLIMERIZAÇÃO** *in situ* **NOS LENHOS JUVENIL E ADULTO DE PINUS**. 2020. Dissertação (Mestrado) – Ciência e engenharia de materiais, Universidade Federal de Pelotas, Pelotas.

RESUMO

Devido a necessidade de programas de melhoramento de madeiras juvenis visando ampliar suas aplicações este estudo teve como objetivo produzir compósitos polímero-madeira utilizando poli (estireno), poli (metacrilato de metila), poli (acetato de vinila) e poli (álcool furfurílico) impregnados nas madeiras juvenil e madura de *Pinus elliottii* sob pressão e polimerizados *in situ*. Para isso, amostras da madeira de Pinus foram cortadas próximas à casca (madeira madura) e à medula (madeira juvenil). Essas madeiras foram impregnadas com monômeros, que foram curados sob aquecimento. Foram avaliados parâmetros de tratamento ganho percentual de peso, massa especifica aparente, morfologia por meio de lâminas anatômicas, características químicas por espectroscopia no infravermelho, estabilidade térmica por termogravimetria, propriedades mecânicas em flexão estática e dureza superficial. A polimerização *in situ* proporcionou propriedades mecânicas maiores e maior estabilidade térmica, atribuídas aos polímeros impregnados, conforme sugerido pelos parâmetros de tratamento e espectros de infravermelho. O tratamento que mais se destacou em relação as propriedades mecânicas e térmicas dentre os analisados, foi o com poli(estireno), devido a melhor fixação do polímero na parede celular . Sendo assim o tratamento de impregnação pode ser uma maneira estratégica de melhorar as propriedades da madeira de Pinus, principalmente da madeira juvenil, que pode superar as propriedades da madeira madura, como foi o caso observado para todos os casos no que tange as propriedades mecânicas.

Palavras-chave: preenchimento da madeira, impregnação, resistência mecânica, polímeros, qualidade da madeira.

ACOSTA, A, P. WOOD-POLYMER COMPOSITES PRODUCED BY POLYMERIZATION *in situ* IN THE JUVENILE AND MATURE PINEWOOD. 2020. Dissertation (Master) - Materials Science and Engineering, Federal University of Pelotas, Pelotas.

ABSTRACT

Need for youth wood improvement programs simplifying your research this study aimed to produce polymer-wood using poly (styrene), poly (methyl methacrylate), poly (vinyl acetate) and poly (furfuryl alcohol) impregnated in juvenile and mature wood of *Pinus elliottii* under pressure and polymerized *in situ*. For this, the lord of the pine wood was cut close to the bark (mature wood) and the pitch (juvenile wood). These woods were impregnated with monomers, which were cured under heating. Treatment parameters adopted were mass gain, apparent specific mass, morphology by means of anatomical sheets, chemical characteristics by infrared spectroscopy, thermal stability by thermogravimetry, mechanical properties in static flexion and surface hardness. *In situ* polymerization provided greater mechanical properties and greater thermal stability, attributed to the impregnated polymers, as suggested by the treatment parameters and infrared spectra. The treatment that stands out the most in relation to the mechanical and thermal properties among the possible ones, was with poly (styrene), due to the better correction of the polymer in the cell wall. Thus, the impregnation treatment can be a strategic way to improve the properties of pine wood, especially juvenile wood, which can surpass the properties of mature wood, as was the case observed for all cases with regard to mechanical properties.

Keywords: wood filling, impregnation, mechanical strength, polymers, wood quality.

SUMÁRIO

ESTRUTURA DA DISSERTAÇÃO

As principais contribuições desta dissertação estão relacionadas a tratamentos de madeira juvenil com a elaboração compósitos que possuam melhores propriedades se comparados a madeira madura. Nesse sentido, o trabalho foi estruturado a começar por uma revisão de literatura, que é seguida por artigos científicos, tendo como objetivo destacar os todos os resultados e levar o leitor um entendimento mais amplo sobre o tema abordado.

O **Artigo 1** apresenta a produção e caracterização de WPC's utilizando o monômero estireno e as madeiras juvenil e madura de Pinus. Este artigo foi publicado na revista International Wood Products Journal.

No **Artigo 2** foi reportado a aplicação do monômero metacrilato de metila nas madeiras juvenil e madura de Pinus. O artigo foi publicado na revista Forests.

A utilização de acetato de vinila com a madeiras juvenil e maduras de Pinus foi reportada no **Artigo 3**. Esse artigo foi aceito na revista Fibers and Polymers.

No **Artigo 4** está apresentada a pesquisa destaque da dissertação. Foram preparados WPC's com álcool furfurílico com a madeira juvenil e madura de Pinus. O artigo foi publicado na revista Wood Material Science and Engineering.

1. INTRODUÇÃO

A madeira é um material renovável, de baixo custo e fácil aquisição, por estas questões vem sendo muito utilizada ao decorrer dos anos pela sociedade. Como produto renovável a madeira, principalmente de florestas de rápido crescimento, possui inúmeras aplicações, por exemplo, fabricação de papel, estruturas, materiais esportivos, decoração, dentre outros. No entanto, apesar da ampla aplicabilidade deste material ainda assim são muito limitadas algumas características, no que diz respeito a sua resistência mecânica e biológica, fazendo com que haja no decorrer dos anos modificações que proporcionem melhorias e amplifiquem sua aplicação. Além disso, principalmente árvores de *Pinus elliottii* com 10 anos de idade estão começando a produzir madeira madura (TREVISAN *et al.*, 2014), enquanto a maioria dos outros pinheiros só se tornam plantas adultas após 15-20 anos de vida (VIDAURRE *et al.*, 2011). É uma característica importante, uma vez que a madeira madura é preferida para a fabricação de produtos sólidos de alta qualidade (VIDAURRE *et al.*, 2011). No entanto de modo geral a madeira juvenil é desperdiçada não sendo usada para inúmeras aplicações devido suas baixas propriedades mecânicas.

Estudos recentes mostram determinadas modificações em escala manométrica que alteram algumas propriedades da madeira, ZANATTA *et al.*, (2017) modificaram a madeira (*Pinus elliottii*) com nanoparticulas de dióxido de titânio afim de proporcionar a madeira melhor resistência biológica, MISSIO *et al.*, (2015a) utilizaram polímeros para proporcionar melhor resistência física e mecânica à uma madeira de rápido crescimento (*Pinus elliottii*), QIN; DONG; LI, (2019) alteraram as propriedades de uma folhosa (*Eucalyptus robusta*) utilizando melanina-ureia-formaldeido afim de proporcionar a madeira melhor resistência mecânica e biológica, OKON *et al.*, 2017; SILVEIRA *et al.*, (2018) retificaram térmicamente uma madeira de folhosa (*Firmiana simplex*) e uma conífera (*Populus nigra*) respectivamente com intuito de proporcionar maior estabilidade térmica e resistência biológica.

Dentre estas modificações algumas são muito utilizadas a nível industrial, como: Indurite ™, VecoWood® e Lignia ™ e Pacific Lumber ™. Dos produtos já comercializados no que se diz respeito à madeira modificada se tem destaque o metil metacrilato, estireno, acetato de vinila e álcool furfurílico. Poli (Metilmetacrilato) (PMMA) é um polímero linear deste tipo consiste em uma longa cadeia de átomos com grupos laterais anexados (YILDIZ; YILDIZ; GEZER, 2005). A utilização do PMMA no tratamento da madeira vem crescendo ao longo do tempo, principalmente pelas características que este produto proporciona à madeira. Atualmente as pesquisas com madeira impregnada com PMMA têm se concentrado nas propriedades físicas e mecânicas do material HADI *et al.*, (2018), principalmente pelo seu excelente desempenho.

O estireno é um precursor sintético de alto valor, pois é usado para produzir vários tipos de isopor. Sua reação de polimerização parte de um radical livre que interage com a molécula de estireno, rompendo as ligações duplas entre os carbonos e formando progressivamente o poli (estireno). O estireno é amorfo e translúcido, esse é um dos motivos de sua ampla utilização pela indústria (KEPLINGER *et al.*, 2015). Mesmo que esses monômeros não interajam diretamente com os principais constituintes da madeira (celulose, hemicelulose e lignina), eles podem alterar algumas propriedades físicas da madeira devido à sua natureza (MATTOS *et al.*, 2015a).

Outro produto com grande potencial de aplicabilidade no tratamento de madeira é o álcool furfurílico. SHELDON, (2014) citam que o uso de carboidratos tem despertado interesse na comunidade científica nos últimos anos, onde um desses compostos é o álcool furfurílico e seus derivados, eles possuem diferentes grupos funcionais, podendo ser obtidos a partir dos açúcares C5 e C6. A aplicação desse carboidrato na madeira atraiu interesse global por ser um processo de modificação química ecologicamente correto (TEMIZ *et al.*, 2007). Este processo visa a modificação química da madeira com o uso de álcool furfurílico em determinadas porcentagens, geralmente utilizando catalisadores para acelerar a polimerização, proporcionando ganho de massa e melhoria consecutiva em determinadas propriedades tecnológicas da madeira (LANDE; WESTIN; SCHNEIDER, 2004). Os benefícios da furfurilação da madeira são: não toxicidade; os produtos de combustão da madeira furfurilada são semelhantes aos da madeira; lixiviado não tóxico otimiza algumas propriedades físicas da madeira.

2. OBJETIVO

Este estudo teve como objetivo produzir e caracterizar compósitos polímero-madeira utilizando poli (estireno), poli (metacrilato de metila), poli (acetato de vinila) e poli (álcool furfurílico) em madeiras juvenis e maduras de *Pinus elliottii* pelo processo de polimerização *in situ*.

3. JUSTIFICATIVA

Devido a grande utilização da madeira juvenil na indústria madeireira e o grande desperdício que ela representa no que se diz respeito a aplicações em madeiras sólidas os tratamentos da madeira surgem como possível solução para esta problematização.

A madeira que anteriormente era considerada de péssima qualidade, para o tratamento se mostra como o material perfeito no que se diz respeito a melhoria de suas propriedades mecânicas e térmicas.

4. REVISÃO GERAL

4.1 MADEIRA E SUAS CARACTERÍSTICAS QUÍMICAS

Desde antes da história registrada, a madeira tem sido usada como combustível para cozinhar e aquecer. Atualmente, seus usos expandiram-se para uma infinidade de produtos, incluindo diferentes ferramentas e manípulos, abrigos e casas, pontes e caminhos, barcos e embarcações, arcos e flechas, sapatos e milhares de outros utensílios e aplicações essenciais (TAGHIYARI *et al.*, 2020). A madeira é considerada um valioso material renovável que ajudou diferentes nações a alcançarem desenvolvimento. melhoria da tecnologia e bem-estar social (VERHAEGEN *et al.*, 2014). Do ponto de vista arquitetônico, madeira maciça, madeira engenheirada e outros produtos à base de madeira são usados para construir casas e edifícios, pontes, madeira para interiores e painéis (ARCE; MOYA, 2015; LEKKA *et al.*, 2016). QIN; DONG; LI, (2019) mencionaram que a madeira é um excelente material em relação à sua relação força/peso. Além disso, esses autores afirmaram que sua ampla variedade de espécies também é um dos pontos mais fortes para seu uso.

Estima-se que existam mais de 12500 espécies de madeira no mundo, das quais 500 são consideradas madeiras de coníferas (BAJPAI, 2018a). Toda essa amplitude de espécies madeireiras aumenta suas características e assim suas aplicações ZABORNIAK; CHMIELARZ; MATYJASZEWSKI, (2019) citaram que as propriedades da madeira são determinadas principalmente pela estrutura da parede celular, variando muito de espécie para espécie. Essa estrutura é composta basicamente por três polímeros naturais: celulose, hemicelulose e lignina (FU *et al.*, 2012; KANG; LIU; HUANG, 2015; ZABORNIAK; CHMIELARZ; MATYJASZEWSKI, 2019).

4.1.1 Holocelulose

A holocelulose (hemicelulose + celulose) é um polímero composto de moléculas de simples açúcares ou monossacarídeo A celulose é um homopolímero linear formado por unidades de d-anidro-glucopiranose que são ligadas por β-1,4–glicosídicas (DONALDSON; NANAYAKKARA; HARRINGTON, 2016). Os mesmos autores citam que o grau de polimerização (DP - número de monômeros de glicose por cadeia de celulose), varia 9000 a 12000. As hemiceluloses são compostas por 5- (arabinose, xilose) e monômeros de açúcar com 6 carbonos (e.g. glicose, manose e galactose) (DONALDSON; NANAYAKKARA; HARRINGTON, 2016). Eles são mais curtos e amorfos por natureza e servem, com a lignina, para formar a matriz na qual as fibrilas de celulose estão embebidas. Segundo JÖNSSON, (2016), As hemiceluloses compreendem cerca de 20% em peso nas madeiras de folhosas e 15%

nas madeiras de coníferas. Os mesmos autores citaram que, nas coníferas, o galactoglucomanano é a mais abundante hemicelulose, seguida de arabinoglucuronoxilano. Já a celulose possui estrutura diferente das hemiceluloses, sendo formada de cadeias longas e pouco ramificadas, ricas em zonas cristalinas. DONALDSON; NANAYAKKARA; HARRINGTON, (2016) citaram que as coníferas possuem cerca de 42% de celulose, enquanto as folhosas aproximadamente 45%. As cadeias de celulose são agrupadas para formar microfibrilas, que são agrupados para formar fibras de celulose (BAJPAI, 2020). Os polímeros da celulose, de cadeia longa, são ligados entre si por ligações de hidrogênio e Van der Waals. De modo geral, a celulose possui determinadas características em relação à suas propriedades que se diferem um pouco das hemiceluloses, como por exemplo, maior estabilidade térmica, menor absorção de água, as quais são devido a presença da cristalinidade em sua estrutura. A Figura 1 ilustra a cadeia química das celuloses e de duas hemiceluloses.

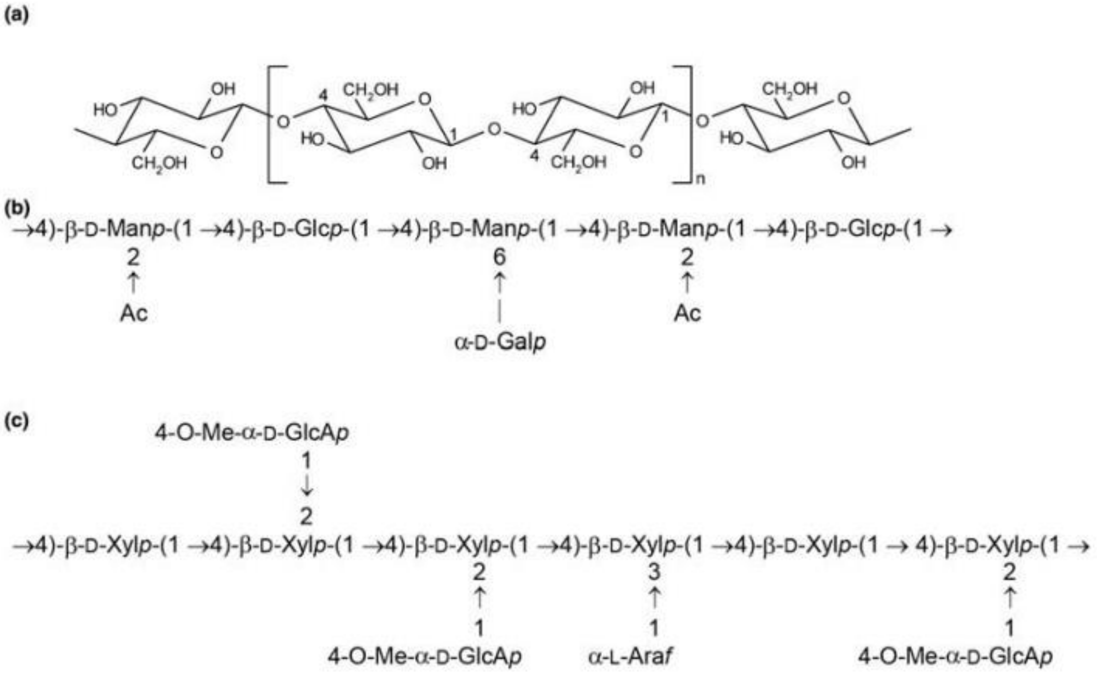


Figura 1: As estruturas químicas de (a) celulose - um polímero de monossacarídeo celobiose; (b) galactoglucomanano; (c) arabinoglucuronoxilano. Fonte: (DONALDSON; NANAYAKKARA; HARRINGTON, 2016)

4.1.2 Lignina

A lignina, por sua vez, é o componente com propriedades que mais chama atenção dos pesquisadores. Juntamente das hemiceluloses, formam a matriz em que a celulose está presente para formar a estrutura da madeira (BAJPAI, 2018b). O mesmo autor menciona que esta é um polímero tridimensional biosintetizado a partir de unidades de fenilpropano que é oriunda de uma molécula grande complicada. A estrutura da lignina varia entre madeiras de coníferas e folhosas. LU *et al.*, (2017) citaram que o conteúdo típico de lignina é de 24 a 33% em madeiras de coníferas e de 19 a 28% em madeiras de folhosas. Grupos funcionais na lignina incluem metoxil, carbonilas, carboxilas e hidroxilas que se ligam a substâncias aromáticas ou alifáticas , levando a diferentes composições e estruturas na lignina (KAI *et al.*, 2016). É sabido que a lignina extraída da madeira é ótima fonte para inúmeros produtos, que vão desde ração animal, até a produção de fibras de carbono. De modo geral, a lignina presente na parede celular da madeira possui propriedades muito interessantes, principalmente no que se refere à sua estabilidade térmica, sendo maior que os demais componentes citados (celulose e hemicelulose). A estrutura proposta por NIMZ, (1974) para a lignina de uma madeira (ilustrada na Figura 2) consiste em 25 unidades de fenilpropano.

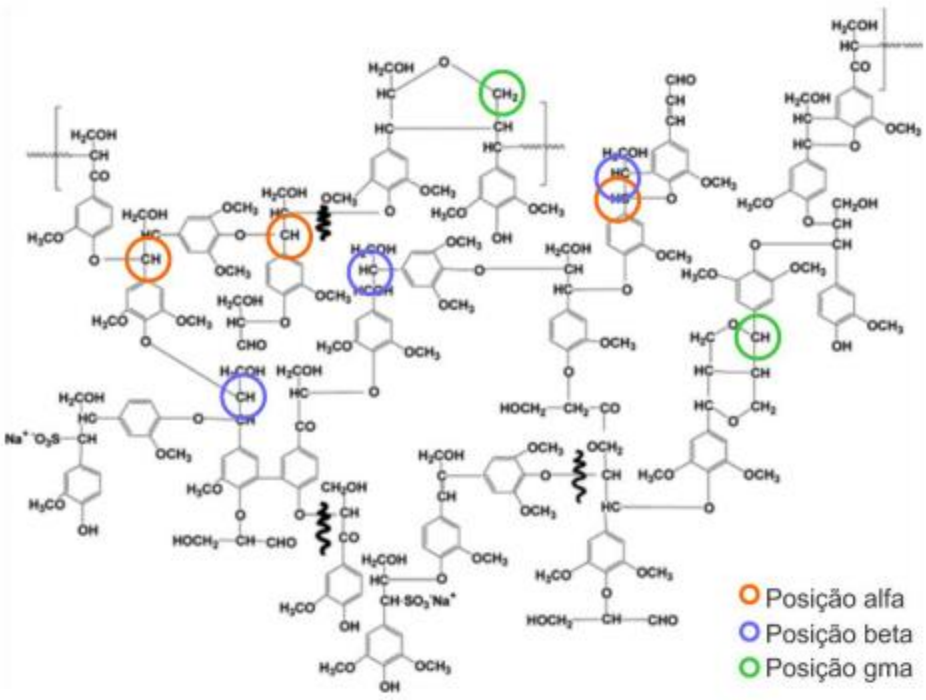


Figura 2: Modelo de lignina proposto por NIMZ, (1974) para a madeira de Fagus (Beech).

4.1.3 Extrativos

Os extrativos (aromáticos e alifáticos) são componentes químicos presentes em resinas naturais, glicosídeos, terpenos, álcoois, gorduras, ceras e taninos representam de 1% a 10% em peso total da madeira. São substâncias não estruturantes e de baixo peso molecular (ISSAOUI; FATIMA CHARRIER - EL BOUHTOURY, 2020). De maneira mais aprofundada, pouco se sabe quanto à química dos extrativos de madeira e, mais recentemente, com o desenvolvimento e incentivos em relação à pesquisa em temas relacionados à biorrefinaria, diversos estudos vêm sendo conduzidos referentes à caracterização química e possíveis aplicações desses compostos (CHENG *et al.*, 2013; KIM; LEE; YUN, 2013).

Os extrativos são responsáveis pela cor, odor, sabor e, ocasionalmente, proporcionam resistência ao ataque de organismos xilófagos à madeira. Existem inúmeros extrativos distintos dentro de uma madeira. Os terpenos são os principais extrativos presentes em coníferas. São uma ampla classe de compostos que aparecem em quantidades altas nas coniferas, onde são coletadas nos dutos de resina dessas espécies (BAJPAI, 2018c).

4.2 ANATOMIA DA MADEIRA

A madeira possui diversificação do ponto de vista morfológico, variando de gênero em gênero e espécie para espécie. No que tange à macroscopia, a madeira é composta de células alongadas, a maioria das quais são orientadas ao longo do tronco da árvore. Estas células alongadas estão conectadas uma à outra através de aberturas (denominadas pontoações) (SJÖSTRÖM, 1993). Essas células (fibras, fibro-traqueídeos, parênquimas, etc..), variam em sua forma de acordo com suas funções, fornecem a resistência mecânica necessária para a sustentação da árvore e também desempenham a função de transporte de líquidos, bem como o armazenamento de reservas alimentares. A madeira possui tecidos de xilema e floema que também têm por função a condução de água e nutrientes. Seus tecidos crescem a partir do câmbio a cada ano (BAJPAI, 2018a). Aprofundando-se mais, há duas amplas categorias de células na madeira que podem classifica-las como folhosas ou coníferas: traqueídeos e fibras (Figura 3).

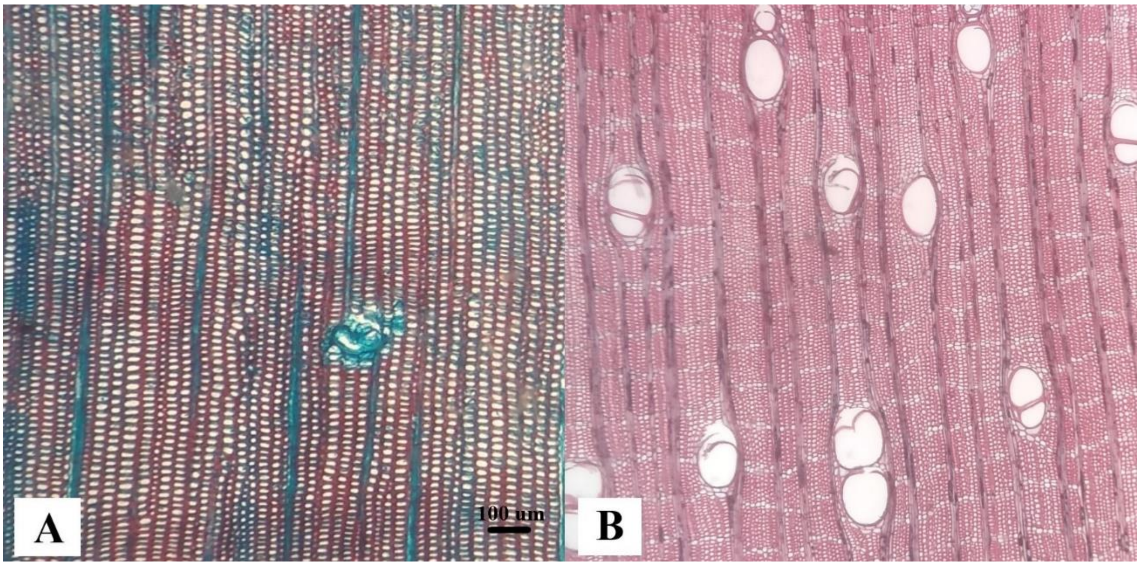


Figura 3 - Estrutura transversal anatômica de uma conífera (*Pinus elliottii*) (A) e uma folhosa (*Couratari multiflora*) (B). Fonte: Autor (2020).

Os traqueídeos ocorrem em coníferas e as fibras ou fibrotraqueídeos ocorrem em folhosas. De modo geral, os traqueídeos são cerca de 2 vezes maiores que as fibras. FERNÁNDEZ *et al.*, (2019) mencionam que o diâmetro do lúmen influencia diretamente na densidade. Logo, quanto mais espaços vazios no interior dessas células, menor será a densidade da madeira. Avançando mais em relação à anatomia da madeira, existem várias camadas formadoras da célula, tal como mostra a Figura 4.

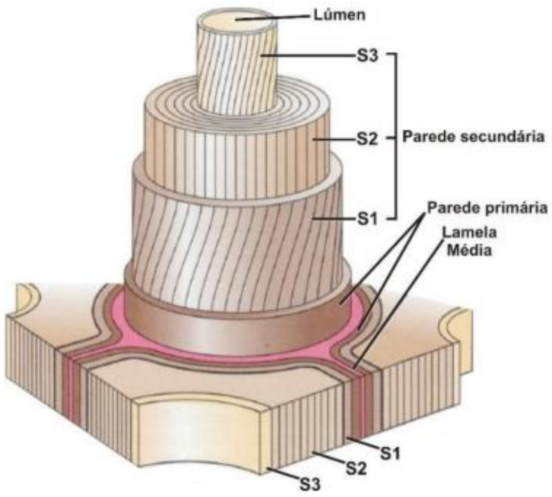


Figura 4: Estrutura de um traqueídeo da madeira. Fonte: (LAZAR, 2003).

As camadas da parede celular da madeira são primeira, secundaria e lamela média. A parede celular secundária das fibras é composta por três camadas (chamadas S_1, S_2 e S_3) e cada camada pode ser considerada como uma fibra natural reforçada, onde a celulose cristalina e hidrofóbica está envolta em uma matriz hidrófilica de celulose amorfa, hemicelulose e lignina (RAFSANJANI *et al.*, 2014). BRÄNDSTRÖM, (2004) relataram que a camada S_1 (com 0,2-0,3 μιη de espessura) consiste de uma única lamela, em que a orientação das microfibrilas é mais ou menos perpendicular ao eixo da célula, salientando que essa camada é homogênea e rígida. Sobre a camada S_2, RAFSANJANI *et al.*, (2014) citaram que a espessura possui importância estrutural para a célula, o que proporciona suporte mecânico para o tecido.

Devido ao grande volume ocupado pela camada S_2, pode-se afirmar que ela contribui nas variações dimensionais, como a contração e inchamento da madeira, densidade, rigidez e resistência mecânica. Também é a camada de maior lignificação, o que foi detectada por microscopia de fluorescência por (DONALDSON; GRACE; DOWNES, 2004). A camada interna (S_3) é uma camada fina (cerca de 0,1 µm) que consiste em várias lamelas que contêm microfibrilas. No que tange a lamela média, sua ocorrência se dá em regiões mais externas da fibra. É possuidora de grandes concentrações de lignina e funcionam como ligantes para as demais camadas.

A lamela média, juntamente com a parede primária, são as principais responsáveis pela permeabilidade da madeira (SJÖSTRÖM, 1993). O mesmo autor mencionou que essa camada é uma fina, com espessura de apenas 0,1-0,2 µm e sua composição consiste em celulose, hemiceluloses, pectina e proteína e completamente incorporada em lignina. Todas essas diferenças, do ponto de vista celular, diferem espécies quanto às suas propriedades, até mesmo dentro de mesmos gêneros.

4.3 *Pinus elliottii* ENGELM.

A madeira de Pinus é uma das matérias-primas mais apreciadas no setor madeireiro brasileiro. Segundo SHIMIZU, (2008), o gênero Pinus vem sendo plantado no Brasil desde o final do século XIX, devido aos imigrantes europeus estabelecidos no estado do Rio Grande do Sul, mas ganhou mais força a partir da metade do século passado, quando o Serviço Florestal do Estado de São Paulo incentivou o plantio de espécies exóticas norte americanas, como *P. palustris*, *P. echinata*, *P. elliottii* e *P. taeda.* Dentre as espécies subtropicais, *Pinus taeda* e o *Pinus elliottii* se destacaram no momento de sua implantação no Brasil pela facilidade nos tratos culturais, rápido crescimento e reprodução intensa nas regiões Sul e Sudeste do país (SHIMIZU, 2008). Dados de 2018 indicam que, dentre os 7,83 milhões de hectares de florestas plantadas no Brasil, 1,6 milhão de hectares (cerca de 20% do total) correspondem a plantações de Pinus (IBÁ - INDÚSTRIA BRASILEIRA DE ÁRVORES, 2019). O *Pinus elliottii* Engelm var. *Elliottii* é originário do sudeste dos Estados Unidos e foi implantado em outros países com intuito da geração de madeira serrada (LAI *et al.*, 2020). Hoje em dia, ocorre naturalmente em certos lugares da América do Norte, Brasil e Austrália (NEIS *et al.*, 2019).

Em específico no Brasil, o *Pinus elliotti* é a espécie mais plantada no sul e no sudeste, pois, dentre as principais coníferas plantadas, apresenta o crescimento mais rápido(SCHNEIDER *et al.*, 2014). Sua madeira possui muitas aplicações tradicionais, incluindo celulose, papel, móveis e construção civil (MISSIO *et al.*, 2015b). Sua resina também possui um importante valor comercial e é fonte para a produção de muitos químicos, incluindo resinas, tintas, vernizes e etc (RODRIGUES-CORRÊA; DE LIMA; FETT-NETO, 2012).

A madeira de *Pinus elliottii* apresenta baixa durabilidade, pois é susceptível ao ataque de fungos (emboloradores, manchadores e apodrecedores) e cupins. No entanto, essa madeira é fácil de tratar sob pressão em autoclave (TARMIAN *et al.*, 2020). Possui fácil trabalhabilidade, nas etapas de desdobro, aplainamento, desenrolo para lâminas, torneamento, colagem, além de permitir bom acabamento. Essa madeira é de fácil secagem, tanto em estufas automatizadas, como ao ar (BAJPAI, 2018a).

4.4 TIPOS DE LENHO

Espécies de rápido crescimento apresentam grandes proporções de lenho juvenil. Esse problema se destaca principalmente nos gêneros *Pinus* e *Eucalyptus*, pois são muito utilizados em sua forma sólida. A madeira de Pinus juvenil apresenta desempenho inferior ao de sua madeira madura devido à sua alta proporção de lenho inicial, que afeta negativamente a qualidade da madeira e limita seu uso, principalmente em determinadas aplicações estruturais. Árvores de *Pinus elliottii* com 10 anos de idade já começam a produzir madeira madura

TREVISAN *et al.*, (2014), enquanto a maioria dos outros pinheiros só se tornam plantas maduras após 15-20 anos de idade (VIDAURRE *et al.*, 2011). É uma característica importante, uma vez que a madeira madura é preferida para a fabricação de produtos sólidos de alta qualidade (VIDAURRE *et al.*, 2011).

Além disso, muitas vezes, o Pinus apresenta propriedades inferiores, como baixa resistência mecânica, baixa resistência a intemperes e baixa estabilidade térmica, quando comparado a pinheiros semelhantes e, consequentemente, deve ser tratado para ser utilizado adequadamente (BAO *et al.*, 2001). Estas propriedades são ainda mais inferiores no seu lenho inicial, em geral, uma floresta pode ser gerenciada de forma que um espaçamento reduzido entre árvores seja aplicado nos primeiros anos de vida das árvores, o que reduz a formação de novas células a partir do meristema cambial e, portanto, mitiga a formação de lenho juvenil (VIDAURRE *et al.*, 2011). PALERMO *et al.*, (2013) estudaram árvores de 35 anos com 25 cm de diâmetro e relataram que a região central do tronco com cerca de 15 cm de diâmetro era composta por madeira juvenil (à altura do peito ou a 1,3 m do solo). A figura 5 ilustra a p corte transversal de uma árvore, onde é possível visualizar as delimitações entre madeira madura e juvenil.

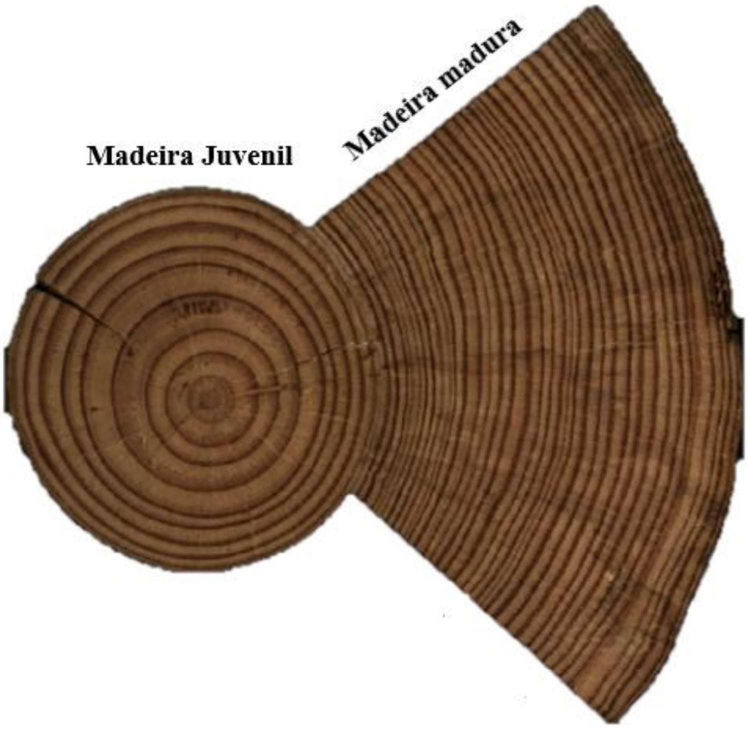


Figura 5: Seção transversal de uma árvore de *Pinus pinaster*. Fonte: (CARVALHO *et al.*, 2013).

. A madeira madura possui imenso apreço pela indústria madeireira, principalmente por sua boa resistência mecânica, esta tem células de menor diâmetro e alta densidade devido a paredes celulares mais espessas (Figura 6).

Figura 6: Imagem microscópica no plano transversal de uma madeira de *Pinus elliottii*. Fonte Autor (2020).

Do ponto de vista morfológico, a madeira madura é composta de maior comprimento traqueídeos (elementos condutores), ângulos microfibrilares menores, traqueídeos apresentam diâmetros menores e paredes celulares mais espessa, o que explica sua maior densidade em comparação com a madeira juvenil (CARVALHO *et al.*, 2013). No que tange às propriedades químicas, há diferenças consideráveis entre os tipos de lenho. PALERMO *et al.*, (2013) mencionam que a madeira madura possui menor conteúdo de lignina. LI; WU; SOUTHERTON, (2012) mencionam que a madeira madura possui maiores conteúdos de holocelulose. Todas essas características proporcionam à madeira madura melhores propriedades mecânicas, se comparadas a madeira juvenil. Por exemplo, BALLARIN; PALMA, (2003), ao avaliar as propriedades mecânicas da madeira de *Pinus elliottii* madura e juvenil por meio do ensaio de flexão estática, encontraram um módulo de elasticidade de 16700 MPa e 10900 MPa.

A madeira juvenil é composta por células de grande diâmetro e baixa densidade. Em madeiras de coníferas, como pinheiros, é de fácil observação a variação no padrão de madeira com base na largura dos anéis de crescimento entre o juvenil e a madeira madura (BAO *et al.*, 2001).

CARVALHO *et al.*, (2013) citaram que a madeira juvenil tem baixa qualidade devido a maior proporção de madeira juvenil do que o da madeira madura. Em uma tora pronta para ser cortada para madeira serrada (cerca de 20 anos) a madeira juvenil pode representar até 50% do volume total de uma tora (WU *et al.*, 2007). Em relação ao módulo de elasticidade os mesmos autores mencionaram que para madeira juvenil é em torno de 6150 MPa e 8110 MPa para madeira madura. BHAT; PRIYA; RUGMINI, (2001) mencionaram que a madeira madura de teca possui valores 20% superiores para MOR e MOE em relação à madeira juvenil, para árvores oriundas de reflorestamentos.

No que tange às propriedades químicas, PALERMO *et al.*, (2013) mencionam que a madeira juvenil possui maior conteúdo de lignina. LI; WU; SOUTHERTON, (2012) mencionam que a madeira juvenil possui menores conteúdos de celulose e hemicelulose, sendo estes citados os componentes majoritários da madeira que fazem com que haja boa resistência mecânica. No que tange aos extrativos, segundo BAO *et al.*, (2001), a madeira juvenil possui maior quantidade, sendo este 1.5 vezes mais se comparada a madura. Os mesmos autores, ao analisar as propriedades químicas de uma madeira de *Pinus elliottii* encontraram sucessivamente na madeira juvenil: 68% de holocelulose, 28,4 % de lignina e 5,03 % de extrativos; para madeira madura: 70,69 % de holocelulose, 27,53 % de lignina e apenas 3,12 % de extrativos. VIDAURRE *et al.*, (2011) também avaliou a constituição química da madeira juvenil e madura de *Pinus radiata* e concluiram que conforme o aumento da idade maior o teor de holocelulose e menor o teor de lignina e extrativos. Por exemplo: a madeira madura de *Pinus radiata* de 26-30 anos apresentou um teor de holocelulose de 55,91 % enquanto na faixa de idade de 4-6 anos 62,09 %, para a lignina observaram um teor de 33,76 % para faixa de 26-30 anos e 38,81 para 4-6 anos.

4.5 TRATAMENTOS CONVENCIONAIS DA MADEIRA POR IMPREGNAÇÃO

A proteção química da madeira se transformou em uma grande indústria mundial. Na maioria dos países, as associações se desenvolveram entre os cientistas da madeira, produtores de conservantes e tratadores da região para desenvolver especificações para conservantes, padrões para tratamentos e promover pesquisas (ZABEL; MORRELL, 2020a). De modo geral, o surgimento do tratamento da madeira deve-se a limitações presentes em determinadas espécies, principalmente no que diz respeito à resistência biológica, instabilidade dimensional e baixa propriedades mecânicas. Em seguida, com a modificação da madeira, visando a resistência a agentes biodeterioradores, pesquisadores propuseram modificações que alteram outras propriedades, como estabilidade dimensional, resistência mecânica, estabilidade térmica e a intemperes (ZABEL; MORRELL, 2020b, 2020a). A modificação da madeira pode dividir-se em quatro tipos: modificação química, modificação térmica, modificação de superfície e modificação por impregnação (ESTEVES; PEREIRA, 2015).

O tratamento de impregnação se dá da seguinte forma: um preservante é inserido nos espaços vazios da madeira, podendo simplesmente causar modificações na parede celular como preencher a mesma. Os tratamentos por impregnação se dividem em: sem pressão e com pressão (American Wood Protection Association, 2017). O tratamento sem pressão pode ser por imersão, escovação e pulverização e requer uma estrutura simples. São frequentemente usados por pequenas empresas para o tratamento de quantidades limitadas de madeira ou fazendeiros que têm uma fonte de baixo custo. Os dois mais usados são pincelamento e revestimentos das extremidades cortadas da madeira, os quais visam proteger a madeira de degradação da luz ultravioleta e ataque de fungos (WILLIAMS; ROTECTING, 2001). Esses tratamentos penetram apenas uma curta distância na madeira para fornecer proteção temporária que pode prolongar a vida útil do produto.

No que tange aos tratamentos com pressão, estes utilizam um conservante para melhorar determinadas características da madeira. Quando realizado adequadamente, o tratamento sob pressão resulta em maior uniformidade e profundidade na penetração do produto químico utilizado. Existem três tratamentos básicos de pressão, conforme ZABEL; MORRELL, (2020b): Tratamento térmico, sob pressão e vácuo-pressão, sendo o último citado o mais eficiente. Nesse processo, há um vácuo inicial (na maioria dos casos, cerca de 0.1 MPa), o qual visa a remoção do ar intracelular presente no material a ser tratado. Após, pela diferença de pressão, há a inserção da solução no interior do equipamento e, após, é aplicada pressão que pode variar de tratamento para tratamento. Em seguida, são retiradas as madeiras tratadas do interior da autoclave e o produto químico restante é reaproveitado para uma próxima impregnação (ZABEL; MORRELL, 2020a).

Dentre os produtos mais utilizados para preservar a madeira, destacaram-se o CCA (Arseniato de Cobre Cromatado), creosoto e o pentaclorofenol. O CCA é um hidrossolúvel que possui, em sua constituição química, o arsênio como principal agente preservante. No entanto, alguns países, como Brasil e Estados Unidos, introduziram recentemente restrições legislativas contra esses produtos químicos, devido a preocupações ambientais TASCIOGLU *et al.*, (2013), principalmente devido a presença do arsênio sendo que há estudos que comprovam seu potencial cancerígeno (AFZAL *et al.*, 2019; KARAMI-MOHAJERI; ABDOLLAHI, 2011; TASCIOGLU *et al.*, 2013). No caso do creosoto, foi muito utilizado antigamente, no entanto, por conta de seu potencial prejudicial ao meio ambiente, foi banido em muitos países, inclusive no Brasil (ZABEL; MORRELL, 2020b). No que tange ao pentaclorofenol, houve a mesma problematização que o em relação ao creosoto. Esse produto se mostrou um eficiente preservativo, no entanto, devido à sua nocividade ao meio ambiente, teve seu uso proibido (ZABEL; MORRELL, 2020a). Com todas essas problematizações em relação a preservantes tradicionais e utilizados pela indústria madeireira houve a necessidade de novos tratamentos que visassem melhorias nas propriedades da madeira sem comprometer tanto o meio ambiente.

4.6 MODIFICAÇÃO DA MADEIRA COM POLÍMEROS

O tratamento da madeira com polímeros vem se mostrando uma excelente alternativa no que se refere à melhoria em suas propriedades (MATTOS *et al.*, 2015b). Essa madeira tratada pode ser considerada um compósito madeira-polímero, o qual consiste em uma madeira sólida impregnada com monômeros insaturados, que em seguida de sua impregnação são submetidos a uma polimerização *in situ* (DING; KOUBAA; CHAALA, 2013; MATTOS *et al.*, 2015b). Este método utiliza a microestrutura da madeira como matriz para um polímero sintetizado *in situ* que age como um reforço (MATTOS *et al.*, 2015b). Assim, as características benéficas de cada componente são aproveitadas e esse compósito pode apresentar propriedades superiores às das fases isoladas (SATYANARAYANA; ARIZAGA; WYPYCH, 2009).

Portanto, madeira de baixa qualidade e crescimento rápido é agora matéria-prima para a fabricação de novos materiais com propriedades físicas, biológicas e mecânicas muito mais altas que a madeira não tratada (ISLAM *et al.*, 2014; YANG *et al.*, 2019). Nesse contexto, já foram utilizados com sucesso diferentes monômeros e resinas sintéticas, incluindo o metacrilato de metila (MMA), o álcool furfurílico, o estireno, a melanina-ureia-formaldeído, entre outros (DING; KOUBAA; CHAALA, 2013; MANTANIS, 2017; QIN; DONG; LI, 2019).

4.6.1 POLI (ESTIRENO)

Dentre os polímeros sintéticos mais consumidas pela indústria, destaca-se o estireno (WEBER *et al.*, 2011). A polimerização do estireno é normalmente iniciada por um radical livre R, que interage com a molécula de estireno, quebrando a dupla ligação entre os carbonos, iniciando a propagação da cadeia desse monômero que transforma-se em um polímero denominado poli(estireno) (Figura 7).

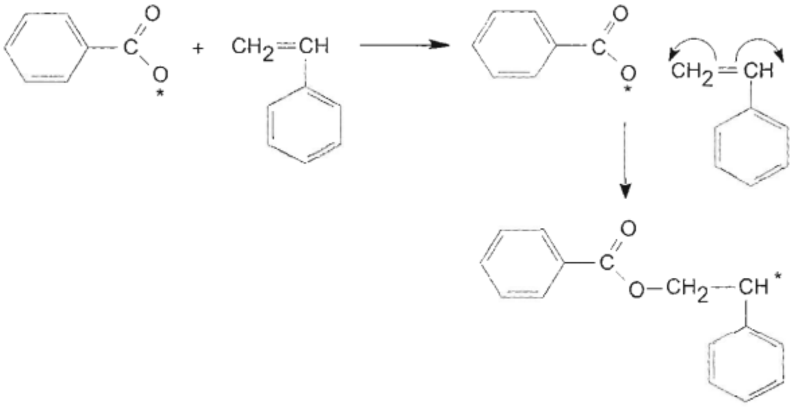


Figura 7 - Estrutura poli (estireno). Fonte: (CANEVAROLO JR, S, 2006).

O poli(estireno) é um polímero termoplástico, amorfo e translúcido e com alta resistência mecânica (MU, 2019). Os principais defeitos são a baixa estabilidade à exposição ao clima, ficando amarelado se exposto a luz do sol. Apesar dessas desvantagens, tem sido amplamente utilizado como recipientes moldados, tampas, garrafas, armários eletrônicos (ROUSSAK, 2012). Segundo os mesmos autores, o estireno é muito aplicado também em tintas à base d’água e revestimentos de proteção para alguns materiais.

No que tange suas aplicações no tratamento da madeira, há poucos estudos utilizando apenas o estireno. EL-AWADY; EL-AWADY, (2003), em seu trabalho com Pinus branco (*Pinus strobus* Linnaeus), produziram WPC por polimerização *in situ* do monômero de estireno sob radiação gama e atingiram maior resistência ao envelhecimento em ambiente aquático do que a madeira de Pinus sem tratamento. CHE *et al.*, (2018) trataram um cerne de pinheiro (*Pinus radiata* Don.) usando soluções aquosas compostas de três diferentes proporções de estireno/ácido acrílico, que resultaram em uma maior resistência a intempéries, atribuída a ligações covalentes desenvolvidas entre o monômero e a lignina da madeira. OLANIRAN *et al.*, (2019) aplicaram a polimerização *in situ* do monômero de estireno em madeiras de abeto norueguês (*Picea abies* L. Karst.) pré-tratadas por metacrilação (reação com anidrido metacrílico). Tais autores relataram que a parede celular e o lúmen da madeira foram parcialmente preenchidos pelo polímero, levando a um aumento da rigidez na flexão e no cisalhamento, embora tenha ocorrido uma redução na rigidez específica devido ao aumento da massa específica.

4.6.2 POLI (ACETATO DE VINILA)

O poli(acetato de vinila) é um polímero amorfo que oferece boa adesão à maioria das superfícies, oferecendo uma capacidade aceitável de preenchimento de lacunas (BHUMKAR; RATHNAM, 2019). Segundo ZIMMERMANN *et al.*, (2014), o poli (acetato de vinila) também é uma matriz promissora para compósitos poliméricos. Outra aplicação possível para o acetato de vinila é utilizado para produzir madeira acetilada (JEBRANE; PICHAVANT; SBE, 2011). A polimerização do poli (acetato de vinila) é ilustrada na Figura 8.

Figura 8: Polimerização do Acetato de vinila em Poli (acetato de vinila). Fonte: Adaptado de (CHANA; FORBES; JONES, 2008).

Este polímero possui baixo custo, alta inflamabilidade e, normalmente, é utilizado juntamente de outro polímero em uma copolimerização. Em aplicações na madeira, é comum encontrar esse monômero em sua forma emulsiva, como cola branca para a indústria de painéis de madeira maciça. Em relação ao tratamento da madeira, há poucos estudos que utilizam esse polímero. JEBRANE; PICHAVANT, (2011), por exemplo, trataram um pinheiro marítimo (*Pinus pinaster*) com acetato de vinila, usando o carbonato de potássio como catalisador, e suas reações de esterificação ocorreram a 90 ºC. Eles relataram reações químicas na celulose e na lignina da madeira estudada.

4.6.3 POLI (METIL METACRILATO)

TSAI *et al.*, (2010) mencionaram que poli(metacrilato de metila) (PMMA) é um típico polímero amorfo, que é usado em vários campos da nossa vida diária. O poli (metil metacrilato) (PMMA), também chamado de plexiglas, lucite ou perspex, é um cristal transparente incolor com excelente estabilidade ao ar livre se forem adicionados absorvedores de UV ao polímero, caso contrário, amarelará com a exposição a luz solar (ROUSSAK, 2012). Tem baixa resistência a arranhões, mas foi o plástico preferido para fabricação de inúmeros materiais (ROUSSAK, 2012).

O PMMA é um dos monômeros mais baratos e acessíveis no mercado, principalmente devido à grande produção na Ásia e à compatibilidade com outros monômeros (MATTOS *et al.*, 2015b). A polimerização do monômero de metacrilato de metila é ilustrada na Figura 9.

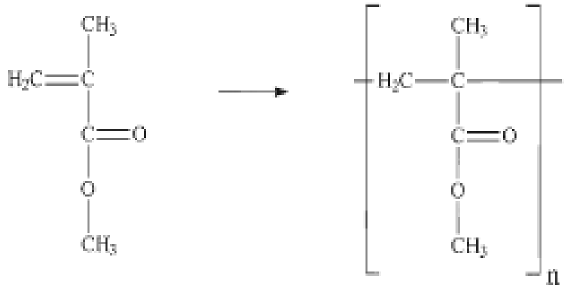


Figura 9 - Estrutura poli (metil metacrilato). Fonte: (CANEVAROLO JR, S, 2006).

O uso do PMMA para produzir peças de madeira impregnadas se deve a sua fácil síntese, baixo custo, translucidez, boa estabilidade química e facilidade de catálise (MATTOS *et al.*, 2015b). DONG *et al.*, (2014) mencionaram que a polimerização *in situ* do MMA em peças de madeira pode fornecer melhorias em vários parâmetros tecnológicos, como estabilidade dimensional, densidade e propriedades mecânicas. Essas alterações estão associadas ao confinamento de segmentos poliméricos em células da madeira e/ou paredes de células de madeira (ROWELL; ELLIS, 2007). Alguns estudos destacam o uso desse polímero na polimerização *in situ* no interior da madeira (MATTOS *et al.*, 2015b).

HADI *et al.*, (2018) polimerizaram *in situ* o MMA em quatro espécies de madeira, sengon (*Falcataria moluccana* Barneby & JW Grimes), jabon (*Anthocephalus cadamba* (Roxb.) Bosser), mangium (*Acacia mangium* Wild) e pinheiro (*Pinus merkusii* Junghuhn & De Vriese). Eles observaram que as madeiras tratadas apresentaram maior resistência ao ataque de cupins subterrâneos em comparação com os respectivos controles. Mais recentemente, o WPC foi produzido por polimerização *in situ* do MMA em três espécies de madeira de rápido crescimento: jabon (*Anthocephalus cadamba*), mangium (*Acacia mangium* Wild) e Pinus (*Pinus merkusii Junghuhn* & De Vriese). Os autores relataram que o tratamento levou a um aumento na densidade e na resistência à flexão (HADI *et al.*, 2018).

4.6.4 POLI (ÁLCOOL FURFURÍLICO)

O uso de carboidratos tem despertado um imenso interesse da comunidade científica nos últimos anos (SHELDON, 2014). O mesmo autor cita que o álcool furfurílico e seus derivados são compostos com diferentes grupos funcionais que podem ser precisamente obtidos a partir dos açúcares C5 e C6 presentes na biomassa (SHELDON, et al., 2014). Este produto foi isolado pela primeira vez pelo químico alemão Johann Wolfgang Döbereiner em 1832 (SIGNORETTO *et al.*, 2019).

O álcool furfurílico é fabricado industrialmente pela redução de um produto tóxico denominado furfural produzido a partir de hemicelulose de produtos agrícolas subprodutos ou serragem. Num reator sob pressão e por catálise ácida, o xilanos de hemicelulose são hidrolisados em xiloses e depois desidratados para forma furfural (ISSAOUI; FATIMA CHARRIER - EL BOUHTOURY, 2020).

O furfural é o principal composto químico elaborado a partir de matéria-prima lignocelulósica, em nível mundial. Além disso, apresenta uma série de derivados, como o álcool furfurílico, ácidos furóicos, furfurilamina, tetrahidrofurano, dentre outros, que juntos constituem a base da química de polímeros furânicos, com imenso potencial de competição com seus similares de origem fóssil, no mercado de adesivos (KIM *et al.*, 2014). TONHI *et al.*, (2002), explicam que a produção dos derivados do álcool furfurílico, portanto, pode ser realizada através de processos eletroquímicos que podem levá-lo à redução, na forma de álcool furfurilico ou oxidado em ácido furóico. A reação de polimerização do álcool furfurilico é mostrada na Figura 10.

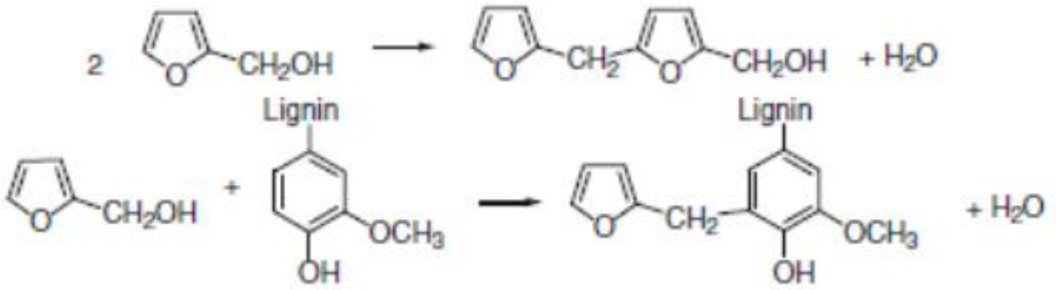


Figura 10 – Polimerização do álcool furfurílico. Fonte: Adaptado de (GÉRARDIN, 2016).

Em 2010, por exemplo, cerca de 85 a 90% da demanda mundial de álcool furfurílico foi empregada na produção de resinas furânicas (SHELDON, 2014). O mercado que demanda em maior quantia estas resinas é a indústria de fundição. Sua aplicação em moldes para peças metálicas se dá graças a características como: excelente estabilidade térmica, resistência à corrosão, ataque ácido e fogo (GANDINI e BELGACEM, 2013).

O processo de modificação por impregnação que mais tem evoluído nos últimos anos é a furfurilação (ESTEVES; PEREIRA, 2015). No que tange a aplicações para o tratamento da madeira, a primeira unidade semi-industrial para produção de madeira tratada com álcool furfurílico foi criada em Porsgrunn (Noruega), mas a primeira unidade de produção em escala comercial foi construída em Heröya, em 2004, e a madeira tratada foi comercializada sobre a marca Kebony (ESTEVES; NUNES; PEREIRA, 2011). Aplicando modificação química da madeira, principalmente madeira furfurilada, espécies de baixa durabilidade podem ser facilmente transformadas em novos produtos de madeira com propriedades aprimoradas, essa abordagem portanto, pode ser considerada como a melhor solução para o problema de algumas limitações deste material (como baixa estabilidade dimensional, baixa resistência mecânica e baixa durabilidade natural) (PAPADOPOULOS; KYZAS, 2019). Recentemente, foram relatadas melhorias em algumas propriedades importantes da madeira, incluindo dureza, rigidez e resistência à flexão, estabilidade térmica e resistência à deterioração (GALLIO *et al.*, 2019).

Para DONG *et al.*, (2015), todas essas melhorias dependem tanto da concentração de álcool furfurílico quanto da relação álcool/catalisador, de uma maneira que parece ser: quanto maior a concentração, maiores as melhorias nas propriedades da madeira. BELGACEM; GANDINI, (2008) explicam que, do ponto de vista químico o que faz com que ocorra ligações químicas entre ambos os materiais são as hidroxilas livres presentes no álcool furfurílico. (MANTANIS, 2017) citaram os benefícios da madeira furfurilada como sendo: A madeira furfurilada apresenta muito boa estabilidade, resistência dimensional e resistência ao intemperismo. A madeira furfurilada tem resistência comparável contra microorganismos com a madeira tratada com biocidas tóxicos convencionais. A madeira furfurilada é resistente a brocas marítimas. A madeira furfurilada é um produto verde.

4.7 EFEITOS DA POLIMERIZAÇÃO *in situ* NAS PROPRIEDADES DA MADEIRA

A indústria destes compósitos teve rápido crescimento na América do Norte e Europa, e a importância comercial destes produtos ampliou esforços para a compreensão de suas propriedades estruturais (SATYANARAYANA; ARIZAGA; WYPYCH, 2009). DONG *et al.*, (2014) polimerizaram *in situ* a madeira de *Muchelia macclurei* com metacrilato de etilglicol dimetílico pelo método vácuo-pressão e observaram um aumento no módulo de ruptura, resistência a compressão, resistência ao impacto e dureza de respectivamente 54%, 60%, 80% e 151%. Os mesmos autores concluiram que a durabilidade, incluindo estabilidade dimensional e resistência à deterioração, também foi aprimorada em comparação com a madeira não tratada. ESTEVES; NUNES; PEREIRA, (2011) polimerizaram *in situ* o alburno de Pinus (*Pinus pinaster*) com poli (álcool furfurílico) e obtiveram um ganho de massa de 38% e um módulo de elasticidade comparável aos controles não tratados, mas um aumento no MOR em 6% e na dureza em 50%, respectivamente. XIE *et al.*, (2013) efetuaram um teste de fluência por flexão por 140 dias e isso revelou que tratamentos parciais de poli (álcool furfurílico) no alburno de pinheiro escocês causaram uma redução na deflexão da fluência e na fluência relativa em 46 e 24%, respectivamente.

Tanto a madeira de Pinus e álamo marítimo modificada com poli (metil metacrilato) exibiram um aumento na compressão de aproximadamente 20–110%, aumentando a faixa de percentual de ganho de massa (WPG) de 34 para 179%; no entanto, a melhoria nas propriedades de flexão foi geralmente inferior a 30% e pouco influenciada pelas mudanças no WPG (YILDIZ; YILDIZ; GEZER, 2005). OLANIRAN *et al.*, (2019) ao tratar a madeira de *Picea abies* com a copolimerização de poli (estireno) e poli (metil metacrilato) observaram um aumento de cerca de 120 % no módulo de elasticidade e concluiram que este aumento deve-se a polimerização *in situ* do poli (estireno). Há inúmeras indústrias que comercializam estes produtos, como é o caso da Indurite ™, VecoWood® e Lignia ™. A figura 11 mostra algumas aplicações de WPC’s.

Figura 11 - Aplicações dos WPC’s. Fonte: Autor, 2020.

A modificação da madeira, com a comercialização de vários processos, tem provado que está aqui para ficar (ESTEVES; PEREIRA, 2015). As quantidades de madeira tratada têm crescido exponencialmente pelo que a madeira modificada poderá, num futuro próximo, vir a substituir a madeira tratada com biocidas. Nas utilizações mais nobres a madeira modificada apresenta já uma considerável cota do mercado principalmente nos países nórdicos (ESTEVES; PEREIRA, 2015). Alguns trabalhos aplicando monômeros para polimerização *in situ* da madeira são expressos na Tabela 1.

Tabela 1: Alguns tratamentos da madeira com monômeros.

Madeira tratada com álcool furfurílico	TEMIZ *et al.*, (2007)
Madeira tratada com álcool furfurílico	YANG; CAO; MA, (2019)
Madeira tratada com álcool furfurílico	LANDE; WESTIN; SCHNEIDER, (2004)
Madeira tratada com metil metacrilato	MATTOS *et al.*, (2015b)
Madeira tratada com metil metacrilato	YILDIZ; YILDIZ; GEZER, (2005)
Madeira tratada com metil metacrilato	TSAI *et al.*, (2010)
Madeira tratada com estireno	OLANIRAN *et al.*, (2019)
Madeira tratada com estireno	MAGALHAES; DA SILVA, (2004)
Madeira tratada com acetato de vinila	JEBRANE; PICHAVANT, (2011)

REFERÊNCIAS

AFZAL, I. *et al.* Plant beneficial endophytic bacteria: Mechanisms, diversity, host range and genetic determinants. **Microbiological Research**, *[S. l.]*, v. 221, n. February, p. 36–49, 2019. Disponível em: https://doi.org/10.1016/j.micres.2019.02.001

ARCE, N.; MOYA, R. Propriedades da Madeira de Clones adultos de Tectona grandis crescendo na Costa Rica. **Cerne**, *[S. l.]*, v. 21, n. 3, p. 353–362, 2015. Disponível em: https://doi.org/10.1590/01047760201521031751

BAJPAI, P. Wood and Fiber—Growth and Anatomy. **Biermann's Handbook of Pulp and Paper**, *[S. l.]*, p. 75–103, 2018 a. Disponível em: https://doi.org/10.1016/b978-0-12-814240-0.00003-3

BAJPAI, P. Wood-Based Products and Chemicals. **Biermann's Handbook of Pulp and Paper**, *[S. l.]*, p. 233–247, 2018 b. Disponível em: https://doi.org/10.1016/b978-0-12-814240-0.00008-2

BAJPAI, P. **Wood and Fiber Fundamentals**. *[S. l.: s. n.]*. *E-book*. Disponível em: https://doi.org/10.1016/b978-0-12-814240-0.00002-1

BAJPAI, P. Biomass composition. **Biomass to Energy Conversion Technologies**, *[S. l.]*, p. 31–40, 2020. Disponível em: https://doi.org/10.1016/b978-0-12-818400-4.00004-9

BALLARIN, A. W.; PALMA, H. A. L. Propriedades de resistência e rigidez da madeira juvenil e adulta de Pinus taeda L. **Revista Árvore**, *[S. l.]*, v. 27, n. 3, p. 371–380, 2003. Disponível em: https://doi.org/10.1590/s0100-67622003000300014

BAO, F. C. *et al.* Differences in wood properties between juvenile wood and mature wood in 10 species grown in China. **Wood Science and Technology**, *[S. l.]*, v. 35, n. 4, p. 363–375, 2001. Disponível em: https://doi.org/10.1007/s002260100099

BELGACEM, M. N.; GANDINI, A. <Chemical Modifi cation of Wood.pdf>. **Elsevier**, *[S. l.]*, v. 29, p. 562, 2008.

BHAT, K. M.; PRIYA, P. B.; RUGMINI, P. Characterisation of juvenile wood in teak. **Wood Science and Technology**, *[S. l.]*, v. 34, n. 6, p. 517–532, 2001. Disponível em: https://doi.org/10.1007/s002260000067

BHUMKAR, A. N.; RATHNAM, M. V. Density, viscosity, and speed of sound of binary liquid mixtures of vinyl acetate with butyl vinyl ether, diisopropyl ether, anisole and dibutyl ether. **Journal of Chemical Thermodynamics**, *[S. l.]*, v. 136, p. 77–87, 2019. Disponível em: https://doi.org/10.1016/j.jct.2019.04.018

BRÄNDSTRÖM, J. Microfibril angle of the S1 cell wall layer of Norway spruce compression wood tracheids. **IAWA Journal**, *[S. l.]*, v. 25, n. 4, p. 415–423, 2004. Disponível em: https://doi.org/10.1163/22941932-90000374

CANEVAROLO JR, S, V. Ia dos. **Artliber**, *[S. l.]*, v. 1, p. 277, 2006.

CARVALHO, A. *et al.* The Transcriptomics of Secondary Growth and Wood Formation in Conifers. **Molecular Biology International**, *[S. l.]*, v. 2013, p. 1–12, 2013. Disponível em: https://doi.org/10.1155/2013/974324

CHANA, J.; FORBES, B.; JONES, S. A. The synthesis of high molecular weight partially hydrolysed poly(vinyl alcohol) grades suitable for nanoparticle fabrication. **Journal of Nanoscience and Nanotechnology**, *[S. l.]*, v. 8, n. 11, p. 5739–5747, 2008. Disponível em: https://doi.org/10.1166/jnn.2008.475

CHE, W. *et al.* Radiata pine wood treatment with a dispersion of aqueous styrene/acrylic acid copolymer. **Holzforschung**, *[S. l.]*, v. 72, n. 5, p. 387–396, 2018. Disponível em: https://doi.org/10.1515/hf-2017-0142

CHENG, S. S. *et al.* Larvicidal activities of wood and leaf essential oils and ethanolic extracts from Cunninghamia konishii Hayata against the dengue mosquitoes. **Industrial Crops and Products**, *[S. l.]*, v. 47, p. 310, 2013. Disponível em: https://doi.org/10.1016/j.indcrop.2013.03.016

DING, W. D.; KOUBAA, A.; CHAALA, A. Mechanical properties of MMA-hardened hybrid poplar wood. **Industrial Crops and Products**, *[S. l.]*, v. 46, p. 304–310, 2013. Disponível em: https://doi.org/10.1016/j.indcrop.2013.02.004

DONALDSON, L. A.; GRACE, J.; DOWNES, G. M. Within-tree variation in anatomical properties of compression wood in radiata pine. **IAWA Journal**, *[S. l.]*, v. 25, n. 3, p. 253–271, 2004. Disponível em: https://doi.org/10.1163/22941932-90000364

DONALDSON, L.; NANAYAKKARA, B.; HARRINGTON, J. **Wood Growth and Development**. Second Edi ed. *[S. l.]*: Elsevier, 2016. v. 1*E-book*. Disponível em: https://doi.org/10.1016/B978-0-12-394807-6.00114-3

DONG, X. *et al.* Structure and Properties of Polymer-Impregnated Wood Prepared by in-situ Polymerization of Reactive Monomers. **BioResources**, *[S. l.]*, v. 10, n. 4, p. 7854–7864, 2015. Disponível em: https://doi.org/10.15376/biores.10.4.7854-7864

DONG, Y. *et al.* Wood/polymer nanocomposites prepared by impregnation with furfuryl alcohol and Nano-SiO2. **BioResources**, *[S. l.]*, v. 9, n. 4, p. 6028–6040, 2014. Disponível em: https://doi.org/10.15376/biores.9.4.6028-6040

EL-AWADY, M. M.; EL-AWADY, N. I. Non-toxic preservatives for wooden objects in sea water. I. Styrene monomer polymerised using gamma irradiation. **Plastics, Rubber and Composites**, *[S. l.]*, v. 32, n. 8–9, p. 334–339, 2003. Disponível em: https://doi.org/10.1179/146580103225004081

ESTEVES, B.; NUNES, L.; PEREIRA, H. Properties of furfurylated wood (Pinus pinaster). **European Journal of Wood and Wood Products**, *[S. l.]*, v. 69, n. 4, p. 521–525, 2011. Disponível em: https://doi.org/10.1007/s00107-010-0480-4

ESTEVES, B.; PEREIRA, H. Novos métodos de protecção da madeira. *[S. l.]*, n. January 2009, 2015.

FERNÁNDEZ, M. E. *et al.* New insights into wood anatomy and function relationships: How

Eucalyptus challenges what we already know. **Forest Ecology and Management**, *[S. l.]*, v. 454, n. September, p. 117638, 2019. Disponível em: https://doi.org/10.1016/j.foreco.2019.117638

FU, Y. *et al.* Hydrophobic modification of wood via surface-initiated ARGET ATRP of MMA. **Applied Surface Science**, *[S. l.]*, v. 258, n. 7, p. 2529–2533, 2012. Disponível em: https://doi.org/10.1016/j.apsusc.2011.10.087

GALLIO, E. *et al.* Influence of thermal rectification and furfurylation treatments on technological properties of a conifer. **Revista Materia**, *[S. l.]*, v. 24, n. 3, 2019. Disponível em: https://doi.org/10.1590/s1517-707620190003.0739

GÉRARDIN, P. New alternatives for wood preservation based on thermal and chemical modification of wood— a review. **Annals of Forest Science**, *[S. l.]*, v. 73, n. 3, p. 559–570, 2016. Disponível em: https://doi.org/10.1007/s13595-015-0531-4

HADI, Y. S. *et al.* Resistance of methyl methacrylate-impregnated wood to subterranean termite attack. **Journal of the Korean Wood Science and Technology**, *[S. l.]*, v. 46, n. 6, p. 748–755, 2018. Disponível em: https://doi.org/10.5658/WOOD.2018.46.6.748

IBÁ - INDÚSTRIA BRASILEIRA DE ÁRVORES. Relatório 2019 Report 2019. **Relatório**, *[S. l.]*, p. 1–80, 2019. Disponível em: https://www.iba.org/datafiles/publicacoes/relatorios/iba-relatorioanual2019.pdf

ISLAM, M. S. *et al.* The chemical modification of tropical wood polymer composites. **Journal of Composite Materials**, *[S. l.]*, v. 48, n. 7, p. 783–789, 2014. Disponível em: https://doi.org/10.1177/0021998313477894

ISSAOUI, H.; FATIMA CHARRIER - EL BOUHTOURY. **Bio-based products from wood materials**. *[S. l.]*: Elsevier, 2020. *E-book*. Disponível em: https://doi.org/10.1016/b978-0-12-818493-6.00007-5

JEBRANE, M.; PICHAVANT, F.; SBE, G. A comparative study on the acetylation of wood by reaction with vinyl acetate and acetic anhydride. **Carbohydrate Polymers**, *[S. l.]*, v. 83, n. 2, p. 339–345, 2011. Disponível em: https://doi.org/10.1016/j.carbpol.2010.07.035

JÖNSSON, A. S. Membranes for lignin and hemicellulose recovery in pulp mills. **Membrane Technologies for Biorefining**, *[S. l.]*, p. 105–133, 2016. Disponível em: https://doi.org/10.1016/B978-0-08-100451-7.00005-0

KAI, D. *et al.* Towards lignin-based functional materials in a sustainable world. **Green Chemistry**, *[S. l.]*, v. 18, n. 5, p. 1175–1200, 2016. Disponível em: https://doi.org/10.1039/c5gc02616d

KANG, H.; LIU, R.; HUANG, Y. Graft modification of cellulose: Methods, properties and applications. **Polymer**, *[S. l.]*, v. 70, p. A1–A16, 2015. Disponível em: https://doi.org/10.1016/j.polymer.2015.05.041

KARAMI-MOHAJERI, S.; ABDOLLAHI, M. Toxic influence of organophosphate, carbamate, and organochlorine pesticides on cellular metabolism of lipids, proteins, and carbohydrates: A systematic review. **Human and Experimental Toxicology**, *[S. l.]*, v. 30, n.

9, p. 1119–1140, 2011. Disponível em: https://doi.org/10.1177/0960327110388959

KEPLINGER, T. *et al.* A versatile strategy for grafting polymers to wood cell walls. **Acta Biomaterialia**, *[S. l.]*, v. 11, n. 1, p. 256–263, 2015. Disponível em: https://doi.org/10.1016/j.actbio.2014.09.016

KIM, H.; LEE, B.; YUN, K. W. Comparison of chemical composition and antimicrobial activity of essential oils from three Pinus species. **Industrial Crops and Products**, *[S. l.]*, v. 44, p. 323–329, 2013. Disponível em: https://doi.org/10.1016/j.indcrop.2012.10.026

KIM, T. *et al.* Thermodynamics and reaction pathways of furfuryl alcohol oligomer formation. **Catalysis Communications**, *[S. l.]*, v. 46, p. 66–70, 2014. Disponível em: https://doi.org/10.1016/j.catcom.2013.11.030

LAI, M. *et al.* Inheritance of resin yield and main resin components in Pinus elliottii Engelm. at three locations in southern China. **Industrial Crops and Products**, *[S. l.]*, v. 144, n. December 2019, p. 112065, 2020. Disponível em: https://doi.org/10.1016/j.indcrop.2019.112065

LANDE, S.; WESTIN, M.; SCHNEIDER, M. Properties of furfurylated wood. **Scandinavian Journal of Forest Research**, *[S. l.]*, v. 19, n. 1596, p. 22–30, 2004. Disponível em: https://doi.org/10.1080/0282758041001915

LAZAR, T. Taiz, L. and Zeiger, E. Plant physiology. 3rd edn. **Annals of Botany**, *[S. l.]*, v. 91, n. 6, p. 750–751, 2003. Disponível em: https://doi.org/10.1093/aob/mcg079

LEKKA, P. *et al.* Effect of mechanical treatment on properties of cellulose nanofibrils produced from bleached hardwood and softwood pulps. **Maderas: Ciencia y Tecnologia**, *[S. l.]*, v. 18, n. 3, p. 457–466, 2016. Disponível em: https://doi.org/10.4067/S0718-221X2016005000041

LI, X.; WU, H. X.; SOUTHERTON, S. G. Identification of putative candidate genes for juvenile wood density in Pinus radiata. **Tree Physiology**, *[S. l.]*, v. 32, n. 8, p. 1046–1057, 2012. Disponível em: https://doi.org/10.1093/treephys/tps060

LU, Y. *et al.* Structural characterization of lignin and its degradation products with spectroscopic methods. **Journal of Spectroscopy**, *[S. l.]*, v. 2017, 2017. Disponível em: https://doi.org/10.1155/2017/8951658

MAGALHAES, W. L. E.; DA SILVA, R. R. Treatment of caribbean pine by in situ polymerization of styrene and furfuryl alcohol. **Journal of Applied Polymer Science**, *[S. l.]*, v. 91, n. 3, p. 1763–1769, 2004. Disponível em: https://doi.org/10.1002/app.13252

MANTANIS, G. I. Chemical modification of wood by acetylation or furfurylation: A review of the present scaled-up technologies. **BioResources**, *[S. l.]*, v. 12, n. 2, p. 4478–4489, 2017. Disponível em: https://doi.org/10.15376/biores.12.2.4478-4489

MATTOS, B. D. *et al.* Thermal tools in the evaluation of decayed and weathered wood polymer composites prepared by in situ polymerization. **Journal of Thermal Analysis and Calorimetry**, *[S. l.]*, v. 121, n. 3, p. 1263–1271, 2015 a. Disponível em: https://doi.org/10.1007/s10973-015-4647-4

MATTOS, B. D. *et al.* Wood-polymer composites prepared by free radical in situ polymerization of methacrylate monomers into fast-growing pinewood. **Wood Science and Technology**, *[S. l.]*, v. 49, n. 6, p. 1281–1294, 2015 b. Disponível em: https://doi.org/10.1007/s00226-015-0761-5

MISSIO, A. L. *et al.* Thermochemical and physical properties of two fast-growing eucalypt woods subjected to two-step freeze-heat treatments. **Thermochimica Acta**, *[S. l.]*, v. 615, p. 15–22, 2015 a. Disponível em: https://doi.org/10.1016/j.tca.2015.07.005

MISSIO, A. L. *et al.* Propriedades mecânicas da madeira resinada de Pinus elliottii. **Ciencia Rural**, *[S. l.]*, v. 45, n. 8, p. 1432–1438, 2015 b. Disponível em: https://doi.org/10.1590/0103-8478cr20130475

MU, A. **済無No Title No Title**. *[S. l.: s. n.]*. v. 53*E-book*. Disponível em: https://doi.org/10.1017/CBO9781107415324.004

NEIS, F. A. *et al.* Multiple industrial uses of non-wood pine products. **Industrial Crops and Products**, *[S. l.]*, v. 130, n. August 2018, p. 248–258, 2019. Disponível em: https://doi.org/10.1016/j.indcrop.2018.12.088

NIMZ, H. Beech Lignin—Proposal of a Constitutional Scheme. **Angewandte Chemie International Edition in English**, *[S. l.]*, v. 13, n. 5, p. 313–321, 1974. Disponível em: https://doi.org/10.1002/anie.197403131

OKON, K. E. *et al.* Effect of silicone oil heat treatment on the chemical composition, cellulose crystalline structure and contact angle of Chinese parasol wood. **Carbohydrate Polymers**, *[S. l.]*, v. 164, p. 179–185, 2017. Disponível em: https://doi.org/10.1016/j.carbpol.2017.01.076

OLANIRAN, S. O. *et al.* Mechanical behaviour of chemically modified Norway spruce (Picea abies L. Karst.): Experimental mechanical studies on spruce wood after methacrylation and in situ polymerization of styrene. **Wood Science and Technology**, *[S. l.]*, v. 53, n. 2, p. 425–445, 2019. Disponível em: https://doi.org/10.1007/s00226-019-01080-5

PALERMO, G. P. de M. *et al.* Delimitação entre os lenhos juvenil e adulto de pinus elliottii engelm. **Revista Arvore**, *[S. l.]*, v. 37, n. 1, p. 191–200, 2013. Disponível em: https://doi.org/10.1590/S0100-67622013000100020

PAPADOPOULOS, A. N.; KYZAS, G. Z. **Nanotechnology and wood science**. *[S. l.]*: Elsevier, 2019. v. 30*E-book*. Disponível em: https://doi.org/10.1016/B978-0-12-814178-6.00009-1

QIN, Y.; DONG, Y.; LI, J. Effect of Modification With Melamine–Urea–Formaldehyde Resin on the Properties of Eucalyptus and Poplar. **Journal of Wood Chemistry and Technology**, *[S. l.]*, v. 39, n. 5, p. 360–371, 2019. Disponível em: https://doi.org/10.1080/02773813.2019.1636821

RAFSANJANI, A. *et al.* Hygroscopic swelling and shrinkage of latewood cell wall micropillars reveal ultrastructural anisotropy. **Journal of the Royal Society Interface**, *[S. l.]*, v. 11, n. 95, 2014. Disponível em: https://doi.org/10.1098/rsif.2014.0126

RODRIGUES-CORRÊA, K. C. da S.; DE LIMA, J. C.; FETT-NETO, A. G. Pine oleoresin: Tapping green chemicals, biofuels, food protection, and carbon sequestration from multipurpose trees. **Food and Energy Security**, *[S. l.]*, v. 1, n. 2, p. 81–93, 2012. Disponível em: https://doi.org/10.1002/fes3.13

ROUSSAK, O. V. **Applied chemistry**. *[S. l.: s. n.]*. v. 7*E-book*. Disponível em: https://doi.org/10.1021/ie50083a031

ROWELL, R. M.; ELLIS, W. D. Determination of dimensional stabilization of wood using the water-soak method. **Wood and Fiber**, *[S. l.]*, v. 10, n. 2, p. 104–111, 2007.

SATYANARAYANA, K. G.; ARIZAGA, G. G. C.; WYPYCH, F. Biodegradable composites based on lignocellulosic fibers-An overview. **Progress in Polymer Science (Oxford)**, *[S. l.]*, v. 34, n. 9, p. 982–1021, 2009. Disponível em: https://doi.org/10.1016/j.progpolymsci.2008.12.002

SCHNEIDER, P. R. *et al.* Crescimento em diâmetro do Pinus elliottii e pinus taeda em areas arenizadas e degradadas no oeste do rio grande do sul. **Ciencia Rural**, *[S. l.]*, v. 44, n. 9, p. 1561–1567, 2014. Disponível em: https://doi.org/10.1590/0103-8478cr20130744

SHELDON, R. A. Green and sustainable manufacture of chemicals from biomass: State of the art. **Green Chemistry**, *[S. l.]*, v. 16, n. 3, p. 950–963, 2014. Disponível em: https://doi.org/10.1039/c3gc41935e

SHIMIZU, J. Y. **Pinus na Silvicultura Brasileira**. *[S. l.: s. n.]*. *E-book*. Disponível em: http://ainfo.cnptia.embrapa.br/digital/bitstream/item/179582/1/Pinus-na-silvicultura-brasileira.pdf

SIGNORETTO, M. *et al.* Catalytic Production of Levulinic Acid (LA) from Actual Biomass. **Molecules (Basel, Switzerland)**, *[S. l.]*, v. 24, n. 15, p. 1–20, 2019. Disponível em: https://doi.org/10.3390/molecules24152760

SILVEIRA, E. A. *et al.* Heat treatment kinetics using three-stage approach for sustainable wood material production. **Industrial Crops and Products**, *[S. l.]*, v. 124, n. July, p. 563–571, 2018. Disponível em: https://doi.org/10.1016/j.indcrop.2018.07.045

SJÖSTRÖM, E. the Structure of Wood. **Wood Chemistry**, *[S. l.]*, p. 1–20, 1993. Disponível em: https://doi.org/10.1016/b978-0-08-092589-9.50005-x

TAGHIYARI, H. R. *et al.* **Nanotechnology for wood quality improvement and protection**. *[S. l.]*: INC, 2020. *E-book*. Disponível em: https://doi.org/10.1016/b978-0-12-817852-2.00019-6

TARMIAN, A. *et al.* Treatability of wood for pressure treatment processes: a literature review. **European Journal of Wood and Wood Products**, *[S. l.]*, v. 78, n. 4, p. 635–660, 2020. Disponível em: https://doi.org/10.1007/s00107-020-01541-w

TASCIOGLU, C. *et al.* Antifungal properties of some plant extracts used as wood preservatives. **International Biodeterioration and Biodegradation**, *[S. l.]*, v. 85, p. 23–28, 2013. Disponível em: https://doi.org/10.1016/j.ibiod.2013.06.004

TEMIZ, A. *et al.* Effect of accelerated weathering on surface chemistry of modified wood. **Applied Surface Science**, *[S. l.]*, v. 253, n. 12, p. 5355–5362, 2007. Disponível em: https://doi.org/10.1016/j.apsusc.2006.12.005

TONHI, E. *et al.* Stationary phases for reversed phase high performance liquid chromatography (RP-HPLC) based on functionalized inorganic oxide surfaces. **Quimica Nova**, *[S. l.]*, v. 25, n. 4, p. 616–623, 2002. Disponível em: https://doi.org/10.1590/s0100-40422002000400017

TREVISAN, R. *et al.* Idade de segregação do lenho juvenil e adulto para Pinus elliottii Engel. **Ciencia Rural**, *[S. l.]*, v. 44, n. 4, p. 634–638, 2014. Disponível em: https://doi.org/10.1590/S0103-84782014000400010

TSAI, T. Y. *et al.* Morphology and properties of poly(methyl methacrylate)/clay nanocomposites by in-situ solution polymerization. **Journal of Physics and Chemistry of Solids**, *[S. l.]*, v. 71, n. 4, p. 590–594, 2010. Disponível em: https://doi.org/10.1016/j.jpcs.2009.12.044

VERHAEGEN, D. *et al.* Eucalyptus robusta pour une production durable de bois énergie à Madagascar: Bilan des connaissances et perspectives. **Bois et Forets des Tropiques**, *[S. l.]*, v. 68, n. 320, p. 15–30, 2014. Disponível em: https://doi.org/10.19182/bft2014.320.a20541

VIDAURRE, G. *et al.* Lenho juvenil e adulto e as propriedades da madeira. **Floresta e Ambiente**, *[S. l.]*, v. 18, n. 4, p. 469–480, 2011. Disponível em: https://doi.org/10.4322/floram.2011.066

WEBER, T. *et al.* Caracterização de artefatos elastoméricos obtidos por revulcanização de resíduo industrial de SBR (Copolímero de Butadieno e Estireno). **Polimeros**, *[S. l.]*, v. 21, n. 5, p. 429–436, 2011. Disponível em: https://doi.org/10.1590/S0104-14282011005000066

WILLIAMS, R. S. a M.; ROTECTING, P. Biodegradation and Weathering : E Valuation of Deck Finish Systems. *[S. l.]*, v. 51, n. 3350, p. 27–32, 2001.

WU, H. X. *et al.* Achievements in forest tree improvement in Australia and New Zealand 8. Successful introduction and breeding of radiata pine in Australia. **Australian Forestry**, *[S. l.]*, v. 70, n. 4, p. 215–225, 2007. Disponível em: https://doi.org/10.1080/00049158.2007.10675023

XIE, Y. *et al.* Effects of chemical modification on the mechanical properties of wood. **European Journal of Wood and Wood Products**, *[S. l.]*, v. 71, n. 4, p. 401–416, 2013. Disponível em: https://doi.org/10.1007/s00107-013-0693-4

YANG, T.; CAO, J.; MA, E. How does delignification influence the furfurylation of wood? **Industrial Crops and Products**, *[S. l.]*, v. 135, n. December 2018, p. 91–98, 2019. Disponível em: https://doi.org/10.1016/j.indcrop.2019.04.019

YANG, X. *et al.* Tin-Functionalized Wood Biochar as a Sustainable Solid Catalyst for Glucose Isomerization in Biorefinery. **ACS Sustainable Chemistry and Engineering**, *[S. l.]*, v. 7, n. 5, p. 4851–4860, 2019. Disponível em: https://doi.org/10.1021/acssuschemeng.8b05311

YILDIZ, Ü. C.; YILDIZ, S.; GEZER, E. D. Mechanical properties and decay resistance of wood-polymer composites prepared from fast growing species in Turkey. **Bioresource Technology**, *[S. l.]*, v. 96, n. 9, p. 1003–1011, 2005. Disponível em: https://doi.org/10.1016/j.biortech.2004.09.010

ZABEL, R. A.; MORRELL, J. J. **Chemical protection of wood (wood preservation)**. *[S. l.: s. n.]*. *E-book*. Disponível em: https://doi.org/10.1016/b978-0-12-819465-2.00019-x

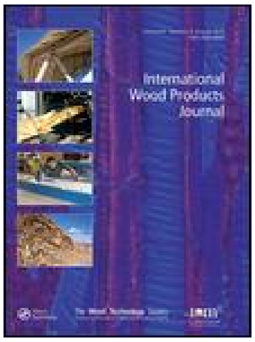
ZABEL, R. A.; MORRELL, J. J. **Wood deterioration agents**. *[S. l.: s. n.]*. *E-book*. Disponível em: https://doi.org/10.1016/b978-0-12-819465-2.00002-4

ZABORNIAK, I.; CHMIELARZ, P.; MATYJASZEWSKI, K. Modification of wood-based materials by atom transfer radical polymerization methods. **European Polymer Journal**, *[S. l.]*, v. 120, n. September, 2019. Disponível em: https://doi.org/10.1016/j.eurpolymj.2019.109253

ZANATTA, P. *et al.* The effect of titanium dioxide nanoparticles obtained by microwave-assisted hydrothermal method on the color and decay resistance of pinewood. **Maderas. Ciencia y tecnología**, *[S. l.]*, v. 19, n. ahead, p. 0–0, 2017. Disponível em: https://doi.org/10.4067/s0718-221x2017005000901

ZIMMERMANN, M. V. G. *et al.* Influência do tratamento químico da fibra de bananeira em compósitos de poli(etileno-co-acetato de vinila) com e sem agente de expansão. **Polimeros**, *[S. l.]*, v. 24, n. 1, p. 58–64, 2014. Disponível em: https://doi.org/10.4322/polimeros.2013.071

5. ARTIGOS



International Wood Products Journal

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/ywpj20

Wood-polymer composites produced by *in situ* polymerization of styrene into juvenile and mature pine woods

Andrey Pereira Acosta , Ezequiel Gallio , Henrique Romer Schulz , Paula Zanatta , Kelvin Techera Barbosa , Rafael De Avila Delucis & Darci Alberto Gatto

To cite this article: Andrey Pereira Acosta , Ezequiel Gallio , Henrique Romer Schulz , Paula Zanatta , Kelvin Techera Barbosa , Rafael De Avila Delucis & Darci Alberto Gatto (2020): Wood-polymer composites produced by *in situ* polymerization of styrene into juvenile and mature pine woods, International Wood Products Journal, DOI: 10.1080/20426445.2020.1776486

To link to this article: https://doi.org/10.1080/20426445.2020.1776486

INTERNATIONAL WOOD PRODUCTS JOURNAL
https://doi.org/10.1080/20426445.2020.1776486

REVIEW

Wood-polymer composites produced by *in situ* polymerization of styrene into juvenile and mature pine woods

Andrey Pereira Acosta, Ezequiel Gallio, Henrique Romer Schulz, Paula Zanatta, Kelvin Techera Barbosa, Rafael De Avila Delucis and Darci Alberto Gatto

Postgraduate Program in Materials Science and Engineering, Federal University of Pelotas, Pelotas, Brazil

ABSTRACT
A wood-based polymer composite was manufactured and characterized using *in situ* polymerization of styrene into juvenile and mature pine wood. Treatment parameters and properties were evaluated by using infrared spectroscopy, thermogravimetry and mechanical testing. Specimens treated by *in-situ* polymerization of styrene showed increased thermal stability as well as improved mechanical properties.

ARTICLE HISTORY
Received 19 February 2020
Accepted 20 May 2020

KEYWORDS
Poly(styrene); impregnation; *Pinus elliottii*; polymers; wood quality; wood modification; Wood treatment; Wood properties

Introduction

Solid wood is a highly versatile material and has been widely used in many applications, including the following sectors: civil construction, furniture and sporting goods. As important features, it has high strength/weight ratio, low thermal and acoustic conductivities, renewability and so on. However, most of the qualified woods (especially those from native forests) have been progressively consumed, due to an improper exploitation and an unsuitable resource planning. Because of that, there is a high investment in some fast growing species, like pines.

Normally, fast growing species produce a large proportion of juvenile wood (JW) when planted in tropical countries, which represents a great challenge for advanced breeding programmes for wood quality control. In general, a forest can be managed in a way that a reduced spacing between trees is applied in the first years of the tree life, which reduces the formation of new cells from the cambial meristem and hence mitigates the formation of JW. According to Palermo et al. (2013), the *Pinus elliottii* wood starts to produce mature wood (MW) at its twentieth year of life if planted in Brazilian environment. The same authors studied 35 years old trees with 25 cm diameter and reported that the central region of the trunk with about 15 cm diameter was composed of JW (at breast height or 1.3 m from the ground).

At an ultrastructural level, compared to the MW, the JW has thinner cell walls, shorter tracheids with larger lumens, smaller tangential cells, larger grain angle, larger microfibril angle and smaller proportion of latewood (Mcdonald and Hubert 2002). Hence, most of the hygroscopic, photochemical, biological and mechanical characteristics of the JW are inferior if compared to the MW (Bao et al. 2001; Li et al. 2011).

Impregnations using certain monomers prior to *in situ* polymerization is a way to improve several unfavourable features in woods. In this procedure, lightweight and permeable solid woods are impregnated with monomers with low molecular weight, low viscosity and/or high reactivity, which must be capable of fill intra- and/or intercellular spaces in wood and/or chemically bond themselves to certain polysaccharides and lignin present in the wood cell wall (Ding et al. 2013; Islam et al. 2014). Currently, some patented products were designed following these concepts and are available on the market, such as Indurite™, VecoWood® and Lignia™. Methyl methacrylate, epoxy, furfuryl alcohol and styrene are some already used monomers in literature. The styrene is a high valuable synthetic precursor since it is used to produce several kinds of styrofoams. Its polymerization reaction is initiated by free radicals, that interact with the styrene molecule, breaking double bonds between carbons and then the poly(styrene) is progressively formed (Lever 2001).

In their work with white pine (*Pinus strobus* Linnaeus), El-Awady and El-Awady (2003) produced WPC via *in situ* polymerization of styrene monomer under gamma radiation and reached increased aging resistance at the aquatic environment. Che et al. (2018) treated a pine heartwood (*Pinus radiata* Don.) using aqueous solutions composed of three different styrene/acrylic acid proportions, which resulted in an increased weathering resistance, attributed to covalent

CONTACT Darci Alberto Gatto gattodarci@gmail.com Postgraduate Program in Materials Science and Engineering, Federal University of Pelotas, Pelotas 96010-260, Rio Grande do Sul, Brazil

bonds developed between the monomer and the lignin from wood. Olaniran et al. (2019) applied the *in situ* polymerization of the styrene monomer into Norway spruce (*Picea abies* L. Karst.) woods pre-treated by methacrylation (reaction with methacrylic anhydride). Such authors reported that both the wood cell wall and wood lumen were partly filled by the polymer, leading to increased stiffness in both flexure and shear, although there was a reduced specific stiffness due to the increase in specific gravity. The present study aimed at the production and characterization of WPC by the *in situ* polymerization, using the poly(styrene) and both JW and MW from pine.

Materials and methods

Raw materials

25 years old trees were selected in a homogeneous pine (*P. elliottii* Engelm.) forest located at Piratini/Brasil. Then, wood samples were cut from near to the pith (first eight growth rings) and near to the bark (after the twentieth growth ring) to represent JW and MW, respectively. Samples were cut according to the requirements of each characterization test and then conditioned under 20 ± 2°C temperature and 65 ± 3% RH until reaching constant mass. Anatomic images were taken from 13 µm thick laminas, which were cut from neat wood samples, using an optical microscope adjusted for 25×.

WPC production

The wood samples were oven dried under 70°C until they reach constant mass to facilitate the monomer impregnation. A high purity (99%) styrene solution (acquired from Sigma Aldrich) was incorporated with 1.5 wt-% of benzoyl peroxide and then magnetically homogenized in a 2 L beaker for 15 min. Afterwards, an amount of almost 1200 cm^3 of wood was placed in a 2300 cm^3 horizontal autoclave and an initial vacuum (−0.1 MPa for 40 min) was applied, using a vacuum pump (Marconi brand), to retire all the trapped air and opening the wood pores. Afterwards, taking advantage of the pressure difference caused by the mentioned vacuum, a valve was opened to pour 1.3 L styrene solution and then a positive pressure of 0.8 MPa was applied for 180 min. The impregnated woods were cured in a laboratory oven at 50°C for 24 h and 70°C for an extra 72 h. Afterwards, the final wood samples were placed in a climatic chamber (20 ± 2°C temperature and 65 ± 3% RH) until reach equilibrium moisture content.

WPC characterization

Specific gravity (ρ) and weight percentage gain (WPG) were determined before and after the wood treatment. For that, a digital caliper (0.0001 mm resolution) and an analytical balance (0.0001 g resolution) were used. Chemical groups were evaluated by Fourier-transform infrared spectroscopy coupled with an attenuated total reflection device (ATR-FTIR) in a Jasco 4100 equipment. A total of 32 scans (600–1800 cm^{-1} range) were performed at 4 cm^{-1} resolution and 2 mm seg^{-1} scanner velocity. Thermal stability was evaluated by thermal gravimetric (TG) analysis, using a TGA-1000 equipment (Navas Brand). The curves were obtained at a heating rate of 10°C.min^{-1} from room temperature (20°C) until a maximum temperature of 600°C. Static bending tests were performed at a speed test of 0.8 mm.min-1, following the ASTM D143. The samples presented a square cross section (side equal to 15 mm) and a length of 250 mm oriented in the longitudinal direction, following the ASTM D143. Load *vs.* deflection curves were manipulated as described by Phuong et al. (2007) to calculate brittleness (B_T). Hardness tests were carried out in prismatic samples (5 × 5 × 15 mm^3 for radial × tangential × longitudinal), following the Janka method. This mechanical test was performed as described in ASTM D143, expect the dimensions of the samples, which were adapted. In this procedure, a 1.13 cm^2 diameter steel hemisphere was inserted on each anatomical plane (transverse, radial and tangential) at a cross-head speed of 6 mm s^{-1}, using a DL 3000 equipment (Emic brand).

Statistical analysis

A completely randomized design (CRD) was applied to analyse all the data. Homogeneity of variances and data normality were verified using Levene and Shapiro–Wilk tests, respectively. When any of these assumptions was not satisfied, the data were transformed using a square root or logarithm. Whenever the null hypothesis was rejected, Fisher tests were used to compare the means. All statistical analyses were developed at a significance level of 1%.

Results and discussion

Both JW and MW reached high means of WPG (above 90%), which were similar if compared to each other (Figure 1(A)). Such WPG levels are in agreement with the literature. Keplinger et al. (2015) and Olaniran et al. (2019) applied methacrylation treatments to Norway pine (*P. abies*) woods, which were followed by *in situ* polymerizations of styrene. They reported means for WPG of about 25% and 95%, respectively. For Magalhães and Da Silva (2004), treatment parameters related to the *in situ* polymerization are dependents of chemical features of the treatment solution (e.g. molecular weight, viscosity and polarity) and physical properties of the wood, such as permeability and specific gravity.

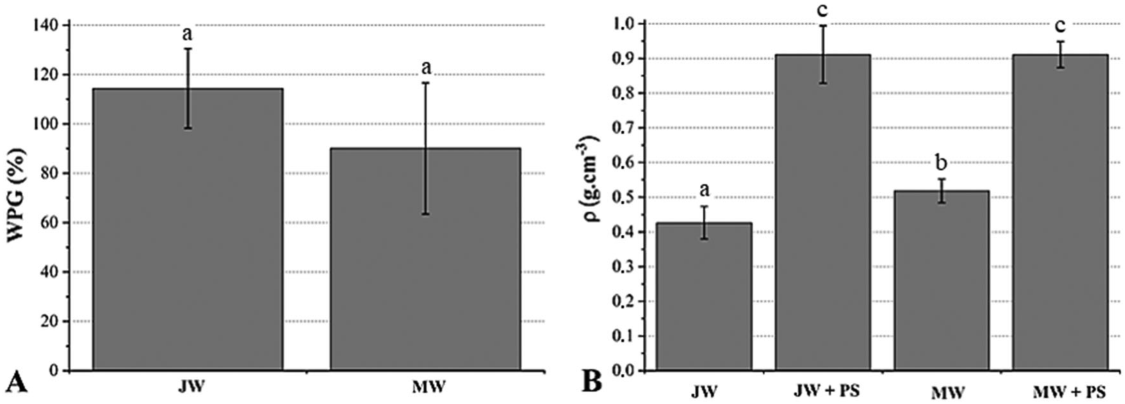


Figure 1. Weight percentage gain (WPG; A) and specific gravity (ρ; B) for juvenile (JW) and mature (MW) pine woods before and after the treatments with poly(styrene) (PS). Where: different letters above the bars represent significant differences.

The impregnated poly(styrene) yielded significant increases of 113.35% and 75.87% in ρ for JW and MW, respectively (Figure 1(B)). The pristine JW presents a smaller ρ than the pristine MW due to its anatomical structures, especially the high proportion of earlywood, which is marked by large lumens and hence large amounts of free voids able to be filled with polymer, as illustrated in Figure 2. Compared to the MW, it also explains the higher increase in specific gravity obtained for the JW. According to Palermo et al. (2013), in temperate countries (where the seasons have well-defined characteristics), rain and sun conditions yield a lightweight pine wood marked by large wood tracheids with large cell lumens that gradually become thicker, wider and longer, especially during spring, due to an intense activity of cambial meristem cells during this season. Because of that, this softwood appears bright if seen on an optical microscope.

Figure 3 shows the infrared spectra for the JW and MW before and after the poly(styrene) insertion. Both the pristine JW and MW presented high peaks at 1725, 1650, 1450, 1275 and 1027 cm^{-1}. It means a similar chemical composition in a comparison between these pine woods (JW and MW), especially regarding their main molecular compounds, namely cellulose, hemicellulose, lignin and extractives.

Two bands at 1490 and 1600 cm^{-1} are prominent for the treated pines, which suggest chemical bonds between the poly(styrene) and the wood cell wall, since they are associated with double bonds between carbons (C=C) in aromatic rings belong to the styrene (Merlatti et al. 2008). These possible chemical bonds could be clarified using further NMR (Nuclear magnetic resonance) or XPS (X-ray photoelectron spectroscopy) studies. On the other hand, both the peaks at 1490 and 1600 cm^{-1} were also attributed to aromatic ring stretching vibrations in the poly(styrene) (Merlatti et al. 2008). In their study, Magalhães and Da Silva (2004) reported chemical bonds between styrene and wood, although these bonds were weak due to the non-polar aromatic structure of the styrene, which was associated with low retention of polymer into the wood.

Compared with the pristine woods, an attenuated peak at 1027 cm^{-1} appeared for the treated pine woods, which also seems to be an effect of the poly (styrene) on the wood cell wall, since this peak is related to stretching of C–O bonds (from cellulose and hemicelluloses) and deformations in C–H in guaiacyl units (from lignin) (Magalhães and Da Silva 2004). The treated pines presented prominent peaks at 755 and 695 cm^{-1}, probably related to bending

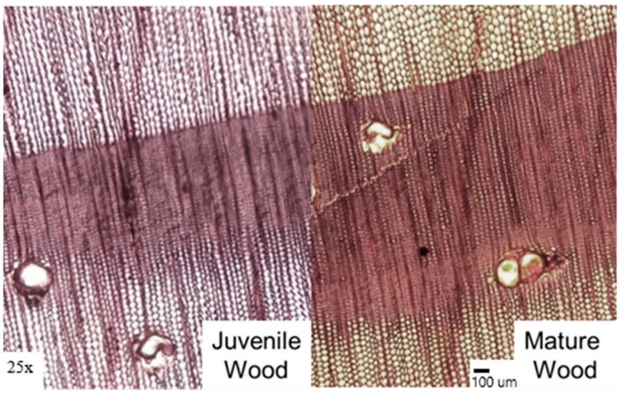


Figure 2. Transverse anatomical plain for both pristine juvenile and mature pine woods.

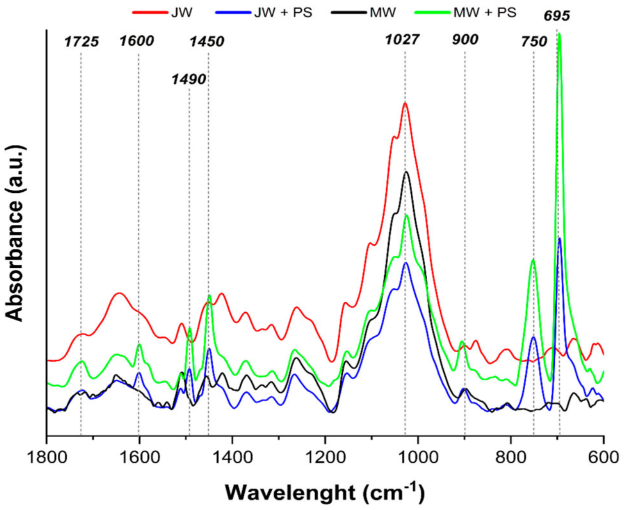


Figure 3. Infrared spectra of the juvenile (JW) and mature (MW) pine woods before and after the treatments with poly(styrene) (PS).

deformation in the C–H plane from aromatic rings of the poly(styrene), which confirms its presence into the pine woods.

Increases of 23.7% and 1.7% in MOE were obtained for JW and MW, respectively (Figure 4(A)). Besides that, the *in situ* polymerization yielded increases in MOR for both JW (70.7%) and MW (52.4%) (Figure 4(B)). Both these improvements in mechanical properties can be attributed to the presence of the synthetic polymer into the pine woods, probably forming covalent linkages with the wood cell wall, as suggested by the infrared spectra. These increases may also be attributed to the solid polymer, which probably acted as mechanical support from inside the wood pores, avoiding the development of micro-cracks when the wood is under mechanical loads.

The *in situ* polymerization of the styrene yielded significant increases in B_{T} (Figure 5) for both JW (95.1%) and MW (277.4%). This is probably related to the well-known high B_{T} attributed to the styrene, which is due to its low crystallinity degree. This way, as suggestion for further researches, impregnation with a polymeric elastomer during the wood processing may lead to a contrary effect in B_{T}, allowing certain applications. Besides that, the aforementioned chemical changes in amorphous segments from hemicelluloses and cellulose probably caused decreases in equilibrium moisture content, which also may lead to an increase in B_{T}. It also explains the obtained increases in stiffness and strength in flexure. In this sense, it is also important to mention that all the samples failed on the compressive face.

The treated pine woods presented higher hardness when compared to each respective untreated wood (Figure 6), especially in a comparison between treated and pristine MW, in which the treated wood presented increases of 94.2%, 101.5% and 48.2% for transverse, radial and tangential planes, respectively. All these increases may be attributed to the same explanations previously ascribed to the gains in stiffness and strength in flexure. The smaller increase for the tangential plan is probably related to the smaller exposition of the wood tracheids on this face. Merlatti et al. (2008) treated a *P. radiata* wood by copolymerization of acrylic styrene dispersed in sodium silicate and reported increases of 28.2% and 44.9% in surface

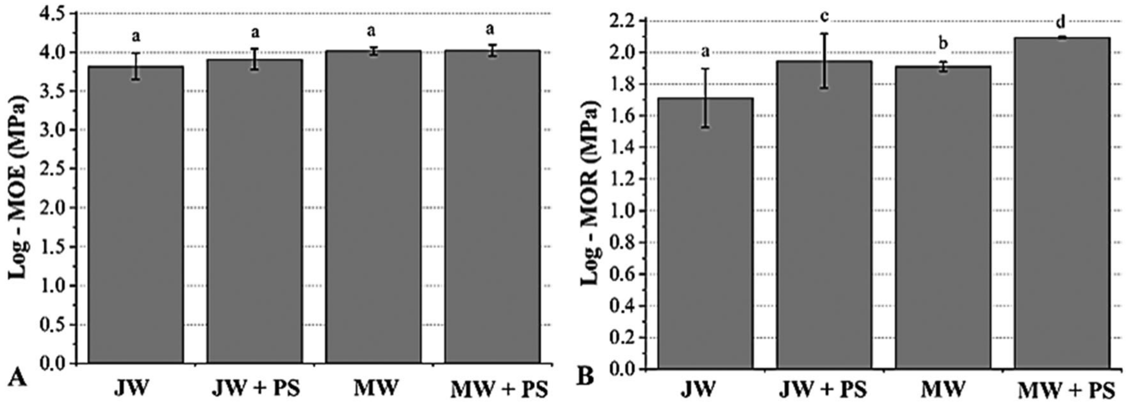


Figure 4. Modulus of elasticity (MOE; A) and modulus of rupture (MOR; B) for the juvenile (JW) and mature (MW) pine woods before and after the treatments with poly(styrene) (PS). Where: different letters above the bars represent significant differences.

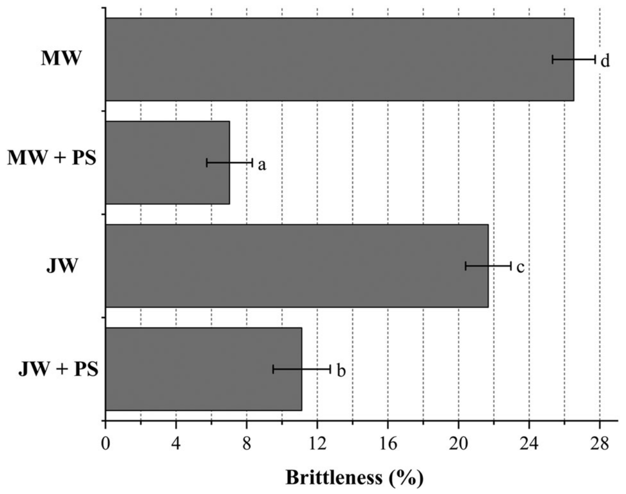


Figure 5. Brittleness (B_T) for the juvenile (JW) and mature (MW) pine woods before and after the treatments with poly(styrene) (PS). Where: different letters aside the bars represent significant differences.

hardness on the transverse plane. Such increases are inferior to those obtained in the present study and can be attributed to anatomical properties of wood and physico-chemical features of the studied styrene solution.

Themogravimetric curves shown in Figure 7 display treated and untreated pine woods. The thermal behaviours of the studied samples are marked by three regions: (I) loss of intra and inter cellular moisture (40–150°C), followed by (II) thermodegradation of hemicelluloses (150–380°C) and then (III) cellulose cleavage (above 380°C). Compared to their respective pristine pine woods, the first region indicates that there was a lower equilibrium moisture content for the treated ones, which is probably related to their smaller content of hydroxyl groups from wood polysaccharides. According to Darwish et al. (2013), those polymers chemically linked to the wood cell wall hinder the absorption-desorption of moisture, creating a modified wood surface marked by a hydrophobic character. The treated woods also presented a higher T_{ONset} in a comparison with the pristine ones, which can be

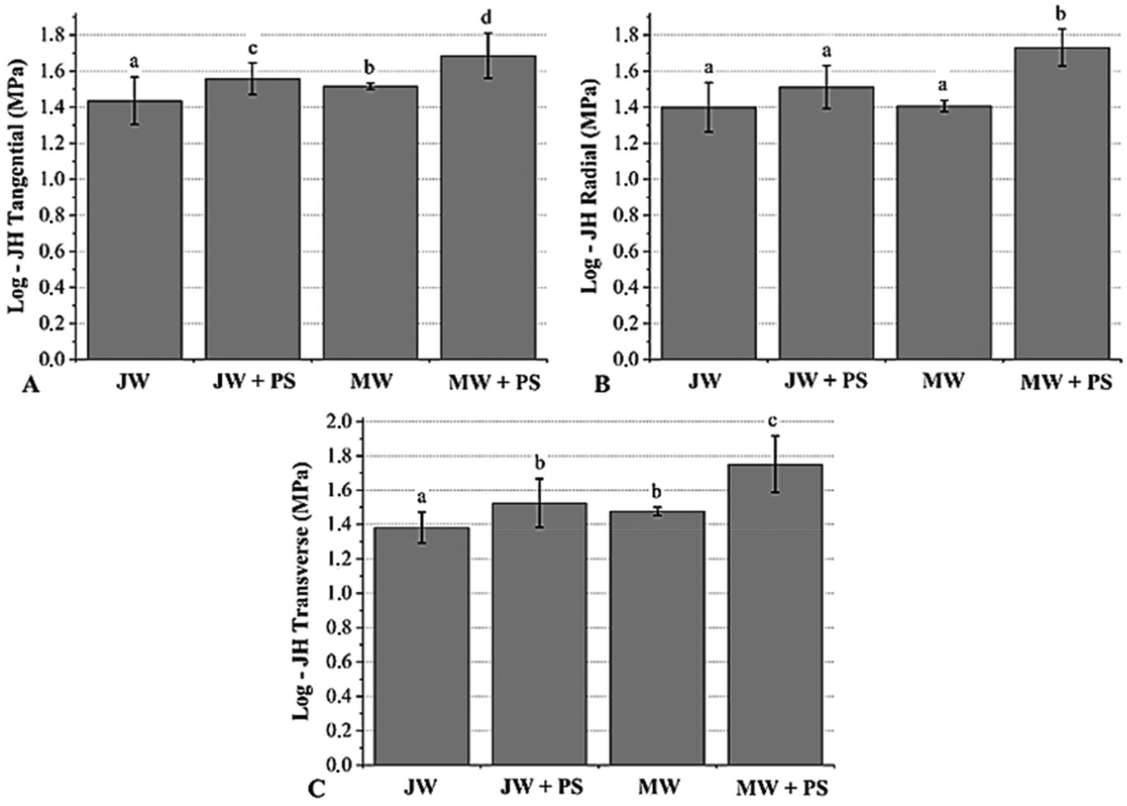


Figure 6. Hardness on transverse (A), radial (B) and tangential (C) planes for the juvenile (JW) and mature (MW) pine woods before and after the treatments with poly(styrene) (PS). Where: different letters above the bars represent significant differences.

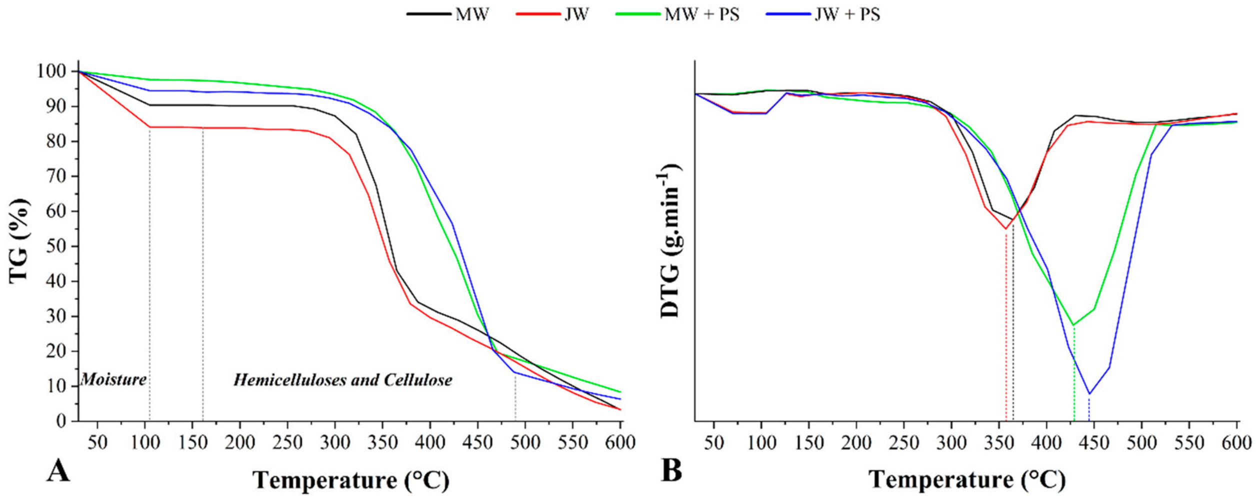


Figure 7. TG (A) and DTG (B) curves for the juvenile (JW) and mature (MW) pine woods before and after the treatments with poly (styrene) (PS).

attributed to below discussed chemical interactions between the polymer and the wood cell wall, as well as the presence of the poly(styrene) itself onto the wood tracheids.

The patterns of the DTG curves and their maximum peaks (Figure 7(B)) indicate higher thermal stability for treated pine woods, especially the treated JW. The slow thermodegradation for the treated woods may be attributed to the presence of the poly(styrene) since there was a maximum peak of degradation above 400°C (Figure 7(B)). For Nguyen et al. (2019), the *in situ* polymerization of the styrene may be followed by an intramolecular bond between carboxyl and ester groups, yielding ring-like anhydrides with high thermal stability. Regarding a *Salmalia malabarica* wood treated with a styrene-co-acrylonitrile, Xie et al. (2013) reported that there was a slowed thermal degradation compared to the respective pristine one. Such a phenomenon was attributed to the high thermal stability of aromatic structures belong to the poly(styrene), corroborating below described results.

Figure 8 shows the microstructure of the JW treated by *in situ* polymerization of the poly(styrene). Most of the wood tracheids were fully filled by the polymer, as highlighted in black colour. The impregnation is homogenous and the wood-polymer interface seems to be intimate. This explains the high obtained WPG and corroborates the possible chemical linkages, previously discussed for the infrared spectra. Similar findings were reported in the literature (Che et al. 2018; Olaniran et al. 2019).

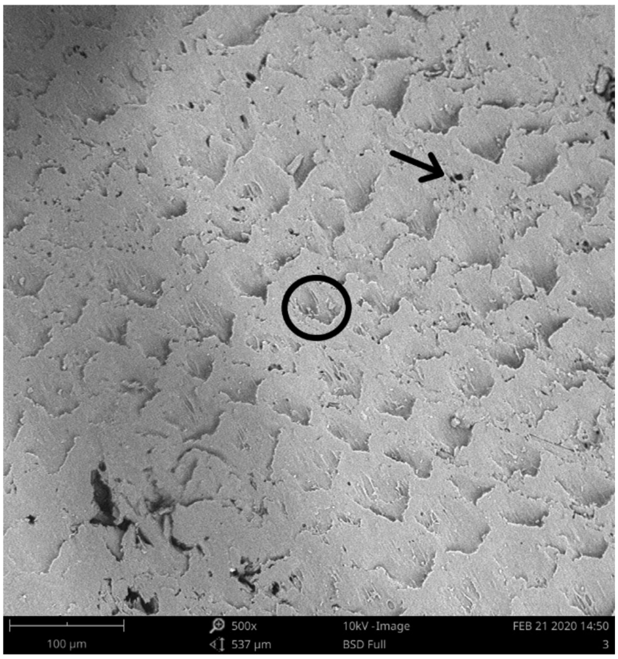


Figure 8. SEM image for the juvenile pine wood treated by *in situ* polymerization of poly(styrene).

Conclusion

The JW presented higher WPG than the MW, which reflected on its increased specific gravity and was attributed to its anatomical structure marked by large tracheids shown on optical micrographs. The treatment by *in situ* polymerization of styrene yielded chemical changes on the wood cell wall and the polymer probably link itself to the wood, as well as filled the wood pores, as suggested by the infrared spectra and treatment parameters. Probably, because of that, the treated JW and MW presented higher mechanical properties in both flexure and hardness, when compared to the pristine ones. The treated woods also showed higher thermal stability, especially the JW. Thus, the JW presented higher treatability than the MW, which may be attributed to its high proportion of earlywood and, consequently, large tracheids and more intra- and intercellular spaces.

Acknowledgements

The authors thank the Professor of the Federal University of Paraná Pedro Henrique Gonzalez de Cademartori for the technical help in the development of this work. This work was carried out with the support of the Higher Education Personnel Improvement Coordination - Brazil (CAPES) – Financing Code 001.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de NÃvel Superior – Brasil (CAPES) – Finance Code 001.

ORCID

Andrey Pereira Acosta http://orcid.org/0000-0002-5074-3772
Ezequiel Gallio http://orcid.org/0000-0002-0603-1065
Henrique Romer Schulz http://orcid.org/0000-0002-8162-7723
Kelvin Techera Barbosa http://orcid.org/0000-0001-9894-703X
Rafael De Avila Delucis http://orcid.org/0000-0002-3657-9216

References

Bao F, Jiang Z, Jiang X, Lu X, Luo X, Zhang S. 2001. Differences in wood properties between juvenile wood and mature wood in 10 species grown in China. Wood Sci Technol. 35:363–375. doi:10.1007/s002260100099.

Che W, Xiao Z, Han G, Zheng Z, Xie Y. 2018. Radiata pine wood treatment with a dispersion of aqueous styrene/acrylic acid copolymer. Holzforschung. 72(5):387–396. doi:10.1515/hf-2017-0142.

Darwish S, El Hadidi N, Mansour M. 2013. The effect of fungal decay on *ficus sycomorus* wood. Int J Conser Sci. 4 (3):271–282.

Ding W, Koubaa A, Chaala A. 2013. Mechanical properties of MMA-hardened hybrid poplar wood. Ind Crops Prod. 46:304–310. doi:10.1016/j.indcrop.2013.02.004.

El-Awady M, El-Awady N. 2003. Non-toxic preservatives for wooden objects in sea water. I. Styrene monomer polymerised using gamma irradiation. Plast Rubber Compos. 32(8–9):334–339. doi:10.1179/146580103225004081.

Islam M, Hamdan D, Hassan A, Talib Z, Sobuz H. 2014. The chemical modification of tropical wood polymer composites. J Compos Mater. 48(7):783–789. doi:10.1177/0021998313477894.

Keplinger T, Cabane E, Chanana M, Hass P, Merk V, Gierlinger N, Burger I. 2015. A versatile strategy for grafting polymers to wood cell walls. Acta Biomater. 11:256–263. doi:10.1016/j.actbio.2014.09.016.

Lever L. 2001 Polymer chemistry – polymerization reactions. 2001. [cited 2019 July 2]. Available from: http://faculty.uscupstate.edu/llever/polymer%20resources/synthesis.htm

Li X, Wu H, Southerton S. 2011. Transcriptome profiling of wood maturation in *Pinus radiata* identifies differentially expressed genes with implications in juvenile and mature wood variation. Gene. 487(1):62–71. doi:10.1016/j.gene.2011.07.028.

Magalhães W, Da Silva R. 2004. Treatment of Caribbean pine by *in situ* polymerization of styrene and furfuryl alcohol. J Appl Polym Sci. 91(3):1763–1769. doi:10.1002/app.13252.

Mcdonald E, Hubert J. 2002. Review of the effects of silviculture on timber quality of Sitka spruce. Forestry. 75 (2):107–138. doi:10.1590/S0100-67622013000100020.

Merlatti C, Perrin F, Aragon E, Margaillan A. 2008. Natural and artificial weathering characteristics of stabilized acrylic–urethane paints. Polym Degrad Stab. 93(5):896–903. doi:10.1016/j.polymdegradstab.2008.02.008.

Nguyen T, Xiao Z, Che W, Trinh H, Xie Y. 2019. Effects of modification with a combination of styrene-acrylic copolymer dispersion and sodium silicate on the mechanical properties of wood. J Wood Sci. 65(1):1–11. doi:10.1186/s10086-019-1783-7.

Olaniran S, Michen B, Mora Mendez D, Wittel F, Bachtiar E, Burgert I, Rüggeberg M. 2019. Mechanical behaviour of chemically modified Norway spruce (*Picea abies* L. Karst.). Experimental mechanical studies on spruce wood after methacrylation and *in situ* polymerization of styrene. Wood Sci Technol. 53(2):425–445. doi:10.1007/s00226-019-01080-5.

Palermo P, De Figueiredo Latorraca J, Severo E, Do Nascimento A, De Rezende M. 2013. Delimitação entre os lenhos juvenil e adulto de *Pinus elliottii* Engelm. Revista Árvore. 37(1):191–200. doi:10.1590/S0100-67622013000100020.

Phuong L, Shida S, Saito Y. 2007. Effects of heat treatment on brittleness of Styrax tonkinensis wood. J. Wood Sci. 53 (3):181–186. doi:10.1007/s10086-006-0841-0.

Xie Y, Fu Q, Wang Q, Xiao Z, Militz H. 2013. Effects of chemical modification on the mechanical properties of wood. Eur J Wood Wood Prod. 71(4):1–2.

forests

Article

Thermochemical and Mechanical Properties of Pine Wood Treated by In Situ Polymerization of Methyl Methacrylate (MMA)

Andrey Pereira Acosta [1], Jalel Labidi [2,*], Henrique Römer Schulz [1], Ezequiel Gallio [1], Kelvin Techera Barbosa [1], Rafael Beltrame [1], Rafael de Avila Delucis [1] and Darci Alberto Gatto [1]

[1] Postgraduate Program in Materials Science and Engineering, Federal University of Pelotas, Technological Development Center (CDTec), Pelotas 96010-290, Brazil; andreysvp@gmail.com (A.P.A.); henriqueschulz09@hotmail.com (H.R.S.); egeng.florestal@gmail.com (E.G.); kelvintecherabarbosa@gmail.com (K.T.B.); beltrame.rafael@yahoo.com.br (R.B.); r.delucis@hotmail.com (R.d.A.D.); darcigatto@yahoo.com (D.A.G.)

[2] Chemical and Environmental Engineering Departement, University of the Basque Country (UPV/EHU), 20018 San Sebastian, Spain

* Correspondence: jalel.labidi@ehu.eus

Received: 25 June 2020; Accepted: 15 July 2020; Published: 17 July 2020

Abstract: The impregnation of low-molecular-weight monomers prior to polymerize them inside the wood may be an efficient way to improve some important wood properties. This work aimed to determine some technological properties of wood-based composites (WPC) produced by in situ polymerization, using a pine wood (*Pinus elliottii* Engelm.) impregnated with methyl methacrylate (MMA). For that, samples taken from both juvenile (JV) and mature (MT) pine woods were treated with MMA. Physical, mechanical, chemical, thermal and morphological features were evaluated. MMA-treated woods from both juvenile and mature woods presented superior physical, mechanical (expect brittleness) and thermal properties when compared to pristine ones. The infrared spectra and morphological analysis by scanning electron microscopy (SEM) confirmed the presence of the monomer inside the pine wood. The juvenile wood presented higher treatability than the mature wood, due to its higher content of intra- and inter-cellular spaces.

Keywords: thermal stability; juvenile wood; infrared spectroscopy; in situ polymerization; wood quality

---

1. Introduction

Pine trees are important raw materials and may meet some current market demand, due to their rapid growth and high adaptability to different environmental conditions. Their woods present a large range of applications, such as for civil construction, panels, furniture and packaging. However, the juvenile pine wood has a lower performance than the mature wood due to its high proportion of early wood, which negatively affects wood quality and limits its use, especially in certain structural applications [1]. Because of that, treatments have been applied to produce modified wood capable of meeting the requirements of each intended purpose.

According to Mantanis [2], some recently developed wood treatments have given rise to new modified products, which gradually changed mistaken perspectives of some customers about wood being a fragile, unstable, and easily degraded construction material. For Sandberg et al. [3], the increased interest during the last decades in wood modification can be satisfactorily explained for four reasons: (i) development of silviculture practices able to produce wood with improved properties, (ii) to avoid the use of rare species with outstanding properties, (iii) to add value to sawn timber and some of its by-products, and (iv) to follow public policies focused on sustainability.

These wood treatments can be divided into four categories: thermal, chemical, surface and impregnation treatments [4]. Currently, impregnation is the most performed method, because of its effects on wood properties. In this context, different synthetic monomers and resins were already in use, including methyl methacrylate (MMA) and furfuryl alcohol [2,5,6]. It is important to mention that some key catalysts also play an important role for the final treated woods. For instance, some cyclic carboxylic anhydrides such as maleic anhydride for furfuryl alcohol may be incorporated in the treatment solution [2].

The use of MMA to produce impregnated wood parts is due to its easy synthesis, low cost, translucency, good chemical stability and ease of catalysis [7]. The in situ polymerization of MMA into wood parts may provide improvements in several technological parameters, such as dimensional stability, density and mechanical properties [8]. These changes are associated with the confinement of polymer segments into wood cells and/or wood cell walls.

High polymer retentions can be reached with in situ polymerization of MMA into the wood, but it may depend on wood anatomical features [9]. Hadi et al. polymerized MMA into four wood species, namely sengon (*Falcataria moluccana* Barneby and JW Grimes), jabon (*Anthocephalus cadamba* (Roxb.) Bosser), mangium (*Acacia mangium* Wild), and pine (*Pinus merkusii* Junghuhn and De Vriese). They observed that the treated woods presented increased resistance to subterranean termite attack compared to their respective pristine ones. More recently, wood-based composite (WPC) was produced by in situ polymerization of MMA into three fast-growing wood species, namely jabon (*Anthocephalus cadamba*), mangium (*Acacia mangium* Wild) and pine (*Pinus merkusii* Junghuhn and De Vriese) [10]. The authors reported that the treatment led to an increase in both density and strength at bending. Also, their lightweight woods presented better treatability than the heavy ones, which suggests that a JV may behave differently to an MT from the same specie if treated by in situ polymerization with MMA.

Therefore, MMA impregnation is a promising treatment and may lead to improvements in physical and mechanical properties of pine woods, especially JV. The objective of this study was to produce and characterize WPC by in situ polymerization of MMA into JV and MT from pine.

2. Materials and Methods

2.1. Raw Material

Pine trees that were 20 years old (*Pinus elliottii* Engelm.) were selected in a homogeneous forest located at Piratini/Brazil. This forest was planted in an initial spacing of 2 m × 2 m and then no silvicultural practice was carried out. Afterwards, 20 prismatic wood samples were cut from near to the pith (juvenile wood; JV) and 20 near the bark (mature wood; MT) with two different dimensions: 25 mm × 25 mm × 100 mm and 15 mm × 15 mm × 250 mm (radial × tangential × longitudinal); of these samples 20 of each were treated. For the JV, only the first 5 growth rings near the pith were selected, while only the last 3 growth rings were selected to represent the MT. Then the samples were placed in a climatic chamber (adjusted to a temperature of 20 ± 2 °C and 65 ± 3% relative humidity) until reaching constant mass.

2.2. Treatment by Methyl Methacrylate (MMA) Impregnation

The wood samples were oven dried at a controlled temperature of 70 °C until reaching constant mass, in order to remove the wood moisture, since the MMA is immiscible in water and this could spoil its polymerization process. Then, benzoyl peroxide (1.5 wt %) was added to an aqueous solution of 99% MMA and this mixture was manually homogenised for 60 s. The dried wood samples were placed inside a small horizontal autoclave (capacity of 2.3 L) and the empty space was filled with a ceramic material. Afterwards, the chamber was subjected to an initial vacuum of 40 min, using a vacuum pump (600 mmHg), in order to remove internal air.

The MMA solution was poured into the autoclave using the difference of pressure between the internal and external environment. After filling the autoclave cavity with about 1.5 L of solution, a pressure of 8 $\mathrm{kgf \cdot cm^{-2}}$ was applied for 180 min, using compressed air. Then, the impregnated samples were coated with aluminium foils and heated at a constant temperature of 50 °C for 24 h, followed by extra 70 °C for 72 h. The final samples were conditioned at room temperature (20 °C) until reaching the equilibrium moisture content.

2.3. Characterization of Physical and Mechanical Properties

Weight percentage gain (WPG) was calculated by a simple perceptual difference between the masse before and after the MMA impregnation, as indicated by Equation (1). The density at 12% of moisture content (ρ) was calculated based on the mass and the volume, as indicated in Equation (2), following an adapted procedure based on the ASTM D2395 [11]. To determine the equilibrium moisture content (M_C), the samples were waterlogged and then oven dried at 103 ± 2 °C until constant mass. Equation (3) was used to calculate M_C.

$$\mathrm{WPG} = \left(\frac{M_A - M_B}{M_B}\right) * 100 \tag{1}$$

$$\rho = \frac{M_{12}}{V_{12}} \tag{2}$$

$$\mathrm{MC} = \left(\frac{M_1 - M_2}{M_2}\right) * 100 \tag{3}$$

where: WPG is weight percentage gain (%), M_B and M_A are masses (g) before and after the treatment, respectively; ρ is density (g $\mathrm{cm^{-3}}$); M_{12} and V_{12} are mass (g) and volume ($\mathrm{cm^3}$), respectively; M_C is the equilibrium moisture content (%); M_1 and M_2 are masses (g) at waterlogged and dry conditions, respectively.

All the mechanical tests were performed with the help of a DL 3000 universal test machine (Emic brand), and according to ASTM D 143 [12]. Modulus of elasticity (MOE), modulus of rupture (MOR) and brittleness (B_T) were determined based on the results obtained by static bending tests, which were carried out in prismatic samples with the dimensions of 25 mm × 25 mm × 100 mm (radial × tangential × longitudinal).

To calculate the B_T, load vs. deflection curves were analysed following the methodology proposed by Phuong et al. [13], as described in Equation (4). Hardness tests were performed on the tangential face of prismatic samples with the dimensions of 15 mm × 15 mm × 250 mm (radial × tangential × longitudinal), using a 0.55 cm diameter steel hemisphere and following the Janka method.

$$B_T = \left(\frac{E_A}{E_A + P_A}\right) * 100 \tag{4}$$

where: B_T is brittleness (%) and E_A and P_A are the elastic and plastic areas from load vs. deflection curves from static bending tests.

2.4. Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier transform infrared (FT-IR) spectroscopy analysis was performed on a 4100 equipment (Jasco brand), wherein each spectrum resulted from 32 scans performed in the 2000 $\mathrm{cm^{-1}}$ to 600 $\mathrm{cm^{-1}}$ wavelength range, with a resolution of 4 $\mathrm{cm^{-1}}$, scanner speed of 2 mm/sec and filter of 30,000 Hz.

2.5. Scanning Electron Microscopy (SEM)

A MMA-treated JV sample was placed on an aluminium stub and pre-coated with gold particles. Then, its transverse plane was analysed in a Pro-X (Phenon World brand) scanning electron microscope (SEM) at an accelerating voltage of 10 kV.

2.6. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed in cubic samples (side equal to 10 mm), using a TGA-1000 equipment (Navas brand). The thermogravimetric curves were obtained using two heating ramps, both of them at a heating rate of 10 °C·min^{-1}, under an inert atmosphere and nitrogen gas flow of 2 L·min^{-1}.The first ramp from 30 °C to 105 °C and the second from 105 °C to 600 °C.

2.7. Statistical Analyses

The statistical design used was completely randomized. The assumptions of homogeneity of variances and data normality were tested by Levene and Shapiro—Wilk methods, respectively. When any assumption was not attended, the data were transformed, using square root or logarithm. Whenever the null hypothesis was rejected based on analysis of variance (ANOVA) tests, Fisher tests were performed in order to compare the averages. All statistical analyses were developed at a significance level of 1%.

3. Results

The treatments with MMA resulted in changes in physical, mechanical, thermal and chemical properties for both JV and MT from pine. This was indicated by significant increases in WPG and ρ (Table 1). The smaller WPG for MT can be attributed to its anatomical features, since the MT is known by a high proportion of latewood, thick wood tracheids and narrow wood lumens [14].

Table 1. Average values for the evaluated physical properties.

Groups	WPG (%)	ρ (g·cm^{-3})	M_C (%)
MT	-	0.577 (0.048) b	14.40 (0.09) a
JV	-	0.536 (0.030) b	14.20 (0.17) a
MT + MMA	73.59 (1.15) b	0.984 (0.040) a	5.76 (0.40) b
JV + MMA	113.97 (1.01) a	0.978 (0.045) a	5.31 (0.62) b

JV: juvenile wood; MT: mature wood; MMA: methyl methacrylate; WPG: weight percentage gain; ρ: density; M_C: equilibrium moisture content; the values in parentheses show the standard deviations and averages in the columns do not differ from each other if followed by the same letter, according to Fisher tests.

Regarding the mechanical properties, the MMA treatment led to a significant increase in hardness, as well as in MOE and MOR for both JV and MT (Table 2). The impregnation and subsequent polymerization of this monomer inside the wood increased the hardness in 108% and 63% for the JV and MT, respectively.

Table 2. Average values for the evaluated mechanical properties.

Groups	Hardness(MPa)	Static Bending (MPa)		
		MOE	MOR	B_T (%)
MT	34.72 (0.08) b	11,409.0 (1.404.2) b	76.91 (1.10) bc	3.15 (1.13) a
JV	31.96 (0.06) b	8,024.9 (1.016.9) c	66.94 (1.03) c	7.81 (1.25) b
MT + MMA	56.67 (1.63) a	13,326.0 (1.200.2) a	127.94 (1.12) a	11.81 (1.25) c
JV + MMA	66.67 (0.42) a	9040.1 (1.753.0) c	83.66 (1.03) b	20.93 (1.35) d

JV: juvenile wood; MT: mature wood; MMA: methyl methacrylate; MOE: modulus of elasticity; MOR: modulus of rupture; B_T: brittleness; values in parentheses show the standard deviations and averages in the columns do not differ from each other if followed by the same letter, according to Fisher tests.

Qualitative chemical analyses before and after the treatment with MMA were performed, by FT-IR (Figure 1). As described in Table 3, it is known that the main chemical components of the wood (namely cellulose, hemicellulose and lignin) have certain functional groups that vibrate in particular wavelengths belong to the infrared spectrum (from 1800 to 600 cm^{-1}). FT-IR spectroscopy is an important tool for evaluating organic components in wood, as each molecule vibrates at a specific wavelength, making this technique a rapid method to ascertain some chemical changes in wood [15].

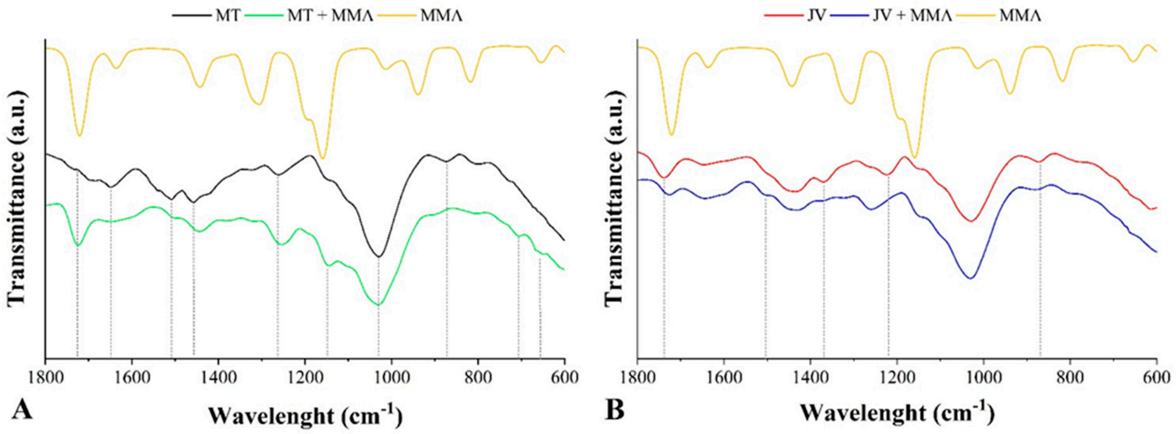


Figure 1. Fourier transform infrared (FT-IR) spectra for MMA-treated and untreated mature (MT; **A**) and juvenile (JV; **B**) woods from pine.

Table 3. Correspondence between infrared spectra wavenumbers with chemical compounds of the wood-based composite (WPC) obtained.

	Wood		
Wavenumber (cm^{-1})	**Molecular Vibrations**	**Wood Compounds**	**Reference**
1740	Stretching of C=O bonds of the carboxylic groups	hemicellulose/lignin	[5,16,17]
1645	Stretching at the C=O conjugated bonds of the alkyl ketones of the carbonyl groups	lignin	[16]
1510	Stretching of C=C bonds on aromatic ring	lignin	[17]
1460	Deformation on C–H bonds of aromatic ring	lignin	[18]
1370	Deformation on C–H bonds	cellulose/hemicellulose	[17]
1260	Stretching on C–O bonds in xylans	hemicellulose	[18]
1030	Stretching on C–O bonds and deformation on C–H bonds of guayacil units	cellulose/hemicellulose/lignin	[18]
870	Stretching on C–OH bonds	cellulose	[16]
	Methyl Methacrylate (MMA)		
Wavenumber (cm^{-1})	**Vibration/Functional Groups**		**Reference**
1725	Stretching on C=O bonds of carbonyl groups		[19,20]
1440	Asymmetric stretching on C–H bonds		[21]
1305	Symmetric stretching on C–H bonds		
1160	Stretching on C–O–R bonds of ester		[20,21]
1010/940/820	Stretching on C–C bonds		[21]

The thermal gravimetric results were used to evaluate the thermal stabilities of studied woods. Based on both the TGA (Figure 2A) and DTG (derived from thermogravimetry) (Figure 2B) curves, it was observed that the impregnation with MMA increased the thermal stabilities of both JV and MT, compared to their respective pristine groups.

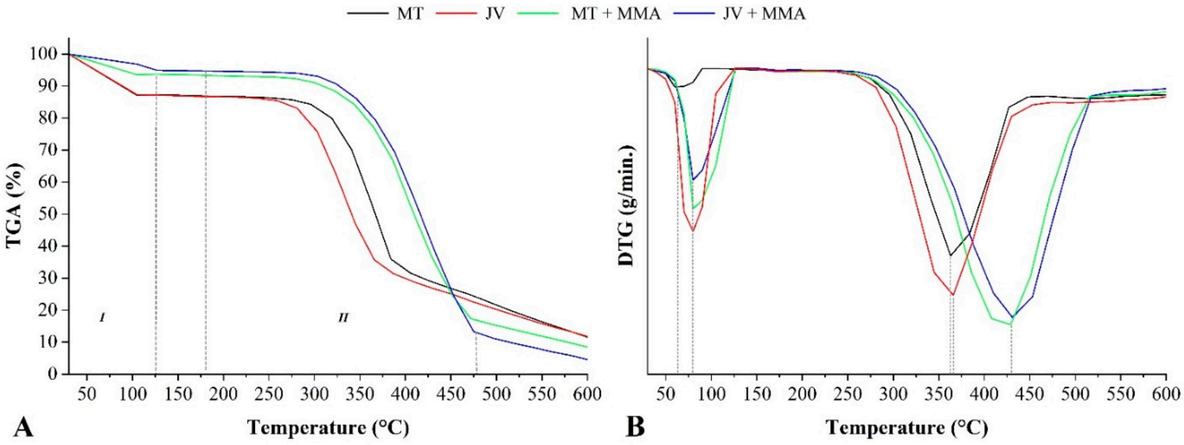


Figure 2. Thermogravimetric analysis (TGA) (**A**) and DTG (derived from thermogravimetry) (**B**) curves for MMA-treated and untreated mature (MT) and juvenile (JV) woods from pine.

The MMA-treated woods presented smaller mass loss (JV ≈ 10% and MT ≈ 5%) in the first region (from 30 °C to 125 °C), which is attributed to simple loss of moisture, confirming that the treatments also induces decreased equilibrium moisture contents. In the second region (from 160 °C to 460 °C), that corresponds to the degradation of hemicellulose and cellulose, the MMA-treated woods prolonged (in approximately 70 °C) the higher peak (i.e., higher thermal degradation in the DTG curve), when compared with their respective control groups. This is proven by the analysis of extrapolated temperatures associated to the beginning (T_{ONset}) and ending (T_{ENDset}) of the studied woods (Table 4).

Morphological details can be seen in Figure 3, which shows two SEM images taken at different magnifications for the JV treated by MMA impregnation. Most of the wood tracheids were fully or partly (as highlighted in white colour) filled by the MMA.

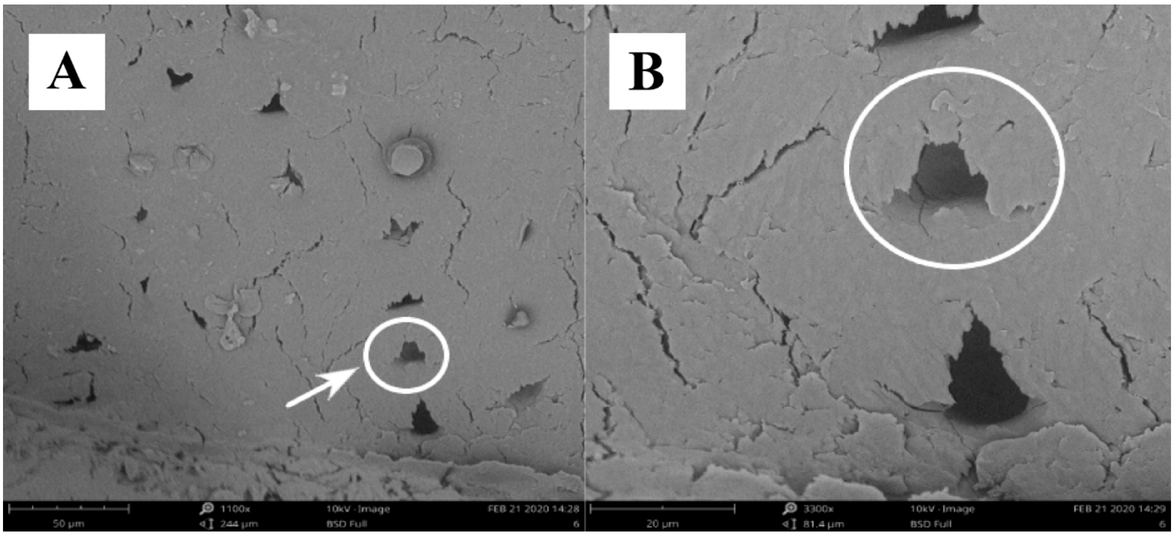


Figure 3. Morphology of treated wood samples; Approximation of 1100× (**A**) and approximation of 3300× (**B**).

Table 4. Main thermal events related to the thermal gravimetric analyses.

Groups	Region I		Region II	
	T_{ONset} (°C)	T_{ENDset} (°C)	T_{ONset} (°C)	T_{ENDset} (°C)
MT	30	105	320	386
JV	30	105	288	365
MT + MMA	30	105	349	465
JV + MMA	30	126	352	470

JV: juvenile wood; MT: mature wood; MMA: methyl methacrylate.

4. Discussion

The ρ was larger for MT when compared to the JV. The treatment with MMA significantly increased this property for both of them (increases of about 80% and 70% for JV and MT, respectively), when compared with the respective control groups. Moreover, the treatment with this monomer significantly reduced the M_C of both the JV and MT (reduction of about 60%).

Normally, JV develops within the first 10–20 growth rings from the pith and presents low density, low stiffness, and poor dimensional stability [22]. This is due to the smaller and shorter fibres in the JV, which also present thinner walls and larger microfibril angles when compared to those of the MT [23]. These characteristics facilitate the impregnation, flow and polymerization of the MMA within the wood, making the JV more susceptible to present a high WPG. Depending on anatomical features, it is well known that monomer loading directly influences WPG [24,25].

This WPG also directly reflects on the increase in ρ. In fact, there was an insignificant change in volume, since most of the synthetic monomers fill the lumens and do not penetrate inside the cell wall. This increase in ρ was also observed in previous studies of impregnation with MMA in jabon [26], and poplar hybrid woods [27], woods with similar ρ compared to the present study reaching increases in ρ of 34% and 200%, respectively. The impregnation with MMA leads to changes in physical properties of wood, mainly due to its hydrophobic nature [21,26,28]. Once the wood is rich in hydroxyl groups with high affinity with water, the polymerized monomer forms a physical barrier inside the wood lumens, which reduces the availability of OH groups on the wood cell wall and directly reflects in the decrease in M_C, since leads impaired desorption and absorption of moisture on overall the wood [7].

This behaviour is also observed for the MOR under bending, wherein JV and MT showed significant increases of 25% and 66%, respectively, compared to their respective untreated ones. While the MOE presented a significant increase for MT (17%), the increase of this parameter in JV (13%) did not differ from the control group. In contrast, significant increases in the B_T for both JV and MT were observed.

The increases in mechanical properties due to the MMA impregnation were also observed in others studies [7,29,30]. This can be attributed to the filling of cellular lumens with the polymer segments of high mechanical properties, which act as mechanical supports from inside the wood pores. The impregnated polymer serves as a conductor and stabilizer of tensions from inside the wood cell wall, leading to increases in strength, while the small increase in MOE may be associated with the plastic nature of the polymer used [27,31]. Also, there is a hardening mechanism, marked by increases in brittleness and hardness, due to the plastic nature of the polymerized MMA, as evidenced in the present study and confirmed by Koubaa et al. [6].

Comparing only the FT-IR spectra of both the pristine JV and MT, the former showed some peaks associated with lignin with smaller intensities (1645 cm^{-1}, 1510 cm^{-1} and 1460 cm^{-1}) when compared to those belonging to the MT. Also, compared to the JV, the MT presented smaller intensities in certain peaks corresponding to cellulose and hemicellulose (i.e., 1740 cm^{-1} and 1370 cm^{-1}). This proves that the JV and MT present different amounts of primary compounds (c.a. cellulose, hemicellulose and lignin) [14,32].

Regarding the impregnation of MMA in the MT (Figure 1A), increases in the intensities of peaks at 1740, 1260, 1150, 710 and 660 cm^{-1} were noted, while the peaks in the wavelengths of 1645, 1510, 1030 and 870 cm^{-1} presented slight decreases. The spectra of JV presented decreases in the peaks at 1740, 1370, 1220 (shifted to ≈ 1260 cm^{-1}) and 870 cm^{-1}, while the intensities at wavelengths of 1030 and 1510 cm^{-1} increased (Figure 2B). When compared to their respective control groups, these changes in the spectra of treated woods may be explained by the filling of the cell wall lumens, possible bonds between the functional groups of the wood and monomer, or overlap of some bands that belong to the MMA with that spectrum related to the wood itself, as in the case of C=O bonds of lignin and MMA in 1730 cm^{-1} [5,30,31].

The peak 1720 cm^{-1} is associated with C=O in carboxylic groups and corresponds to two main components of wood: lignin and hemicellulose. This finding also indicates what possibly happened to the monomer inside the lumen, in other words, there were strong bonds between the monomer and both lignin and hemicelluloses from wood.

For instance, the peak at 1030 cm^{-1} corresponds to the elongation in C–O bonds and deformation in C–H bonds in guaiacyl units, which indicates the presence of the three main wood components: cellulose, hemicellulose and lignin. Gallio et al. [15]. reported that reductions in this peak for their treated MT and increases in this peak for their treated JV. It is probably due to the high absorption of MMA on the wood cell wall in the JV, promoting a strong chemical change, which was captured by this peak.

However, the mass loss at the end of the second thermal region event (≈430 °C) was higher for those woods treated with MMA, possibly due to the degradation of the monomer. Among the main chemical compounds, the hemicellulose is the most thermally unstable, while lignin undergoes a slow thermal degradation (by means of complex transformations) from 220 °C until almost 400 °C [33].

The polymerization using MMA probably increased the thermal stability of the wood due to the physical barrier formed during the polymerization process and filling of the wood lumen [33], avoiding the degradation of wood compounds. In general, the MT tends to present a high thermal stability due its high amounts of cellulose and hemicellulose. The MMA exhibits a high resistance when subjected to high temperatures with a maximum degradation peak at approximately 400 °C, and becoming totally degraded at approximately 425 °C [21,34].

The wood cell wall seems to have been penetrated by the MMA, which was also reported in some previous studies [28]. According to Georgiena et al. [35], impregnated vinyl monomers fill the capillaries, vessels, and other void spaces in the wood structure, where the MMA attaches itself to the wood cell wall, becoming a protective barrier [36]. This morphological feature explains the gains found in mechanical and thermal properties.

5. Conclusions

The impregnation of MMA into both the JV and MT provided improvements in all their evaluated physical properties, especially for the JV, due to its large tracheids, leading to a high WPG. Regarding the mechanical properties, although there were increases in hardness, MOE and MOR, the treatment also increased the wood brittleness. TG results indicated that both the MMA-treated JV and MT woods presented higher thermal stabilities than their respective untreated ones. FT-IR spectra and SEM images confirmed the presence of the MMA inside the wood, but it is not clear if the MMA is chemically linked to the wood. Further studies may include hygroscopic and bonding properties in order to ascertain the potential of this treated wood for outdoor use.

Author Contributions: Conceptualization, A.P.A., J.L. and K.T.B.; methodology, A.P.A. and R.d.A.D.; software, K.T.B.; validation, D.A.G., J.L. and A.P.A.; formal analysis, A.P.A. and H.R.S.; investigation, A.P.A. and E.G.; resources, A.P.A. and R.B.; data curation, R.d.A.D. and E.G.; writing—original draft preparation, A.P.A., J.L. and R.d.A.D.; writing—review and editing, A.P.A. and R.d.A.D.; visualization, A.P.A.; supervision, D.A.G. and R.B.; project administration, A.P.A.; funding acquisition, D.A.G. and J.L. All authors have read and agreed to the published version of the manuscript.

Funding: Higher Education—CAPES (Financing Code 001) and National Council for Scientific and Technological Development—CNPq (Financing Code 301758/2019-0).

Acknowledgments: This work was supported by Coordination for the Improvement of Higher Education—CAPES (Financing Code 001) and National Council for Scientific and Technological Development—CNPq (Financing Code 301758/2019-0).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Lasserre, J.P.; Mason, E.G.; Watt, M.S. Influence of initial planting spacing and genotype on microfibril angle, wood density, fibre properties and modulus of elasticity in *Pinus radiata* D. Don core wood. *For. Ecol. Manag.* **2009**, *258*, 1924–1931. [CrossRef]
2. Mantanis, G.I. Chemical modification of wood by acetylation or furfurylation: A review of the present scaled-up technologies. *Bioresources* **2017**, *12*, 4478–4489. [CrossRef]
3. Sandberg, D.; Kutnar, A.; Mantanis, G. Wood modification technologies-a review. *iForest Biogeosciences For.* **2017**, *10*, 895–908. [CrossRef]
4. Esteves, B.; Pereira, H. Wood modification by heat treatment: A review. *Bioresources* **2009**, *4*, 370–404.
5. Ding, W.; Koubaa, A.; Chaala, A. Dimensional stability of methyl methacrylate hardened hybrid poplar wood. *Bioresources* **2012**, *7*, 0504–0520.
6. Koubaa, A.; Ding, W.D.; Chaala, A.; Bouafif, H. Surface properties of methyl methacrylate hardened hybrid poplar wood. *J. Appl. Polym. Sci.* **2012**, *123*, 1428–1436. [CrossRef]
7. Dong, X.; Sun, T.; Liu, Y.; Li, C.; Li, Y. Structure and properties of polymer-impregnated wood prepared by in-situ polymerization of reactive monomers. *BioResources* **2015**, *10*, 7854–7864. [CrossRef]
8. Rowell, R.M.; Ellis, W.D. Determination of dimensional stabilization of wood using the water-soak method. *Wood Fiber Sci.* **2007**, *10*, 104–111.
9. Hadi, Y.S.; Massijaya, M.Y.; Zaini, L.H.; Abdillah, I.B.; Arsyad, W.O.M. Resistance of methylmethacrylate-impregnated wood to subterranean termite attack. *J. Korean Wood Sci. Technol.* **2018**, *46*, 748–755. [CrossRef]
10. Hadi, Y.S.; Massijaya, M.Y.; Zaini, L.H.; Pari, R. Physical and mechanical properties of methyl methacrylate-Impregnated wood from three fast-growing tropical tree species. *J. Korean Wood Sci. Technol.* **2019**, *47*, 324–335. [CrossRef]
11. ASTM D 2395: Standard Test Methods for Density and Density (Relative Density) of Wood and Wood-Based Materials. Available online: https://www.astm.org/Standards/D2395.htm (accessed on 2 February 2020).
12. ASTM D 143: Standard Test Methods for Small Clear Specimens of Timber. Available online: https://www.astm.org/Standards/D143.htm (accessed on 2 February 2020).
13. Phuong, L.X.; Shida, S.; Saito, Y. Effects of heat treatment on brittleness of *Styrax tonkinens* is wood. *J. Wood Sci.* **2007**, *53*, 181–186. [CrossRef]
14. Esteban, L.G.; Simón, C.; Fernández, F.G.; de Palacios, P.; Martín-Sampedro, R.; Eugenio, M.E.; Hosseinpourpia, R. Juvenile and mature wood of *Abiespinsapo boissier*: Sorption and thermodynamic properties. *Wood Sci. Technol.* **2015**, *49*, 725–738. [CrossRef]
15. Gallio, E.; Zanatta, P.; Ribes, D.D.; Lazarotto, M.; Gatto, D.A.; Beltrame, R. Fourier transform infrared spectroscopy in treated woods deteriorated by a white rot fungus. *Maderas. Ciencia y Tecnología* **2018**, *20*, 479–488. [CrossRef]
16. Zhang, X.; Wang, F.; Keer, L. Influence of surface modification on the microstructure and thermo-mechanical properties of bamboo fibers. *Materials* **2015**, *8*, 6597–6608. [CrossRef] [PubMed]
17. Tomak, E.D.; Topaloglu, E.; Gumuskaya, E. An FT-IR study of the changes in chemical composition of bamboo degraded by brown-rot fungi. *Int. Biodeterior. Biodegrad.* **2013**, *85*, 131–138. [CrossRef]
18. Darwish, S.S.; El Hadidi, N.M.N.; Mansour, M. The effect of fungal decay on *Ficussy comorus* wood. *Int. J. Conserv. Sci.* **2013**, *4*, 271–282.
19. Tommasini, F.J.; Ferreira, L.D.C.; Tienne, L.G.P.; Aguiar, V.D.O.; da Silva, M.H.P.; Rocha, L.F.D.M.; Marques, M.D.F.V. Poly (methyl methacrylate)-sic nanocomposites prepared through *in situ* polymerization. *Mater. Res.* **2018**, *21*, 6. [CrossRef]
20. Biswas, M.; Libera, J.A.; Darling, S.B. Kinetics for the sequential infiltration synthesis of alumina in poly (methyl methacrylate): An infrared spectroscopic study. *J. Phys. Chem. C* **2015**, *119*, 14585–14592. [CrossRef]

21. Ahmad, S.; Ahmad, S.; Agnihotry, S.A. Synthesis and characterization of in situ prepared poly (methyl methacrylate) nanocomposites. *Bull. Mater. Sci.* **2009**, *30*, 31–35. [CrossRef]
22. Dinwoodie, J.M. *Timber: Its Nature and Behavior*, 2nd ed.; E & FN Spon: New York, NY, USA, 2000; p. 270.
23. Darmawan, W.; Nandika, D.; Sari, R.K.; Sitompul, A.; Rahayu, I.; Gardner, D. Juvenile and mature wood characteristics of short and long rotation teak in Java. *IAWA J.* **2015**, *36*, 428–442. [CrossRef]
24. Ding, W.D.; Koubaa, A.; Chaala, A.; Belem, T.; Krause, C. Relationship between wood porosity, wood density and methyl methacrylate impregnation rate. *Wood Mater. Sci. Eng.* **2008**, *3*, 62–70. [CrossRef]
25. Mattos, B.D.; de Cademartori, P.H.G.; Magalhães, W.L.E.; Lazzarotto, M.; Gatto, D.A. Thermal tools in the evaluation of decayed and weathered wood polymer composites prepared by *in situ* polymerization. *J. Therm. Anal. Calorim.* **2015**, *12*, 1263–1271. [CrossRef]
26. Hadi, Y.S.; Rahayu, I.S.; Danu, S. Physical and mechanical properties of methyl methacrylate impregnated jabon wood. *J. Indian Acad. Wood Sci.* **2013**, *10*, 77–80. [CrossRef]
27. Ding, W.; Koubaa, A.; Chaala, A. Mechanical properties of MMA-hardened hybrid poplar wood. *Ind. Crops Prod.* **2013**, *46*, 304–310. [CrossRef]
28. Ghorbani, M.; Shahmirzadi, A.N.; Amininasab, S.M. Physical and morphological properties of combined treated wood polymer composites by maleic anhydride and methyl methacrylate. *J. Wood Chem. Technol.* **2017**, *37*, 443–450. [CrossRef]
29. Zhang, Y.; Zhang, S.Y.; Chui, Y.H.; Wan, H. Effect of impregnation and in-situ polymerization of methacrylates on hardness of sugar maple wood. *J. Appl. Polym. Sci.* **2006**, *99*, 1674–1683. [CrossRef]
30. Li, Y.F.; Gong, D.W.; Dong, X.Y.; Liu, Z.B. Mechanical properties of wood-polymer composite prepared by in-situ polymerization of methyl methacryalte and styrene. *Appl. Mech. Mater.* **2012**, *166*, 2938–2941. [CrossRef]
31. Islam, M.S.; Hamdan, S.; Hassan, A. The chemical modification of tropical wood polymer composites. *J. Compas. Mater.* **2014**, *48*, 783–789. [CrossRef]
32. Simón, C.; Esteban, L.G.; de Palacios, P.; Fernández, F.G.; Martín-Sampedro, R.; Eugenio, M.E. Thermodynamic analysis of water vapour sorption behaviour of juvenile and mature wood of Abiesalba Mill. *J. Mater. Sci.* **2015**, *50*, 7282–7292. [CrossRef]
33. Gérardin, P. New alternatives for wood preservation based on thermal and chemical modification of wood—A review. *Ann. For. Sci.* **2016**, *73*, 559–570. [CrossRef]
34. Gałka, P.; Kowalonek, J.; Kaczmarek, H. Thermogravimetric analysis of thermal stability of poly (methyl methacrylate) films modified with photoinitiators. *J. Anal. Calorim.* **2014**, *115*, 1387–1394. [CrossRef]
35. Georgieva, M.; Harata, M.; Miloshev, G. The nuclear actin-related protein Act3p/Arp4 influences yeast cell shape and bulk chromatin organization. *J. Cell. Biochem.* **2008**, *104*, 59. [CrossRef] [PubMed]
36. Xie, Y.; Fu, Q.; Wang, Q. Effects of chemical modification on the mechanical properties of wood. *Eur. J. Wood Wood Prod.* **2013**, *71*, 401–416. [CrossRef]

Fibers and Polymers 0000, Vol.0, No.0, 1-6
DOI 10.1007/s12221-000-0000-0

ISSN 1229-9197 (print version)
ISSN 1875-0052 (electronic version)

Juvenile and Mature Pinewoods Treated by *in situ* Polymerization with (poly)vinyl Acetate

Andrey Acosta, Ezequiel Gallio, Paula Zanatta, Henrique Schulz,
Rafael de Avila Delucis, and Darci Gatto*

Postgraduate Program in Materials Science and Engineering, Federal University of Pelotas, Pelotas 96010-260, Brazil

(Received January 8, 2020; Revised March 27, 2020; Accepted April 7, 2020)

Abstract: This study aims to produce and characterize wood-based composites (WPC) by *in situ* polymerization with (poly)vinyl acetate into juvenile and mature woods from a pine specie. Vacuum-pressure method was used to impregnate the wood with a vinyl acetate monomer and benzoyl peroxide (1.5 wt%) was used as initiator. The studied WPC were characterized for treatment parameters (weight percentage gain and specific gravity), as well as chemical (by infrared spectroscopy), thermal (by thermogravimetric analysis) and mechanical (by flexure and hardness tests) features. The *in situ* polymerization yielded improved mechanical properties and increased thermal stabilities, which were attributed to the impregnated (poly)vinyl acetate (especially on the wood surface) as suggested by treatment parameters and infrared spectra. The presented wood treatment may be a key strategy to improve pinewood properties, especially from juvenile wood, which may overcome the properties of the pristine mature wood.

Keywords: Wood quality, Wood treatment, Wood-based composites, *In situ* polymerization, Wood properties

Introduction

In tropical countries (marked by a temperate climate), fast-growing woods may be important alternatives to meet demands for lumber and other solid products, avoiding the use of some scarce native forests. However, such species normally produce a large proportion of juvenile wood (JW), which presents low properties and unsuitable quality for several purposes, including the pulp and paper industry and the lumber sector. Palermo *et al*. evaluated a Brazilian *Pinus elliottii* wood and reported that it starts to produce mature wood (MW) only after 20 years of life [1], which may represent an economic issue regarding certain wood products, especially those designed for structural applications. For this reason, MW from certain species are scarce in many countries and it is necessary to encourage the use of their JW.

Rowell divided the treatments for wood improvement into four categories, namely chemical, thermal and impregnation methods [2]. Regarding of the last one, most of the impregnation procedures also lead to chemical changes in the wood cell wall, since the impregnated chemicals attach itself or become inside coatings in the wood lumens [3,4]. These treatments are possible when low viscosity substances are impregnated into permeable woods.

Different polymeric materials were already impregnated into wood parts, including methyl methacrylate, furfuryl alcohol, epoxy, among others [5]. For instance, Dong *et al.* impregnated two vinyl monomers (glycidyl methacrylate and ethylene glycol dimethacrylate) into a champak wood and reported both the filling of wood lumens and chemical bonds with the wood substrate [6]. Hadi *et al*. impregnated the jabon wood (*Anthocephalus cadamba*) with methyl methacrylate and reported significant increases in physical and mechanical properties, including volume shrinkage, modulus of elasticity and modulus of rupture [7].

The (poly)vinyl acetate (PVA) is an amorphous thermoplastic polymer with good adhesion to many surfaces and, because of that, has been used for several applications, including general repairs such as filling of holes and imperfections [8]. According to Zimmermann *et al*., the PVA is also a promising matrix for polymer composites [9]. Jebrane *et al*. presented other possible application for the vinyl acetate, using it to produce acetylated wood products [10]. They treated a maritime pine (*Pinus pinaster*) with vinyl acetate, using potassium carbonate as catalyst, and their esterification reactions occurred at 90 ºC. They reported chemical reactions on both cellulose and lignin from their studied wood.

The polymerization of vinyl monomers into the wood occurs in presence of catalysts or radiation techniques. For Dong *et al*., it occurs via a free radical mechanism at an almost neutral pH, which is suitable for wood parts, since certain wood compounds may be hydrolysed when condensation reactions are induced during the polymerization process [6].

Since PVA present a non-polar structure, its impregnation on wood containing high numbers of hydroxyl groups may lead to poor interactions. However, there are compatibilizers (for instance: maleic anhydride, glycidyl methacrylate and ethyl glycol dimethyl methacrylate) able to improve the compatibility between wood and nonpolar polymers, such as the (poly)vinyl acetate [6,11].

On the other hand, previous studies already reported that the impregnation with vinyl monomers led to improvements inhygroscopic, biological, thermal and mechanical properties

---

*Corresponding author: gattodarci@gmail.com

[11], although the PVA-treated wood may show less-dimensional stability in the presence of moisture, due to the retention of monomers in the cell lumen instead of the cell wall. Although the effects of the PVA impregnation into wood parts were deeply studied, these effects for JW and MW have not yet been elucidated by a comparative study. This work aims to produce and characterize wood-based composites via *in situ* polymerization of PVA into JW and MW from a pine species.

Experimental

Raw Material Selection

25 years old pine (*Pinus elliotti* Engelm.) trees were overturned in a homogenous forest located at Piratini/Brazil. Specimens from both the first 8 growth rings and the last 5 growth rings were selected to represent the JW and MW, respectively. These specimens were cut following those requirements of each used standard and then placed in a climatic chamber (20±2 °C temperature and 65±3% RH) until reach constant mass. Anatomic images were taken from 13 µm thick laminas cut from untreated wood samples, using an optical microscope (adjusted for 25×), using a commercial software, called as Klonk Image Measurement.

WPC Processing

A 98.5 % vinyl acetate aqueous solution (acquired from Sigma Aldrich) was homogenised with 1.5 wt% of benzoyl peroxide in a 2 *l* beaker for 15 min, using a magnetic stirrer. The wood samples were oven-dried at 50 ºC until reaching constant mass, in order to open the wood pores and facilitate the monomer impregnation. Then, a certain amount of pinewood (about 1200 cm^3) was placed into a 2300 cm^3 horizontal autoclave, wherein an initial vacuum (-0.1 MPa for 40 min) was applied, using a vacuum pump (Marconi brand). Afterwards, using the pressure difference caused by the mentioned vacuum, a valve was opened to pour 1.3 *l* of a vinyl acetate solution and then it was applied a positive pressure of 0.8 MPa for 180 min. The impregnated woods were subsequently coated using aluminium foils and placed in a laboratory oven at 70 °C for 72 h.

WPC Characterization

Specific gravity (ρ) and weight percentage gain (WPG) were determined before and after the wood treatments. For that, a digital calliper (0.0001 resolution) and an analytical balance (0.0001 g resolution) were used. Chemical groups were evaluated by Fourier-transform infrared spectroscopy (FTIR), using an attenuated total reflection (ATR) device in a Jasco 4100 equipment. A total of 32 scans (600-1800 cm^{-1} range) were performed at 4 cm^{-1} resolution and 2 $mm{\cdot}seg^{-1}$ scanner velocity. Thermal stability was evaluated by thermal gravimetric (TG) analysis, using a TGA-1000 equipment (Navas Brand). It was applied a heating rate of 10 $°C{\cdot}min^{-1}$ from room temperature (20 ºC) until 105 ºC (moisture ramp), followed by a heating ramp from 105 ºC to 600 ºC at the same heating rate. Static bending tests were performed in prismatic samples (15×15×250 mm^3) at a speed of 0.8 $mm{\cdot}min^{-1}$, as described in ASTM D143. Load *vs.* deflexion curves were manipulated as described by Phuong *et al*. [12] in order to calculate brittleness. Hardness tests were performed in prismatic samples (5×5×15 cm^3), following the Janka method described in ASTM D143. In this procedure, a 1.13 cm^2 diameter steel hemisphere was inserted on each anatomical plane (transverse, radial and tangential) at a cross-head speed of 6 $mm{\cdot}s^{-1}$. All mechanical tests were carried out using a DL 3000 equipment (Emic brand). The transverse plane of the PVA-treated JW was analysed in a Pro-X (Phenon brand) scanning electron microscope (SEM).

Statistical Analyses

A completely randomized design (CRD) was applied to analyse all the data. Homogeneity of variances and data normality were verified using Levene and Shapiro-Wilk tests, respectively. Whenever any of these assumptions was not satisfied, the data were transformed using square root or logarithm. Also, whenever the null hypothesis was rejected, LSD Fisher tests were performed to compare the means. All statistical analyses were developed at a significance level of 1 %.

Results and Discussion

Treatment Parameters

Regarding the WPG, the JW and MW reached 10.78 %± 0.036 % and 8.93 %±0.019 %, respectively. These levels are probably related to the high proportion of early wood, large wood tracheids and free voids in JW, as shown in Figure 1. Besides that, the MW (627 $kg{\cdot}m^{-3}$±0.024 $kg{\cdot}m^{-3}$) presented a higher average value for ρ compared to the JW (539 $kg{\cdot}m^{-3}$± 0.014 $kg{\cdot}m^{-3}$), which can be attributed to their anatomical

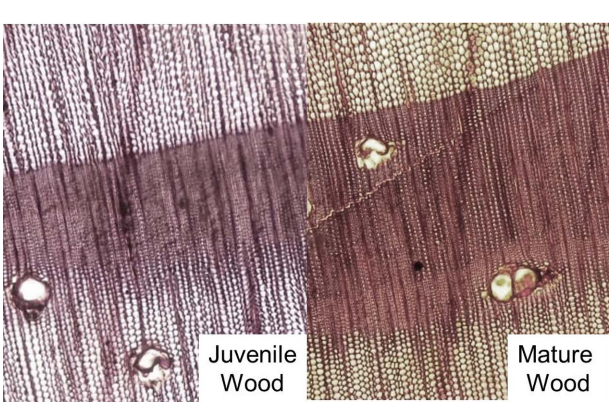


Figure 1. Anatomical images taken from transverse anatomical plains of juvenile (JW) and mature (MW) pinewoods.

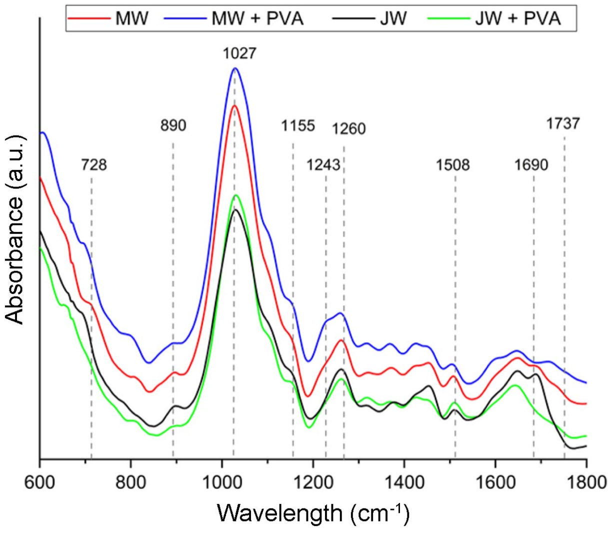


Figure 2. Infrared spectra of the juvenile (JW) and mature (MW) pinewoods prior and after the treatments with (poly)vinyl acetate (PVA).

features, since the MW is marked by a high proportion of latewood, thick wood tracheids and narrow wood lumens. Nonetheless, the wood permeability may also depend on anatomical features from wood, including, fibre length, fibre width, and wall thickness [13], which are all larger for MW than the JW [1]. WPG levels above 30 % are common in literature for other monomers [7,8], which indicates that the present WPG is low, probably due to the low polarity of the PVA.

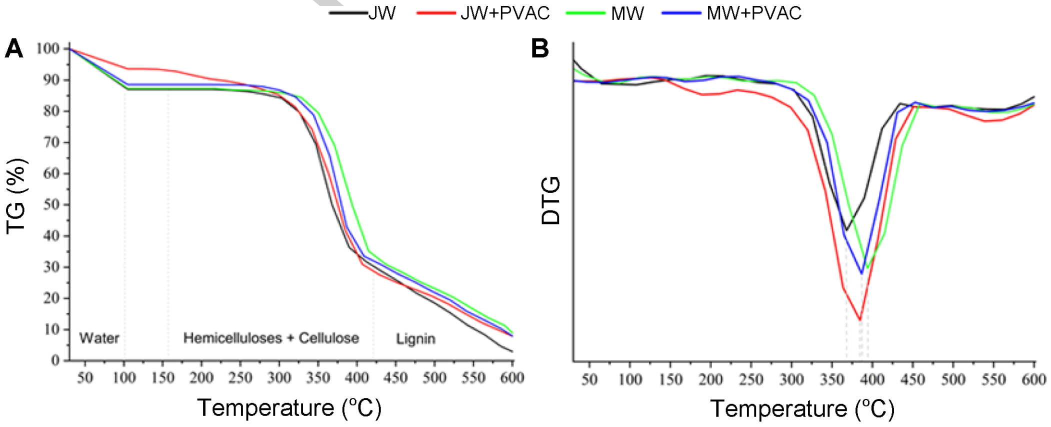
Infrared Spectroscopy

Figure 2 shows qualitative results about the main chemical groups for the pristine and treated pinewoods. The untreated JW and MW showed infraredspectra with similar shapes, which are marked by typical peaks, as those located at 890 cm^{-1}, 1027 cm^{-1}, 1155 cm^{-1}, 1260 cm^{-1} and 1508 cm^{-1}. Thismeansa similar chemical composition in a comparison between these woods. Compared to the pristine woods, the peaks 890 cm^{-1}, 1027 cm^{-1}, 1508 cm^{-1} and 1690 cm^{-1} showed slight attenuations for the treated ones. All these differences are attributed to the presence of the PVA into the wood lumens, since these peaks represent typical chemical groups belong to the PVA [14]. For instance, according to Marcilla *et al*., the peak at 1690 cm^{-1} is related to stretching vibrations in C=C bonds from =CH_2 groups belong to the PVA, which indicates the presence of PVA molecules attached to the wood cell wall [14].

Moreover, in a comparison between JW and MW at pristine conditions, the attenuation of the peak at 1027 cm^{-1} can also explain why the JW presented a larger permeability than the MW, since this peak can be associated with the presence of wood extractives [15]. It is known that the MW presents a larger extractives content than the JW, which may negatively affect its permeability [13].

Thermal Gravimetric Analyses

Figure 3 displays both TG and DTG curves for pristine and treated pinewoods, as well as the main thermal events. All samples showed three thermo-degradation stages, wherein the first (from 30 °C to 105 °C) is attributed to their drying process. Those TG curves related to the treated pinewoods presented minor slopes along this region, which



Thermal event	JW	JW + PVA	MW	MW + PVA
T_{ONset} (°C)	330.74	328.91	347.56	345.08
T_{ENDset} (°C)	383.03	397.77	416.55	394.64

Figure 3. TG (A) and DTG (B) curves and main thermal events for the juvenile (JW) and mature (MW) pinewoods prior and after the treatments with (poly)vinyl acetate (PVA).

appear as nearly constant lines in the DTG curves, indicating that the treated pinewoods acquired hydrophobic characteristics, probably due to chemical reactions occurred in the amorphous segments from wood polysaccharides.

Based on the second thermo-degradation stage (from about 150 °C to 380 °C), compared to the treated one, the pristine MW presented a lower mass loss, which is confirmed by their T_{ONset} and T_{ENDset}. This is probably related to the low PVA retention for MW, as well as its high natural thermal stability, since the PVA under heating starts a deacetylation reaction at 300 ºC [16]. For pristine woods, this thermo-degradation stage is associated with degradation of volatiles, hemicelluloses and cellulose. Therefore, it seems that the low amount of retained PVA into the MW did not bond itself to crystalline segments in cellulose and, because of that, did not protect them. On the other hand, the treated JW presented an increased thermal stability compared to the pristine one and seems to become thermally similar to the pristine MW.

Regarding the third thermo-degradation region (above 420 ºC), the pristine JW presented the highest mass loss, followed by the treated JW. This seems to be related to the composition of its lignin and possible reaction with the impregnated PVA. The pristine and treated MW presented similarly shaped TG curves, which may be attributed to the low retention of the impregnated PVA. DTG curves also confirm this last thermal behaviour. Normally, the thermo-degradation kinetics of the PVA develop until about 500 ºC [16]. The final chars for JW and MW are probably related to different mechanisms, whereas the amount of PVA into the pine wood yields an increased content of inorganic compounds, meanwhile the lignin from wood partially becomes fixed carbon.

Mechanical Properties

The treatment by *in situ* polymerization with PVA yielded both increased stiffness and strength, except for the MOE in the JW (Figure 4A). The increases in MOR were of 32.11 % and 25.87 % for JW and MW, respectively. It is also important to highlight that the treated JW overcame the pristine MW, which may be useful when pristine MW is unavailable. Additionally, a small increase of 6.65 % in MOE was found for the MW. Therefore, it seems that the presence of PVA itself did not induce changes in the mechanical properties and these aforementioned improvements may be attributed to the reduced equilibrium moisture content from the chemical changes in the amorphous segments of hemicelluloses and cellulose. The increase in MOE for the MW may be attributed to the elastoplastic nature of the impregnated PVA [17,18]. Besides, increases in brittleness for treated pinewoods can be attributed to the high amorphous chemical structure of the PVA and may

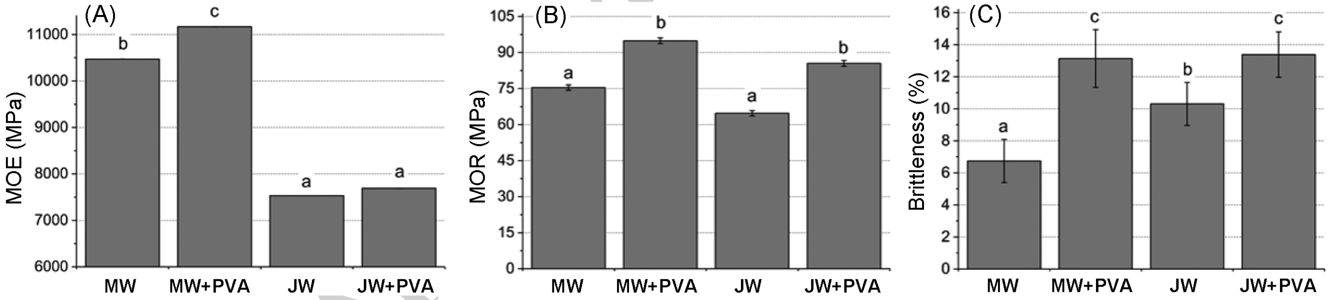


Figure 4. Modulus of elasticity (MOE; A), modulus of rupture (MOR; B) and brittleness (C) for the juvenile (JW) and mature (MW) pinewoods prior and after the treatments with (poly)vinyl acetate (PVA). Where: different letters above the bars represent significant differences.

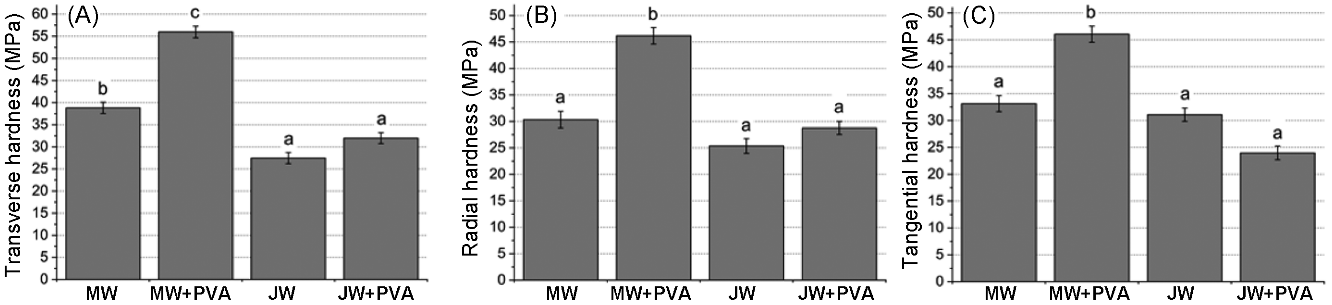


Figure 5. Transverse hardness (A), radial (B) and tangential (C) planes for the juvenile (JW) and mature (MW) pinewoods prior and after the treatments with (poly)vinyl acetate (PVA). Where: different letters above the bars represent significant differences.

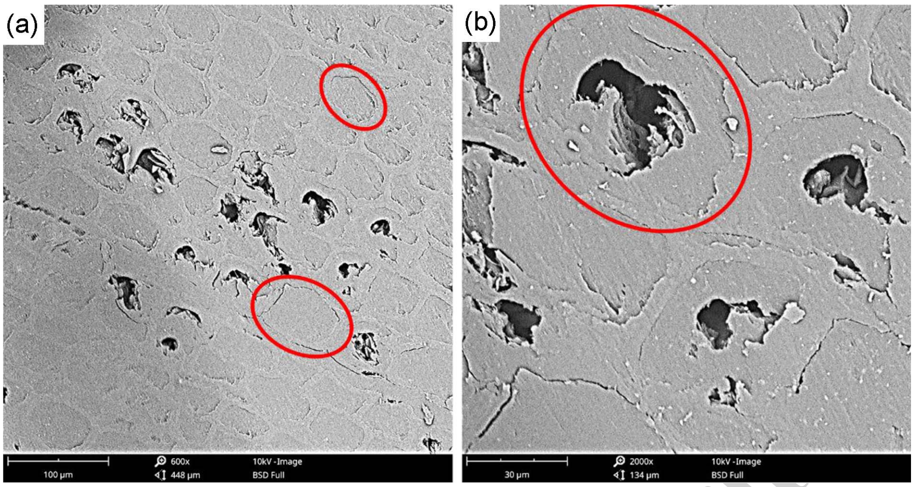


Figure 6. SEM images for the transverse view of the juvenile pine wood (JW) treated by *in situ* polymerization with (poly)vinyl acetate (PVA) taken at two different magnifications (a and b).

depend on the groups attached to the carbon-carbon backbone (Figure 4C).

The hardness for MW was increased by the treatment with PVA on the three anatomical planes (Figure 5). These increases were more than 35 % in all cases. On the other hand, for the treated JW, these parameters did not change when compared to the pristine one. This may be attributed to the low equilibrium moisture content on the surface of the treated MW, since there was a low retention of PVA for that case. Thus, particular chemical changes lead to a hydrophobic surface and, consequently, increased hardness. This decrease in equilibrium moisture content was already reported in previous studies [7].

Figure 6 shows SEM images taken at different magnifications in order to illustrate some morphological features of the PVA-treated pine woods. It is observed that most the wood tracheids are filled with solid PVA. According to Georgieva *et al*., impregnated vinyl monomers fill the capillaries, vessels, and other void spaces in the wood structure [19]. The PVA clearly bulked the wood cell wall, what explains the achieved gains in mechanical and thermal properties. The Figure 6 also suggests that the wood cell wall was penetrated by the PVA, which was reported in some previous studies [11,19]. A wood-PVA interfacial region appears in some filled tracheids (highlighted in red), what suggests a weak chemical interaction, probably related to previously explained mechanisms.

Conclusion

Treated pinewoods presented low WPG and unchanged ρ, which may be related to the low polarity of the PVA. Slight chemical changes in the wood cell wall were detected based on infrared spectra. The impregnated PVA led to increased thermal stability for the JW, especially from 150 °C to 420 °C. Increases in MOR were found for all cases, but only the MW presented increase in MOE after the treatment with PVA. Increases in brittleness were found for all cases and there was an increase in hardness for the treated MW, which seems to be related to an increased hydrophobicity on the MW surface. The MOR for treated JW overcame that of the pristine MW and the thermal stability for treated JW was similar to both treated and pristine MW. This may be important to supply certain structural applications needs, especially when there is a demand for MW due to its naturally higher thermal and mechanical properties compared to the JW. The solid PVA filled the pine wood tracheids, although it seems that the polymer was detached from the wood cell wall, which suggests a weak interaction.

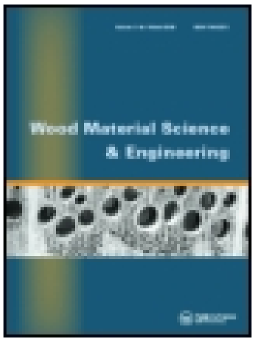
Acknowledgements

This work was supported by Coordination for the Improvement of Higher Education - CAPES (Financing Code 001).

References

1. G. P. Palermo, J. V. F. Latorraca, E. T. D. Severo, M. A. do Nascimento, and M. A. de Rezende, *Rev. Arvore*, **37**, 191 (2013).
2. R. Rowell, *Cellul. Chem. Technol.*, **46**, 443 (2012).
3. E. Cabane, T. Keplinger, V. Merk, P. Hass, and I. Burgert, *Chem. Sus. Chem.,* **7**, 1020 (2014).
4. V. Merk, M. Chanana, T. Keplinger, S. Gaan, and I. Burgert, *Green Chem.*, **17**, 1423 (2015).
5. W. D. Ding, A. Koubaa, and A. Chaala, *BioResources*, **7**, 504 (2012).

6. X. Dong, T. Sun, Y. Liu, C. Li, and Y. Li, *BioResources*, **10**, 7854 (2015).
7. Y. S. Hadi, I. S. Rahayu, and S. Danu, *J. Indian Acad. Wood Sci.*, **10**, 77 (2013).
8. A. N. Bhumkar and M. V. Rathnam, *J. Chem. Thermodyn.*, **136**, 77 (2019).
9. M. Jebrane, F. Pichavant, and G. Sèbe, *Carbohydr. Polym.*, **2**, 339 (2011).
10. M. V. Zimmermann, T. C. Turella, A. J. Zattera, and R. M. Santana, *Polim.: Cienc. Tecnol.*, **24**, 58 (2014).
11. M. Ghorbani, Z. A. Aghmashadi, S. M. Amininasab, and R. Abedini, *J. Appl. Polym. Sci.,* **136**, 47467 (2019).
12. L. X. Phuong, S. Shida, and Y. Sait, *J. Wood Sci.*, **53**, 181 (2007).
13. E. E. P. Baraúna, J. T. Lima, R. da S. Vieira, J. R. M. da Silva, and T. C. Monteiro, *Cerne*, **20**, 529 (2014).
14. A. Marcilla, A. Gómez, and S. Menargues, *Polym. Degrad. Stab.*, **89**, 145 (2005).
15. R. A. Delucis, W. L. E. Magalhães, C. L. Petzhold, and S. C. Amico, *J. Appl. Polym. Sci*., **135**, 45684 (2017).
16. A. Badiee, I. A. Ashcroft, and R. D. Wildman, *Int. J. Adhes. Adhes.*, **68**, 212 (2018).
17. W. D. Ding, A. Koubaa, and A. Chaala, *Ind. Crops Prod.*, **46**, 304 (2013).
18. S. Islam, S. Hamdan, A. Hassan, Z. A. Talib, and H. R. Sobuz, *J. Compos. Mater.*, **48**, 783 (2014).
19. M. Georgieva, M. Harata, and G. Miloshev, *J. Cell. Biochem.*, **104**, 59 (2008).



Wood Material Science & Engineering

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/swoo20

Juvenile and mature woods from pine subjected to *in situ* polymerization with furfuryl alcohol

Andrey Pereira Acosta , Rafael Beltrame , André Luiz Missio , Rafael de Avila Delucis & Darci Alberto Gatto

To cite this article: Andrey Pereira Acosta , Rafael Beltrame , André Luiz Missio , Rafael de Avila Delucis & Darci Alberto Gatto (2020): Juvenile and mature woods from pine subjected to *in situ* polymerization with furfuryl alcohol, Wood Material Science & Engineering, DOI: 10.1080/17480272.2020.1810118

To link to this article: https://doi.org/10.1080/17480272.2020.1810118

WOOD MATERIAL SCIENCE & ENGINEERING
https://doi.org/10.1080/17480272.2020.1810118

Taylor & Francis
Taylor & Francis Group

ORIGINAL ARTICLE

Juvenile and mature woods from pine subjected to *in situ* polymerization with furfuryl alcohol

Andrey Pereira Acosta [a], Rafael Beltrame [a], André Luiz Missio [b], Rafael de Avila Delucis [a] and Darci Alberto Gatto [a]

[a]Postgraduate Program in Materials Science and Engineering, Federal University of Pelotas, Pelotas, Brazil; [b]Postgraduate Program in Forest Engineering, Federal University of Santa Maria, Santa Maria, Brazil

ABSTRACT
This article presents an elucidative research that aims to bring new uses for the juvenile pine wood, which is highly available and commercially undervalued. For that, specimens from adult pine trees were cut from near to both their pith and bark in order to present the juvenile and mature pine woods, respectively. These specimens were then impregnated with a furfuryl alcohol-based solution, which was *in situ* polymerized by heating. Treatment parameters (weight percentage gain and density), as well as chemical (by infrared spectroscopy), thermal (by thermogravimetry) and mechanical (by flexure and hardness tests) features were evaluated. Typical mechanisms reported in previous studies for pine woods subjected to furfurylation were also obtained here, including reactions of the furfuryl alcohol with lignin and hemicelluloses from the pine wood, increase in thickness of the wood cell wall, as well as certain increases in thermal and mechanical features. Additionally, thermal stability (in all temperatures) and hardness of the furfurylated juvenile wood overcame the same properties of the untreated mature wood. Still regarding this comparison, the stiffness in flexure was similar for both of them.

ARTICLE HISTORY
Received 13 April 2020
Revised 13 July 2020
Accepted 11 August 2020

KEYWORDS
Wood treatment; eco-friendly treatment; wood composites; furfuryl alcohol; mechanical stiffness

Introduction

Fast-growing woods are alternative supplies for many wood-based industries and indirectly relive the pressure on some native forests (Dong *et al*. 2016). However, their high growth rate also restricts some applications of lumbers cut from these woods, since it confers some negative effects, including low density, low mechanical properties, dimensional instability, and susceptibility to xylophagous agents (He *et al*. 2013; Dong *et al*. 2014; Kunstler *et al*. 2016).

This low quality attributed to fast-growing woods is due to their high proportion of juvenile wood (JW) (Gapare *et al*. 2006; Acosta *et al*. 2020). In fact, the JW is often unsuitable for structural applications, since it may have low mechanical properties and low durability. Compared to the mature wood (MW), the JW presents smaller fiber length, smaller fiber diameter and higher lignin content (Palermo *et al*. 2013). Because of that, researches on the development of new uses for the JW through chemical or physical modifications have a key role in literature.

The treatments for improvement of wood properties are divided into three categories: impregnations, chemical modifications and thermal modifications (Rowell 2012). The impregnation methods consist of impregnating polymers or carbohydrates into the wood lumens and/or other intercellular spaces (Mattos *et al*. 2015). According to Magalhães and Da Silve (2004), softwoods are normally suitable to be impregnated by chemicals with low viscosity due to their simple anatomical structure, which is important for the *in situ* polymerization of unsaturated monomers.

Furfuryl alcohol (FA) is a possible chemical for wood treatment. The FA is obtained from renewable resources, presents different functional groups and can be functionalized to synthetize several polymeric materials (Kim *et al*. 2014; Sheldon 2014). The furfurylation (reaction with FA) of wood pieces has attracted much attention since is an eco-friendly method. Improvements in some important wood properties were recently reported, including hardness, both stiffness and strength in flexure, thermal stability and decay resistance (Gallio *et al*. 2019). For Dong *et al*. (2016), all these improvements are dependent of both the FA concentration and FA/catalyst, in a way that seems to be: the higher the FA concentration, the higher the improvements in wood properties. In this sense, the FA concentration can be defined as the proportion of FA in the treatment solution.

In Brazil, *Pinus elliottii* is one of the mostly planted fast-growing specie, especially in south and southeast. This wood is mainly destined to lumber production, although its resin is also valuable (Aguiar *et al*. 2014). According to Palermo *et al*. (2013), Brazilian *Pinus elliottii* trees only produce MW after their 10–15 years of life, which indicates that most of the overturned trees are entirely composed by JW. Schulz *et al*. (2019) treated a Brazilian pine wood (PW) by furfurylation and reached increased stiffness in compression. Also, they reported similar compression strengths comparing treated and untreated PW, which was attributed

CONTACT Darci Alberto Gatto gattodarci@gmail.com Postgraduate Program in Materials Science and Engineering, Federal University of Pelotas, Pelotas, RS, Brazil

Figure 1. Anatomical images taken from transverse anatomical plains of both juvenile and mature woods from pine.

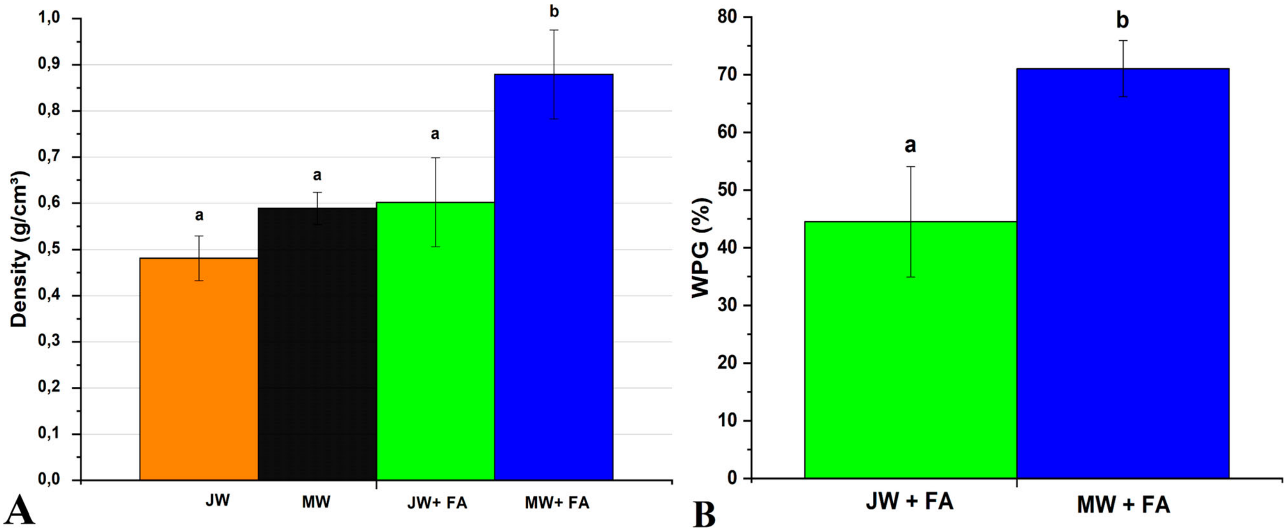


Figure 2. Density (A) and weight percentage gain (B) for juvenile (JW) and mature pine (MW) woods at both pristine and treated (+ FA) conditions (different letters inside the bars indicate a statistically significant difference). Note: Vertical lines represent the standard deviation of each treatment.

to decreases in wood hydrophilicity and filling of wood tracheids. However, the effect of the furfurylation in the performance of the JW and MW from pine is still not yet comprehended. This study aims the production of wood-polymer composites by *in situ* polymerization using FA and the JW and MW from pine, in order to bring new uses for the former PW.

Materials and methods

Raw material and wood treatment

Twenty years old pine (*Pinus elliottii* Engelm) trees were selected in a homogeneous forest located at Piratini/Brazil. Prismatic PW samples were cut from near to both the pith and bark, in order to represent the JW and MW, respectively. The specimens were produced in two different dimensions: (15 × 15 × 250 (I) and 25 × 25 × 100 (II)) mm^3, respectively, attributed to radial × tangential × longitudinal. The PW samples were then placed in a climatic chamber adjusted to a temperature of (20 ± 2)°C and (65 ± 3)% relative humidity until reaching the constant mass. Anatomy images were taken from 13 µm thick laminas cut from both JW and MW, using an optical microscope (adjusted for 25×) and a commercial software (called as Klonk Image Measurement).

A high purity (98 wt%) FA-based solution was acquired from Sigma Aldrich. This was manually mixed with maleic anhydride 1 wt% for 10 min. The PW specimens (about 1200 cm^3) were placed in a horizontal autoclave with an internal volume of about 2300 cm^3, wherein an initial vacuum of −0.1 MPa was applied for 40 min, using a vacuum pump (Marconi brand), in order to retire all the possible trapped air. A valve was opened to pour the prepared solution (about 1.3 L), taking advantage of the pressure difference

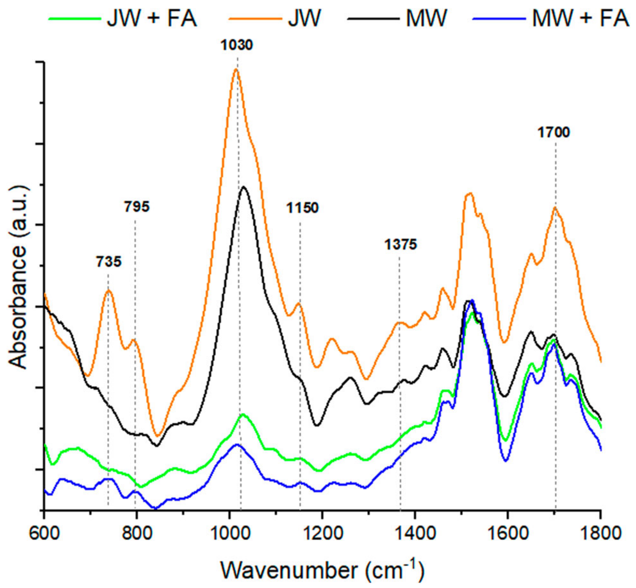


Figure 3. Infrared spectra for juvenile (JW) and mature (MW) pine woods at both pristine and treated (+ FA) conditions.

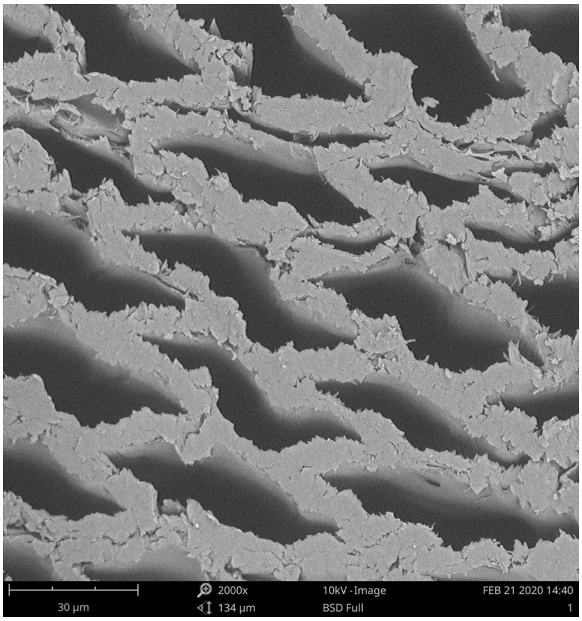


Figure 4. SEM image taken for the juvenile pine wood treated by *in situ* polymerization of furfuryl alcohol.

caused by the mentioned vacuum, and then a positive pressure of 0.6 MPa was applied for 120 min. The impregnated PW were oven-heated at 60°C for 24 h. Afterwards, all the PW samples were conditioned using the mentioned climatic chamber until reach equilibrium moisture content.

Characterization

Density (ρ) and weight percentage gain (WPG) were evaluated with the aid of a digital calliper (0.0001 mm resolution) and an analytical balance (0.0001 g resolution). Chemical groups were evaluated by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) in a Jasco 4100 equipment. A total of 32 scans 600–1800cm^{-1} range were performed at 4 cm^{-1} resolution and 2 mm s^{-1} scanner velocity. Thermal stability was evaluated by thermal gravimetric (TG) analyses, using a Navas TGA-1000 equipment. In this procedure, a moisture ramp from room temperature (about 20°C) until 105°C, was followed by a heating ramp from 105°C to a maximum temperature of 600°C. Both these ramps were performed at a heating rate of 10°C min^{-1}. Static bending tests were performed in prismatic samples (I) at a speed test of 0.8 mm min^{-1}. Hardness tests were carried out following the Janka method described in ASTM D143 (2014). In this procedure, a 1.13 cm^2 diameter steel hemisphere was inserted on each anatomical plane (transverse, radial and tangential) of prismatic samples (II) at a cross-head speed of 6 mm s^{-1}. All the mechanical tests were carried out using a DL 3000 equipment (Emic brand). The surface morphology of the transverse plane (in relation to the fibers orientation) of treated JW was also analyzed, using a Phenom World Pro-X scanning electron microscope.

Statistical analyses

A completely randomized design (CRD) was applied to analyze all the data. Homogeneity of variances and data normality were verified using Levene and Shapiro–Wilk tests, respectively. Whenever any of these assumptions was not satisfied, the data were transformed using square root or logarithm. Also, whenever the null hypothesis was rejected, LSD Fisher tests were performed to compare the averages. All statistical analyses were developed at a significance level of 1%.

Results and discussion

Figure 1 shows optical micrographs of the transverse planes of both the pristine JW and MW. The JW presented tracheids with higher diameters than those from the MW, especially its spring wood (highlighted using black braces). In countries with tropical climates, like Brazil and India, meristematic cells (responsible for wood growth) present an intense physiological activity during the spring, which explains these different cell diameters. That wood grown during this season is called as spring wood and is marked by long and wide tracheids with a fine cell wall (Pacheco *et al.* 2019).

As shown in Figure 2, the *in situ* polymerization with poly (furfuryl alcohol) (PF) into both the JW and MW from PW led to both high WPG (above 40%) and high densities (above 0.6 g cm^{-3}). Such WPG levels are in agreement with the literature. For instance, Lande *et al.* (2004) produced a PF-based WPC using a *Pinus sylvestris* wood and reported WPG levels ranging from 30% to 47%. Temiz *et al.* (2007) studied a *Pinus sylvestris* wood treated by furfurylation and obtained a WPG of 40%. As aforementioned, according to the literature, these treatment parameters are closely related to the FA concentration and FA/catalyst ratio.

MW and JW presented similar WPG levels, which may be occurred due to the content and composition of their lignin, since the PF has a high chemical affinity with this wood compound (Lande *et al.* 2004). In all, the obtained treatment parameters may be related to the PF located inside the PW cell

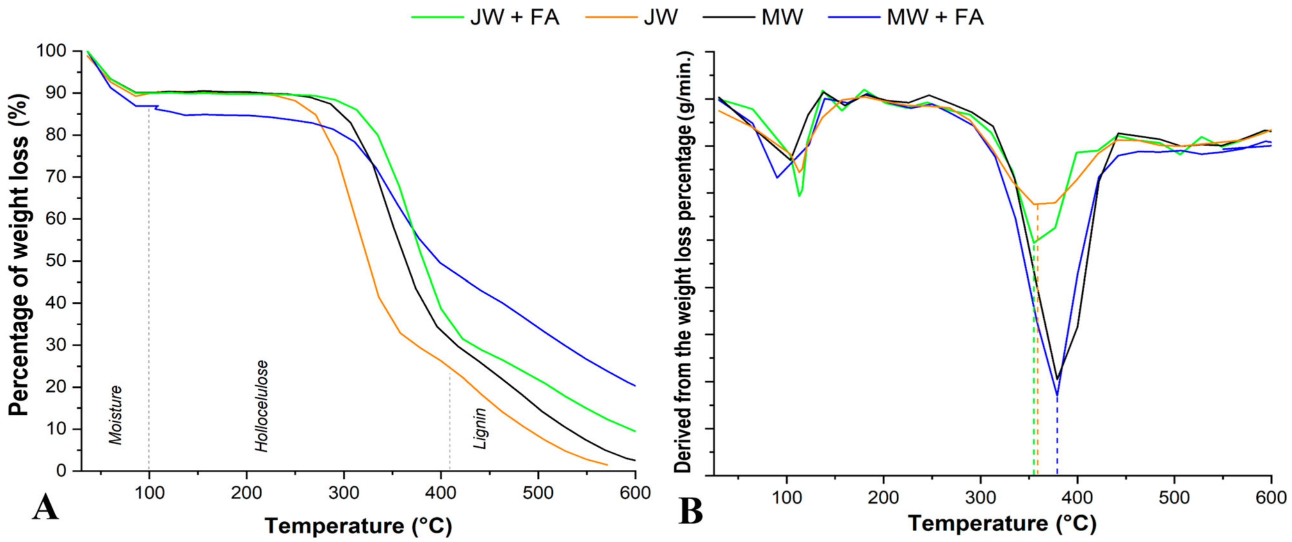


Figure 5. TG (A) e DTG (B) curves for juvenile (JW) and mature (MW) pine woods at both pristine and treated (+ FA) conditions.

structure. Esteves *et al*. (2011) mentioned that the PF may attach itself to the lumen wall, forming an inner layer that partially or totally occupies all intercellular spaces of the wood. The changes in the main chemical groups from the pristine and treated PW were analyzed and shown in Figure 3 by infrared spectra.

The pristine JW presented major bands attributed to its lignin at 1720, 1150, 795, and 735 cm^{-1}, which are, respectively, assigned to C=O stretch (unconjugated), guaiacyl C–H, C=O bonds, and C–H out-of-plane deformation (Pandey 1999; Barsberg and Thygesen 2017). The spectrum of treated JW did not show these prominent bands, which may be due to hydrolysis of certain chemical groups from lignin induced by the furfurylation. This can also be affirmed about the bands at 1490, 1375, and 1150 cm^{-1}, which represent some chemical groups belong to the wood sugars (Darwish *et al*. 2013). Compared to the MW, the JW presents a higher lignin content (Palermo *et al*. 2013), which explains the absence of these bands in the pristine MW. Additional details on the influence of the furfurylation in the anatomical structure of the JW are shown in Figure 4.

The furfurylated PW seems to have thicker cell walls than the normal for pristine PW. Guigo *et al*. (2010) reported that the PF may homogeneously permeating the wood cell wall, leading to an inner coverage. These interactions between the PF and the wood cell wall yielded thermal changes in the overall PW, as indicated by Figure 5.

Regarding the TG curves (Figure 5(A)), after 240°C, the treated JW starts to present a higher thermal stability compared to its respective pristine PW, but the same only happens for the treated MW after 320°C. This temperature range (i.e. 240–320°C) is driven by thermal decomposition of crystalline segments from the cellulose and the overall lignin (Poletto *et al*. 2012). Yang *et al*. (2019) reported that the FA presents a high chemical affinity with the lignin, which explains why the furfurylation only impacts the thermal stability of the wood at a high temperature range, since the lignin only becomes to be thermally decomposed at high temperatures. According to Kong *et al*. (2018), this temperature also coincides with the degradation of structural compounds from the PF itself, which involves cleavage of many hydrogen bonds.

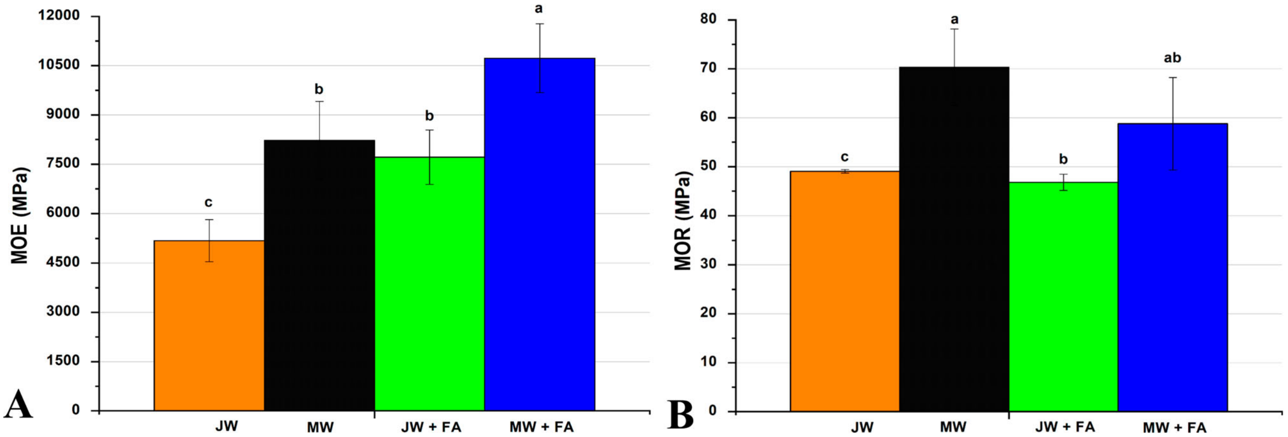


Figure 6. Modulus of elasticity (MOE; A), modulus of rupture (MOR; B) for juvenile (JW) and mature (MW) pine woods at both pristine and treated (+ FA) conditions (different letters inside the bars indicate a statistically significant difference). Note: Vertical lines represent the standard deviation of each treatment.

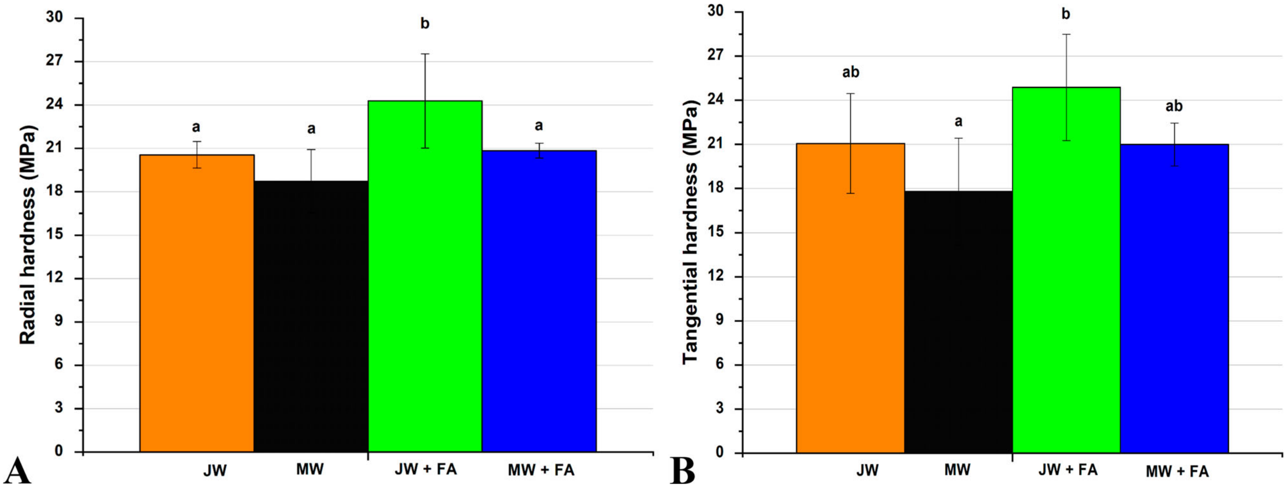


Figure 7. Radial (A) and tangential (B) hardness for juvenile (JW) and mature (MW) pine woods at both pristine and treated (+ FA) conditions (different letters inside the bars indicate a statistically significant difference). Note: Vertical lines represent the standard deviation of each treatment.

The treated JW was more thermally stable than the treated MW until 380°C and thereafter took place a contrary behavior. This seems to be attributed to the chemical composition of each PW, since compared to each other, the MW presents a smaller lignin content and the JW presents a smaller hemicellulose (Palermo *et al.* 2013). Compared to the pristine MW, the treated JW was more thermally stable in all temperatures, which is an important feature for several applications. Both the treated PW also showed the two highest residues contents (above 10 wt %) after 600°C, which indicates that the PF itself also partly became fixed carbon.

The furfurylation conferred increases of 48.83% and 30.38% in MOE for the JW and MW, respectively (Figure 6 (A)). Both of these treated PW also presented smaller MOR than each respective pristine version. These changes in mechanical properties can be attributed to the presence of the polymer into the PW microstructure. The elasticity of the studied WPC seems to be related to the PF-wood chemical bonds (indirectly indicated by infrared spectra and SEM images) and the strength may be associated with the fragile nature of the PF. These increases in MOE may also be related to the mechanical support of the solid polymer located inside the wood voids, preventing the development of micro cracks generated during mechanical loads. Additionally, the treated JW reached a higher stiffness than the pristine MW, which indicates that the furfurylation may bring new uses for JW from pine.

Schulz *et al.* (2019) reported that their furfurylated PW presented similar mechanical properties compared to their respective untreated samples, including strength in both compression and flexure, as well as stiffness in flexure. According to Barsberg and Thygesen (2009), possible increases in mechanical properties induced by furfurylation treatments are associated to balanced FA/catalyst ratios. For Dong *et al.* (2016), the increases in mechanical properties are higher as higher is the FA concentration in the treatment solution. Therefore, it seems to have optimal parameters to be adjusted in order to reach a maximized performance for each treated raw material.

The *in situ* polymerization with the PF conferred an increase in hardness for the radial plane of the JW, as indicated in Figure 7. This difference between radial and tangential planes is attributed to the orientation of ray cells, which may be filled by the PF and contribute to the overall hardness. Thereby, the radial plane shows the axial direction of these filled anatomical elements, while only their cross sections appear on the tangential plane. Regarding the other cases (both hardnesses of the MW and the tangential hardness of the JW), treated and untreated PW did not showed different properties. Besides of that, the treated JW overcame the pristine MW in both radial and tangential hardnesses, which can be related to its anatomical features (such as long and wide lumens shown by optical images) which were internally coated with PF (as shown in SEM image).

Conclusion

JW and MW presented similar WPG levels, which may attributed to its lignin composition and great chemical affinity with the PF. The treatment by *in situ* polymerization yielded chemical changes in the wood cell wall and the PF partly filled the wood pores, as suggested by the treatment parameters, infrared spectra, and SEM images. The treated JW presented higher thermal stability in the 0–600°C range, higher stiffness in flexure, and higher hardness compared to the pristine mature wood. This indicates that the furfurylation is probably able to confer new uses to the JW from pine.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was supported by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior [001].

ORCID

Andrey Pereira Acosta http://orcid.org/0000-0002-5074-3772
Rafael Beltrame http://orcid.org/0000-0002-8132-7587
André Luiz Missio http://orcid.org/0000-0001-9373-6313
Rafael de Avila Delucis http://orcid.org/0000-0002-3657-9216
Darci Alberto Gatto http://orcid.org/0000-0002-6805-3243

References

Acosta, A. P., Gallio, E., Schulz, H. R., Zanatta, P., Barbosa, K. T., De Avila Delucis, R. and Gatto, D. A. (2020) Wood-polymer composites produced by in situ polymerization of styrene into juvenile and mature pine woods. International Wood Products Journal, 1–7. doi:10.1080/20426445.2020.1776486

Aguiar, A., Gavioli, D. and Ferraz, A. (2014) Extracellular activities and wood component losses during *Pinus taeda* biodegradation by the brown-rot fungus *Gloeophyllum trabeum*. International Biodeterioration & Biodegradation, 82, 187–191. doi:10.1016/j.ibiod.2013.03.013

ASTM D 143 (2014) Standard test methods for small clear specimens of timber.

Barsberg, S. and Thygesen, L. G. (2009) Poly(furfuryl alcohol) formation in neat furfuryl alcohol and in cymene studied by ATR-IR spectroscopy and density functional theory (B3LYP) prediction of vibrational bands. Espectroscopia Vibracional, 49(1), 52–63. doi:10.1002/slct.201702104

Barsberg, S. T. and Thygesen, L. G. (2017) A combined theoretical and FT-IR spectroscopy study of a hybrid poly (furfuryl alcohol)–lignin material: Basic chemistry of a sustainable wood protection method. Chemistry Select, 2(33), 10818–10827. doi:10.1002/slct.201702104

Darwish, S. S., El Hadidi, N. M. N. and Mansour, M. (2013) The effect of fungal decay on *Ficus Sycomorus* wood. International Journal of Conservation Science, 4(3), 271–282.

Dong, Y., Yan, Y., Zhang, S. and Li, J. (2014) Wood/polymer nanocomposites prepared by impregnation with furfuryl alcohol and nano-SiO_2. BioResources, 9(4). doi:10.15376/biores.9.4.6028-6040

Dong, Y., Qin, Y., Wang, K., Yan, Y., Zhang, S., Li, J. and Zhang, S. (2016) Assessment of the performance of furfurylated wood and acetylated wood: Comparison among four fast-growing wood species. BioResources, 11(2), 3679–3690. doi:10.15376/BIORES.11.2.3679-3690

Esteves, B., Nunes, L. and Pereira, H. (2011) Properties of furfurylated wood (*Pinus pinaster*). European Journal of Wood and Wood Products, 69(4), 521–525. doi:10.1007/s00107-010-0480-4

Gallio, E., Zanatta, P., Cruz, N., Zanol, G. S., Schulz, H. R. and Gatto, D. A. (2019) Influência dos tratamentos de termorretificação e furfurilação em propriedades tecnológicas de uma conífera. Matéria, 24(3). doi:10.1590/s1517-707620190003.0739

Gapare, W. J., Wu, H. X. and Abarquez, A. (2006) Genetic control of the time of transition from juvenile to mature wood in *Pinus radiata* D. Don. Annals of Forest Science, 63(8), 871–878. doi:10.1051/forest:2006070

Guigo, N., Mija, A., Vincent, L. and Sbirrazzuoli, N. (2010) Eco-friendly composite resins based on renewable biomass resources: Polyfurfuryl alcohol/lignin thermosets. European Polymer Journal, 46(5), 1016–1023. doi:10.1016/j.eurpolymj.2010.02.010

He, W., Zhang, Q. S. and Jian, S. X. (2013) Modification of fast growing poplar with styrene and glycidyl methacrylate. International Wood Products Journal, 5(2), 98–102. doi:10.1179/2042645313y.0000000058

Kim, T., Assary, R. S., Pauls, R. E., Marshall, C. L., Curtiss, L. A. and Stair, L. C. (2014) Thermodynamics and reaction pathways of furfuryl alcohol oligomer formation. Catalysis Communications, 46, 66–70. doi:10.1016/j.catcom.2013.11.030

Kong, L., Guan, H. and Wan, X. (2018) *In situ* polymerization of furfuryl alcohol with ammonium dihydrogen phosphate in poplar wood for improved dimensional stability and flame retardancy. ACS Sustainable Chemistry & Engineering, 6(3), 3349–3357. doi:10.1021/acssuschemeng.7b03518

Kunstler, G., Falster, D., Coomes, D. A., Hui, F., Kooyman, R. M., Laughlin, D. C. and Aiba, M. (2016) Plant functional traits have globally consistent effects on competition. Nature, 529(7), 204–207. doi:10.1038/nature16476

Lande, S., Westin, M. and Schneider, M. (2004) Properties of furfurylated wood. Scandinavian Journal of Forest Research, 19(5), 22–30. doi:10.1080/0282758041001915

Magalhães, W., and Da Silva, R. (2004) Treatment of Caribbean pine by in situ polymerization of styrene and furfuryl alcohol. Journal of Applied Polymer Science, 91(3), 1763–1769. doi:10.1002/app.13252

Mattos, B. D., de Cademartori, P. H. G., Magalhães, W. L. E., Lazzarotto, M. and Gatto, D. A. (2015) Thermal tools in the evaluation of decayed and weathered wood polymer composites prepared by *in situ* polymerization. Journal of Thermal Analysis and Calorimetry, 121(3), 1263–1271. doi:10.1007/s10973-015-4647-4

Pacheco, A., Camarero, J. J., Pompa-García, M., Battipaglia, G., Voltas, J. and Carrer, M. (2019) Growth, wood anatomy and stable isotopes show species-specific couplings in three Mexican conifers inhabiting drought-prone areas. Science of the Total Environment, 13–40. doi:10.1016/j.scitotenv.2019.134055

Palermo, G. P. M., Latorraca, J. V. F., Severo, E. T. D., Nascimento, A. M., and Rezende, M. A. (2013). Delimitação entre os lenhos juvenil e adulto de Pinus elliottii Engelm. Revista Árvore, 37(1), 191–200. doi:10.1590/S0100-67622013000100020

Pandey, K. K. (1999) A study of chemical structure of soft and hardwood and wood polymers by FTIR spectroscopy. Journal of Applied Polymer Science, 71(12), 1969–1975. doi:10.1002/(sici)1097-4628(19990321)71:12<1969::aid-app6>3.3.co;2-4

Poletto, M., Zattera, A. J. and Santana, R. M. C. (2012) Structural differences between wood species: Evidence from chemical composition, FTIR spectroscopy, and thermogravimetric analysis. Journal of Applied Polymer Science, 126(S1), E337–E344. doi:10.1002/app.36991

Rowell, R. (2012) Chemical modification of wood to produce stable and durable composites. Cellulose Chemistry and Technology, 46, 443.

Schulz, H. R., Gallio, E., Acosta, A. P., Barbosa, K. T. and Gatto, D. A. (2019) Efeito da furfurilação em propriedades físicas e mecânicas da madeira de *Pinus elliottii*. Matéria, 24(3). doi:10.1590/s1517-707620190003.0756

Sheldon, R. A. (2014) Green and sustainable manufacture of chemicals from biomass: state of the art. Green Chemistry, 16(3), 950–963. doi:10.1039/C3GC41935E

Temiz, A., Terziev, N., Eikenes, M. and Hafren, J. (2007) Effect of accelerated weathering on surface chemistry of modified wood. Applied Surface Science, 253(12), 5355–5362. doi:10.1016/j.apsusc.2006.12.005

Yang, T., Cao, J. and Ma, E. (2019) How does delignification influence the furfurylation of wood. Industrial Crops and Products, 135, 91–98. doi:10.1016/J.INDCROP.2019.04.019

6. CONSIDERAÇÕES FINAIS

A impregnação dos monômeros na JV e na MT proporcionaram melhorias em todas as suas propriedades físicas, especialmente para a JV, devido aos seus grandes traqueídeos, levando a um alto WPG. A respeito de propriedades mecânicas, houveram aumentos na dureza, MOE e MOR. Os resultados de TG indicaram que tanto a JV quanto a MT tratadas com os monômeros as madeiras apresentaram maior estabilidade térmica que suas respectivas não tratadas. Espectros FT-IR e imagens do MEV confirmaram a presença dos monômeros dentro da madeira, mas não está claro se estes estão quimicamente ligados a mesma.

As madeiras tratadas com Poli(estireno) se mostraram mais resistentes mecanicamente e mais estáveis termicamente. A madeira juvenil obteve maiores ganhos no que se diz respeito as propriedades mecânicas e térmicas. Sendo assim neste estudo pôde-se proporcionar a madeira juvenil propriedades semelhantes ou até mesmo superiores se comparadas a madeira madura não tratada, ampliando seu leque de aplicações.

As editoras liberam a utilização dos artigos utilizados nesta dissertação.