UNIVERSIDADE FEDERAL DE LAVRAS

MATHEUS FELIPE FREIRE PEGO

PAPERS DEVELOPMENT FROM BLENDING OF DIFFERENT NATURAL FIBERS AND NANOCELLULOSE ADDITION

LAVRAS - MG
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Tese apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-graduação em Ciência e Tecnologia da Madeira, área de concentração Processamento e utilização de materiais lignocelulósicos e derivados, para obtenção do título de Doutor.

Profa. Dra. Maria Lúcia Bianchi
Orientadora

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PAPERS DEVELOPMENT FROM BLENDING OF DIFFERENT NATURAL FIBERS AND NANOCELLULOSE ADDITION

DESENVOLVIMENTO DE PAPÉIS A PARTIR DA MISTURA DE DIFERENTES FIBRAS NATURAIS E ADIÇÃO DE NANOCELULOSE

Tese apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-graduação em Ciência e Tecnologia da Madeira, área de concentração Processamento e utilização de materiais lignocelulósicos e derivados, para obtenção do título de Doutor.

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2020

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Dedico

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RESUMO GERAL

A indústria de papel e celulose tem atualmente diversos desafios que devem ser superados, além de metas que devem ser atingidas, sejam elas produtivas, ambientais ou referentes à qualidade. A qualidade de seus produtos é um desses desafios, principalmente no que se refere a papéis especiais ou superiores, com propriedades específicas para determinada utilização. Nesse sentido, faz-se necessário o desenvolvimento de novos produtos para suprir demandas mais exigentes do mercado. Assim, este trabalho teve como objetivo desenvolver papéis que apresentem propriedades superiores por meio da mistura de fibras naturais obtidas de diferentes matérias-primas e da adição de micro/nanofibrilas de celulose, além de compreender como esses dois fatores afetam a qualidade dos papéis. Para isso, amostras de polpa celulósica de sisal, eucalipto e pinus foram utilizadas. As polpas foram misturadas nas combinações possíveis e nas proporções de 5/95%, 25/75% 45/55%, sendo posteriormente destinadas a produção dos papéis. Papéis virgens (100% de cada polpa) também foram produzidos. A adição de nanofibrilas de celulose de sisal foi realizado por dois métodos: mistura durante a formação das folhas - MT- (3, 5 e 10% de nanofibrilas) e recobrimento superficial de folhas já formadas -CT- (10% de nanofibrilas). Os papéis reforçados e não reforçados foram submetidos aos ensaios mecânicos, físicos e óticos, além da análise da estrutura, espectroscópica e da resistência de suas ligações. Para melhor compreensão dos resultados e conclusões, a tese foi dividida em três tópicos: I – Efeitos da mistura de diferentes fibras nas propriedades físico-mecânicas; II – Efeitos da mistura de diferentes fibras nas propriedades óticas, estruturais e de resistência de ligação); e III – Impacto da adição de nanocelulose em papéis misturados. No tópico I, foi observado que ocorreram diferenças estatísticas entre os tratamentos para as propriedades físico-mecânicas e estas foram relacionadas à morfologia das fibras. A espessura dos papéis tendeu a decrescer com a mistura de fibras. As menores resistências mecânicas foram relacionadas à fibra do eucalipto e suas misturas enquanto as maiores foram relacionadas ao sisal e pinus. A adição de pequenas quantidades de sisal em misturas contribuiu significativamente para melhoria das propriedades mecânicas, evidenciando o efeito sinergético da mstura de fibras. No tópico II, os tratamentos com eucalipto apresentaram maiores resistência de ligação, alvura e permeância ao ar. Papéis misturados apresentaram melhores propriedades físicas que papéis virgens, evidenciadas por diferenças estruturais em imagens eletrônicas. No tópico III, a adição de nanofibrilas em papéis misturados aumentou a espessura, volume, gramatura, densidade aparente, opacidade, rugosidade e todas as propriedades mecânicas e reduziu bulk, alvura e permeância ao ar. A adição de nanofibrilas foi diferente entre os dois métodos de reforço. O método MT promoveu a melhora das propriedades mecânicas com o aumento do teor de nanocelulose. Papéis obtidos pelo método CT apresentaram menores valores de resistência mecânica se comparados com os obtidos pelo método MT. Finalmente, conclui-se que tanto a mistura de diferentes fibras como a adição de nanofibrilas contribuem para melhoria de propriedades qualitativas do papel, podendo se tornar potenciais métodos para produção de papéis que demandem grande qualidade ou mesmo para aumento do valor agregado desses produtos.

Palavras-chave: Folhas. Métodos de reforço. Qualidade dos papéis. Polpação. Resistência.

GENERAL ABSTRACT

The pulp and paper industry currently have several challenges that must be overcome, as well as goals that must be reached, whether productive, environmental or related to quality. The product quality is one of these challenges, especially for special or superior papers, with specific properties for a particular use. In this sense, we seek for development of new products to meet market demands. Thus, this study aimed to develop superior papers by mixture of natural fibers obtained from different raw materials and by addition of micro / nanofibrils of cellulose, as well as to understand how these two factors affect the paper quality. Then, samples of cellulosic pulp from sisal, eucalyptus and pine were used. Morphological analyzes of these fibers were performed. The pulps were mixed in different combinations and proportions (5/95%, 25/75% 45/55%,), and destined to the paper production. Virgin papers (100% of each pulp) were also produced. The addition of sisal nanocellulose was performed by two methods: mixing during handsheet formation - MT- (3, 5 and 10% nanofibrils) and surface coating of formed papers - CT- (10% nanofibrils). The reinforced and unreinforced papers were submitted to mechanical, physical and optical tests, besides the structure analysis, spectroscopic and bond strength. For a better understanding of results and conclusions, the thesis was divided into three topics: I - Effects of different fibers blending on the physical-mechanical properties; II - Effects different fibers blending in optical, structural and bond strength properties; and III - Impact of nanocellulose addition on mixed papers. In topic I, it was observed that statistical differences occurred between treatments for physical-mechanical properties and these were related to fiber morphology. The paper thickness tended to decrease with the fiber blend. Lowest mechanical strengths were related to eucalyptus fiber and its mixtures while highest were related to sisal and pine. The addition of small amounts of sisal in mixtures significantly contributed to the improvement of mechanical properties, evidencing the synergistic effect of fiber blending. In topic II, treatments with eucalyptus presented higher bond strength, brightness and air permeability. Mixed papers had better physical properties than virgin papers, evidenced by structural differences in electronic images. In topic III, the addition of nanofibrils to mixed papers increased thickness, volume, weight, apparent density, opacity, roughness, all mechanical properties and reduced bulk, brightness and air permeability. The addition of nanofibrils was different between the two reinforcement methods. The MT method promoted mechanical properties improvement as nanocellulose content was increased. Papers obtained from CT method presented lower mechanical strength values compared to the MT method. Finally, it is concluded that both the mixing of different fibers and the addition of nanofibrils contribute to the improvement of paper quality properties and can become potential methods for high quality paper production or even to increase the added value of these products.

Keywords: Handsheets. Reinforcement methods. Paper quality. Pulping. Strength.

SUMÁRIO

PRIMEIRA PARTE

1 INTRODUÇÃO

O setor de papel e celulose apresenta destaque no Brasil. A produção brasileira de celulose em 2018 foi de aproximadamente 21,1 milhões de toneladas, sendo grande parte desse montante destinado à exportação. A produção de papel no mesmo período foi de 10,4 milhões de toneladas, destinados em maioria ao mercado interno. (INDÚSTRIA BRASILEIRA DE ÁRVORES - IBÁ, 2019). Esse setor apresenta demandas crescentes e muitos desafios nos dias atuais. Os principais desafios são a autossuficiência nos processos produtivos, a redução dos danos ambientais e o desenvolvimento de produtos com características e propriedades específicas para atendimento de um mercado cada vez mais exigente.

A qualidade da polpa e do papel são alguns dos principais parâmetros para o bom desempenho das indústrias de papel e celulose, pois são os principais produtos provenientes dessas indústrias e possuem íntima relação com os consumidores. A qualidade desses produtos está vinculada com sua utilização.

Existem inúmeros fatores que interferem na qualidade do papel, sendo o principal é a matéria-prima. Sua qualidade, quando usada na produção de papel e celulose, depende da espécie e o tipo de material (madeira e outros materiais lignocelulósicos) e de suas propriedades. Existem também fatores relacionados aos processos de produção, destacando-se os equipamentos, as variáveis do processo de cozimento, o processamento da polpa e o branqueamento. Na produção do papel destacam-se ainda o preparo da massa, os aditivos, os equipamentos e a consistência da massa. Além destes, existem também os fatores associados ao meio-ambiente e à mão-de-obra. Dentro da influência da matéria-prima na qualidade do papel, suas propriedades afetam fortemente a qualidade do produto final e/ou processo, como por exemplo, a facilidade de deslignificação e determinado comprimento de fibra que seja adequado para determinada aplicação. Além desses, outros fatores também podem afetar a qualidade como a composição química, idade, densidade, defeitos e propriedades anatômicas (vasos, parênquima e outras propriedades morfológicas). Portanto, faz-se necessário conhecer e entender como esse fator afeta a qualidade dos produtos finais, potencializando propriedades adequadas para cada aplicação e a combinação de fibras obtidas de diferentes matérias-primas pode ser uma alternativa em busca da melhoria da qualidade do papel.

A mistura de polpas celulósicas é a combinação de diferentes tipos de polpas (matérias-primas) em diferentes proporções. Busca-se, dessa maneira, obter um material com boa interação entre os vários tipos de fibras, que pode ter uma influência positiva na qualidade do papel produzido. Além disso, combinar diferentes fibras pode diminuir deficiências que polpas isoladas podem apresentar, como por exemplo, fracas interações e ligações interfibras provenientes de polpas de fibras com comprimento longo.

A mistura de fibras já é uma prática utilizada na preparação de muitos tipos de compósitos utilizados na construção civil, na indústria automobilística, etc. O objetivo é melhorar as propriedades dos materiais, principalmente a ductibilidade e a resistência mecânica.

Outra forma de melhorar a qualidade dos papéis produzidos é por meio da adição de micro ou nanofibrilas à estrutura do papel. A adição dessas pode melhorar a resistência mecânica dos papéis aos diversos tipos de solicitações, a hidrofilicidade, a ligação entre as fibras, as propriedades óticas dos papéis, entre outras, contribuindo para a produção de papéis com características superiores.

Diante do exposto, a mistura de polpas celulósicas, juntamente com a adição de micro e nanofibrilas, pode ser uma alternativa para a produção de papéis superiores e embalagens, conferindo a esses, propriedades diferenciadas, devido à grande variação nas propriedades e interações das diferentes fibras, principalmente a biometria e ligações interfibras, que irão afetar a qualidade dos produtos. A mistura de polpas pode potencializar as qualidades e minimizar os problemas que são encontrados em polpas puras, como a contribuição da melhoria das ligações entre fibras e melhoria de propriedades físicas, químicas, óticas e mecânicas. Além disso, a mistura de diferentes matérias-primas para a produção de papéis pode contribuir para a diversificação das fontes de matérias-primas usadas nas industrias, de forma a retirar a pressão sobre a madeira e utilizar novas fontes renováveis/resíduos.

Portanto, esta tese teve como objetivo desenvolver papéis que apresentam qualidades superiores utilizando a mistura de polpas celulósicas obtidas de diferentes fontes, em diferentes proporções. Além disso, objetiva-se avaliar como as características da matéria-prima afetam a qualidade dos papéis produzidos e a influência da adição de nanofibrilas de celulose de sisal na qualidade do papel.

2 REFERENCIAL TEÓRICO

2.1 Matérias-primas

A principal fonte de matéria-prima para a produção de papel e celulose no mundo provém da exploração das árvores, sejam elas coníferas ou folhosas. Dentre as espécies de folhosas mais utilizadas destacam-se *Populus sp., Eucalyptus sp., Betula sp., Acacia sp.* e *Quercus sp*. Já para as coníferas destacam-se o *Pinus sp., Picea sp., Abies sp.* e *Spruce sp*.. Além destas, em alguns países são produzidos significativamente celulose e papel a partir de outras matérias-primas como o bambu, resíduos agrícolas, gramíneas e outras espécies arbóreas (ILVESSALO-PFĂFFLI, 1995).

As principais matérias-primas utilizadas no Brasil para a produção de papel e celulose são eucalipto e pinus, conhecidas comumente por celulose de fibra curta e longa, respectivamente e correspondem a mais de 95% da produção brasileira de papel e celulose (IBÁ, 2019). Embora no Brasil ainda seja inexpressível, outras matérias-primas fibrosas não-madeira também são utilizadas nas indústrias.

Fibras não madereiras podem futuramente se tornar potenciais fontes de matéria-prima no mundo. Essas fibras podem se tornar alternativa para caso de colapso no fornecimento de madeira em muitos países. Em geral, dentre as principais vantagens de se utilizar essas matérias-primas estão: alto rendimento de matéria seca por hectare; menor teor de lignina; facilidade de deslignificação e baixo custo da matéria-prima. No entanto, exigem maiores estudos; readequações; custos operacionais; fornecimento adequado em quantidade e qualidade; baixa densidade e alto volume; alto teor de sílica e dificuldade no manejo de algumas matérias-primas (ASHORI, 2006).

Existem variadas matérias primas que podem ser utilizadas para a produção de papel e celulose que não são comumente utilizadas. Diversas pesquisas são realizadas com objetivo de apresentar as potencialidades de matérias-primas não convencionais e destiná-las para a produção de papel e celulose. Alguns exemplos são o uso de palhas de trigo (IHNÁT et al. 2015), palha de milho (ROMÃO, 2015; LATIBARI; POURALI, 2019), folhas de palmeiras (SAEED et al. 2017), bagaço de cana (SAMARIHA et al., 2013; MAMAYE et al., 2019) haste de painço (SAEED et al. 2017), entre outras. Existe ainda, a possibilidade do uso de algas para a produção de papel e celulose (SANANDIYA et al. 2017; KUMAR; PATHAK; BHARDWAJ, 2020) ou mesmo plantas marinhas (SYED; ZAKARIA; BUJANG, 2016).

Portanto, existe grande diversidade de matérias-primas que podem ser utilizadas para a produção de celulose e papel. A utilização dessas matérias-primas depende de vários aspectos, dentre eles a disponibilidade em quantidade e qualidade; fatores econômicos, sociais e ambientais, além de fatores tecnológicos e culturais. Essas matérias-primas apresentam diferentes propriedades que precisam ser caracterizadas e entendidas de forma a maximizar a utilização de suas propriedades.

Dentre as matérias-primas usadas para produção de celulose e papel no Brasil, merecem destaque o eucalipto e o pinus, devido à grande produtividade, adaptabilidade, qualidade e por ter um parque industrial consolidado. A fibra do sisal também pode se tornar potencial fonte de fibra no Brasil e, juntamente com eucalipto e sisal, serão objeto de estudo nessa pesquisa. As principais características médias desses materiais estão apresentadas na Tabela 1.

Tabela 1- Composição química e anatômica média das principais propriedades nas diferentes matérias-primas.

Propriedade	**Sisal**	**Eucalipto**	**Pinus**
Comprimento da fibra (mm)	1,5 - 4	0,7 - 1,2	2,7 - 3,5
Largura fibra (mm)	10 - 30	15 - 25	30 - 45
Espessura parede (mm)	6 - 9	4 - 8	6 - 10
Celulose (%)	65 -75	45 - 55	40 - 50
Polioses (%)	7 - 20	20 -35	20- 30
Lignina (%)	7 - 13	20 -27	25 - 30
Extrativos (%)	5- 10	3 - 10	5 - 10
Minerais (%)	< 1	< 1	< 1

Fonte: Guimaraes et al. (2010); Martin et al. (2009); Rowell (2004).

2.1.1 Sisal

O sisal é uma planta pertencente à família Agavaceae, que possui suas fibras muito exploradas em indústrias têxteis, construção civil e cordoarias. O sisal é representado principalmente pela espécie *Agave sisalana*. A Bahia é o estado que mais explora comercialmente essa fibra, com mais de 95% do total da produção brasileira (MEDEIROS et al. 2016).

Diferentemente de outras espécies, as fibras estão localizadas na folha. É uma planta muito rústica, sendo cultivada em diferentes climas, principalmente em regiões semiáridas.

Realiza-se cortes a cada seis meses a partir dos três anos de idade e seu manejo é facilitado. Por ser muito resistente, a fibra é usada para confecção de produtos como cordas, barbantes e na indústria têxtil (EMBRAPA, 2008). Suas fibras possuem elevada resistência mecânica à tração, alongamento e alto módulo de elasticidade.

As fibras do sisal, por apresentarem alto teor de celulose e baixo teor de lignina juntamente com alta resistência mecânica, podem ser aplicadas para a melhoria de algumas propriedades dos papéis. As fibras do sisal foram usadas para realizar misturas com outras fibras, melhorando as qualidades de papéis reciclados por Behera, Patel e Mishra (2015). A característica que mais impactou a melhoria das propriedades dos papéis foi a resistência à tração das fibras de sisal, que conferiu incremento na resistência das fibras de pior resistência dos papéis reciclados.

2.1.2 Eucalipto

As fibras de árvores são as mais usadas em processos de polpação e fabricação de papel no Brasil. Dentre as árvores utilizadas, o eucalipto destaca-se, representando mais de 86% da produção de papel e celulose no Brasil (IBÁ, 2019). As fibras do eucalipto são consideradas curtas e possuem boas características morfológicas, permitindo qualidades essenciais ao produto final, referentes às ligações entre fibras, estrutura e propriedades físicas. Sendo assim, os papéis produzidos por fibras de eucalipto são apropriados para múltiplos usos, como para o papel de escrita, impressão e para a confecção dos papéis tissue.

No entanto, no tocante à resistência mecânica, para algumas utilizações do papel como é o caso de embalagens e outros tipos de utilizações, a fibra do eucalipto não oferece boas condições de resistência, principalmente quando é levada em consideração a resistência ao rasgo e ao arrebentamento. Além disso, a sua qualidade pode ser comprometida por fatores relacionada ao processo de produção, como na polpação ou no branqueamento (FOELKEL, 2010). Portanto, considerando essas desvantagens, a fibra de eucalipto necessita de melhorias em suas propriedades mecânicas.

2.1.3 Pinus

A “fibra” (traqueíde) de pinus é a segunda em maior destaque dentro do setor de celulose e papel no Brasil, sendo superadas apenas pelas fibras de eucalipto. Segundo o IBÁ (2019), a produção de celulose de Pinus atingiu 2,3 milhões de toneladas. A celulose proveniente da polpação do Pinus é usada principalmente na produção de embalagens e papéis cartões.

A composição do pinus difere do eucalipto principalmente nas características químicas e anatômicas. O Pinus apresenta boas características anatômico-morfológicas para um certo uso, tendo uma menor rigidez e resistência alta, principalmente na resistência ao rasgo. Além disso, apresentam elevado teor de lignina e extrativos que são indesejáveis para a polpação e branqueamento. Outra característica está no tipo de lignina presente nesses materiais, ou seja, o tipo majoritário de estruturas monoméricas para formação da lignina (SILVA JÚNIOR et al., 1994).

Embora apresente parâmetros adequados à polpação e qualidade de vários papéis e embalagens, a ligação entre as “fibras” do pinus necessita de melhorias, já que é uma matéria-prima que não apresenta uma interligação adequada, principalmente quando se leva em consideração características como a resistência a tração, a formação da folha, propriedades superficiais, velocidade da máquina de papel, propriedades da polpa, entre outras propriedades (CIT, 2013).

2.2 Qualidades das matérias-primas

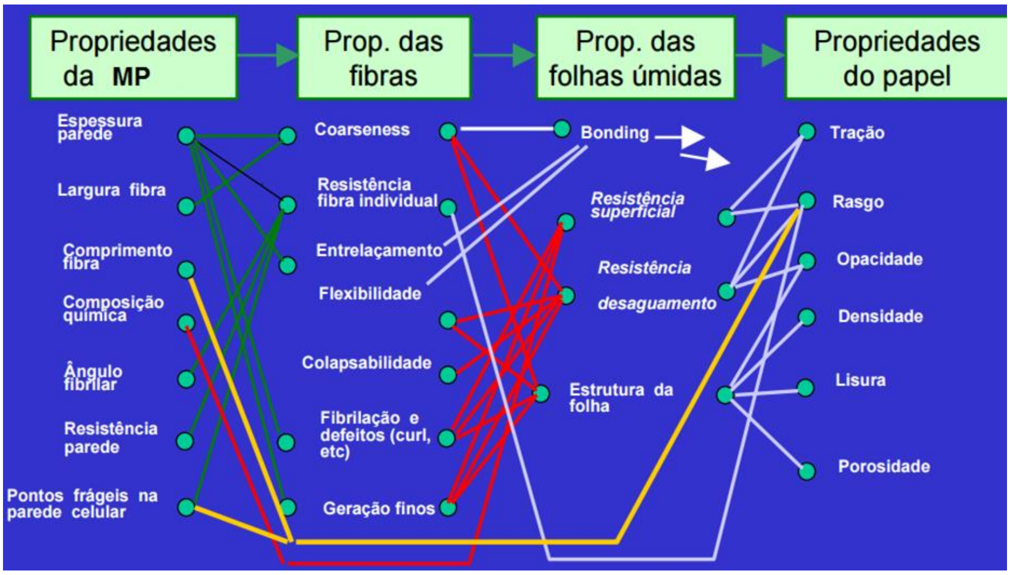
As características das matérias-primas têm relação muito forte com a qualidade do produto final. Essa relação pode ser direta ou indireta dependendo da característica (BIERMANN, 1996). Dentre as principais características das matérias-primas que estão relacionadas a qualidade da polpa e do papel podem-se destacar a morfologia das fibras (comprimento e largura das fibras, espessura da parede e largura do lume), a densidade, higroscopicidade, porosidade, a composição química (teor de celulose, hemicelulose e lignina, tipo de lignina, tipo e teor de extrativos, minerais, grau de polimerização e cristalinidade da celulose), propriedades anatômicas (proporção de lenho inicial e tardio, vasos, relação cerne/alburno, parênquima, percentagem de fibras, ângulo microfibrilar), elementos indesejados (teor e tipo de minerais e impurezas) e os defeitos (nós, madeira de reação e lenhos diferenciados) (POPA, 2013). Assim, diferentes tipos de papéis requerem diferentes propriedades e estas são dependentes principalmente da qualidade da matéria-prima

A morfologia das fibras é uma das principais características usadas no setor, já que pode ser mensurada rapidamente e impacta negativa ou positivamente as propriedades dependendo da aplicação. Por exemplo, o uso de fibras curtas, comparado com fibras longas, melhora a formação e estrutura da folha, a maciez, a superfície, ligação entre fibras, a resistência à tração e as propriedades óticas. Por outro lado, reduz a resistência mecânica principalmente ao rasgo, a porosidade, a drenagem e a velocidade da máquina de papel. Assim, a morfologia das fibras afeta diretamente a aplicação e pode ser predita baseado nas propriedades dos papéis em determinado uso. (NANDKUMAR, 2009).

As principais associações envolvendo características das matérias-primas com a qualidade do processo e do produto final no setor de papel e celulose são: As fibras curtas, afetando a formação da folha, a resistência ao rasgo e a melhoria das propriedades superficiais; a lignina, afetando o consumo de reagentes, o tempo de cozimento, o teor de lignina residual e branqueamento; as fibras longas, afetando a velocidade da máquina de papel, a resistência ao rasgo e propriedades da polpa. Além disso, outros elementos anatômicos impactam a resistência, a formação das folhas e o teor de finos. O teor de cinzas e extrativos é indesejado ao processo, afetando o rendimento, a recuperação de reagentes e causando entupimentos nos equipamentos (EK; GELLERSTEDT; HENRIKSSON, 2009).

Portanto, alguns fatores que impactam a qualidade do papel estão relacionados à matéria-prima. A relação entre as características e as propriedades não são harmônicas, conforme Figura 1. Existem propriedades do papel que são diretamente relacionadas com as características da matéria-prima, e outras são indiretamente relacionadas. Ainda, as propriedades são em maioria inter-relacionadas.

Figura 1- Relação entre as propriedades da matéria-prima e as propriedades do produto/processo.



Fonte: Foelkel (2017).

2.3 Mistura de fibras para produção de papel

A mistura de fibras é o ato de juntar/mesclar/combinar diferentes fibras com objetivo de melhorar propriedades do papel, principalmente quando comparadas com fibras isoladas. A combinação de fibras possibilita o aprimoramento da qualidade dos papéis através de associações entre diferentes matérias-primas, uma vez que essa interação pode trazer incrementos na resistência e propriedades físicas (HENDRY; HANSSENS, 1987).

A mistura de fibras pode apresentar sinergismo em determinadas combinações. O efeito sinergético ocorre quando existe a combinação de dois ou mais produtos causando um ganho em relação à soma dos efeitos individualizados (GEHLEN, 2014; MASROL et al., 2020). No caso da mistura de fibras, algumas propriedades podem ser potencializadas e apresentar melhores resultados quando utilizadas em conjunto, do que quando comparadas isoladamente. Caso o resultado seja inferior aos efeitos individualizados, ocorre o efeito antagônico, no qual as associações apresentam desempenhos insatisfatórios quando são comparados ao desempenho isolado, podendo haver características que afetem negativamente outras.

A mistura de fibras longas com fibras curtas pode apresentar inúmeras vantagens e aplicações na indústria de papel e celulose. Devido à grande variabilidade de suas características, a mistura de fibras visa trabalhar com as diferentes propriedades em busca de alcançar algum objetivo, potencializando vantagens e reduzindo desvantagens de determinadas matérias-primas. Assim, essas características podem ser melhor trabalhadas de forma a adequar a uma determinada aplicação. Por exemplo, em geral, fibras de coníferas apresentam drenagem ruim, menor resistência à umidade, altos teores de extrativos/resina e deficiência na formação da folha e ligações interfibras. Em contrapartida, apresentam boas propriedades mecânicas, especialmente à resistência ao rasgo, menor heterogeneidade, afeta a velocidade da máquina de papel e textura adequada (BARRICHELO, 1980). É possível, com a mistura de fibras, usar diferentes características em busca de um objetivo final.

Segundo Manfredi et al. (2008), a adição de polpas de eucalipto em polpas branqueadas kraft de *Pinus radiata* promoveu aumento da força de ligação entre as fibras, melhorando as propriedades de índice de tração, índice de estouro e opacidade.

No entanto, algumas propriedades mecânicas podem ser reduzidas quando são adicionadas grandes quantidades de polpas provenientes de folhosas em misturas. As principais propriedades são o índice de tração, o rasgo e índice de estouro. Isto se deve às características intrínsecas das matérias-primas, principalmente parâmetros morfológicos das fibras e ligações interfibras. Já as propriedades óticas (opacidade e brilho) são melhoradas com a adição de fibras de folhosas na mistura (SAMARIHA et al. 2013).

Portanto, a mistura de fibras pode trazer diferentes consequências às propriedades dos papéis, com efeitos sinergéticos ou antagônicos, mas que, dependendo da aplicação que o produto irá desempenhar, pode gerar ganhos e apresentar propriedades superiores aos papéis provenientes de polpas isoladas. A Tabela 2 mostra algumas pesquisas envolvendo a mistura de fibras entre coníferas e folhosas e a consequência da mistura de fibras em suas propriedades.

Tabela 2- Levantamento bibliográfico de estudos envolvendo a mistura de fibras de madeira (coníferas e folhosas).

Autor	**Mistura**	**Resultados e Conclusões**
Foelkel e Barrichelo (1975)	Polpas karft de *Eucalyptus saligna* e *Pinus caribaea* (20, 40, 60 e 80 e 100% de cada polpa)	- Adição de pinus na mistura não afetou a resistência a tração. Em contrapartida, aumentou a resistência ao rasgo, dobramento, arrebentamento e o peso específico. - Adição de pinus na mistura reduziu a espessura.
Bugajer e Kuan (1980)	Polpas celulósicas comerciais de *Eucalyptus sp.* e *Pinus sp.* (33, 50 e 66% de cada polpa) em diferentes graus de refino	- Grau de refino influenciou as propriedades resultantes. Grau de refino em até 44° SR aumentou todas propriedades mecânicas - Adição de polpa de Eucalipto refinada na polpa de Pinus não refinada gerou elevado aumento nas ligações interfibras. Aumentou também a resistência mecânica.
Bassa et al. (2007)	Polpas *Eucalyptus grandis* x *Eucalyptus urophylla* e *Pinus taeda* (10 a 50 % de pinus na mistura)	- Aumento de pinus ocasionou diminuição da drenabilidade, número de fibras por grama, solubilidade, dos rendimentos brutos e depurados, viscosidade e do índice de tração e estouro. Em contrapartida, aumentou teores de lignina na polpa, consumo específico de madeira, coarseness e índice de rasgo.
Cit (2013)	Polpas de *Eucalyptus dunni M.* e *Pinus taeda* (5 a 30% de eucalipto na mistura)	- Aumento de eucalipto na mistura reduziu o número kappa, a viscosidade e refinabilidade das polpas. - Nos papéis formados ocorreram aumentos na espessura, gramatura, volume específico, alvura, permeabilidade e índice de rasgo e reduções no índice de tração, arrebentamento e permanência do ar.
Bassa (2008)	Polpas comerciais de *Eucalyptus globulus* e *Pinus taeda* no branqueamento	- Aumento de pinus na mistura (50%) aumentou o consumo de ClO_2 em 44%, e cloro ativo em 41% e reduziu a viscosidade em 17%. - Pequenas adições de pinus (10%) na mistura aumenta a resistência dos papéis devido à adição de fibras longas sem comprometer o branqueamento.

A mistura de fibras também pode ser realizada utilizando fontes de matérias-primas incomuns. Essas matérias-primas podem ser resíduos provenientes da exploração industrial e agropecuária, oferecendo vantagens quando utilizadas para esse fim, como é o caso da grande variabilidade de características, além de vantagens ambientais e econômicas. Alguns trabalhos que buscam utilizar essas matérias-primas de forma a atender determinado objetivo estão resumidos na Tabela 3. Por exemplo, Kim et al. (2014) estudaram a mistura de fibras de cânhamo em alguns papéis com o objetivo de melhorar a preservação de papéis. Foram variadas as quantidades de fibras de cânhamo presentes na mistura e determinadas as propriedades físicas, mecânicas e óticas nos papéis formados. Como resultados, o aumento da proporção de fibras de cânhamo melhorou significativamente as propriedades mecânicas, mas decresceu a opacidade dos papéis. Comparando as melhorias alcançadas, a mistura de pequenas proposições de fibras de cânhamo ao papel (10%) foi uma importante ferramenta para aumentar a preservação dos papéis.

Existe também a possibilidade da utilização da mistura de fibras para a melhoria da qualidade de polpas e papéis reciclados. Polpas semi-químicas virgens e recicladas foram misturadas por Ghasemian et al. (2012). Foram utilizadas polpas e papéis corrugados reciclados. Para a formação das folhas foram utilizadas misturas na proporção polpas recicladas:polpas virgens de 0:100, 20:80, 30:70 e 40:60. Houve tendência de aumento médio em aproximadamente 20% das propriedades mecânicas das folhas com o aumento da proporção de polpas recicladas, excetuando o teste de esmagamento por anel e teste de ondulação. Esse aumento foi devido à morfologia das fibras longas presentes no papel reciclado.

Andrade et al. (2001) usaram a mistura de fibras de bambu (*Dendrocalamus giganteus*) e bagaço de cana com de papéis reciclados (aparas) para a produção de papéis artesanais. Os papéis formados apresentaram boas propriedades. A adição de 20% ou mais de bagaço obtiveram papéis mais resistentes ao rasgo e ao dobramento (fold endurance). Alto teor de aparas (80%) e 20% de bagaço apresentaram melhor resistência ao arrebentamento e lisura. A adição de fibras de bagaço foi superior que o bambu para a melhoria nas propriedades dos papéis artesanais, uma vez que as fibras de bagaço apresentaram maiores interações entre as fibras (potencial de ligações) e fibras mais individualizadas.

Tabela 3- Levantamento bibliográfico de estudos envolvendo a mistura de fibras pouco comuns e resíduos com outras fibras.

Autor	**Mistura**	**Resultados e Conclusões**
Omari, Belfkira e Brouillette (2016)	Fibras de *Typha latifolia*, *Agave americana* e *Pennisetum alopecuroides* misturadas com polpas kraft comerciais (7,5; 15; 22,5; 30%)	- Adição das fibras melhorou propriedades mecânicas em 4x. - Fibras podem ser utilizadas como alternativa em misturas.
Veisi e Mahdavi (2016)	Polpas branqueadas de *Populus alba* e palha de trigo (25, 50 e 75% de cada polpa)	- Mistura de fibras apresentou sinergismo. - Resistências mecânicas maiores ou similares a papéis de jornais comerciais. - Maior quantidade de palha de trigo, melhores índices mecânicos.
Chaiarrekij et al. (2011)	Polpas Kapok (*Ceiba pentandra*) com polpas comerciais branqueadas de pinos e eucalipto (25% de Kapok)	- Adição de 25% de Kapok aumentou a resistência à tração (8%), arrebentamento (10%) e reduziu o rasgo (16%) e alongamento (7%).
Shamariha et al. (2013)	Polpas de bagaço de cana com polpa quimiomecânica de folhosa	- Adição de bagaço contribuiu para a redução de custos dos papéis produzidos e com qualidades comparáveis aos comerciais.
Zhang, He e Ni (2011)	Polpas de palha de trigo branqueada refinada com polpas de alto rendimento	- A adição de 5-10% de fibras de palha de trigo na mistura aumentou a resistência à tração de 10-20%.
Zao et al. (2010)	Polpas de bambu com polpa kraft de acácia	- Adição de bambu como fibra de reforço apresentou melhora nas propriedades mecânicas e óticas.
Azeez, Andrew e Sithole (2016)	Polpas de *Gmelina arborea* com o bambu (25, 50 e 75%)	- Índice de rasgo foi praticamente duplicado com aumento da proporção do bambu (25% para 75%).
Huang et al. (2016)	Polpas de bambu e conífera para papel de isolamento	- Adição de 10% bambu melhorou propriedades de isolamento elétrico.
Sridach e Paladsongkhram (2014)	Polpas de *Trema orientails* com polpas de *Typha angustifólia*.	- Maior proporção de fibras não madeireira (>50%) aumentou o índice de tração (45%), arrebentamento (112x) e rasgo (23%). - Aumento na resistência foi devido ao comprimento das fibras e ligação das fibras, fornecidas pela fibra não-madeira.

2.3.1 Variações da mistura de fibras

A mistura de diferentes fibras pode acontecer antes ou após a polpação. O período da mistura tem influência sobre a polpação e a qualidade dos papéis formados. Quando a mistura é realizada antes da polpação, os fatores que estão relacionados ao cozimento podem influenciar nas características das fibras como o teor de álcali ativo, a sulfidez e a relação licor/matéria (HENDRY; HANSSENS, 1987). Assim, nessa modalidade de mistura de fibras, as diferentes matérias-primas utilizadas devem ter propriedades próximas de modo a reduzir o impacto da polpação nas características das fibras.

O meio mais prático de realizar a mistura de fibras é após o cozimento. Após essa etapa, as polpas resultantes são então misturadas de acordo com determinada proporção ou combinação para a formação dos papéis. Esse método oferece vantagens e poucas desvantagens para a mistura de fibras, já que cada matéria-prima apresenta características diferenciadas e que, por isso, requerem processos diferenciados. Outra forma de realizar a mistura de fibras é misturar as diferentes matérias-primas antes da polpação, ou seja, durante a preparação da matéria-prima (mistura de cavacos). Assim, após as misturas, os processos subsequentes são realizados em conjunto (CHAUHAN et al. 2011). Esses processos são diferentes e também podem apresentar resultados desiguais, dependendo dos fatores que podem afetar a produção dos papéis, podendo inclusive melhorar algumas características e apresentar vantagens como o melhor desfibramento, fibras inteiras, cozimento mais uniforme e menor teor de rejeitos. Portanto, não há regra sobre a qualidade dos produtos caso sejam realizados de uma forma ou outra, já que existem muitos fatores que podem afetar as propriedades.

Neste sentido, Hou et al. (2011) estudaram o efeito do co-refino (refino conjunto) entre misturas de polpas de resíduo agrícola (palha de trigo) e folhosa com objetivo de reduzir gastos. O co-refino foi capaz de reduzir o consumo de energia gasto no refino em 30% sem afetar as propriedades de resistência à tração e rasgo dos papéis. A redução do consumo de energia foi determinada pelo conteúdo de palha de trigo na mistura.

O cozimento conjunto com diferentes matérias-primas pode trazer benefícios para propriedades mecânicas. Levit et al. (2013) estudaram a polpação conjunta de resíduos agrícolas (palha de trigo e milho) e cavacos comerciais de folhosas. As condições do cozimento Kraft foram razão licor/biomassa 4:1; alcalinidade de 16.0%; sulfidez de 22.0%; temperatura máxima de 165 °C e fator H 800. O rendimento da polpação e o número kappa foram pouco alterados em relação às misturas e a matéria-prima virgem. A mistura aumentou as propriedades mecânicas quando comparadas com polpas isoladas. Houve aumento máximo de 29% no índice de tração e de 12% no índice de rasgo para as amostras que continham palha de trigo na mistura. O aumento da resistência foi atribuído ao aumento no conteúdo de xilanas das polpas provocadas pelos resíduos agrícolas. O conteúdo de xilanas é um parâmetro crucial para as ligações interfibras e que por isso afeta as propriedades de resistência dos papéis.

A mistura de diferentes cavacos de madeira em diferentes proporções foi estudada por Gulsoy e Tufek (2013). Os autores misturaram cavacos de *Pinus pinaster* e *Populus tremula* em diferentes proporções (0, 25, 50, 75 e 100%) e submeteram ao cozimento kraft e posteriormente a produção de papéis. Como resultados, as polpas com maior número kappa, viscosidade e percentual de rejeitos foram observados em mistura com maior teor de Pinus. Maiores teores de Pinus resultaram em menores rendimentos totais e depurados. Já o aumento no teor de *Populus tremula* melhorou propriedades de refinabilidade. Para as propriedades do papel, o aumento no percentual de cavacos de Pinus contribuiu para melhoria das propriedades de resistência, no entanto, reduziu propriedades óticas e de aspereza dos papéis produzidos.

Jahan, Sarkar e Rahman (2015) realizaram uma mistura de cavacos de bambu e *Trema orientalis* e submeteram à polpação. Foram formados papéis e determinada suas propriedades. As misturas foram na percentagem de 0, 25, 50, 75 e 100%. A adição de *Trema orientalis* culminou em aumento no rendimento da polpação e redução no número kappa. Houve também aumento na resistência a tração com a adição da madeira de folhosa. A maior resistência ao arrebentamento foi obtida na proporção 50:50. Além disso, todas as misturas apresentaram capacidades similares de sofrer branqueamento. Os autores concluíram que a proporção de 50:50 dessas matérias-primas pode ser utilizado de forma a melhorar as deficiências de matérias-primas isoladas sem comprometer a qualidade dos papéis formados.

O refino pode também ser realizado de maneira isolada ou conjunta. Caso realizado de maneira conjunta, o grau do refino pode afetar as propriedades das polpas, principalmente daquelas oriundas de matérias-primas menos resistentes. Assim, a intensidade de refino tem que se dar pela matéria-prima menos resistente. Quando realizado de forma isolada, o refino é realizado respeitando as características e condições ótimas de cada matéria-prima (HOU et al., 2011).

Assim, pode haver a mistura de fibras provenientes de processos diferentes, ou seja, polpas refinadas e não refinadas. Segundo Kibblewhite (1977), a adição de polpas não refinadas em polpas refinadas pode levar a produção de papéis com qualidades físico-mecânicas comparáveis às polpas totalmente refinadas e com menor uso de energia durante o processo.

Já Nandkumar (2009) avaliou a mistura de polpas de *Ipomoea carnea* e bambu antes da polpação, depois da polpação sem refino, e depois da polpação com refino. O aumento (50%) no percentual de bambu na mistura aumentou a porosidade (25%), o índice de arrebentamento (21%), o índice de rasgo (22%) e reduziu a alvura (1%), o comprimento de autoruptura (12%) e o índice de tração (7%). A mistura dessas fibras depois da polpação e refino obtiveram melhores propriedades mecânicas, comparados com os demais. Além disso, a mistura das fibras após a polpação e sem refino apresentou melhores qualidades que a mistura de cavacos (antes da polpação).

Colson et al. (2016) promoveram uma mistura entre fibras longas e finos provenientes de processos mecânicos com objetivo de avaliar o comportamento reológico. Foram misturadas nas proporções de 25, 50, 75 e 100% de cada constituinte. Depois de misturados, foi realizada a caracterização da qualidade da polpa e avaliada para produção de nanofibrilas. Como resultados, o acréscimo de fibras longas em 50% reduziu a viscosidade em 22%. Já os finos de fibras utilizados melhoram a reologia das polpas podendo ser destinadas para a produção de nanofibrilas a partir da mistura.

A qualidade do papel é afetada por diferentes fatores, principalmente em misturas de fibras. Nesse sentido, Sim et al. (2012) avaliaram o efeito da composição das fibras e do refino na qualidade dos papéis nos testes de dobras. Para isso, os autores avaliaram o efeito da proporção na mistura de polpas de folhosas e coníferas branqueadas e o grau de refino das polpas. Os papéis formados foram afetados pela mistura de fibras, sendo o de melhor resultado 90:10, com maior proporção de folhosa. Valores fora dessa proporção apresentaram resultados insatisfatórios. Além disso, as polpas com maior intensidade de refino obtiveram melhor resultado nas propriedades mecânicas e para o teste de dobras.

Além disso, alguns tratamentos podem ser aplicados à mistura de diferentes polpas celulósicas com o objetivo de melhorar algumas propriedades, ou mesmo tornar o processo de mistura menos oneroso. O tratamento por enzimas pode ser aplicado em misturas de polpas celulósicas de matérias-primas diferentes, podendo reduzir o tempo de refino das matérias-primas e produzir polpas com qualidade similares às refinadas. Esse resultado se dá pela alta fibrilação e inchaço das fibras provocadas pelo tratamento enzimático (DIEN et al., 2014).

Uma combinação de polpas provenientes de diferentes processos (químicas e químiomecânicas) de uma mesma matéria-prima foi estudada por Xu (2007). A adição de 20% de polpas químiomecânicas nas polpas químicas apresentou sinergismos nas propriedades mecânicas dos papéis, sendo que as polpas misturadas resultaram em uma melhor resistência de ligação entre as fibras. Assim, o uso dessa mistura de polpas pode ser utilizado para melhorar os processos de formação de papéis.

2.4 Utilização de fibras como reforço

Atualmente, o uso de fibras como reforço em uma matriz é uma prática bastante comum, conferindo características marcantes aos produtos formados. As fibras naturais podem ser melhor utilizadas, já que oferecem vantagens sobre outros tipos de materiais. Dentre as vantagens destacam-se o fato de ser um recurso renovável, a abundância, o baixo custo, alta aplicabilidade, baixa densidade e alta resistência, mas também apresentam algumas desvantagens como é o caso da baixa durabilidade em alguns casos, a biodegradação e a variabilidade das propriedades (NECHWATAL; MIECK; REUßMANN, 2003).

As fibras celulósicas provenientes da polpação são largamente utilizadas para reforçar filmes. Fibras de resíduos de biomassa de frutos foram estudadas por Abdul Khalil et al. (2017) para reforçar filmes produzidos à base de algas marinhas, havendo melhoria nas propriedades mecânicas de mais de 2x com a adição de 50% de fibras.

O uso de mistura de fibras é muito utilizado como reforço em compósitos com objetivo de melhorar as propriedades reológicas dos materiais. Ren et al. (2015) desenvolveram polímeros biodegradáveis reforçados por fibras longas e curtas. A adição de 20% de fibras melhorou a rigidez em 69% e a resistência ao impacto em 37%.

A adição de fibras provenientes do bagaço de cana e de bambu em outras polpas celulósicas pode ser utilizada com objetivo de melhorar algumas propriedades do papel. Além disso, a adição dessas fibras pode ser promissora e viável em papéis reciclados, podendo torná-los reutilizáveis, com boas propriedades e qualidade adequada, como alta ligação interfibras e resistências mecâncias elevadas (ANDRADE et al., 2001).

O uso de fibras celulósicas é também utilizado como reforço em papéis a partir da mistura com outros tipos de fibras (ZHAO et al., 2010). Mansfield, Kibblewhite e Riddell (2004) estudaram a caracterização do potencial de reforço do papel usando diferentes coníferas para misturas de fibras. As fibras eram provenientes do *Pinus radiata* e abeto. O potencial de reforço das matérias-primas nas misturas foi facilmente caracterizado e predito pela mensuração do índice da energia de fratura dos papéis formados por 100% de fibras de coníferas. As fibras apresentaram de potencial para serem usadas como reforço, principalmente devido as propriedades morfológicas das fibras.

2.5 Qualidade da polpa e papel

A qualidade dos produtos da indústria de papel e celulose tem como objetivo atender determinados requisitos, tais como as exigências dos consumidores e de fábricas. Portanto, é sempre necessários o aprimoramento e a busca da qualidade dos diferentes tipos de produtos.

De maneira geral, a qualidade dos produtos produzidos pelas indústrias de papel e celulose pode ser afetada basicamente por quatro fatores. O primeiro deles é a influência da estrutura das fibras e das propriedades da matéria-prima na qualidade dos produtos. Além deste, avalia-se o efeito dos processos de polpação e branqueamento, o impacto de aditivos e modificações e a influência das etapas de produção na qualidade dos produtos finais (SCOTT; TROSSET, 1989).

A melhoria da qualidade dos papéis pode ser realizada com intuito de alcançar diferentes objetivos. Dentro da melhoria da qualidade, diversas ações podem ser realizadas. A melhoria da qualidade pode ser realizada compreendendo os diferentes fatores que impactam a qualidade do produto final (DIAS; SIMONELLI, 2013). Os fatores que podem influenciar as propriedades do papel podem ser divididos em material (tipo, defeitos, composição, características, espécie); maquinário (equipamentos, processamento da polpa, cozimento, branqueamento); métodos (formação das folhas, preparo da massa, refino, aditivos); o meio ambiente (desperdícios, reaproveitamento, uso da água) e a mão-de-obra (qualificação e treinamento).

Entender como esses fatores influenciam a qualidade de determinado produto é primordial para o desenvolvimento de produtos que atendam determinada finalidade. Como exemplo, é possível destacar a densidade da matéria-prima. Segundo Ciolacu, Pitol-Filho e Ciolacu (2012), matérias-primas menos densas tendem produzir menos celulose por volume, economizar álcali e reagentes, ter menos rejeitos, ter refinação mais fácil, permitir menores velocidades de máquinas, produzir papel mais liso e apresentar maiores índices de tração (tensile index). Já matérias-primas densas tendem a produzir papéis com propriedades opostas aos produzidos por matérias-primas menos densas e com maior resistência ao rasgo (tear strenght), além de maior dificuldade para a polpação e maior quantidade de celulose por volume. Em geral, a densidade ideal para a produção de papel e celulose encontra-se na faixa de 0,4 a 0,6 g/cm³.

Algumas qualidades requeridas de papéis e sua relação com as propriedades das fibras estão relatadas na Tabela 4. O sisal positivo (+) indica que determinada propriedade da fibra tem relação direta (afeta positivamente) com a propriedade do papel, enquanto o sinal negativo (-) indica relação contrária.

Tabela 4**-** Correlações entre a qualidade das fibras e do papel.

Propriedade do papel	**Propriedade das fibras**
Resistência à tração (Tensile Strenght)	Comprimento da fibra (+) Diâmetro do lume (+) Espessura da parede da fibra (-) Coeficiente de flexibilidade (+) Fração parede (+) Índice de Runkel (-)
Resistência ao rasgo (Tear Strenght)	Comprimento da fibra (+) Espessura da parede da fibra (-) Largura da fibra (-) Coeficiente de flexibilidade (+) Índice de enfeltramento (+) Fração parede (+) Índice de Runkel (+)
Resistência ao arrebentamento (Bursting Strenght)	Comprimento da fibra (+) Diâmetro do lume (+) Espessura da parede da fibra (-) Largura da fibra (-) Coeficiente de flexibilidade (+) Índice de Runkel (+)
Peso específico (Apparent density)	Espessura da parede da fibra (+) Coeficiente de flexibilidade (+)
Opacidade (Opacity)	Espessura da parede da fibra (+)

Fonte: Barrichelo e Brito (1976)

Segundo Tasman (1992) a qualidade do papel é influenciada pela sua formação, direção das fibras, espessura, densidade, lisura, opacidade, propriedades mecânicas, porosidade, absorção de líquidos, estabilidade dimensional e defeitos. Além dessas, outras características que podem afetar a qualidade estão associadas ao comportamento da polpa durante a formação do papel, como a drenagem, retenção, floculação, orientação, teor de sólidos e gramatura.

As aplicações dos papéis são diversas, podendo ser utilizadas em uma grande variedade de funções. Os principais usos dos papéis são: papel imprensa, papel escrita e impressão, embalagens, papéis tissue (absorventes), papel cartão e cartolina e papéis especiais (filtros, fotográficos, coloridos, artesanato, capacitores, isolantes, antimicrobiano). Essas diferentes aplicações exigem diferentes propriedades dos papéis e assim, diferentes qualidades (VIDAL; HORA, 2012).

O uso do papel para impressão e escrita exige lisura (smothness/roughness), opacidade, boas ligações interfibra, alta resistência mecânica, gramatura e espessura adequada, adequadas propriedades óticas (optic properties), alto teor de hemicelulose, coarseness, imprimabilidade, estabilidade dimensional, resistência à água, porosidade (air permeance) e orientação das fibras. Para o papel imprensa ou jornal, não é necessária tanta resistência mecânica quanto o papel escrita ou embalagem, mas é necessária uma mínima resistência. A gramatura, porosidade, lisura, alvura e estabilidade dimensional são requeridas para essa aplicação (BIERMANN, 1996).

Para o uso em embalagens, o papel necessariamente tem que possuir alta resistência mecânica. Em embalagens mais rústicas e que exigem transporte de cargas, a resistência ao rasgo é a propriedade mecânica mais requerida. Para outras finalidades, outras propriedades podem ser essenciais, como a resistência à tração e ao arrebentamento. Em alguns casos, como para embalagens para embrulhos ou alimento, a aparência é fundamental. A impermeabilidade também é uma característica importante para o uso do papel como embalagem. Para embalagens de alimentos características como a permeabilidade ao ar e aspereza são importantes (LOPEZ, 1998).

Papéis tissue são papéis usados para fins sanitários e de absorção. Esses papéis devem apresentar grande capacidade de absorção (Cobb test), maciez, baixo teor de hemicelulose, teor de finos, espessura adequada, resistência a úmido, baixa gramatura, suavidade e textura agradável. Papel cartão deve apresentar alta gramatura, rigidez, boa orientação das fibras e formação, lisura, alta resistência e boas propriedades óticas (RATNIEKS; FOELKEL, 1996).

Os papéis especiais possuem propriedades singulares de acordo com a aplicação. Por exemplo, em papéis usados para cigarros, o controle da velocidade da queima do papel é determinante. Para papéis filtros é necessário ter resistência a úmido. Para papéis isolantes é necessário alto isolamento elétrico, resistência mecânica e ausência de materiais metálicos. Papéis fotográficos exigem lisura e brancura elevadas. Papéis usados em artesanato apresentem características de receberem coloração, elementos metálicos, resinas e outros materiais. Os papéis ainda podem apresentar características antimicrobianas e características de segurança no caso de papel-moeda, ingressos (FERREIRA, 2008).

2.6 Papéis superiores

Segundo Ferreira (1988) a definição de superior pode ser caracterizada como algo que está acima, de melhor qualidade e que se apresenta como muito bom, excelente e distinto. Este conceito pode ser aplicado em diferentes materiais quando apresentam características que os diferenciam da maioria, sendo estas características melhores para determinada aplicação.

Os papéis superiores podem ser aqueles que apresentem características que sejam desejadas para determinado tipo de uso/aplicação. Assim, os papéis superiores podem não apresentar todas as características apropriadas para algum uso, mas se destacam em alguma característica que impacta significativamente alguma aplicação (GATTI, 2008).

Com isso, é possível a criação de papéis superiores de forma a atender alguma finalidade, como a grande resistência às diversas solicitações requisitadas no caso de embalagens, o revestimento superficial e impermeabilização no caso de hidrofobicidade da água, a hidrofilicidade para papéis absorventes, a aceitação de acabamentos e o contato com alimentos. Portanto, a qualidade final do produto estará diretamente vinculada com sua aplicação e com os consumidores.

2.7 Micro e nanofibrilas

Fibras com dimensões reduzidas são utilizadas para melhorar a qualidade em materiais. Neste caso, são usadas partes de fibras em escala reduzida (nano e micro) com objetivo de melhorar alguma propriedade. Dentre as principais melhorias das propriedades com adição dessas fibras, a de maior destaque é o aumento na resistência mecânica (AL-SALEH; SUNDARARAJ, 2011; LU et al., 2020).

As micro e nanofibrilas podem ser utilizadas como reforço em materiais com objetivo principal de aumentar a resistência mecânica. Além disso, a adição de micro e nanofibrilas pode afetar a hidrofilicidade, características reológicas, revestimento e acabamento de muitos materiais. A adição das micro e nanofibrilas é comumente utilizada em filmes (MACHADO et al. 2012), polímeros (SAÏDI et al. 2017), papéis (CHARANI et al. 2013) para a melhoria de propriedades, conferindo qualidades desejáveis para a estrutura dos materiais a serem reforçados, como a melhoria nas ligações e nas propriedades físico-mecânicas.

A adição dessas fibras com dimensões reduzidas pode ser realizada como reforço para a estrutura dos papéis. Essa adição pode ser realizada por diferentes fibras, provenientes de matérias-primas com propriedades distintas e por diferentes metodologias (NOGI et al., 2009). Várias pesquisas são realizadas no intuito de melhorar propriedades com a adição dessas fibras na estrutura do papel.

A adição de micro e nanofibrilas podem aumentar as propriedades de resistência mecânica, além de outras propriedades físicas como as propriedades óticas, sem reduzir o conteúdo de sólidos no papel. Além disso, a adição dessas estruturas melhora propriedades de ligação entre as fibras e com outros produtos comumente utilizados na fabricação do papel, como elementos de enchimento, cargas e aditivos (HII et al., 2012). Podem ainda afetar propriedades físicas como a permeabilidade, lisura, e uniformidade podendo, portanto, impactar a qualidade dos diferentes produtos. Por exemplo, a permeabilidade a gás pode ser diminuída em até quatro vezes com a adição de celulose microfibrilada. Já a adição de nanofibrilas na estrutura do papel pode tonar o papel mais hidrofóbico (ZHANG et al., 2013).

Dentre as principais consequências que a adição de micro e nanofibrilas pode trazer para a qualidade do papel estão: a melhoria das propriedades mecânicas; a melhor transferência de tensão durante as diferentes solicitações; a redução da massa dos papéis (requer menos quantidade de massa para atingir determinada resistência) e principalmente a melhoria nas interações interfibras (CHARANI et al., 2013; BALEA et al., 2018).

Neste sentido, Kose, Yamaguchi e Okayama (2015) verificaram a influência da adição dessas fibras nas propriedades e estrutura do papel. Os autores também examinaram os benefícios da adição de fibras de diferentes tamanhos no papel. Para isso, usaram micro, submicro e nanofibrilas. A adição de 10% aumentou o índice de tração em 40%, o alongamento até a ruptura em 35% e a absorção de energia por tração em 80% das folhas formadas e reforçadas. Isso ocorreu devido ao aumento das forças de ligação entre as fibras provocadas pela adição. Além disso, as diferenças na estrutura dos papéis (rede de fibras, porosidade, entreleçamento) também influenciaram a resistência mecânica dos papéis. Fibras de diferentes tamanhos conferiram propriedades de reforço também diferenciadas.

O uso de celulose nanofibrilada com o objetivo de aumentar a resistência em estruturas de papéis foi estudado por Sehaqui, Zhou e Berglund (2013). Neste estudo, os autores produziram papéis provenientes de fibras de madeira e celulose nanofibrilada. Assim, 10% de celulose nanofibrilada foi misturada com a polpas de fibras de abeto. A adição de nanofibrila de celulose aumentou a resistência à tração e a densidade em aproximadamente 75%. O aumento na resistência e densidade foram altamente correlacionados, demostrando que o aumento nas propriedades mecânicas é em decorrência do aumento da densidade dos papéis. Além disso, a absorção de energia por tração melhorou fortemente através da interação fibra-fibra favorável.

Nanofibrilas foram usadas como reforços de papéis provenientes de diferentes matérias-primas (bagaço de cana, conífera e folhosa). A adição de 5% de nanofibrilas melhorou as propriedades de resistência ao arrebentamento em 116%, tração em 20% e rasgo em12% em papéis formados tanto por fibras refinadas, como por não refinadas. No entanto, as propriedades óticas não foram influenciadas, não diferindo dos papéis sem adição de nanofibrilas (KUMAR, SINGH, SINGH; 2016).

A mistura de diferentes polpas celulósicas e o reforço de celulose microfibrilada (CM) de Kenaf e *Pinus sylvestris* foi estudado por Charani et al. (2013). As propriedades avaliadas foram a gramatura, a espessura, densidade aparente, resistência à tração, modulo de elasticidade, rigidez à tração e permeabilidade ao ar. A adição de polpas aumentou todas as propriedades excluindo a gramatura, comparadas com a polpa virgem de conífera. Já na adição do reforço de celulose microfibriladas houve aumento das propriedades, embora pequeno, para as pequenas proporções (2, 4 e 6% CM). No entanto, a adição de uma maior quantidade (10% CM) para as duas diferentes polpas apresentou aumentos de até 60% para o índice de arrebentamento e 30% para o índice de tração quando comparados com os papéis produzidos apenas por polpas virgens de coníferas. Os autores ainda relataram que a adição de celulose microfibrilada melhorou a interação fibras-fibras nos papéis produzidos.

A adição de diferentes qualidades de celulose microfibrilada (0, 2,5 e 5%) foi estudada por Hii et al. (2012) e teve como consequência a redução da drenagem da polpa e a melhoria de propriedades mecânicas dos papéis formados. Além disso, aumentou a resistência à passagem de ar e as ligações internas dos papéis.

3 CONSIDERAÇÕES GERAIS

Neste estudo, foram desenvolvidos papéis a partir da mistura de diferentes fibras e pela adição de nanofibrilas de celulose. A partir dos resultados, as seguintes conclusões e considerações podem ser feitas:

- A mistura de fibras pode afetar propriedades físico-mecânicas dos papéis trazendo melhorias em suas propriedades graças ao efeito sinergético provocado pelo uso de fibras de diferentes propriedades. Em geral, melhores resultados foram obtidos em misturas envolvendo as fibras do sisal e pinus, na proporção de 45/55%.

- O uso de fibras com propriedades morfológicas discrepantes favorece o sinergismo obtido com misturas de fibras.

- A adição de nanofibrilas em papéis misturados afeta propriedades físicas e melhora significativamente a resistência mecânica dos papéis.

- Os métodos de adição de nanofibrilas diferiram-se quanto aos resultados. O método de mistura durante a formação dos papéis apresenta melhores resultados mecânicos quando comparado ao método de recobrimento superficial dos papéis já formados.

- Em cada propriedade dos papéis, os tratamentos que obtiveram resultados destaques foram apontados e possíveis implicações foram sugeridas.

- Ambas técnicas melhoram propriedades dos papéis quando comparadas com papéis produzidos por polpas virgens e podem tornar-se potenciais tecnologias para melhoria desses produtos. Tipos de papéis com determinadas propriedades exigidas podem ser produzidos baseados em misturas de fibras e propriedades pré-estabelecidas. Pequenas e médias empresas que visem o aproveitamento de resíduos/aparas/papel reciclado podem utilizar a mistura de fibras para produção de novos produtos. O uso das nanofibrilas de celulose nas empresas de papel e celulose apresenta grande horizonte de exploração e melhoria de produtos em um futuro próximo.

-Sugere-se novos estudos envolvendo diferentes tipos de fibras (gramíneas, resíduos agrícolas, fibras não madeireiras, fibras madeireiras) em diferentes proporções e para determinar a percentagem ideal de nanofibrilas em determinados tipos de papéis.

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SEGUNDA PARTE – ARTIGOS

ARTIGO 1 - PHYSICAL AND MECHANICAL PROPERTIES OF PAPERS PRODUCED FROM DIFFERENT CELULOSIC PULPS BLENDING

Artigo redigido conforme normas do periódico científico Cellulose, sendo uma versão preliminar, que pode sofre alterações.

Abstract

Blending of different fibers can be an alternative for paper production due to synergetic effect. This study aimed to evaluate the effect of different fiber blending in physical-mechanical properties of papers and understand to what extent the fiber blending affects quality of produced papers. Three different commercial cellulosic pulps were used: eucalyptus, sisal and pine pulp. Fiber morphological analysis were performed after refining in each pulp. After refining, three pulps were blended two by two in 5/95%, 25/75% and 45/55% in all possible combinations. Virgin pulps (without blending) were also used for handsheet production. Handsheets were formed (2% consistency and 60 g/m²) in a lab paper-making machine and tested by physical and mechanical properties. Fibers differ regarded to morphological properties and indexes. Greatest differences were related to fibers length. There were statistical differences in all physical and mechanical properties. Differences was due to morphological properties. Highest and lowest treatments (blend proportion) were pointed out for each property. Thickness tend to decreased with fiber blending in all proportion. Thickness and grammage were not related. For all mechanical properties, lowest values were obtained in eucalyptus treatment and blending involving it. Highest values were obtained in pine, sisal and mixtures treatments. Small addition of sisal (5%) in eucalyptus pulp improved the tensile strength, tensile index, stretch, bursting index, tear index and fold endurance in approximately 41.5, 54.8, 51.4, 28.9, 37.5 and 33.3%, respectively. Same addition using pine instead of sisal resulted in improvement of 15.9, 22.7, 22.7, 37.4, 46.7 and 133.3%. Fiber blending presented synergetic effect for physical and mechanical properties.

Keywords: Fiber morphology, Handsheet, Mixing ratio, Mixture, Short fibers, Long fibers, Strength.

Introduction

Pulp and paper industries are crucial for the planted forest sector, and consequently, for Brazilian industries and economy, contributing to gross domestic product, taxes, trade balance and employments Pulp and paper are the main industrial consumer segment of planted forests in the country. Currently, Brazil is the world's second largest pulp producer and the eighth largest paper producer. Pulp production was approximately 21.1 million of tons in 2018, while paper production was 10.4 million of tons. Considering Brazilian production history, a clear trend towards increased pulp production is observed, while paper industries have stagnated (IBA 2019). This stagnation may be a result of Brazilian economy, internal consumption, insertion of digital technologies or even the need to create new enhancements and products which meet an increasingly demanding market for quality. Thus, paper industry is a potential and challenging industry within Brazilian context, which will demand new ideas, products, technologies and researches over the years to continue and increase competitiveness.

Papers are required in various purposes, such as writing, printing, packaging, special papers, newsprint and tissue papers. These applications request specific qualities, whether physical, mechanical or morphological. Mechanical properties are associated with materials strength and elasticity when submitted to stress. Physical properties are related to the structure, arrangement and the behavior when submitted to a certain action (Biermann 1996; Durán et al. 2018). Depending on properties and quality, papers can be suitable or intended for some applications. Papers used for packaging need high resistance, mainly to tear and bursting. Papers used in writing and printing need to be smooth, present proper printability and optical properties, dimensional stability and tensile strength (Scott et al. 1995; Bektas 2018).

Paper quality depend specially on the raw material used for production of the papers. Among the factors that affect quality, fiber morphology plays an important role. Fibers characteristics vary between the different materials used as raw material, including in the same species. Such variation can bring consequence to papers properties and affect application (Barrichelo and Brito 1975). These differences can be highlighted when working with distinct vegetable groups, as well as other chemical and anatomical differences. Hardwood tend to present shorter fiber length, width and cell wall thickness. Softwood tracheid are usually the opposite of those presented by the hardwoods. Non-wood fibers present great variation of these characteristics, and may be completed different from those presented by softwoods and hardwoods (Ashori 2006). Then, the large variation in raw materials characteristics can be better understood and worked aiming to obtain different behavior and papers qualities

Therefore, combination and blending of different types of cellulosic fibers can be an alternative for creating papers that have satisfactory qualities. Fiber blending is the act of merge, mixture and combine differentiated fiber properties, mainly regarding to morphology. Virgin pulps can present some drawbacks in paper production (Cit 2013; Danielewicz and Ślusarska 2019). For example, long fibers have not high tensile strength, suitable interfiber bonding, smoothness and paper formation. In contrast, short fibers need improvement in tear and bursting resistance and larger coarseness. Thus, as both have disadvantages, different fiber blending can increase paper properties, reducing deficiency and leveraging the benefits that certain virgin pulps may present.

Fibers blending have been targeted from some studies in the world. Researchers have studied and combined various fiber sources aiming to develop strong and quality papers. Generally, these studies look for improvement of physical-mechanical properties in deficient virgin pulps (Manfredi et al. 2008; Samariha et al. 2013; Chaiarrekij et al. 2011; Zao et al. 2010; Danielewicz and Ślusarska 2019; Kumar et al. 2019), paper preservation (Kim et al. 2014), reuse of recycled paper (Ghasemian et al. 2012; Claramunt et al. 2020), improvement of electrical properties (Hung et al. 2016; Mo et al. 2019), nonwoven materials (Hemamalini and Dev 2019) and interfiber bonding (Sridach and Paladsongkhram 2014) is also studied worldwide.

Most large pulp and paper industries use only one source of raw material due to logistical problems, variation and differences in species properties (Gulsoy and Tufek 2013). The main raw material used by these industries are wood. In Brazil, most used species are eucalyptus and pine, commonly known as short and long fibers, respectively (IBA 2018). Another alternative is non-wood fibers, such as annual plants and agricultural waste. These fibers have been already used in many countries, but are still incipient in Brazil (Ashori 2006). A great example is sisal, which has immense possibilities due to its fiber morphologic properties and production cycle (Embrapa 2008). The cited raw materials are examples of material which have huge variations in properties, besides considerable potential and can be used in fibers blending.

From this perspective, the blending of fibers with distinct characteristics can be an alternative to enhance paper properties and become a potential technique for improving paper quality. Thus, the combination of these fibers can have results not always expected and synergetic effect can be performed, enabling acquirement of papers that meets a particular application.

Therefore, this study aimed to evaluate the effect of different fiber blending (eucalyptus, sisal and pine fibers) in physical-mechanical properties of papers and understand how fiber blending affects quality of produced papers.

Material and methods

Material

Three cellulosic pulps were used for handsheet production: the eucalyptus pulp (*Eucalyptus sp)*, sisal pulp *(Agave sisalana)* and pine pulp *(Pinus sp)*. Pulps were partially bleached. Sisal and eucalyptus pulps were furnished by Lwarcell company, located at Lençóis Paulista in São Paulo state, Brazil. Pine pulp was furnished by Klabin company, located at Telêmaco Borba, in Paraná state, Brazil.

The choice of raw materials used in this study was performed according to difference in fiber properties, whether chemical or physical, but mainly morphological, and then, that could be engineered in order to obtain a product with desired characteristics.

Refining

First, a pulp refining pre-test was performed in order to obtain the ideal refining time for each pulp. Refining curves were elaborated for each pulp in the times of 15, 30, 45 and 60 minutes and then evaluated according to Schopper-Riegler test, following TAPPI T221 standard. An ideal refining time was obtained for each pulp. A laboratory hollander beater - REGMED HV-10 was used for refining. The Schopper-Riegler pneumatic -REGMED SR/A was used for refining evaluation.

Fibers morphological analysis

Subsequently, pulps were analyzed morphologically in order to know raw material properties after refining and how fiber properties could affect the quality of handsheets. Thereunto, a small portion of refined pulp was placed in a flask with water, and colored with two drops of safranin. Temporary slides were prepared for evaluations.

Measurements of fibers length and width, cell wall thickness and lume width were performed based on Iawa (1989) recommendations. Cell wall was obtained according to Equation 1. Twenty measurements were performed for each characteristic, and posteriorly descriptive statistics were determined. Measurements were conducted in a Ken-A Vision optic microscope, model TT-1010, in Dinocapture 2.0 software. Using these measurements, the main morphological indexes that impact paper quality were calculated. They are described in Table 1.

$$E\ (\mu m) = \frac{L - d}{2} \tag{1}$$

Where:

L= Fiber width (µm)

d= Lume width (µm)

Table 1 Morphological indexes for paper quality

Designation	Ratio
Felting rate	L / W
Elasticity coefficient	(d/W) x 100
Wall fraction	(2C/W) x 100
Runkel index	2C / d
Mulsteph index	$(W^2 - d^2) / W^2$
Boiler index	$(W^2 - d^2) / (W^2 + d^2)$

Where: L=Length, W= Width, d= lumen diameter, C= cell wall thickness

Handsheet forming and fibers blending

The pulp preparation for each raw material was performed in 2% consistency. Then, 200 g of pulp (absolutely dried) were weighted and added 10 L of water, during 48 hours to achieve hydration and swelling of fibers. After, pulps were disintegrated for cellulose suspensions production in a REGMED D-3000 pulp disintegrator. Propeller rotation was 2000 rpm. The time of each portion for disintegration was 2 minutes.

After suspension preparation, each pulp was refined according to ideal refining time, determined in the previous step. The equipment used for refining was the same used for the preparation of the refining curves. Ideal refining time for eucalyptus was 30 minutes and 45 minutes for sisal and pine. Pulps reached approximately 25 °SR in ideal refining time.

The different pulps were combined two by two in 5/95%, 25/75% and 45/55% ratio. 18 treatments were generated using all possible combinations of raw material and the three different ratios. In addition, 3 virgin pulps (without blending) were also used for comparisons, totalizing 21 treatments. Table 2 shows a summary of fiber blending and respective treatments. Fiber blending was performed taking into account the proportion of each constituent based on volume.

Table 2 Scheme of cellulosic pulps blending

Treatment	Eucalyptus (%)	Sisal (%)	Pine (%)
T1(100E)	100	-	-
T2 (100S)	-	100	-
T3 (100P)	-	-	100
T4 (5E 95S)	5	95	-
T5 (25E 75S)	25	75	-
T6 (45E 55S)	45	55	-
T7 (5E 95P)	5	-	95
T8 (25E 75P)	25	-	75
T9 (45E 55P)	45	-	55
T10 (95E 5S)	95	5	-
T11 (75E 25S)	75	25	-
T12 (55E 45S)	55	45	-
T13 (5S 95 P)	-	5	95
T14 (25S 75P)	-	25	75
T15 (45S 55P)	-	45	55
T16 (95E 5P)	95	-	5
T17 (75E 25P)	75	-	25
T18 (55E 45P)	55	-	45
T19 (95S 5P)	-	95	5
T20 (75S 25P)	-	75	25
T21 (55S 45P)	-	55	45

The mechanical stirrer Fisatom model 713d was used for homogenization and preparation of the different cellulosic pulps. Neither collage and pigmentation products nor retention agents were applied during handsheet forming. Recipients were adjusted for volume measurement, homogeneous mixture and blinding. Agitation was kept constantly during pulp blending. Figure 2 illustrates how was the suspension preparation and blending for handsheet forming.

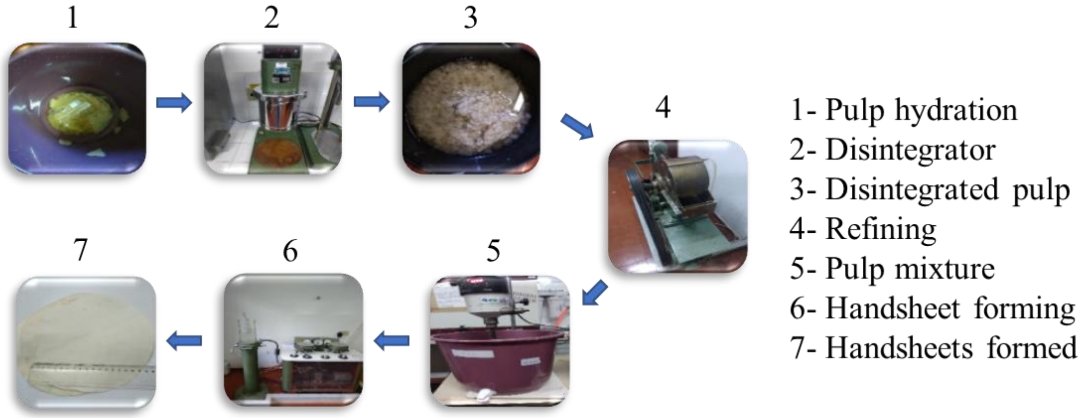

Fig. 1 Experiment scheme and recipient prepared for blending

Handsheets forming was performed based on consistency of approximately 2%, in order to reach 60 g/m² grammage, required to carry out paper tests. Handsheets were formed in a laboratory paper-making machine REGMED F/SS-2 with 20.2 cm diameter. Handsheets forming was based on TAPPI 205 standard. Three handsheet by treatment (repetitions) were formed.

After formed, handsheets were dried and subsequently conditioned in acclimatized room with temperature of 20°C ± 2°C and moisture of 65% ± 5ºC, aiming to eliminate moisture effect on paper properties and keep all samples in the same condition.

Handsheets were tested by physical and mechanical properties, shown in Table 3, along with respective standards. Regards to mechanical properties, handsheets were split following TAPPI T220 standard.

Table 3 Standards used for physical and mechanical properties

Properties	Standard
Thickness	TAPPI T 220
Volume	TAPPI T 220
Apparent density	TAPPI T 220
Grammage	TAPPI T 220
Specific volume (Bulk)	TAPPI T 220
Tensile properties	TAPPI T 494
Bursting strength	TAPPI T 403
Tear strength	TAPPI T 414
Fold endurance	TAPPI T 511

Statistical analysis

Experiment was conducted in a completely randomized design. The experimental unit were the handsheets produced from fiber blending and, as treatment, the variation among fiber type (raw material) and proportion. Three repetitions for each treatment were performed.

Handsheet properties were analyzed from analyses of variance (Anova) and having statistical differences between the averages of each property, a Tukey test (95% probability) was performed. Statistical analysis was performed in SISVAR software.

Variation graphs according to ratio of each pulp in the blends were generated. Correlations and regression analysis were carried out in order to relate raw material and paper properties, seeking for ideal proportion for some application, based on intrinsic characteristics.

Results and discussion

Table 4 shows fibers morphological parameters presented in cellulosic suspension after refining. Values comply with expected and reported in literature for these cellulosic pulps (Li et al. 2000; Gomide et al. 2005; Castelo et al. 2008). These characteristics are essential, impacting morphological indexes and then, paper quality. The fiber length is distinguished considering the materials. Fibers can be classified in three distinct groups. Eucalyptus fibers (881 µm) can be considered as moderately short fibers. Pine and sisal fibers (2808 e 3566 µm) can be considered as greatly long and extremely long fibers, respectively (Metcalfe and Chalk 1983). Fibers length affect paper mechanical properties, influencing interfiber bonding and strength. Generally, papers produced from long length fibers present high tear strength, possibility of high speed in paper machine and higher elasticity. On the other hand, fibers present low tensile strength, weak interfiber bonding and smaller softness (Nandkumar 2009). Cell wall thickness did not present great variation comparing the three materials, and was higher for sisal (6.1 µm) and similar for eucalyptus and pine. This characteristic impact coarseness, interfiber bonding and fibers network. Increasing of cell wall thickness improves tear strength and bulk, but handsheet forming, flexibility and interfiber bonding is compromised, rendering a more porous paper (Baldin et al. 2017).

Fibers width also presented same tendency of cell wall thickness, and was slightly larger in pine (19.9 µm), followed by sisal and eucalyptus (17.8 e 15.8 µm). Fiber width acts on collapsibility, slenderness and interfiber bonding. Lumen width is a characteristic that affect cell wall thickness and also interfiber bonding. Pine fibers presented higher lume width compared to eucalyptus and sisal who were statistically equal According to Pereira et al. (2003), low values of lumen width (fewer than 4 µm) negatively impact physical and mechanical properties, which is not the case of the fibers studied. Higher lume width was obtained from pine fibers, followed by eucalyptus and sisal.

Table 4 Fiber morphological measures in pulp after refining

Fibers morphology characteristics	Parameters	Material		
		Eucalyptus	Sisal	Pine
Length	Mean (µm)	880.8 c	3565.8 a	2807.5 b
	CV (%)	10.8	14.9	12.4
	Maximum (µm)	1087	4679	3475
	Minimum (µm)	734	2752	2263
Width	Mean (µm)	15.8 b	17.8 ab	19.9 a
	CV (%)	19.2	12.6	20.3
	Maximum (µm)	24	21	27
	Minimum (µm)	12	14	15
Lume width	Mean (µm)	7.1 b	5.5 b	11.6 a
	CV (%)	30.3	24.1	33.1
	Maximum (µm)	12	8	19
	Minimum (µm)	4	3	7
Cell wall thickness	Mean (µm)	4.4 b	6.1 a	4.2 b
	CV (%)	22.2	15.1	21.4
	Maximum (µm)	6	8	6.5
	Minimum (µm)	2.5	4.5	3

Means followed by same letter in row do not differ statistically from each other by Tukey test at 5% de significance level.

Morphological indexes, which was based on characteristics of fibers studied, are shown in Table 5. These indexes are associated with physical and mechanical properties of papers. Considering all indexes, all materials are potential fiber types for papermaking. However, they presented some difference related to fiber morphology, and will differently affect qualities and possible applications from papers. The indexes are also in agreement with literature and with similar species to those studied (Manfredi et al. 2008; Benites et al. 2018; Silva 2017).

Table 5 Morphological indexes related to paper quality after refining

	Material		
Parameters	Eucalyptus	Sisal	Pine
Felting rate	55.75	200.89	141.08
Elasticity coefficient (%)	44.62	30.99	58.29
Wall fraction (%)	55.38	69.01	41.71
Runkel index	1.24	2.23	0.72
Mulsteph index	0.80	0.90	0.66
Boiler index	0.67	0.82	0.49

Felting rate was quite different comparing the fibers, since this index is influenced by fiber length. Eucalyptus, pine and sisal felting rate can be considered as low, high and huge, respectively. This index is related to fiber slenderness and then, with tear and bursting strength (Mogollón and Aguilera 2002). Elasticity coefficient is related to fibers elasticity and possibility of connections between fibers, besides collapse. Higher index value turns fiber more flexible and presents greater rupture strength. Values are also different, especially for sisal that presents low value (30.99%). Wall fraction is connected with fiber stiffness and interfiber bonding. High wall fraction (above 60%) is not recommend for many applications, mainly those that require high tensile strength (Foelkel and Barrichelo 1975). Runkel index also indicates interfiber bonding capacity. Index values is directly related to interfiber bonding capacity. Therefore, especial attention must be observed for sisal fiber in some applications. According to Carrillo et al. (2015), values close and smaller to 1 are desirable and considered as favorable for paper properties, especially for writing and printing. Mulsteph and Boiler indexes are similar and related to fibers collapse. All materials present same tendency and can be considered suitable for paper making. However, high values (above 0.8 for both indexes) may compromise some applications, especially for sisal.

Fiber morphology, as well as its respective indexes, are crucial characteristics for paper application. For instance, long fiber papers tend to be used for packaging, corrugated papers and cardboard. Short fiber papers are more applied for writing, printing and tissue. Other parameters also influence physical, mechanical and optic paper properties and, therefore, must be understood (Biermann 1996).

The physical properties of blended papers are presented in Table 6 as well their statically analysis between treatments.

Table 6 Physical properties of blended handsheets

Treatment	Thickness (mm)	Volume (cm^3)	Grammage (g/m^2)	Apparent density (g/cm^3)	Bulk (cm^3/g)
T1 (100E)	0.170 ab	5.448 ab	67.3 ab	0.399 b	2.518 ab
	(± 0.03)	(± 0.87)	(±4.4)	(±0.04)	(± 0.26)
T2 (100S)	0.166 abc	5.325 abc	63.2 abcde	0.382 b	2.629 a
	(± 0.01)	(±0.41)	(±0.9)	(±0.03)	(±0.23)
T3 (100P)	0.156 abcd	4.999 abcd	66.4 abcd	0.427 ab	2.352 ab
	(±0.01)	(±0.30)	(±1.0)	(±0.03)	(±0.17)
T4 (5E 95S)	0.185 a	5.929 a	69.2 a	0.375 b	2.673 a
	(±0.01)	(±0.47)	(± 1.3)	(±0.02)	(±0.17)
T5 (25E 75S)	0.147 bcd	4.721 bcd	59.1 defg	0.401 ab	2.491 ab
	(±0.01)	(±0.42)	(±3.6)	(±0.02)	(±0.09)
T6 (45E 55S)	0.158 abcd	5.069 abcd	59.8 cdefg	0.378 b	2.644 a
	(±0.01)	(±0.16)	(±1.2)	(±0.01)	(±0.04)
T7 (5E 95P)	0.142 bcd	4.564 bcd	64.1 abcde	0.450 ab	2.232 ab
	(±0.01)	(±0.11)	(±5.4)	(±0.04)	(±0.17)
T8 (25E 75P)	0.147 bcd	4.711 bcd	65.7 abcd	0.448 ab	2.236 ab
	(±0.01)	(±0.25)	(±0.6)	(±0.02)	(±0.12)
T9 (45E 55P)	0.154 abcd	4.938 abcd	67.4 ab	0.437 ab	2.288 ab
	(±0.01)	(±0.10)	(±2.5)	(±0.02)	(±0.08)
T10 (95E 5S)	0.151 bcd	4.836 bcd	61.8 abcdef	0.410 ab	2.442 ab
	(±0.01)	(±0.19)	(±0.6)	(±0.01)	(±0.08)
T11 (75E 25S)	0.150 bcd	4.810 bcd	60.7 bcdefg	0.405 ab	2.471 ab
	(±0.01)	(±0.09)	(±0.8)	(±0.01)	(±0.05)
T12 (55E 45S)	0.155 abcd	4.975 abcd	64.0 abcde	0.413 ab	2.427 ab
	(±0.01)	(±0.37)	(±0.3)	(±0.03)	(±0.19)
T13 (5S 95P)	0.137 cd	4.407 cd	67.2 abc	0.490 a	2.052 b
	(±0.01)	(±0.24)	(±3.0)	(±0.05)	(±0.20)
T14 (25S 75P)	0.146 bcd	4.676 bcd	64.5 abcde	0.443 ab	2.264 ab
	(±0.01)	(±0.34)	(±1.8)	(±0.03)	(±0.18)
T15 (45S 55P)	0.137 cd	4.377 cd	57.3 efg	0.421 ab	2.386 ab
	(±0.01)	(±0.29)	(±2.0)	(±0.04)	(±0.21)
T16 (95E 5P)	0.147 bcd	4.708 bcd	64.3 abcde	0.438 ab	2.286 ab
	(±0.01)	(±0.14)	(± 1.6)	(±0.01)	(±0.06)
T17 (75E 25P)	0.145 bcd	4.644 bcd	64.6 abcde	0.446 ab	2.245 ab
	(±0.01)	(±0.05)	(±1.7)	(±0.02)	(±0.08)
T18 (55E 45P)	0.144 bcd	4.620 bcd	66.3 abcd	0.460 ab	2.178 ab
	(±0.01)	(±0.08)	(±1.8)	(±0.02)	(±0.10)
T19 (95S 5P)	0.135 d	4.316 d	53.3 g	0.397 b	2.524 ab
	(±0.01)	(±0.26)	(±0.3)	(±0.03)	(±0.16)
T20 (75S 25P)	0.142 bcd	4.553 bcd	55.6 fg	0.393 b	2.557 ab
	(±0.01)	(±0.32)	(±1.6)	(±0.04)	(±0.23)
T21 (55S 45P)	0.150 bcd	4.826 bcd	61.8 abcdef	0.411 ab	2.449 ab
	(±0.01)	(±0.22)	(±4.3)	(±0.04)	(± 0.26)
CV (%)	6.72	6.72	3.79	6.84	6.80

Means followed by same letter in column do not differ statistically from each other by Tukey test at 5% de significance level.

The paper thickness is dependent basically from fiber morphologic characteristics, specially fiber length and width, as well as factors related to paper production process (paper forming), which mainly affect fiber quantity in each treatment, and consequently paper thickness. Statistical difference occurred between treatments. The lower values were corresponded to treatment T19 (95S 5P), T15 (45S 55P) and T13 (5S 95P) and higher values were corresponded to treatments T4 (5E 95S), T1 (100E) and T2 (100S). It is observed that higher values may be associated to treatments with virgin pulps (100%). This allows to indicate that fiber blending tend to decrease paper thickness, since the different fibers are combined and reflect on this characteristic.

Generally, higher values in thickness are observed in handsheets produced using eucalyptus in the blending. This increase can be related to the participation of eucalyptus short-fiber in the formation of the interlacing network, making the paper less compact (Cit 2013). This same hypothesis can be related to pine and sisal long-fiber, which in general, presented lower values of thickness. It is not possible associate thickness variation with the ratio increase for the three materials. Thickness results from blended handsheets are in concordance with values found by por Cit (2013), Aqueela et al. (2018) who worked with fiber blending using similar raw materials. Also, thickness and grammage was not related as observed in Figure 2. This allows to conclude that grammage had small influence on thickness results and thickness was probably more impacted by the fiber morphology.

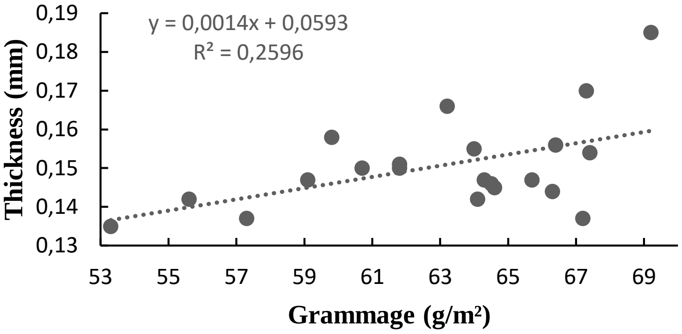

Fig. 2 The relationship between grammage and thickness

The physical property of volume presented the same thickness behavior, since it is a variable that is dependent of thickness and handsheet surface area, which remained constant for all treatments due to same diameter of handsheet former.

Grammage is a variable that affects other paper properties, especially strength properties and expresses the mass quantity present in a paper with pre-established area. Surface area for all treatment was approximately 320.5 cm². In handsheet forming, grammage was adjusted to be close to 60 g/m² for all treatments. According to Table 6, statistical differences occurred between treatments. Considering all treatments, a variation of approximately 30% among the higher and lower value occurred. The treatment with higher grammage was the treatment T4 (69.2 g/m²), while the lower value was obtained by treatment T19 (53.3 g/m²). Apparently, there is no relationship between the fiber ratio in blending, or even morphological characteristics of fibers and the grammage. It is more likely that the variation of this property is exclusively governed by factors related to handsheet forming, since the measurement for each proportion was based on volume and probably affected grammage.

The apparent density is an important parameter of conformability of individual fibers in fiber networks. According to Table 6, there are statistical differences between treatments, although these differences are not as significant as other physical properties. Differences can be related to individual fiber characteristics, such as flexibility and factors inherent in the production process. The highest values of handsheet density are associated to treatments which contained pine in their composition, such as T13 (5S 95P), T18 (55E 45P) T7 (5E 95P) and T8(25E 75P). These higher values can be associated to high flexibility of pine fiber (see elasticity coefficient in Table 5). According to Latifah et al. (2009) the increase in apparent density of blended paper is associated to insertion of more flexible fibers, which can render the paper more compacted and with higher number of fibers per volume unit, due to interfiber bonds and the fiber accommodation during handsheet forming.

Values obtained by treatments T1 (100E) and T2 (100P) and their respective combinations can be also related to fibers flexibility presented in Table 5. However, there is no clear behavior of this property as the proportion of material is increased or reduced in blending. This can be explained by variations in paper grammage during handsheet forming, which, in turn, reflected in the density. Another factor which can affect handsheet density is pulp chemical constitution, such as hemicelluloses content, which can contribute to the increase in density (Casey 1980). Besides, other morphological factors affect the interfiber bonding and, therefore, handsheet density, such as the fiber length. For instance, Latifah et al (2009) detected increase in handsheet density as the proportion of long kenaf fiber increased. However, such increment was very low, tending to stability. According to Jahan and Rawshan (2009), the addition of short fibers in blends can increase handsheet density, but this increment is mainly dependent of pulp refining rate, since the fibrillation affects in handsheet forming and in their volume.

The Bulk (specific volume) is an essential paper property, directly affecting application, mainly because influence paper structure and speed in paper machine. The bulk is affected by grammage and thickness. Statistical difference occurred between treatments. The higher values were treatments T4 (5E 95S), T6 (45E 55S) and T2 (100S) and the lowest value was treatment T13 (5S 95P). Generally, the bigger the bulk is, more consistent is the paper. Bulk differences can be related to compaction during paper formation. Cit (2013) reported that addition of short fibers can increase the paper bulk, since a more open fiber network is formed. However, such behavior was not observed in this study. Bhardwaj et al. (2018) also detected few variations in bulk and lack of a clear trend in blended papers.

Table 7 and Figure 3 present mechanical properties of blended handsheets. The mechanical properties are essential properties since affect paper quality and applications. Mechanical properties are represented by the ability of papers to withstand the action of external forces. Depending on application, paper must have a required amount of strength. For example, the higher tear strength value is, more appropriate the paper to be used in packaging.

Statistical results are presented in Table 7. According to this table, statistical differences occurred in all properties between treatments. Treatments obtained significant variation depending on property, like fold endurance. Considering the lowest and highest values, a difference of approximately 2.2, 2.3, 3.5, 3.3, 4.3 and 76.7 times occurred for tensile strength, tensile index, stretch, bursting index, tear index and fold endurance, respectively. Difference can be addressed to large variation in morphological properties and behavior of this properties when the fiber was blended since no additive, pigment or collage products was added in paper structure and physical properties do not influenced strength properties as illustrated in Figure 4. Generally, an enhancement in mechanical strength with increase of density or grammage is expected in virgin papers, since no variation are performed. However, this relation is not presented in blended paper since morphological differences play a key role in mechanical properties.

Table 7 Mechanical properties of blended handsheets

Treatment	Tensile strength (N/m)	Tensile index (N·m/g)	Stretch (mm)	Bursting index (kPa·m²/g)	Tear index (mN·m²/g)	Fold endurance (number)
T1 (100E)	1129 g	16.09 e	1.772 h	1.07 e	5.84 k	3 c
T2 (100S)	2424 ab	37.03 a	6.141 a	3.56 a	24.98 a	145 abc
T3 (100P)	2232 abc	32.59 abc	5.592 abc	2.99 ab	17.65 defg	115 abc
T4 (5E 95S)	2366 ab	32.96 abc	5.181 abcd	2.76 abc	22.99 abc	95 bc
T5 (25E 75S)	1699 cdefg	27.71 abcd	3.432 defgh	2.3 abcde	19.72 cde	36 bc
T6 (45E 55S)	1525 efg	24.72 cde	3.506 defgh	2.4 abcd	16.69 defg	22 bc
T7 (5E 95P)	2185 abcd	32.81 abc	5.964 ab	3.23 ab	17.28 defg	230 a
T8 (25E 75P)	2261 abc	33.39 abc	5.085 abcde	2.72 abc	15.37 gh	66 bc
T9 (45E 55P)	2015 abcde	28.87 abcd	3.627 defgh	2.14 bcde	11.52 ij	25 bc
T10 (95E 5S)	1598 defg	24.91 cde	2.683 fgh	1.38 de	8.03 jk	4 c
T11 (75E 25S)	1663 cdefg	26.44 bcd	2.985 fgh	2.08 bcde	11.28 ij	10 c
T12 (55E 45S)	1889 abcdef	28.68 abcd	3.158 efgh	2.09 bcde	15.72 fg	21 bc
T13 (5S 95P)	2445 a	35.00 ab	4.115 bcdef	3.22 ab	16.25 efg	201 ab
T14 (25S 75P)	2255 abc	34.04 abc	4.313 abcdef	3.19 ab	19.2 def	110 abc
T15 (45S 55P)	1832 bcdef	30.99 abc	4.148 bcdef	3.19 ab	19.83 bcd	112 abc
T16 (95E 5P)	1309 fg	19.75 de	2.174 gh	1.47 cde	8.57 ijk	7 c
T17 (75E 25P)	1750 cdef	26.38 bcd	2.906 fgh	1.6 cde	10.54 ij	11 c
T18 (55E 45P)	1893 abcdef	27.62 abcd	3.117 fgh	2.3 abcde	11.97 hi	23 bc
T19 (95S 5P)	1974 abcde	35.97 ab	4.147 bcdef	3.21 ab	23.28 ab	85 bc
T20 (75S 25P)	2007 abcde	34.84 ab	3.868 cdefg	2.63 abcd	22.99 abc	154 abc
T21 (55S 45P)	1969 abcde	30.75 abc	3.335 defgh	3.55 a	18.06 defg	114 abc
CV (%)	10.10	10.47	16.06	16.58	9.31	30.93

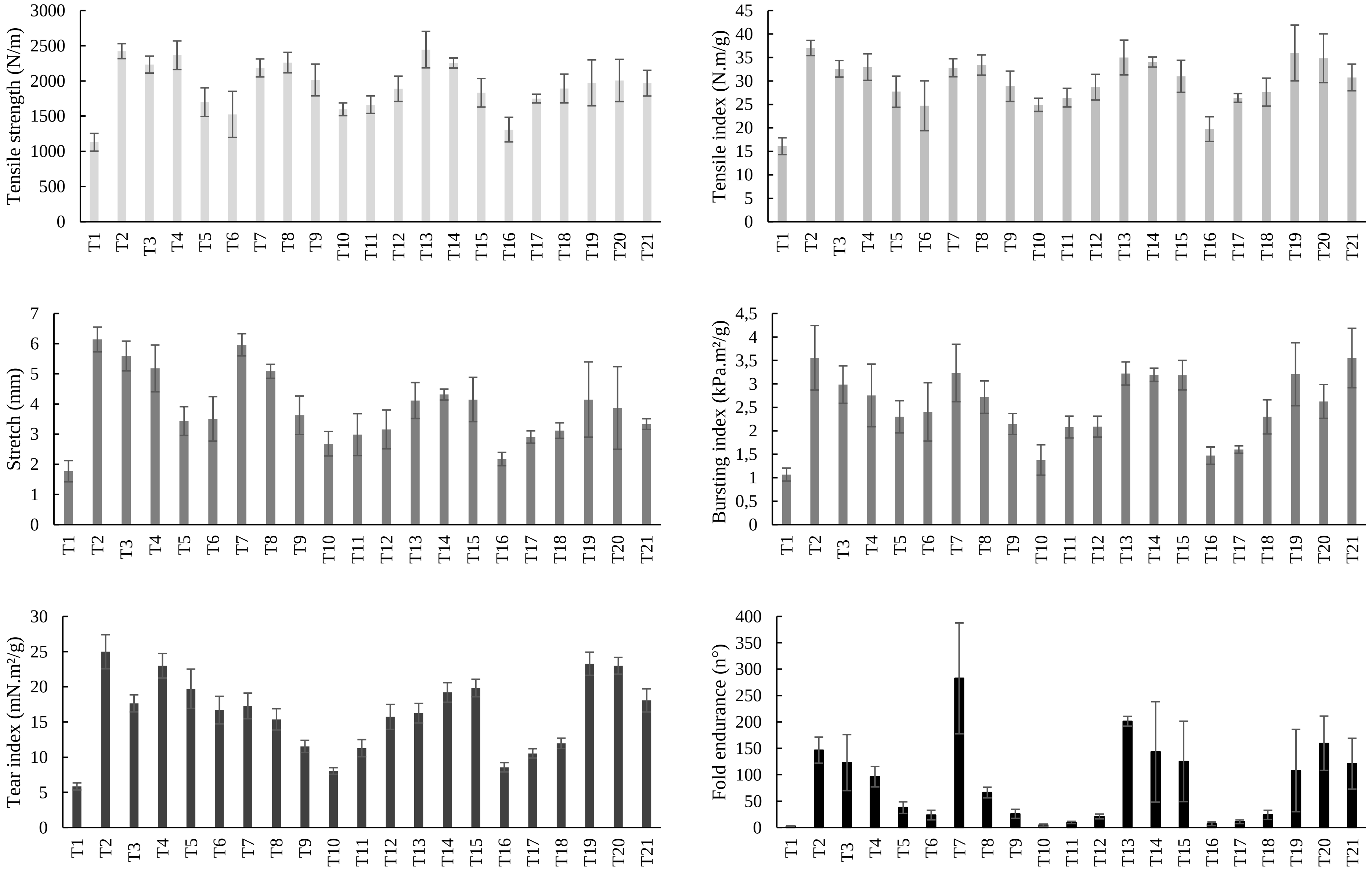

Fig. 3 Mechanical properties of blended handsheets in graphic

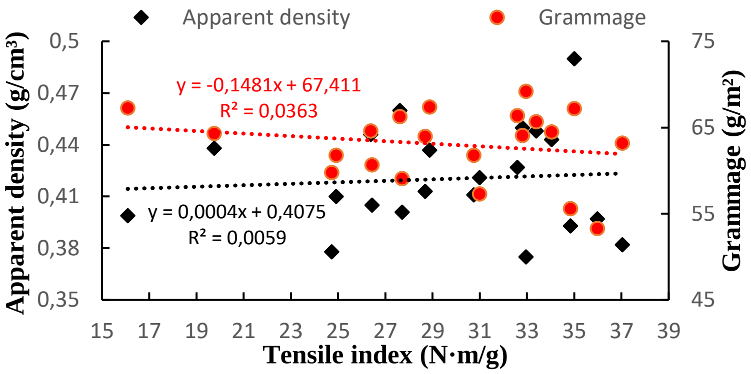

Fig. 4 Relationship of tensile index and physical properties

In general, the lowest values for all mechanical properties were represented by eucalyptus pulp or mixtures involving it. Small values of fold endurance, bursting and tear index was expected due to morphological properties of eucalyptus fiber, such as short fiber length, felting rate and individual fiber strength. According to Munawar et al. (2018), tear and bursting strength is impacted by fiber morphology, especially fiber length, interfiber bonding and small values of these properties is obtained by short fibers. Fold endurance follows same tendency (Tanifuji et al. 2018). However, low values in the tensile properties was not expected especially on blending with long fibers. Short fiber from eucalyptus pulp could have acted as fine structures in fiber network and improved tensile tension transference between fibers and tensile properties. As stated in Motamedian et al. (2019), the fine addition on long fiber pulps have a substantial contribution to the increased strength and stiffness of the handsheets. Zhang et al. (2011) reported that short fibers can act like connection elements and improve interfiber bonding. Despite that, similar result to those obtained in this study was found by Cit (2013), who reported a reducing tendency in tensile index values as the participation of eucalyptus in the mixture with pine pulp increases.

Highest values were found in sisal, pine and in blending of this fibers for all mechanical properties. This result can also be explained by morphological properties (long fibers) and high individual fiber strength. The biggest differences are for the tear resistance and fold endurance. As reported by Desmaisons et al. (2018), long fiber fraction is very important for improving the tear resistance, since distribute the efforts suffered among the links between the fibers and fiber individual strength. According to Fao (2019), sisal fibers presents great bulk, porosity and fold endurance, making these fibers potential for their use in packaging. Pine fibers also present great properties. Cit (2013) reported increase in mechanical properties with the increase of pine percentage in mixtures. Also, Bektaş (2018) considered suitable the insertion of pine in blending with other long fibers for improving mechanical properties due to morphological properties of pine fibers. Generally, highest values in blending fiber were in sisal and pine blending or in blending with large amounts of any of these fibers. Some values were comparable and including larger than virgin pulps in some properties. This result can be related to improvement of paper property when combining two different fibers. According to Gehlen (2014), fiber blending can present a synergetic effect, developing gains with different combinations when compared to the individualized effects. Veisi and Mahdavi (2016) reported a synergetic effect due to blending of long fibers from one pulp and fines content from another pulp.

Figure 5 presents the behavior of strength properties according to fiber percentage in blending with other fibers. As observed, as the sisal or pine percentage in blending with eucalyptus is increased, all strength properties are improved. The relationships between property value and increase of fiber percentage follow a linear trend, some with very high coefficients of determination. Small amount of sisal (5%) added in eucalyptus fibers improved the tensile strength, tensile index, stretch, bursting index, tear index and fold endurance in approximately 41.5, 54.8, 51.4, 28.9, 37.5 and 33.3%, respectively. Same addition of pine in eucalyptus fibers resulted in improvement of 15.9, 22.7, 22.7, 37.4, 46.7 and 133.3%. This increasing tendency can be addressed to the behavior of sisal and pine fibers compared to eucalyptus fibers as reported in previous paragraph, especially due to high individual resistance, fiber length and interfiber bonding. Increase of sisal in blending with pine fiber showed no tendency for all strength properties. This can be related to the similar characteristics of these two fibers. In some cases, the values of blending were greater than the individual effects. Mari et al (2019) stated significant increment in paper strength even with small additions (3-5%) of abaca fibers in blending. Authors explained that fiber morphology (extremally long and thin cell wall fibers) was the main factor affecting mechanical properties.

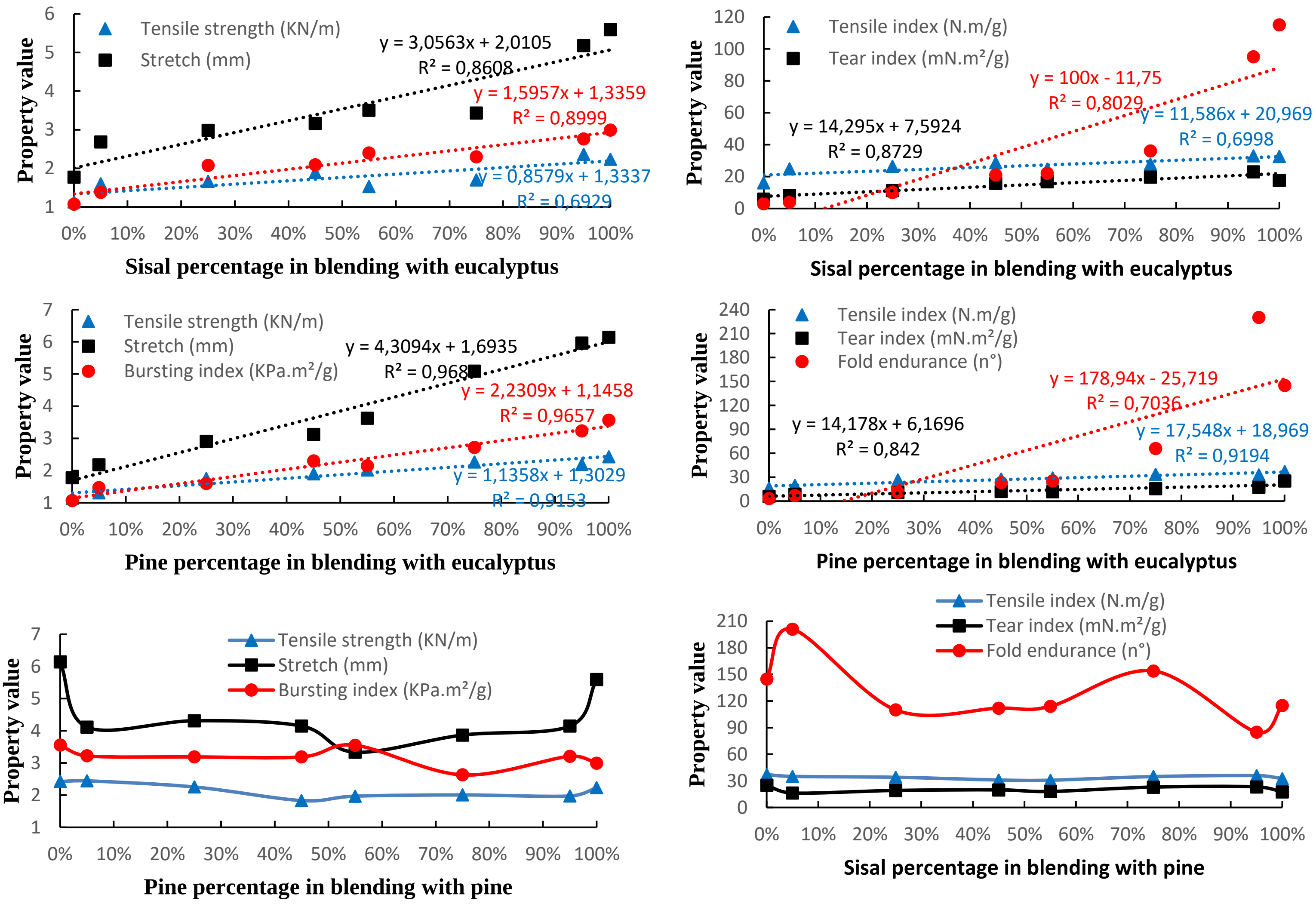

Figure 5. Behavior of mechanical properties due to percentage enhancement of one fiber in blending with another fiber.

Tensile properties are related to durability and utility of a paper. These properties are also largely important for printing papers because of rupture possibility during printing process. Highest values were found in treatments T13 (5S 95P) and T2 (100S) for tensile strength, T2 and T19 (95S 5P) for tensile index, T2 and T7 (5E 95P) for stretch. Lowest values were in T1 (100E) and T16 (95E 5P) for all tensile properties. Highest values were correspondent to sisal and pine fibers. Lowest values were correspondent to eucalyptus pulp. According to Zanão et al. (2019), no significant effect was observed in the mixture of eucalyptus and pine fibers for tensile strength values. Some authors found similar result to those obtained in this study for tensile properties (Chaiarrekij et al. 2011; Kim et al. 2014). However, it is more common the increment in tensile properties with addition of short fibers, especially in blending of different fibers as studied by Laukala et al. (2019), Zhang et al. (2011), Bassa et al. (2007). Authors converge that short fibers can act like fines. Fines are capable of fill small spaces in the paper structure and provide binding sites between long fibers improving tensile properties. We could not point out a convincing explanation for this result. This behavior can be related to pulp property used in this study or insufficient pulp preparation, such as refining. Besides, the species of eucalyptus or pulping condition used is different in each study.

Bursting and tear strength are proprieties related to use of paper as packaging, bags, wrapping papers, corrugated cardboard and cards. Highest values were found in treatments T2 and T21 (55S 45P) for bursting index, T2 and T19 (95S 5P) for tear index. Lowest values were in T1 and T10 (95E 5S) for both bursting and tear indexes. As observed in tensile properties, highest values were correspondent to sisal and pine fibers while lowest values were correspondent to eucalyptus fibers. Explanation for these results can also be given by morphological properties. Fiber flexibility (coefficient of elasticity) presents great influence in bursting strength. Low fiber diameter and lumen can affect the bursting index (Veisi and Mahdavi, 2016). The tear index is affected by relationship between the cell wall thickness and fiber diameter (wall fraction) followed by fiber length. As reported by Veisi and Mahdavi (2016), the improvement of tear strength in blending can be associated to long fibers addition. The bursting and tear indexes were improved by increasing the proportion of pine fiber in blending with eucalyptus fibers (Zanão et al.2019). The addition of long fibers in short fiber pulps increases the bursting and tear indexes (Jahan and Rawshan, 2009).

Fold endurance is defined as the ability of paper to support multiple folds before rupture. It has been useful in determining degradation with aging process. It is an important property for paper used in applications subjected to multiple folds such as paper money, maps, books, pamphlets. As seen in Table 7, highest values do fold endurance were obtained in treatments T7 (5E 95P) and T13 (5S 95P). These results were obtained from blending of different fibers and were greatly superior than isolated fibers. Blending presented a synergetic effect, superior than individualized effects. These results can be associated to combining effect of very flexible fibers (pine's elasticity coefficient), very long fibers (sisal's fiber length) as shown in Table 4 and 5 and possibility of connection between short and long fibers. According to Fathi and Kasmani (2019), long and flexible fibers provide high resistance to fold endurance. On the other hand, lowest values were obtained in treatments T1 (100E), T10 (95E 5S), T11 (75E 25S), T16 (95E 5P) and T17 (75E 25P). All treatments were represented by eucalyptus fibers. This result can be related to morphology of eucalyptus fiber, such as short length and elasticity coefficient. Cit

(2013) also found small fold endurance using eucalyptus fibers and in blending involving eucalyptus fibers.

Conclusion

Fibers used in this study for blending presented distinct characteristics regarding to morphological properties. Fibers differed in length and width, besides lumen width and cell wall thickness. Morphological indexes showed that fibers are proper for papermaking despite great variability. Felting rate was the most divergent index and was impacted by fiber length.

Blending of different fibers (pulp blending) during handsheet forming affected physical and mechanical properties. The thickness, volume, grammage, apparent density, bulk, tensile properties, bursting index, tear index and fold endurance were affected. Differences between treatments were governed by difference between fibers related to morphological properties. Thickness had a decreasing tendency with blending. Thickness and grammage were not related. Other physical properties were influenced by fiber blending. Long-fibers (sisal and pine) presented better mechanical properties than short-fibers (eucalyptus). As long-fibers percentage increased in blending with eucalyptus, handsheet became stronger. Addition of small quantities of long fiber (5%) in short fiber pulps dramatically increased strength properties.

Fiber blending present synergetic effect for some properties. In other words, mix different fibers were better than virgin pulps (individualized fibers) for some properties. The best results were obtained in blending of sisal and pine pulps.

Acknowledgments

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ARTIGO 2 - PAPERS PRODUCED FROM DIFFERENT FIBER BLENDING: PHYSICAL, OPTIC, STRUCTURAL AND INTERFIBER BONDING ANALYSIS

Artigo redigido conforme normas do periódico científico Cellulose, sendo uma versão Preliminar, que pode sofre alterações.

Abstract

Blended papers can present suitable mechanical properties. However, regarded to physical properties, few studies are conducted. This study aimed to evaluate optic, structural, interfiber bonding and other physical properties from blended papers and try to understand how these properties can affect applications. Eucalyptus, sisal and pine pulp were used for handsheet forming. Pulps were disintegrated, refined, and then, blended two by two in 5/95%, 25/75% and 45/55% ratios in all possible combination. Also, virgin pulps (100% of each pulp) were used for handsheet forming. Handsheets were formed and evaluated by bond strength, cobb test, air permeance, roughness, optic, Fourier transform infrared Spectroscopy (FTIR) and scanning electron microscopy (SEM). Treatments differed statistically in bond strength, cobb test, optic, air permeance and roughness. Generally, treatments with eucalyptus presented higher bond strength, brightness and air permeance. Treatments with sisal presented higher opacity and roughness. Blended handsheets presented higher values than virgin handsheet on most properties. Spectra of virgin handsheet presented differences in 2170-2000 and 2360 cm^{-1} bands, probably related to residual lignin content. SEM images revealed structural differences between blended and virgin pulps. Fiber blending can present suited physical properties, providing synergetic effect and can affect paper applications.

Keywords: Cellulose, Handsheet, Natural fibers, Mixture, Papermaking properties.

Introduction

Paper industries are an important sector in economy of many countries and can also be basis of other business. As well as any industries, they are facing demands regarding to sustainability, efficiency and quality of products, especially in the current century, besides other technologies competitions (Schneider et al. 2016). This leads to a constant search for improvements. One possibility for improvement of paper quality is through fiber blending. Fiber blending is a tendency in researches and paper industries aimed at achieving requested properties of their final products.

Fiber blending is a technique of paper production based on combination and mixture of different fibers. Instead of an isolated fiber, fibers are blended in different combinations in order to improve paper properties, trying to reduce drawbacks and potentialize advantages that one fiber can present (Mansfield et al. 2004; Claramunt et al. 2020). Compared to virgin pulps, blended pulps can improve paper properties, and be a technique for production of superior paper (Karlsson 2010).

Physical properties are important for paper application. For example, optic properties are requested for writing and printing paper; structural and surface properties affect fibers arrangement and mechanical properties (Biermann 1996). These properties involve the behavior of paper when exposed to some requirements, making possible the characterization of structure, arrangement, surface and fibers connections. As well as other paper properties, physical properties can be strongly affected by fiber blending due to large variation in fiber characteristics (Cit 2013). Then, physical properties need to be considered in studies involving fiber blending.

Among other properties, interfiber bonding is an important property due to influence in paper structure and mechanical properties. Interfiber bonding can be defined as connections between fibers by chemical bonding, Wan der Waals' interaction and molecular entanglement. Interfiber bonding keep fiber together (fibers network) contributing to internal cohesion of paper and consequently to physical and mechanical properties (Retulainen et al. 1997). Interfiber bonding is essential for fiber blending. Since fiber blending deal with distinguished fibers, a consequence in interfiber property is expected. Additions of short fiber in long fiber pulps may improve dramatically interfiber bonding when compared to virgin pulps (Yan and Li 2013; Kimura et al. 2020).

Interfiber bonding is a crucial property for some applications. All applications require a minimum amount of this property. For example, packaging and especial papers requires high tensile strength and interfiber bonding play an important role. Generally, interfiber bonding can be improved by two methods: Addition of different papermaking furnishes and fiber treatment. Both methods intend to improve fiber connections through different morphology and surface fiber treatment. Interfiber bonding could be improved by pulp refining, addictive and fines additions (Vainio and Paulapuro 2007).

The majority of researches involving fiber blending seek for improvements in mechanical properties (Zhang et al. 2011; Sheikhi et al. 2013; Bhardwaj et al. 2019). Regarding to physical properties, structure and interfiber bonding, few studies aim at associating these results to mechanical properties, besides understanding the influence of these properties on the main applications.

Therefore, this study aimed to evaluate the physical properties and structure from blended papers and understand the connection between different fibers (eucalyptus, sisal and pine) in paper structure.

Material and methods

Material and handsheet forming

Cellulosic commercial pulps of eucalyptus *(Eucalyptus sp.)*, sisal (*Agave sisalana*) and pine (*Pinus sp.*) were used for fiber blending and paper forming. Pulps were provided by Lwarcell and Klabin companies in form of cellulose sheets.

Pulps were soaked with distillated water for 48 hours in order to improve fiber swelling and hydration. Water volume was 10 liters and consistency were 2%. After, pulps were disintegrated in REGMED D-3000 disintegrator. Each pulp was subjected to refining in REGMED HV-10 refiner. Refining time was 30, 45 and 45 minutes for eucalyptus, sisal and pine, respectively, determined by refinability pre-tests. Pulps reached approximately 25 °SR in ideal refining time. After refining, pulps were blended taking into account all possible combinations of materials in 5/95%, 25/75% and 45/55% ratios. Virgin pulps from each material (eucalyptus, sisal and pine) were also used for handsheet forming, totalizing 21 treatments. All treatments are described in Table 1. The pulp blending was based on volume. A mechanical stirrer FISATOM 713d model was used for blending.

Table 1 Percent composition of the cellulose pulps in each treatment

Treatment	Blending composition
T1 (100E)	100% eucalyptus
T2 (100S)	100% sisal
T3 (100P)	100% pine
T4 (5E 95S)	5% eucalyptus e 95% sisal
T5 (25E 75S)	25% eucalyptus e 75% sisal
T6 (45E 55S)	45% eucalyptus e 55% sisal
T7 (5E 95P)	5% eucalyptus e 95% pine
T8 (25E 75P)	25% eucalyptus e 75% pine
T9 (45E 55P)	45% eucalyptus e 55% pine
T10 (95E 5S)	95% eucalyptus e 5% sisal
T11 (75E 25S)	75% eucalyptus e 25% sisal
T12 (55E 45S)	55% eucalyptus e 45% sisal
T13 (5S 95P)	5% sisal e 95% pine
T14 (25S 75P)	25% sisal e 75% pine
T15 (45S 55P)	45% sisal e 55% pine
T16 (95E 5P)	95% eucalyptus e 5% pine
T17 (75E 25P)	75% eucalyptus e 25% pine
T18 (55E 45P)	55% eucalyptus e 45% pine
T19 (95S 5P)	95% sisal e 5% pine
T20 (75S 25P)	75% sisal e 25% pine
T21 (55S 45P)	55% sisal e 45% pine

Handsheets were formed based on consistency of 2% and nominal grammage around 60 g/m². The TAPPI 205 om-88 standard and a REGMED F/SS-2 paper-making machine was used for handsheets forming. Three handsheets were formed for each treatment and evaluated.

Bond strength

Bond strength between fibers were evaluated following methodology proposed by Page (1969), which relate paper strength properties and fiber characteristics, shown in equations 1 and 2.

$$B = \frac{96\, A\, \rho\, g\, Z\, T}{(8Z-9T)P\, L\, RBA} \quad (1) \qquad RBA = \frac{So-S}{So} \quad (2)$$

Where:

B= Bond strength index (N/mm²);

T= Handsheet tensile strength – Breaking length (km)

Z= Zero-span tensile strength – Breaking length (km)

A= Average fiber cross section (cm²)

g= Gravity Acceleration (m/s²)

ρ= Cell wall density of fiber (g/cm3)

P= Fiber cross section perimeter (cm)

L= Fiber length (cm)

RBA= Handsheet relative bonded area (%);

So= Light scattering coefficient of unbound fiber network (m²/kg);

S= Light scattering coefficient of handsheet (m²/kg).

Some items in bond strength index determination were considered constant. The values of 9.80665 m/s² and 1.53 g/cm³ were designed for gravity acceleration (g) and cell wall density (ρ), respectively. Parameters related to tensile strength (T and Z) and morphological properties of fibers (L, P, A) were measured in laboratory. The formed handsheet for each treatment were tested by tensile properties according to TAPPI T 494 standard. Handsheet density and grammage was performed according to TAPPI T 220. Measurements of fiber morphology was carried out in Ken-A Vision optic microscope, model TT-1010, Dinocapture 2.0 software. Only measurements of virgin refined pulps (T1, T2 and T3) were conducted. Mean values from each pulp were obtained and then, the other treatments were calculated taking in account fiber type percentage.

RBA was calculated based on method proposed by Tao and Liu (2011) who develop a method to determine sheet relative bonded area using the fiber flexibility index (FFI) and obtained suitable result between calculated and measured RBA. FFI were obtained by equation 3. RBA was obtained by equation 4 using FFI.

$$Sheet\ density = 5.5887E - 17 * (FFI) + 342.67 \quad (3)$$

$$RBA = 8.045E - 20 * (FFI) + 0.4935 \quad (4)$$

Fourier Transform Infrared Spectroscopy

Infrared spectroscopy analysis (FTIR) from handsheets was carried out aiming to observe and identify possible chemical structures. FTIR was performed only for handsheets produced from virgin pulps (T1, T2 and T3) due to small differences in spectra for blended papers, as previously evaluated. Spectra were obtained in IRAffinity – Shimadzu spectrophotometer in diffuse reflection by ATR, spectral range of 4000 to 400 cm^{-1}, 4 cm^{-1} resolution and 32 scans.

Physical properties (Cobb test, optic properties, air permeance and roughness)

The water absorption capacity (Cobb60 test) was performed according to TAPPI T441 standard. This test express absorption capacity on 1 m² paper surface. In this analysis, water absorption time was 60 seconds and surface area of each sample was 25 cm². Blotting paper of approximately 258 g/m² grammage was used. Cobb test was performed in all treatment in triplicate. The determination of Cobb test was performed following equation (3).

(3)

$$Water\ absorption\ capacity\ \left(\frac{g}{m^2}\right) = (m_1 - m_0) * 400$$

Where:

m_1 = Mass after water exposure (g)

m_0 = Mass before water exposure (g)

Optic properties of handsheets were performed by brightness and opacity determination. Analyses were carried out according to TAPPI T 452 (brightness) and TAPPI T 519 (opacity) standards for all treatments in triplicate. A REGMED brightness meter with a directional reflectance level of 457 nm was used for analysis.

Air permeance and roughness were performed according to TAPPI T 460 and TAPPI T 538, respectively.

Scanning electron microscopy

Structure analysis of handsheets was carried out using scanning electron microscopy (SEM). Virgin handsheets (T1, T2 and T3) and handsheets with 45:55 ratio (T6, T9 and T15) were submitted to SEM for evaluating physical structure and fibers arrangement. Analyses were carried out in Evo40 LEO XVP equipment, with 25kV voltage. Handsheets were cut in small fragments for samples preparation. Samples were fixed in aluminum stubs, coated with aluminum foil film, using carbon double-sided tape and covered with a thin gold layer. Images were obtained in transversal and longitudinal section.

Results and discussion

Bond strength

Interfiber bonding can be a weak point in paper strength, being able to be broken with simple hydration. However, they act decisively together with intrinsic fiber resistance to determine the mechanical properties of papers, mainly tensile strength. (Retulainen 1997). Table 2 presents results of lab measured and calculated data for parameters required to bond strength (B), along with the respective results obtained. Bond strength data presented a coefficient of variation of approximately 10.1% between replicates. Statistical differences occurred between treatments for bonding strength index. Results found in this study are in accordance with Area et al. (2010) who evaluated bond strength in eucalyptus Kraft pulps who obtained results around to 12 N/mm².

Table 2 Measured and calculated handsheets properties and bond strength indexes

Treatment	D (kg/m^3)	G (g/m^2)	FFI (N^{-1} m^{-2})	RBA (%)	T (km)	Z (km)	L (cm)	A (cm^2)	P (cm)	B (N/mm^2)
T1 (100E)	399	67.3	1.02E+18	0.576	1.64	2.39	0.0881	2.5E-06	4.96E-03	12.73 a
T2 (100S)	382	63.2	7.2E+17	0.551	3.77	5.91	0.3566	3.17E-06	5.59E-03	6.95 efgh
T3 (100P)	427	66.4	1.52E+18	0.616	3.32	4.97	0.2807	3.96E-06	6.25E-03	8.84 bcde
T4 (5E 95S)	375	69.2	5.9E+17	0.541	3.35	4.79	0.3432	3.13E-06	5.56E-03	8.65 bcde
T5 (25E 75S)	401	59.1	1.06E+18	0.579	2.82	4.72	0.2895	3E-06	5.43E-03	5.13 fgh
T6 (45E 55S)	378	59.8	6.5E+17	0.546	2.52	4.19	0.2358	2.87E-06	5.31E-03	5.91 fgh
T7 (5E 95P)	450	64.1	1.94E+18	0.650	3.34	5.14	0.2711	3.89E-06	6.19E-03	7.98 cdef
T8 (25E 75P)	448	65.7	1.9E+18	0.646	3.41	5.15	0.2325	3.59E-06	5.93E-03	9.63 bcd
T9 (45E 55P)	437	67.4	1.7E+18	0.630	2.95	4.33	0.1940	3.3E-06	5.67E-03	10.81 ab
T10 (95E 5S)	410	61.8	1.22E+18	0.592	2.54	4.06	0.1015	2.53E-06	5.00E-03	13.03 a
T11 (75E 25S)	405	60.7	1.12E+18	0.584	2.70	4.41	0.1552	2.66E-06	5.12E-03	9.04 bcde
T12 (55E 45S)	413	64.0	1.27E+18	0.596	2.93	4.55	0.2089	1.37E-06	2.73E-03	7.68 cdefg
T13 (5S 95P)	490	67.2	2.66E+18	0.707	3.56	5.23	0.2845	3.92E-06	6.22E-03	8.62 bcde
T14 (25S 75P)	443	64.5	1.81E+18	0.639	3.46	5.36	0.2997	3.76E-06	6.09E-03	7.38 defg
T15 (45S 55P)	421	57.3	1.42E+18	0.608	3.15	5.47	0.3148	3.6E-06	5.95E-03	5.12 fgh
T16 (95E 5P)	438	64.3	1.72E+18	0.632	2.01	3.11	0.0977	2.57E-06	5.03E-03	10.99 ab
T17 (75E 25P)	446	64.6	1.86E+18	0.643	2.69	4.15	0.1362	2.86E-06	5.29E-03	11.01 ab
T18 (55E 45P)	460	66.3	2.11E+18	0.663	2.81	4.20	0.1748	3.16E-06	5.54E-03	10.04 bc
T19 (95S 5P)	397	53.3	9.9E+17	0.573	3.66	6.84	0.3528	3.21E-06	5.63E-03	4.68 h
T20 (75S 25P)	393	55.6	9.2E+17	0.568	3.56	6.33	0.3376	3.37E-06	5.76E-03	5.32 fgh
T21 (55S 45P)	411	61.8	1.24E+18	0.593	3.14	5.02	0.3224	3.52E-06	5.89E-03	5.95 fgh

Where: D=Sheet density, G=Grammage, FFI=Fiber flexibility index, RBA=Relative bonded area, T=Tensile index, Z= Zero-span tensile index, L= Fiber length, A= Average fiber cross section, P= Fiber cross section perimeter and B= Bond strength. Means followed by same letter in column do not differ statistically from each other by Tukey test at 5% de probability level.

Highest B values were obtained in treatments T1 (100E) and T10 (95E 5S), which corresponded to higher content of eucalyptus. Lowest B value was obtained in treatment T19 (95S 5P), with sisal and pine blending. Expressive differences were observed comparing the three virgin pulps (T1, T2 and T3). Bond strength in eucalyptus handsheet were approximately 83.1% and 44% higher than sisal and pine handsheets, respectively. Such result can suggest that eucalyptus fiber is more likely to connect to other fibers and increase fiber bonding. In general, treatments containing eucalyptus in composition presented higher values of bond strength while treatments with sisal and pine presented lower values. As observed in Figure 1, increasing eucalyptus percentage in the blending tended to present higher values of bond strength, both for sisal and pine blending, although eucalyptus and sisal blending fitted better. According to Zhang (2011), short fibers addition in blending, such as eucalyptus, improve interfiber bonding due to fibers acting as connecting elements in paper network.

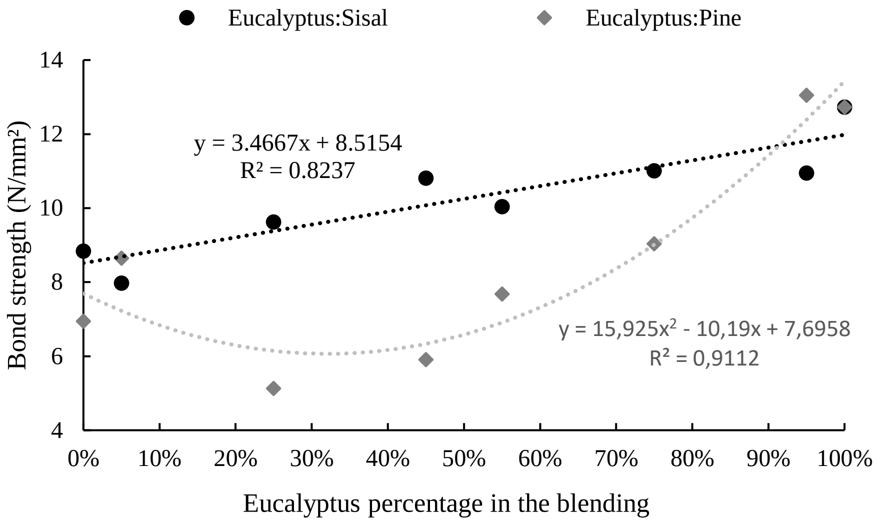

Fig. 1 Bond strength behavior of blended paper with increasing of eucalyptus percentage

Differences in fiber bonding strength can be related to fibers morphology, especially fiber length. The three materials presented discrepant fiber length. Eucalyptus fibers averaged approximately 880 µm in length while sisal and pine fibers averaged 3500 and 2800 µm, respectively. According to Page equation, B and fiber length are indirectly related. Therefore, short fibers tended to present high values of bond strength. Long fibers tended to present reversed tendency. Short fibers can act as a bridge between long fibers contributing to bond connection and strength, consequently improving paper network. According to Larsson et al. (2018), long fibers tend to present pour interfiber bonding and bond resistance.

Other factors also can affect fibers bond strength such as refining. Increasing in refine degree can modify B value, since frequency of bonding between fibers is enhanced (Dasgupta 1994). However, considering that studied fibers were submitted to proper refining time, refining played not a key role in bonding strength. Besides, bleaching, chemical content and production process should also be considered (Area et al. 2010), although these factors are not significant in our target.

Some expressive B values are from fibers blending. They may be larger or equivalent to virgin fibers. This result can be due to synergetic effect when blending totally different fibers. Blended papers can show higher values of bond strength than papers prepared with single fibers (Cappelletto et al. 2000; Danielewicz and Ślusarska, 2019).

Results from bond strength can suggest that eucalyptus handsheet presents better mechanical properties than the other fibers. With increase of fiber bonding, intermolecular interactions (van der Waals forces and hydrogen bonds) can occur, contributing to internal cohesion and affecting paper properties (Vainio and Paulapuro 2007). However, when it comes to strength properties, many other properties (fiber length, fiber flexibility, chemical content, fiber surface wettability, network structure, interlacement, intrinsic fiber resistance, etc.) should be considered, especially on a specific request. Therefore, bond strength is just an indicative and paper produced from sisal and pine fibers can present better strength properties than eucalyptus because of better other properties, previously mentioned.

Fourier Transform Infrared Spectroscopy

Figure 2 shows spectra of handsheets produced from virgin pulps (T1, T2 and T3). The band located at 3500-3100 cm^{-1} can be related to hydroxyl (OH) stretching vibrations, which may include water and other structures, mainly celluloses and hemicelluloses (Kazayawoko et al. 1997). The band at approximately 1032 cm^{-1} can be related to C-O stretching. The band at 2900 cm^{-1} can be assigned to C-H stretching (Huang et al. 2016). The band at 1640 cm^{-1} can be assigned to double bond (C=C) or water adsorption. Bands between 1400-1300 cm^{-1} are associated to C-H stretching and CH_2 bending and rocking vibrations and can be related to cellulose crystallinity (Hajji et al. 2016).

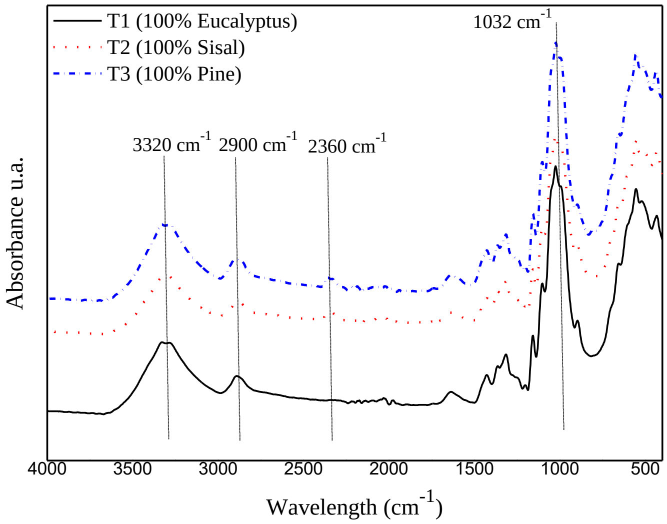

Fig. 2 FTIR handsheet spectra from virgin pulps (T1, T2 and T3)

According to Figure 2, spectra from eucalyptus, sisal and pine handsheets present a high degree of similarity. Then, FTIR analysis was not sufficiently capable of discriminating chemical difference in handsheets. However, some minor differences can be visualized between 2170 and 2000 cm^{-1}. These differences can be associated to different sugars from hemicelluloses or even different residual lignin contents present in handsheets. Eucalyptus spectrum did not present the band at 2360 cm^{-1}, differently from sisal and pine spectra. This absorption peak can be assigned to lignin structure, indicating that eucalyptus pulp obtained greater delignification when compared to the other materials (Puntambekar et al., 2016).

Physical properties (Cobb test, optic properties, air permeance and roughness)

The table 3 presents the results from Cobb test, optic e other physical properties of blended papers.

Table 3 Cobb test, brightness, opacity, air permeance and roughness in each treatment

Treatment	Cobb$_{60}$ (g/m^2)	Brightness (%iso)	Opacity (%iso)	Air permeance µm/Pa·s	Roughness mL/min
T1 (100E)	138 ab (±8.5)	54.73 a (±1.53)	90.57 abc (±2.12)	110.65 a (±8.45)	1573 abc (±110)
T2 (100S)	140 a (±5.6)	44.90 i (±0.36)	92.57 a (±2.28)	42.37 cde (±2.61)	1943 ab (±161)
T3 (100P)	112 c (±2.8)	52.60 abc (±1.45)	82.03 g (±0.93)	38.26 cde (±1.89)	1536 abc (±169)
T4 (5E 95S)	136 abc (±5.6)	46.57 ghi (±0.38)	91.57 ab (±1.4)	44.66 cde (±5.82)	1925 ab (±115)
T5 (25E 75S)	118 abc (±8.4)	47.53 fghi (±1.25)	89.67 abcd (±2.06)	60.99 bcde (±2.19)	1315 bc (±32)
T6 (45E 55S)	120 abc (±5.6)	49.47 defg (±0.47)	89.50 abcd (±0.53)	45.37 cde (±7.09)	1462 abc (±55)
T7 (5E 95P)	114 bc (±2.8)	51.13 bcde (± 1.56)	82.47 g (±1.59)	24.79 e (±3.04)	1499 abc (±32)
T8 (25E 75P)	116 abc (±5.7)	53.47 ab (±0.4)	83.83 efg (±1.45)	28.43 de (±2.8)	1425 abc (±380)
T9 (45E 55P)	132 abc (±5.9)	53.17 abc (±1.36)	83.43 fg (±0.9)	53.8 bcde (±5.8)	1629 abc (±58)
T10 (95E 5S)	136 abc (±3.5)	54.37 a (±0.46)	88.67 abcd (±2.06)	68.72 bc (±7.93)	1555 abc (±115)
T11 (75E 25S)	138 ab (±2.8)	52.13 abcd (±1.19)	87.97 bcde (±0.85)	62.93 bcd (±2.7)	1462 abc (±166)
T12 (55E 45S)	132 abc (±1.9)	50.70 bcde (±0.26)	90.23 abcd (±0.59)	55.48 bcde (±5.78)	1962 ab (±123)
T13 (5S 95P)	118 abc (±7.6)	51.90 abcd (±1.47)	82.43 g (±1.72)	32.37 cde (±3.4)	2147 a (±134)
T14 (25S 75P)	120 abc (±2.3)	50.40 cdef (±0.44)	83.00 fg (±0.66)	31.45 cde (±2.37)	1610 abc (±89)
T15 (45S 55P)	116 abc (±5.7)	48.53 efgh (±0.55)	82.37 g (±1.86)	33.29 cde (±5.46)	1573 abc (±135)
T16 (95E 5P)	132 abc (±5.9)	54.50 a (±0.78)	87.97 bcde (±0.4)	66.89 bc (±1.25)	1092 c (±96)
T17 (75E 25P)	132 abc (±7.9)	53.73 ab (±1.0)	87.00 cdef (±1.42)	52.13 bcde (±4.41)	1240 bc (±102)
T18 (55E 45P)	126 abc (±8.4)	52.73 abc (± 075)	87.1 cdef (±0.62)	42.4 cde (±3.46)	1555 abc (±160)
T19 (95S 5P)	118 abc (±2.8)	44.67 i (± 1.12)	86.07 defg (±1.55)	86.92 ab (±2.96)	1740 abc (±168)
T20 (75S 25P)	114 bc (±2.8)	45.83 hi (±1.08)	86.30 cdefg (±1.4)	66.41 bcd (±1.83)	1795 abc (±110)
T21 (55S 45P)	114 bc (±3.0)	47.47 fghi (±0.45)	86.00 defg (±1.1)	34.21 cde (±3.76)	1518 abc (±134)
CV (%)	4.97	1.94	1.64	23.77	15.86

Means followed by same letter in column do not differ statistically from each other by Tukey test at 5% de probability level.

The cobb test shows the water absorption capacity of papers and is an important property specially for absorbent and printing papers. According to Table 3, all treatments presented great hydrophilicity. This is due to the fact that handsheets have no additive or charge added in their structure during formation, or even modification in surface energy of papers, which would probably change the hydrophilicity. Statistical difference between treatments occurred. Differences can be related to porosity and grammage of papers, since these characteristics influence surface energy and wettability. However, it is not possible to observe increasing or decreasing trend according to variation in material percentage. Bhardwaj et al. (2019) also detected no tendency of variation in blending of agro-residues and hardwood pulp. Authors just reported big difference in water absorption when was added chitosan charge during handsheet forming.

Optic properties of papers have huge importance in several applications and final destination of the products, such as newspaper, writing and printing papers. The optic properties of brightness and opacity for all treatments are presented in Table 3. Some variable affect optical properties, like refining rate, residual lignin content, fines content, factors related to forming, among others. Pulps used in this study have already been partially bleached, but probably differed in some chemical, such as the residual lignin content.

Evaluating Table 3, it is possible to observe that higher brightness content was obtained in treatment T1 (100E) and in others treatments which contained eucalyptus in the blending, such treatments T10 (95E 5S) and T16 (95E 5P), which shows an increasing trend in paper whiteness as eucalyptus percentage is increased in paper blended, as also evidenced in Figure 3. The increase in brightness with eucalyptus percentage can be explained by the fact of original eucalyptus pulp possibly have a lower residual lignin content (which contributes to greater brightness in the papers from mixtures with higher eucalyptus percentual). Cit (2013) also observed increments in brightness in blended papers from the increase of short eucalyptus fibers percentage in mixtures. On the other hand, the treatment which presented the lowest brightness value was treatment T2 (100S), represented by 100% sisal. Besides, as the proportion of sisal in the blending increases, a reduction in brightness happened, as observed in the same Figure 3, considering the decreasing trend in brightness and the consequent increase of sisal in blending. This reduction is probably related to a high content of residual lignin in the original sisal pulp. Pine pulp (T3) presented high brightness when compared to sisal pulp (T2), similar to that obtained by eucalyptus pulp. As a consequence, papers with pine pulp in mixture also presented brightness increment with increase of pine percentage.

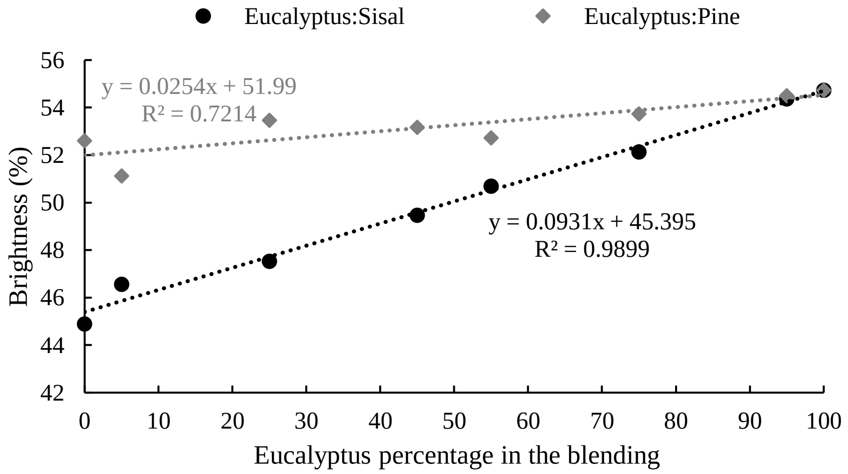

Fig. 3 Brightness behavior of blended paper with increasing of eucalyptus percentage

The addition of small quantities (25%) of eucalyptus and pine in sisal pulp enhance pulp brightness in approximately 6 and 2 %, respectively. The use of fiber combination can be suitable when some application demand mechanical properties that sisal fiber can offer, like high tear strength, and brightness appropriate for a particular situation.

Opacity is related to the capacity of light transmitted by paper and is an important property for printing papers. This property suffers great influence of fibers network and its interlacement, besides physical properties (grammage and thickness), bleaching and filling materials. According to Table 3, statistical difference between treatments happened, and materials with greater opacity were treatments with sisal and eucalyptus in their composition. Eucalyptus presented high opacity probably due to their short fibers and the possibility of connections in fiber network, making the material very compact and hard for light passage. Sisal behavior can be due to good compaction of handsheets or, most likely, the impact of process variable in handsheet forming like grammage and apparent density. Lower values of opacity were obtained in treatment T3 and others treatments involving pine pulp in composition. This low value can be related to fiber properties, such as high length and width of fibers, which can affect handsheet forming and fiber interlacement.

The values of optic properties, both for brightness and opacity, are in concordance with others studies that worked the effect of fiber blending in these properties (Veisi and Mahdavi 2016; Fathi and Kasmani 2019; Bhardwaj et al. 2019). It is important to note that optical properties are dependent of bleaching intensity from virgin pulps.

The air permeance is an important property from papers and refer to facility of air volume pass on paper structure. Air permeance affects many applications such as food packaging, papers with barrier properties and filter papers. Air permeance is also related to empty spaces in paper structure and, consequently, with permeability, since this property is dependent from number, size, distribution and format of pores. According to Ek et al. (2009) air permeance is an indication of paper structure and is controlled by both the pore volume, diameter and pore network connectivity. Papers with low air permeance value is less porous and more impermeable. They could be used in paper that require barrier properties such as waterproof papers, food packaging and other packaging applications. On the other hand, paper with high air permeance could be used other paper applications such as tissue, cardboard, writing and printing papers

According to Table 3 and Figure 4, statistical difference occurred between treatment. Highest values were obtained in T1 (100E) and T19 (95S 5P), while fewest values were obtained in T7 (5E 95P) and T8 (25E 75P). Highest values were correspondent to treatments containing eucalyptus while lowest values were corresponded to pine treatments. Differences can be related to fiber morphology between fibers and how this difference affect fiber accommodation during handsheet forming and, consequently, paper structure. Generally, papers produced from long fibers tend to have higher air permeance values compared to short fibers, since short fibers stay more compacted during forming and can present better interfiber bonding, reducing porosity and permeability. Laukala et al. (2019) reported a reduction in air permeance with addition of short hardwood fibers in blending with long softwood fibers. However, such behavior was not presented in studied papers. This behavior could be due to influence of handsheet forming conditions (variations on fiber accommodation and physical properties), fiber morphological properties or even poor fibers connections between fiber due to insufficient refining or specific pulp characteristic.

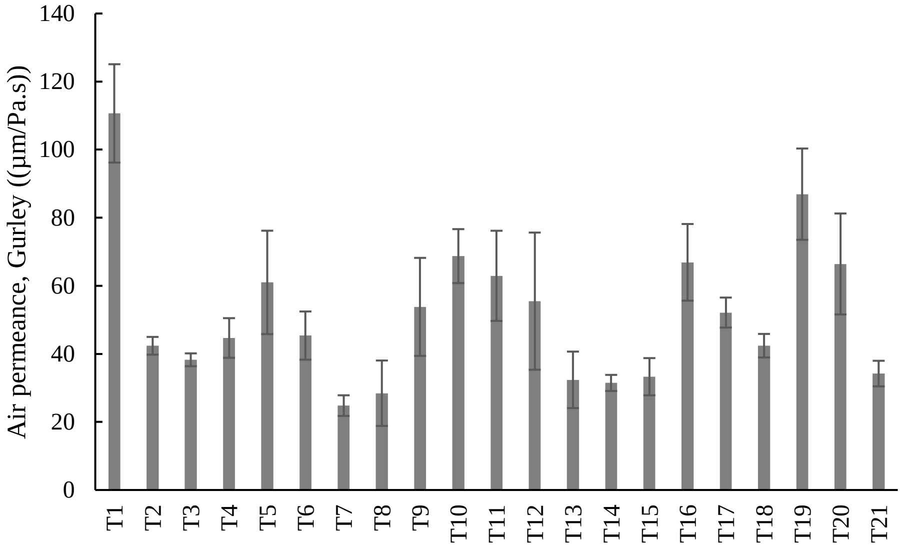

Fig. 4 Air permeance behavior in each treatment

Air permeance did not present a clear tendency with increase or decrease of fibers proportion in blending, except for eucalyptus addition. In summary, short fiber from eucalyptus presented higher air permeance (T1). As eucalyptus content increased in fiber blending the air permeance tended to increase in blending with sisal and pine fibers, as observed in Figure 5. Cit (2013) also found increases in air permeance with addition of eucalyptus pulp in pine pulp, enhancing possibility of air passage as the amount of short fibers in blending increased. According to author eucalyptus addition affected fiber interlacing network generating more spaces in a three-dimensional analysis. Zanão et al. (2019) found no tendency in air permeance with blending eucalyptus and pine fibers.

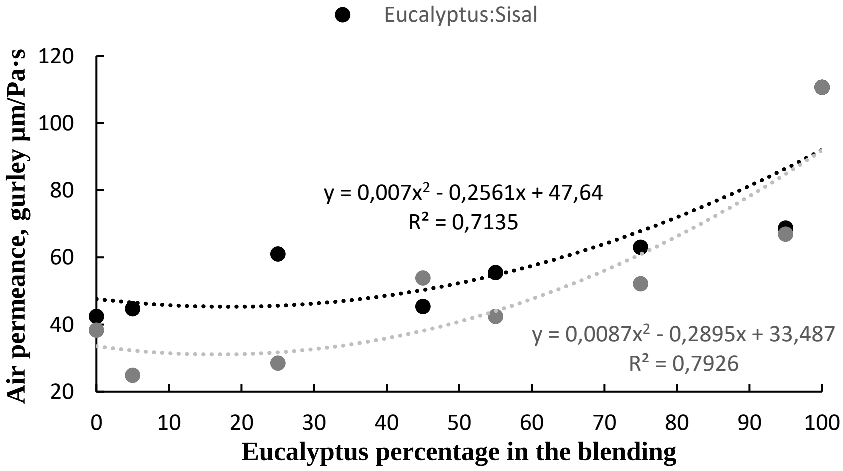

Fig. 5 Air permeance behavior of blended paper with increasing of eucalyptus percentage

The paper roughness expresses numerically the presence of irregularities on paper structure and affect the performance and uses of papers in different applications. For example, writing, printing and absorbent papers requires an appropriated smoothness level while other papers application do not need so much requirement. According to Table 3 and Figure 6, statistical differences occurred between treatments. Highest values were obtained in T13 (5S 95P), T12 (55E 45S), T2 (100S) and T4 (5E 95S), while fewest values were obtained in T16 (95E 5P) and T17 (75E 25P). Apparently, no tendency in roughness was observed with ratio variation in fiber blending. Fiber blending and morphologic fibers features had small influence in roughness. Differences can be related to variation in fiber accommodation happened in handsheet forming step, since no additive or collage product was added in handsheet production and on surface which could affect the roughness. However, highest values were correspondent to sisal and pine fibers. According to Omari et al. (2017) paper roughness is related to the presence of long fibers in blends. Additionally, fiber conformability can also affect surface roughness. According to author, the longer agave fibers lead to the highest surface roughness, as founding in this study for sisal and pine fibers. Gülsoy and Pekgözlü (2019) reported same behavior with these fibers. Shorten and fine fibers tend to present lower roughness due to better conformability. Authors also stated to the action of vessel elements and influence on roughness.

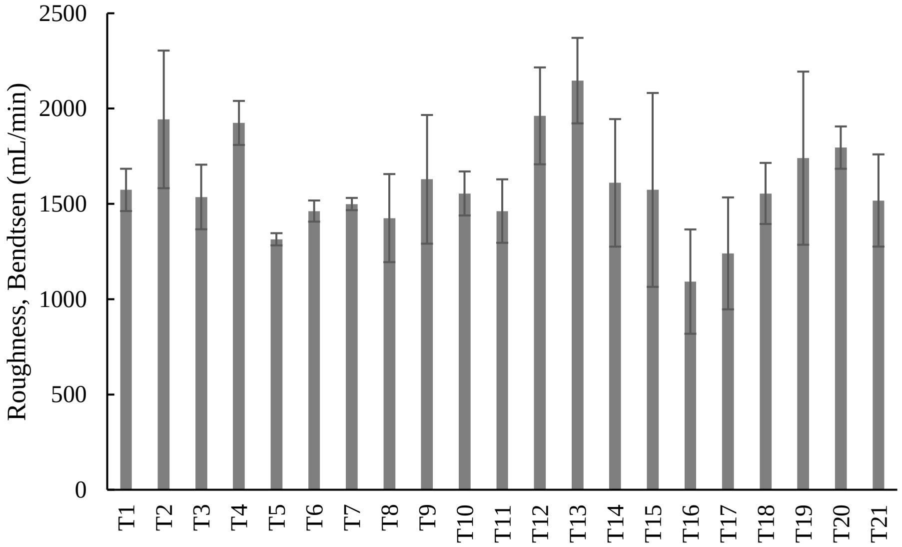

Fig. 6 Roughness behavior in each treatment

Scanning electron microscopy (SEM)

SEM analysis are important when working with different fiber blending. Some characteristics seen in SEM images affect other paper properties such as strength and physical properties. Morphological features, strength of individual fibers, their arrangement and the amount of interfiber bonding are the most important factor affecting these paper properties (Page 1969; Mossello et al. 2010).

Figure 7 and 8 shows SEM images of transversal and longitudinal sections from virgin and blended handsheets. Virgin handsheets (T1, T2 and T3) were treatments with just one type of fiber in paper structure. Blended handsheets (T6 - 45E 55S, T9 - 45E 55P and T15 – 45S 55P) were treatments with blending of two fiber in combination of eucalyptus, sisal and pine fibers at 45/55 ratio. Differences are observed in transversal section of handsheets (Figure 7) especially related to morphological properties. As expected, blended papers (T6, T9, T15) presented intermediate structure when compared to virgin paper (T1, T2 and T3).

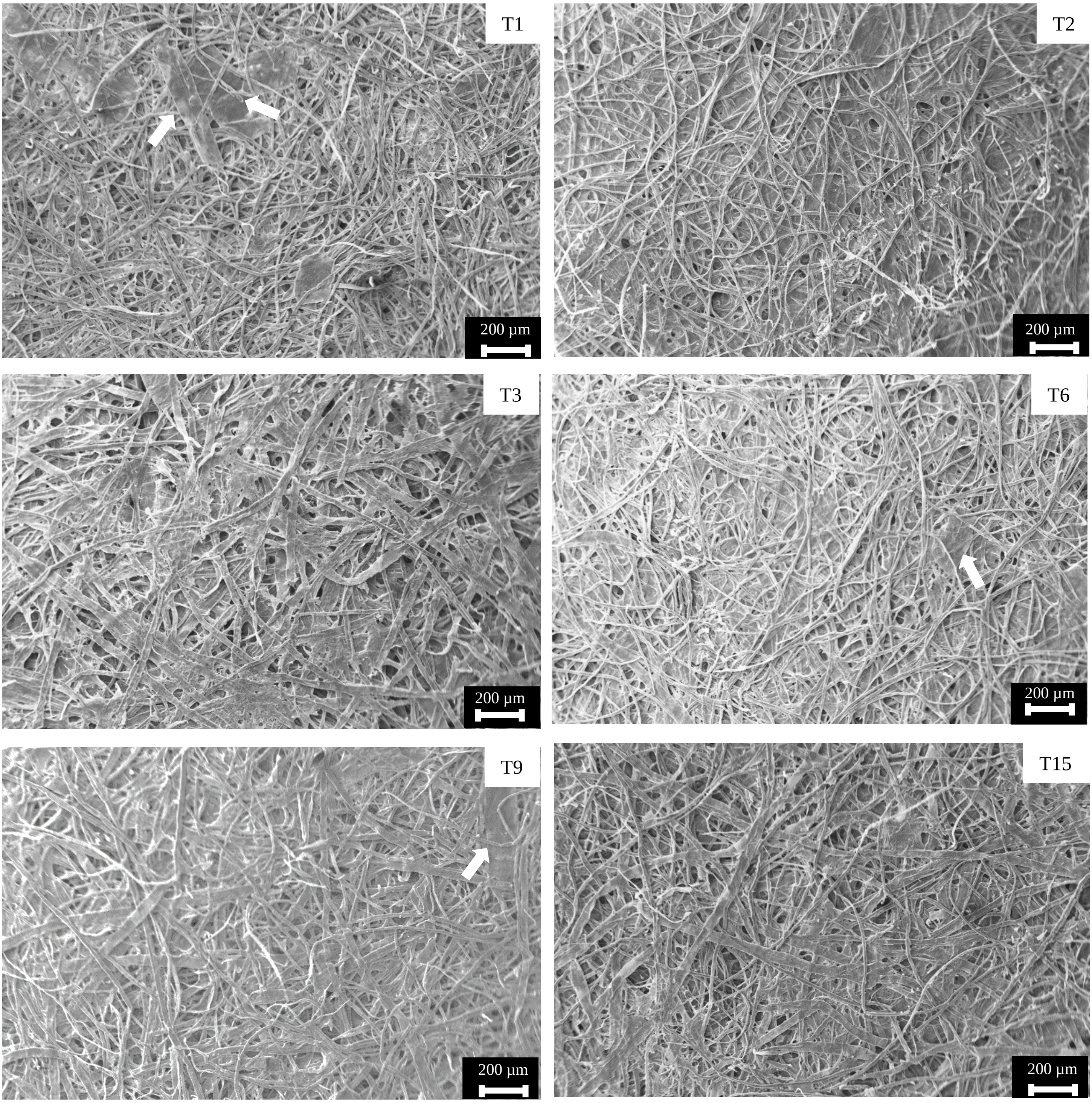

Fig. 7 Scanning electron micrographs of handsheets surface from T1, T2, T3, T6, T9 and T15 at 100x magnification (arrows show vessel elements)

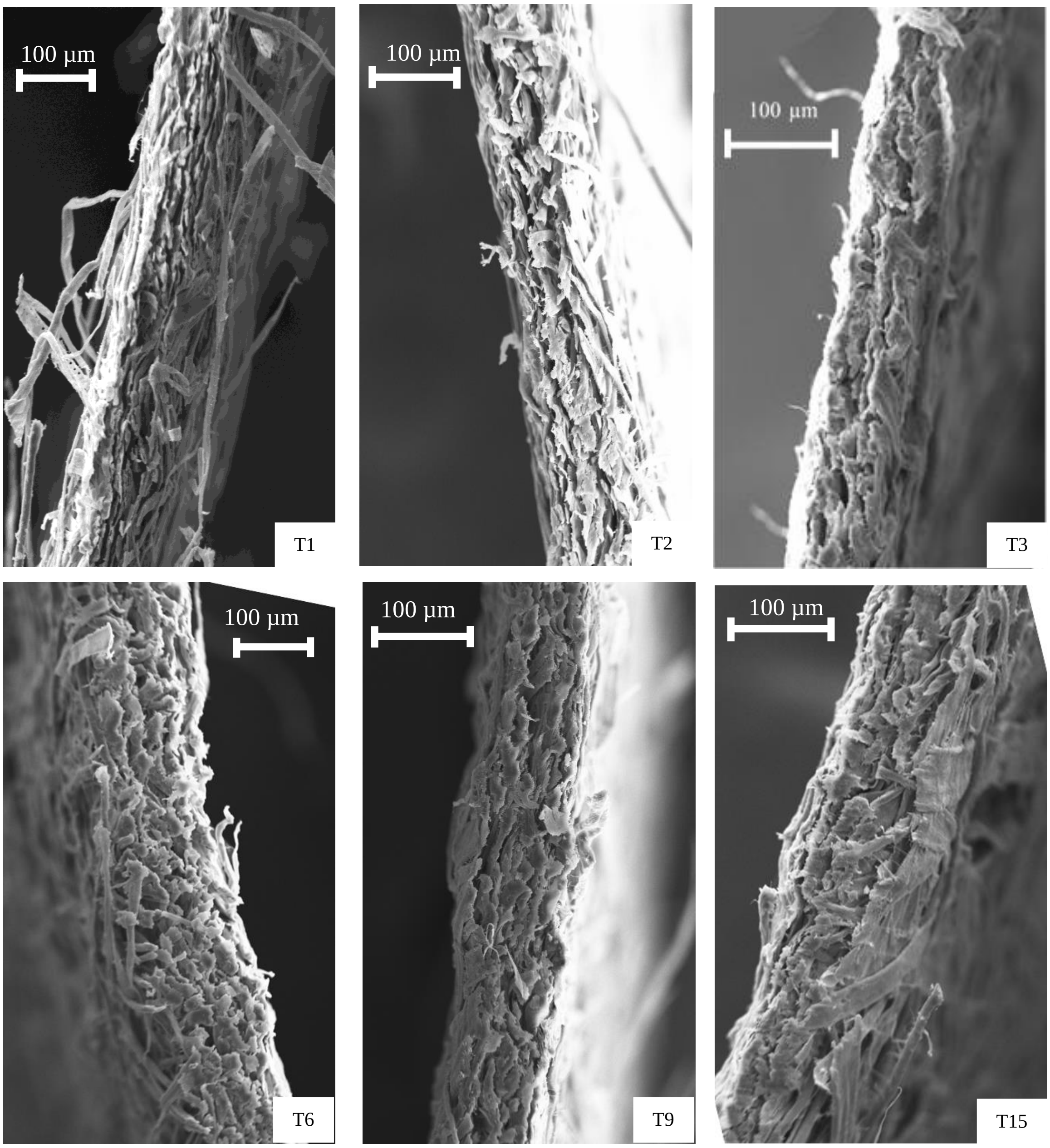

Fig. 8 Scanning electron micrographs of handsheets cross-section from T1, T2, T3, T6, T9 and T15 at 300x magnification

According to figure 7, fibers in T1 were thin and short as expected for eucalyptus fibers. Also, vessel elements were seen in surface. Vessel elements can bring poor mechanical characteristics to paper properties since they can act as weak link due to low individual strength and connections possibilities (Zhao et al. 2019). T1 also presented some voids in paper structure and fibers more scattered. This could result in reduction of handsheets density and increase of porosity (Vallejos et al. 2016). Increase of porosity can be checked in Table 3. T1 and other treatment with eucalyptus content obtained higher values of air permeance. T1 presented a more irregular structure which could affect physical properties such as thickness. As a result, T1 seemed to be thicker than others treatment as observed in Figure 8.

Fibers presented similar width in T2 as in T1. However, the fiber length was dramatically different. T2 fibers were quite long and could probably contribute to strength of papers. Although smaller than T1, T2 also presented some voids in paper structure and this could also reflect in density and porosity. In the other hand, T2 seemed to be more compacted as observed in Figure 7 and 8. Such behavior can affect thickness and density. A compacted paper may also present appropriated strength property due to better stress transfer during the requests (Tabarsa et al. 2017). T2 structure is better distributed and oriented, making a more closed structure. This can be due to better fiber accommodation in handsheet forming and morphological properties. T2 also presented a more regular structure, increasing surface uniformity (less coarse and more collapsed surface). The surface uniformity may have contributed to handsheet roughness (Table 3). Highest values for roughness were obtained in treatments containing sisal fibers. According to Banerjee et al. (2009), SEM images are able to determine measurements of the surface roughness of paper since this technique can detect subtle changes in sheet structure.

T3 fibers seen in Figures 7 and 8 seemed to have large width compared to T1 (eucalyptus fibers) and T2 (sisal fibers). Also, fibers seemed to present great lengths, higher than T1 and lower that T2. This is a well-known characteristic of some conifer's fibers especially for pine. Morphological properties of pine fiber can contribute to better strength properties. As well as T2, T3 presented a compacted structure. This can be due to better interfiber bonding of these fibers and better accommodation since pine fibers are more flexible. This result could reflect in thickness. Apparently, T3 presented the smallest thickness, according to Figure 8. Fibers seemed to be flat compared to the other fibers and this could have contributed to fiber flexibility and the arrangement of one fiber on top of another, affecting thickness, interfiber bonding and fiber-to-fiber interaction (Kim et al. 2014). According to Karademir et al. (2004), flat fiber is expected to create a larger contact area between fibers, better conformation and stronger resultant papers.

As already pointed out, SEM images from blended paper (T6, T9 and T15) presented different features compared to virgin papers. These features were a compiled of virgin characteristics seen in images. In other words, T6, T9 and T15 presented intermediate behavior of the two fibers that made up the blending. For example, blending with eucalyptus presented some amounts of vessel elements, thin and short fibers in paper structure along with other different fibers. According to Figures 7 and 8, fibers blending affected paper properties seen by SEM images and differences can reflect in interfiber bonding, surface uniformity, fiber arrangement, physical and strength properties. Therefore, papers properties could be improved depending on blending of different fibers since proper properties from each pulp could be engineered aiming to a specific situation. This behavior can be seen in treatment T15 by SEM images. T15 were blending of sisal and pine and presented suitable features from each fiber. As a consequence, T15 seemed to be more compacted due to better fiber accommodation and interfiber bonding. Morphological properties varied and could have improved connections between fibers. Thickness in T15 seemed to be lower than other treatment. Fibers in T15 were better distributed and arranged, presenting few voids in structure. This could probably affect porosity, as observed in Table 3. Surface was also uniform reflecting in roughness. Handsheet properties observed in SEM images suggested that T15 can present better strength properties. Even interfiber bonding can be improved with fiber blending. Motamedian et al. (2019) observed by SEM images occurrence and formation of bridges/connections between fibers by other morphologically different fibers. However, fiber blending can also bring different consequences depending on fiber type. Aqueela et al. (2018) observed by SEM images the effect of fiber blending in thickness. Blended papers were approximately 2x thicker than virgin papers. Besides, blended papers were less uniform due differences in fiber shapes and dimensions.

Conclusions

In this study, the effect of different fiber blending in bond strength, physical, optical and structural properties was investigated. Statistical differences were observed between blended and virgin handsheet in all properties. In some cases, values from blended handsheet were higher than respective virgin handsheets, highlighting synergetic effect.

Treatments containing eucalyptus fibers presented higher values of bond strength. An increasing trend was observed as eucalyptus percentage enhanced in blending. Lower values were obtained for sisal and pine handsheets. In general, eucalyptus handsheets were 83.1% and 44% higher than sisal and pine for bond strength. FTIR spectra showed similarity between the three different virgin handsheets. Differences were related to 2170-2000 cm-1 and 2360 cm-1 peak, probably related to chemical content in pulps, especially residual lignin. All treatments presented great hydrophilicity. No tendency was observed in Cobb test. Treatment containing eucalyptus and pine presented higher brightness. Addition of eucalyptus in blending caused brightness increase in blended handsheets, as well as pine treatments. Small additions of eucalyptus and pine in sisal pulp can enhanced paper brightness. Treatments containing sisal and eucalyptus presented higher opacity while pine treatments presented opposite results. Treatments with eucalyptus also presented higher values of air permeance. Increasing tendency was also reported for air permeance in blending with sisal and pine. Higher values for roughness were obtained for sisal and pine treatments, probably due to its long fibers. However, no tendency was observed in fiber blending. SEM images revealed differences between handsheets regarded to morphological properties of fibers. Blended handsheets presented intermediate structure compared to virgin handsheets. Other handsheet properties such as porosity, width, roughness, surface uniformity, interfiber bonding were possible to compare by SEM images.

Acknowledgments

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ARTIGO 3 - NANOCELLULOSE REINFORCEMENT IN PAPERS PRODUCED FROM FIBER BLENDING

Artigo redigido conforme normas do periódico científico Cellulose, sendo uma versão preliminar, que pode sofre alterações.

Abstract

Nanocellulose reinforcement is a promising technique for improving paper properties, especially strength. This study aimed to evaluate the effect of nanocellulose addition on physical-mechanical properties of papers produced from different fiber blending, apart from to compare two nanocellulose addition methods. Three different fiber were used for fiber blending (eucalyptus, sisal and pine). Handsheets were formed based in blending of all possible combination at 45/55 ratio in 2% consistency and 60 g/m². Handsheets reinforcement were performed by two methods: Mixture method (MT) were mixture of nanocellulose along with pulps during paper formation in 3,5 and 10% addition; Coating method (CT) were the superficial coating of dry formed papers in 10% addition. Nanocellulose were produced by mechanical microfibrillation of sisal pulp. Handsheets were evaluated by physical and strength properties. Nanocellulose addition increased thickness, volume, grammage, apparent density, opacity, roughness, tensile strength, tensile index, stretch, bursting index, tear index and fold endurance in 8.7, 8.8, 10.4, 2.1, 4.1, 23.2, 45.7, 31.8, 20.1, 14.2, 21.1 and 271.6% but reduced bulk, brightness and air permeance in 1.9, 3.4 and 71.7%, respectively. Reinforcement methods presented distinct results. In physical properties, an increasing tendency with increment of nanocellulose (MT) were observed in thickness, grammage and apparent density despite decreasing tendency in air permeance. No tendency was observed in other physical properties. In general, CT presented higher values of thickness, grammage, bulk and brightness but lower values of apparent density and opacity, compared to MT. Mixture method presented increasing tendency in strength properties with increment of nanocellulose content. CT obtained fewer strength properties compared to MT.

Keywords: Strength. Interfiber bonding. Handsheet. Cellulose nanofibers. Paper properties.

Introduction

Brazil has one of the greatest pulp and paper industries in the world. These industries are responsible for annual production of approximately 21.1 and 10.4 million tons of pulp and paper, respectively, contributing to Brazilian economy and society in many aspects (IBA 2019). Despite expressive numbers, these industries are constantly facing concerns and possibilities regarded to quality improvement of its products. Then, quality products demand, especially for noble applications is appellant, requiring studies and development of new products, beyond competition with other technologies. One of the major possibilities is the insertion of nanocellulose into their production process aiming to improve products quality.

Cellulose nanofibers are suspensions formed by small cellulose structures, with diameters in nanometric order (lower than 100 nm), commonly produced by cellulosic fibers exposure to mechanical microfibrillation (Lavoine et al. 2012). Currently, nanocellulose has drawn great attention from scientists and industries with the purpose of improving properties and product quality and creation of new nanomaterials, due to intrinsic characteristics of nanocellulose, such as large specific surface area, high aspect ratio, suitable physical and rheological properties and also because renewable and biodegradable aspect (Joahnson et al. 2012). However, when we bought our attention to nanocellulose application in pulp and paper industries, this reality is far below its potentialities. This is, mainly, due to high obtaining cost, high energy consumption, besides operational bottlenecks. Therefore, studies which approach this research area are increasingly required latterly.

Several researchers have directed their studies toward improvement of pulp and paper products and nanocellulose, aiming to enhance properties and applications, mainly of non-satisfactory quality product, such as the use of nanofibrils to improve mechanical properties and fine reduction of recycled paper (Balea et al. 2018); improve interfibers bonding (Vallejos et al. 2016); increase number of cycles during the use of paper (Delgado-aguilar et al. 2015a); improve softness and printability (Ghazali et al. 2014); optical properties (Kasmani 2016); structure and physical properties (Kose et al. 2015; Miao et al. 2020) barrier properties (Lavoine et al. 2012); hydrophobic behavior (Qi et al. 2020). Nevertheless, studies involving combined effect of nanocellulose and different fiber blends in paper properties have been insufficiently researched

Fiber blending is the act of combining, merging and mixing different types of fibers, which have different properties from the other, especially related to morphology, seeking improvements in product quality when compared to virgin pulps (Kibblewhite 1977; Akeem Azeez et al. 2016). The blend of different fiber sources is also a possibility of development and production of papers that meet certain requirements or even for improvement of deficit papers. Combining different fiber properties can bring advances in physical-mechanical properties, and induce synergistic effect on many other properties. In some countries, like India, companies have carried out fiber blending (hardwoods, softwoods, annual plants, agricultural waste) to obtain papers with a desired quality level (Chauhan et al. 2011).

Papers formed from different fiber blending can present disadvantages, which may be linked to the fiber’s characteristics, such as disabled interfiber bonding besides unsatisfactory mechanical properties, like tear and tensile strength. The use of nanocellulose during paper formation or even coating of dry formed papers can improve interfiber bonding, and then, physical-mechanical properties.

Therefore, this study aimed to evaluate the effect of nanocellulose addition on reinforcement and physical-mechanical properties of papers produced from different fiber blending, apart from to compare two nanocellulose addition methods: mixture of nanocellulose along with the cellulosic pulps during paper formation and the superficial coating of dry formed papers.

Material and methods

In this study, three different cellulosic pulps were engineered for fiber blending. The commercial pulps of eucalyptus (*Eucalyptus sp.*), sisal (*Agave sisalana*) and pine

(*Pinus sp.*) were used. Cellulosic pulps were donated by Lwarcell and Klabin Brazilian companies in rectangular sheet format. Pulps were hydrated for 48 hours, disintegrated in REGMED D-3000 and refined in REGMED HV-10 equipment for 30 minutes for eucalyptus and 45 minutes for sisal and pine. Refining time were set based in previous refinability pre-test. Pulps reached approximately 25 °SR in ideal refining time. Then, pulps were blended in 45/55% ration in all possible combinations. A mechanical stirrer (Fisatom-713d model) was used for homogenization and assistance in suspensions mixing. Pulp blending was based on volume.

Handsheets forming were performed according to TAPPI T 205. Handsheets were formed based on 2% consistency (suspension) and 60 g/m² grammage, in a laboratory paper-making machine REGMED F/SS-2. Three handsheets were formed for each treatment.

Handsheets were reinforced using two methods: mixture of nanocellulose along with pulp blending during handsheets forming (mixture method-MT) and superficial coating of formed handsheets (coating method-CT). In the first process, the mixture of nanocellulose was performed before handsheets forming, adding 3, 5 and 10% of nanocellulose in the 45:55% ration of all combinations. The addition was based on the dry mass of the handsheets (approximately 2 g). In the second process, a one-sided coating was performed with the superficial addition of 10% of nanocellulose on handsheets. Addition was also based on dry mass. The coating was carried out through spatula coating. Stainless steel spatulas with blade width of 12 cm were used for manual coating. Therefore, considering all sources of variation, 24 treatments were performed. After forming and coating stage, reinforced handsheets were conditioned in a controlled humidity and temperature environment (20°C ± 2ºC and 65% ± 5ºC) for the subsequent evaluation of properties.

Nanocellulose were produced using sisal pulp as raw material. The sisal nanofibers were obtained through mechanical microfibrillation of pure and refined sisal pulp. Thereunto, a mechanical microfibrillator mill (Grinder) Super Masscolloider Masuko Sangyo MKCA6-3 at 1500 rpm was used following methodology proposed by Bufalino et al. (2015). The distance between silicon carbide stones was 100 μm. The pulp was immerged in distillated water during 48 hours in order to provide the swelling and hydration of fibers. The consistency was 1.5%, based on dry mass of pulp. Before being submitted to microfibrillation, the pulp was agitated by mechanical stirrer three times a day (15 minutes each) for homogenization and disintegration. The pulp suspension passed 5 times on microfibrillator until obtaining of gel consistency. Final suspension was kept in temperature of 4 ±0.5°C up to reinforced handsheet production. The final suspension consistency was determined using equation 1. Moisture content was set using the wet base. Then, a nanocellulose sample was dried in forced air circulation oven (103 ±2°C) during 24 hours for obtaining of dry mass.

$$Consistency\ (\%) = 100 - moisture\ content(\%) \qquad (1)$$

Table 1 described all treatments used in this research. Figure 1 summarizes and illustrates experimental design.

Table 1 Summary of all treatments and different conditions studied

Process	Treatment	Percentage of cellulosic pulp			Nanocellulose (%)
		Eucalyptus (%)	Sisal (%)	Pine (%)	
Mixture method	MT1	45	55	-	3
	MT2	45	-	55	3
	MT3	55	45	-	3
	MT4	-	45	55	3
	MT5	55	-	45	3
	MT6	-	55	45	3
	MT7	45	55	-	5
	MT8	45	-	55	5
	MT9	55	45	-	5
	MT10	-	45	55	5
	MT11	55	-	45	5
	MT12	-	55	45	5
	MT13	45	55	-	10
	MT14	45	-	55	10
	MT15	55	45	-	10
	MT16	-	45	55	10
	MT17	55	-	45	10
	MT18	-	55	45	10
Coating method	CT19	45	55	-	10
	CT20	45	-	55	10
	CT21	55	45	-	10
	CT22	-	45	55	10
	CT23	55	-	45	10
	CT24	-	55	45	10

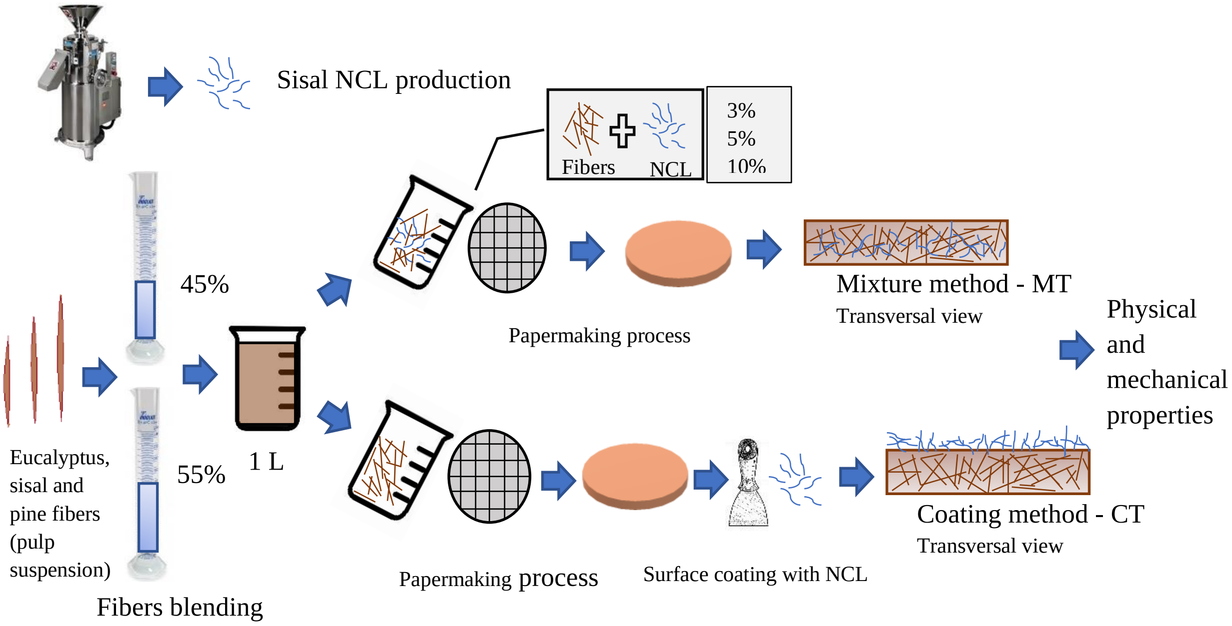

Fig. 1 Schematic preparation of blended handsheets with nanocellulose reinforced by two methods

Nanocellulose reinforced handsheets were evaluated considering its physical and mechanical properties. Each handsheet was divided in small sections according to TAPPI T 220 sp-01 for mechanical properties. Regarding to physical properties, the thickness (TAPPI T 220), grammage (TAPPI T 220), apparent density (TAPPI T 220), bulk (TAPPI T 220), air permeance (TAPPI T 460), roughness (TAPPI T 538) brightness (TAPPI T 452) and opacity (TAPPI T 519) were evaluated. Tensile properties (TAPPI T 494), bursting strength (TAPPI T 403), tear strength (TAPPI T 414) and fold endurance (TAPPI T 511) were evaluated to understand the mechanical properties of reinforced handsheets, making possible the comparison of these along with non-reinforced handsheets and nanocellulose reinforcement methods

A completely randomized design was conducted during the experiment. Three repetitions for each treatment were performed, totaling 63 samples. The results from physical-mechanical properties were evaluated by Anova and when statistical difference happened, the Tukey test ($p < 0.05$) was carried out. Graphs according to nanocellulose percentages and comparing two reinforcement methods were generated. The statistical tests were performed in SISVAR software (Ferreira 2011).

Results and discussion

Nanocellulose consistency in suspension was 1.12%. Considering initial consistency (1.5), a reduction in consistency of approximately 25% occurred. This reduction was due to mass losses and water addition during microfibrillation in order to facilitate the operation and reduce energy consumption. Final consistency was used for determination of volume and mass quantity (in relation to dry mass) from nanocellulose suspensions added to mixtures and coating. Then, in proportions of 3, 5 and 10%, approximately 5.5, 8.9 and 17.8 mL of nanocellulose suspension was added in mixture and coating.

The result of variation in fiber blending excluding nanocellulose addition is presented in Table 2. In other words, just the proportion of 45:55 is used in this study for comparison with nanocellulose reinforced handsheets.

Table 2 Physical properties of blended handsheets in 45:55 proportion

Variation	T. (mm)	Vol. (cm³)	Gr. (g/m²)	Ap. Den. (g/cm³)	Bulk (cm³/g)	Brig. (%)	Op. (%)	Air perm. (µm/Pa·s)	Rough. (mL/min)
45E 55S	0.158	5.069	59.8	0.378	2.644	49.47	89.50	45.37	1462
45E 55P	0.154	4.938	67.4	0.437	2.288	53.17	83.43	53.8	1629
55E 45S	0.155	4.975	64.0	0.413	2.427	50.70	90.23	55.48	1962
45S 55P	0.137	4.377	57.3	0.421	2.386	48.53	82.37	33.29	1573
55E 45P	0.144	4.620	66.3	0.460	2.178	52.73	87.10	42.4	1555
55S 45P	0.150	4.826	61.8	0.411	2.449	47.47	86.00	34.21	1518
Mean	0.150	4.801	62.8	0.420	2.395	50.35	86.44	44.09	1616.5

Where: E (Eucalyptus pulp), S (Sisal pulp), P (Pine pulp), T (Thickness), Vol (Volume), Gr (Grammage), Ap Dens (Apparent density), Brig (Brightness), Op (Opacity), Air perm (Air permeance), Rough (Roughness).

Comparing average values of physical properties with values presented in Table 3 (nanocellulose reinforced), it is possible to observe that, in general, nanocellulose addition, either by mixture or coating reinforced method, provoked increase in thickness, volume, grammage, apparent density, opacity and roughness and in 8.7, 8.8, 10.4, 2.1, 4.1 and 23.2%, respectively. On the other hand, nanocellulose addition reduced bulk, brightness and air permeance in 1.9, 3.4 and 71.7%, respectively.

The increase in thickness, volume, grammage and apparent density can be explained to mass increment realized with nanocellulose addition in papers. Even with low consistency, the addition of determined nanocellulose volume contributes to increase mass and form a thin layer in paper surface, or between the fibers. The increase in opacity can be related to possibility of increase in interfiber connections by the addition of fine and small size structures, besides forming a well-structured layer. These consequences can certainly increase the opacity and become material more opaque, impending light passage during analysis performance.

The increase of roughness with addition of nanocellulose can be related to nanofilm formed in paper surface in coated treatment and accumulation of nanocellulose in paper structure and consequence in thickness. Addition of nanocellulose in mixture method affected thickness and probably roughness. When nanocellulose was added to fiber suspension, fiber accommodation could be affected, bringing increase in roughness as consequence. Majority of researchers reported decrease of roughness with addition of nanocellulose (González et al. 2014; Huang et al. 2018;). Similar resulted was observed in mixture method with increase of nanocellulose percentage (see means of mixture method in Table 3). However, mean values of roughness was dramatically impacted by coating method and mixture method (3%) values. Also, fiber morphology of different blending ratio could have affected handsheet roughness.

Bulk reduction with nanocellulose addition can be associated to intrinsic nanocellulose properties, such as improving accommodation of fibers during handsheet forming, entailing handsheets more compacted, with fewer volume for a given mass added. Bulk reduction was also observed by González et al. (2014), with addition of nanocellulose in paper structure.

Brightness reduction can be related pulp type used for nanocellulose production. It was expected that brightness would not be so impacted, since nanocellulose have high transparency. According to Hu et al. (2013), papers with nanocellulose addition tend to have better optical properties, including brightness. Nanocellulose have as property almost transparency, since the size of nanocellulose is much less than the wavelength of visible light, with large light scattering and transparency. However, sisal pulp was used for nanocellulose production and consequently mixture and coating of papers. Sisal pulp was partially bleached and had a substantial residual lignin content when compared to eucalyptus and pine pulps, which may have contributed to the reduction in brightness.

Air permeance was dramatically reduced with nanocellulose addition in paper structure. Nanocellulose probably acted as fine structure and blocked the voids presented in fiber network among larger fibers. This consequence probably reduced the facility of air volume passage on paper structure, since compacted nanocellulose provides longer tracks for air molecules to diffuse through (Nair et al. 2014). According to Sirviö and Nurminen (2004), small amounts of fines added to paper structure can have a remarkable influence on porosity and air permeance. Adnan et al. (2018) reported a reduction in air permeance by 50% with addition of nanocellulose nanocellulose up to 10%. This property could lead nanocellulose to a material that can be applied to papermaking industries because of huge barrier property, especially for food packaging (El-Samahy et al. 2017).

Air permeance is also related to porosity. Porosity could be also calculated by relation between apparent density of samples and density of crystalline cellulose. Then, a reduction in porosity probably must happen since of reduction of air permeance and apparent density with addition of nanocellulose. According to González et al. (2014), the reduction in porosity is as important property because of its close relationship with mechanical properties. Paper with small porosity tend to present higher mechanical properties due to the increase of hydrogen bond promoted by high specific area of nanocellulose.

Table 3 shows values obtained for physical properties of blending papers with nanocellulose in the two reinforcement methods (Mixture-MT and Coating-CT). The Figure 1 also shows the same results, but presented in graphic form (bar chart) for better comprehension of results.

The variations of physical properties between the blending proportion can be related to ranges in morphologic and chemical properties between the three fibers or even factors associated to the process handsheet forming, such as fibers accommodation, interfiber bonding, variations in volume mensuration, among others.

According to Table 3 and Figure 1, thickness was affected by reinforcement method and proportion of nanocellulose in mixture method. Statistical differences occurred between treatments. In general, thickness presented increasing trend as nanocellulose content increased. Highest values were obtained in treatments which had the addition of nanofibers superficially, such as CT19 (45E 55S 10), CT24 (55S 45P 10) and CT21 (55E 45S 10). In all blending proportion, the coating method presented highest values of thickness. This can be explained by surface deposition and the lack of losses of nanocellulose when compared to mixture method, during handsheet forming. After suspension drying, nanocellulose connect to each other and form a network of interlaced nanofibers creating a film on the paper surface. This film certainly contributed to expressive increase of final paper thickness. Souza et al. (2009) and Viana et al. (2017) reported thickness of nanocellulose films ranging from 10 to 70 µm depending on consistency and film grammage. Minor thickness values were obtained in treatments from mixture method and in low proportions. It also important to emphasize that, between treatments from mixture, the variation was low and did not follow a clear trend as nanocellulose was increased in mixture. This behavior can be explained by possibility of losses in handsheet forming process, since because of their low dimensions, nanocellulose could be drain along with water during drainage and suction step for the formation of fiber network.

Table 3 Physical properties of blended handsheets with nanocellulose reinforcement

Treatment	Thickness (mm)	Volume (cm³)	Grammage (g/m²)	Apparent density (g/cm³)	Bulk (cm³/g)	Brightness (%)	Opacity (%)	Air permeance (µm/Pa·s)	Roughness (mL/min)
MT1 (45E 55S 3)	0.158 def	5.058 def	65.73 cd	0.417 bcdef	2.404bcde	48.9 cdefgh	91.67 abcd	19.24 abc	2128 abc
MT2 (45E 55P 3)	0.148 ef	4.759 ef	66.15 bcd	0.446 abcd	2.245 cde	52.27 ab	87.37 fg	16.32 abcde	1647 bc
MT3 (55E 45S 3)	0.162 cdef	5.184 cdef	66.15 bcd	0.410 cdef	2.445 abcd	47.47 efghi	91.97 abcd	21.43 ab	1462 c
MT4 (45S 55P 3)	0.152 ef	4.874 ef	68.23 bcd	0.449 abcd	2.230 cde	46.87 ghi	90.07 cdef	17.27 abcd	2646 ab
MT5 (55E 45P 3)	0.152 ef	4.868 ef	68.23 bcd	0.450 abcd	2.225 cde	47.43 fghi	91.77 abcd	14.82 abcdef	2461 abc
MT6 (55S 45P 3)	0.171 bcde	5.493 bcde	68.44 bcd	0.400 cdef	2.509 abc	47.17 fghi	89.67 cdefg	27.37 a	1925 abc
Mean	0.157	5.039	67.15	0.429	2.343	48.35	90.42	19.41	2044.8
MT7 (45E 55S 5)	0.171 bcde	5.485 bcde	67.40 bcd	0.395 cdef	2.540 abc	46.40 hi	93.23 abc	17.51 abcd	2073 abc
MT8 (45E 55P 5)	0.142 f	4.535 f	63.65 d	0.449 abcd	2.231 cde	50.9 abcd	87.76 fg	13.26 bcdef	1962 abc
MT9 (55E 45S 5)	0.160 cdef	5.122 cdef	66.46 bcd	0.416 bcdef	2.406 bcde	46.93 fghi	93.27 abc	17.53 abcd	2091 abc
MT10 (45S 55P 5)	0.157 ef	5.026 ef	67.71 bcd	0.433 abcd	2.317 cde	47.03 fghi	89.27 defg	13.49 bcdef	1814 abc
MT11 (55E 45P 5)	0.150 ef	4.799 ef	68.96 bcd	0.461 abc	2.173 cde	51.3 abc	88.6 defg	12.35 bcdef	1703 bc
MT12 (55S 45P 5)	0.162 cdef	5.192 cdef	68.34 bcd	0.422 bcde	2.371 bcde	47.27 fghi	89.1 defg	13.04 bcdef	2128 abc
Mean	0.157	5.027	67.087	0.429	2.340	48.31	90.21	14.53	1961.8
MT13 (45E 55S 10)	0.167 bcdef	5.357 bcdef	73.12 ab	0.437 abcd	2.286 cde	47.13 fghi	94.30 a	4.81 def	2498 abc
MT14 (45E 55P 10)	0.144 ef	4.617 ef	71.46 abc	0.496 a	2.017 e	50.23 bcde	87.3 fg	2.72 f	1906 abc
MT15 (55E 45S 10)	0.167 bcdef	5.363 bcdef	72.91 abc	0.436 abcd	2.295 cde	47.53 efghi	93.90 ab	4.07 ef	2147 abc
MT16 (45S 55P 10)	0.157 ef	5.023 ef	70.73 abcd	0.453 abcd	2.213 cde	47.03 fghi	90.2 bcdef	6.28 cdef	1906 abc
MT17 (55E 45P 10)	0.141 f	4.519 f	67.50 bcd	0.479 ab	2.089 de	49.7 bcdef	87.7 fg	2.72 f	1647 bc
MT18 (55S 45P 10)	0.151 ef	4.834 ef	68.65 bcd	0.456 abcd	2.196 cde	45.7 i	89.70 cdefg	5.14 def	1481 c
Mean	0.155	4.952	70.73	0.460	2.183	47.89	90.52	4.29	1930.8
CT19 (45E 55S 10)	0.203 a	6.516 a	71.77 abc	0.355 f	2.839 a	48.4 defghi	91.63 abcde	16.77 abcde	1758 bc
CT20 (45E 55P 10)	0.171 bced	5.483 bced	71.98 abc	0.421 bcdef	2.378 bcde	53.1 a	87.23 fg	14.89 abcdef	1740 bc
CT21 (55E 45S 10)	0.186 abc	5.955 abc	72.50 abc	0.390 def	2.564 abc	49.7 bcdef	89.97 cdef	12.1 bcdef	2387 abc
CT22 (45S 55P 10)	0.185 abcd	5.929 abcd	76.87 a	0.416 bcdef	2.408 bcde	49.43 cdefg	89.90 cdefg	11.48 bcdef	1740 bc
CT23 (55E 45P 10)	0.161 cdef	5.159 cdef	71.46 abc	0.444 abcd	2.253 cde	52.37 ab	86.2 g	9.05 bcdef	1703 bc
CT24 (55S 45P 10)	0.193 ab	6.177 ab	70.00 abcd	0.364 ef	2.752 ab	47.57 efghi	87.93 efg	6.05 def	2831 a
Mean	0.183	5.870	72.43	0.398	2.532	50.10	88.81	11.72	2026.5
Pooled Mean	0.163	5.222	69.35	0.429	2.349	48.66	89.99	12.49	1990.9
CV (%)	5.34	5.34	3.31	4.89	5.44	1.82	1.32	33.39	16.71

Means followed by same letter in column do not differ statistically from each other by Tukey test at 5% de probability level.

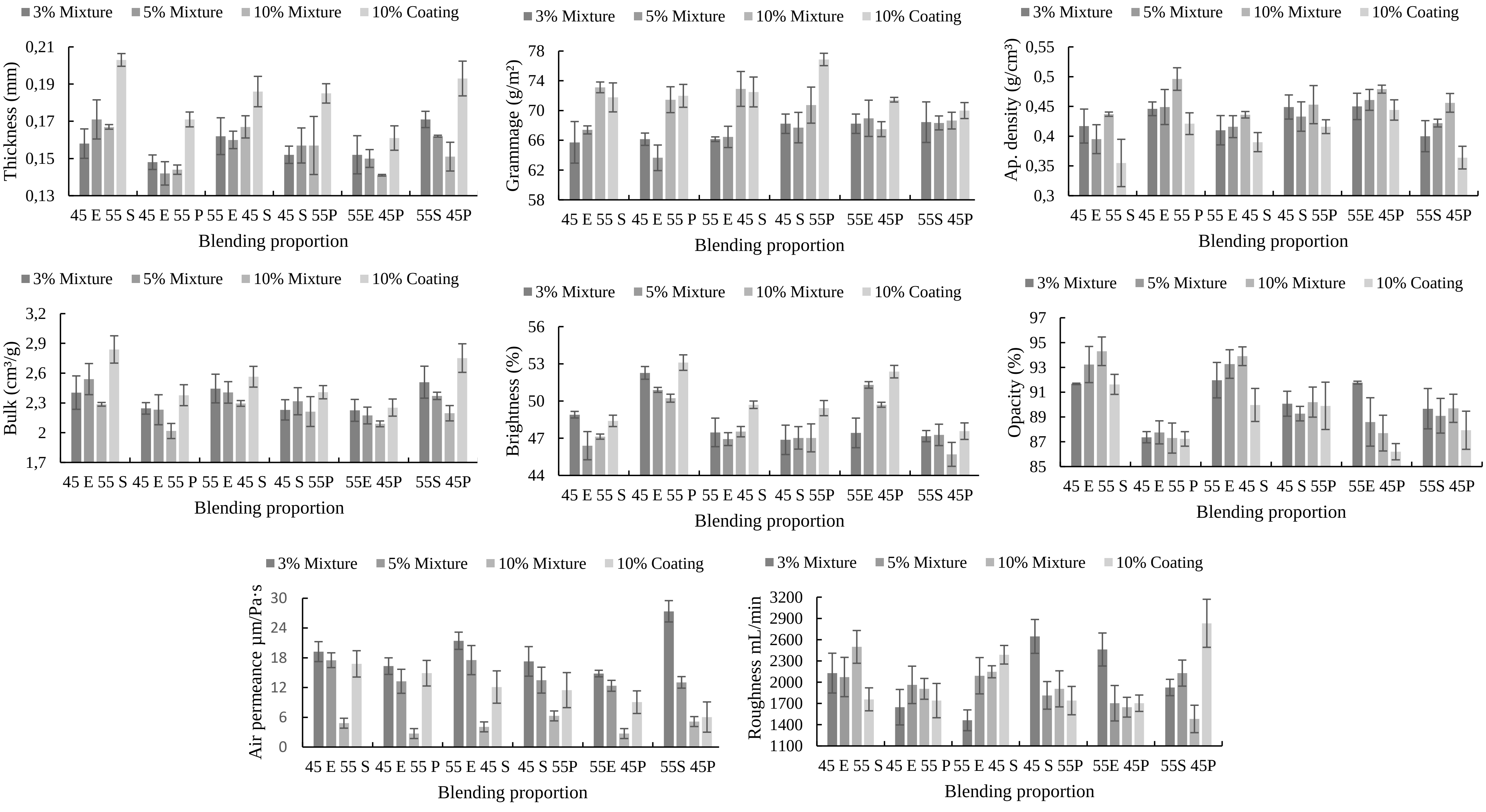

Fig. 1 Physical properties behavior due to blending proportion and nanocellulose and reinforced method

The volume presented same tendency to the results obtained in thickness, showed in Table 3, since volume was a consequence of multiplication of surface area of handsheets (constant for all treatments) and thickness of each treatment.

Grammage exhibited similar tendency to that presented by thickness. Statistical differences between treatment occurred and, in general, presented increasing tendency as nanocellulose content raised. Highest values were obtained in surface coating at 10%, represented by treatments CT19, CT24 and CT21, same obtained in thickness analysis. The increase in paper grammage can also be related to losses during reinforced method. In coating, small quantity of nanocellulose is lose during procedure, implicating in increase of grammage, since small quantity in mass (approximately 200 mg) was placed in paper surface. The lowest values in grammage were obtained in treatments MT8 (45E 55P 5) and MT1(45E 55S 3), which contained smaller amounts of nanocellulose and from mixture method. The lower the amount of nanofiber percentage is, the smaller the amount of mass added for mixture. This reflected in the paper grammage. Besides, losses during handsheet forming affect grammage. In some treatments from mixture method at 10% (MT13, MT14 and MT15) the grammages was high, assimilated to that observed in coating method. Presumably, in these treatments, nanocellulose losses were lower due to better fiber accommodation.

Statistical differences between treatments happened for apparent density. Highest values were obtained in treatments MT14 (45E 55P 10) and MT17 (55E 45P 10). Lowest values were obtained in treatments CT19 (45E 55S 10) and CT24 (55S 45P 10). Apparent density had an increasing as nanocellulose percentage was raised in mixture method. This increase can be related to mass increment performed by increasing nanocellulose content, besides it could be placed in empty spaces among fiber network, blocking pores and consequently increasing density (Balea et al. 2016). González et al. (2014) also reported increasing trend in paper density as the nanocellulose percentual was raised in papers. However, a decrease in coating method occurred when compared to mixture method, including small quantity of nanocellulose in mixture method. This decrease can be associated to greater thickness found in the treatments with coating method. The increase in thickness was fundamentally higher than the mass increase with surface nanocellulose addition.

The bulk presented similar tendencies but inversely proportional to apparent density, as observed in Table 3 and Figure 1. Highest values were obtained in treatments CT19 and CT24. Lowest values were obtained in treatments MT14 and MT17. Same explanation of apparent density can be used for differences between treatments in bulk.

Regarded to optic properties, addition of nanocellulose affected both brightness and opacity. According to Table 3, statically difference occurred between treatments. Highest values of brightness and opacity were found in treatments CT20 (45E 55P 10) and MT13 (45E 55S 10), while lower values were found in treatments MT18 (55S 45P 10) and CT23 (55E 45P 10), respectively. Both brightness and opacity did not follow a tendency depending on nanocellulose addition in mixture method. Similar result was obtained in the study of González et al. (2012), wherein opacity did not present increase or decrease trend with nanocellulose addition, but was, in average, higher than paper without addition. Delgado-Aguilar et al. (2015b) reported that the opacity is decreased with nanocellulose content, due to its distribution and dispersion in handsheet forming. According to Balea et al. (2016), large quantities of small dimensions nanofiber tend to reduce brightness.

However, the coating method presented higher brightness and lower opacity than mixture method. This can be explained by the nanofilm formed in paper surface after suspension drying and his interaction with light. The film probably responded in greater intensity than the remaining fibers. Generally, paper produced from common fibers are opaque. However, paper become transparent when in nanoscale due to a denser structure (Zhu et al. 2014). According to Brodin et al. (2014), the coating method of paper can reduce opacity due to bonds in surface reduce the light scattering coefficient.

Statistical differences occurred in air permeance. Highest values were found in treatments MT6 (55S 45P 3) and MT3 (55E 45S 3), while lower values were found in treatments MT14 (45E 55P 10) and MT17 (55E 45P 10). In general, highest values were obtained from mixture method and low nanocellulose percentage, while fewest values were obtained from mixture method and high nanocellulose percentage. Air permeance presented a decreasing tendency with addition of nanocellulose, especially with increase of nanocellulose content in mixture method. This result agrees with Adnan et al. (2018) and El-Samahy et al. (2017), who reported air permeance behavior. Reduction in air permeance can be explained by reduction in paper porosity with addition of nanocellulose. Nanocellulose occupy voids in paper structure (fiber-fiber voids) blocking air passage during air permeance analysis. In coating method, a decreasing tendency also happened with addition of nanocellulose, but was not as significant as mixture method. Previous explanation can be addressed for decreasing with nanocellulose addition. Differences between mixture and coating method can be related to nanocellulose application mode. Differently from mixture method, one side application is performed in coating method, forming a superficial film. This application mode does not block empty spaces in paper structure, allowing air passage. The obstruction is only on the surface, not being sufficiently able to reduce the air flow compared to mixture method with high nanocellulose content (Hubbe et al. 2017).

No tendency was observed for roughness with addition of nanocellulose. Statistical differences occurred between treatments. Differences can be related to fiber morphology or variations during handsheet forming. Highest values were found in treatments CT24 (55S 45P 10) and MT4 (45S 55P 3), while lower values were found in treatments MT18 (55S 45P 10) and MT3 (45E 55S 10). It was expected that coating treated presented fewer roughness than others treatment. However, this tendency does not happen. Just few treatments presented low roughness. Nanocellulose addition in surface was probably not regular, since the nanocellulose dispersal was performed manually by stainless spatula. This could affect nanofilm in surface and affected roughness. According to Charani et al. (2013), coating paper surface with nanofibrilated cellulose gives a denser and smooth surface and affect porosity of papers.

The result of mechanical properties in 45:55 blended papers excluding nanocellulose addition is presented in Table 4. Mechanical values of reinforced paper (pooled mean) are presented in Table 5. Comparing mean values of two tables, it is possible to observe that, in general, nanocellulose addition, either by mixture or coating reinforced method, caused increase in all mechanical property. The tensile strength, tensile index, stretch, bursting index, tear index and fold endurance were increased in 45.7; 31.8; 20.05; 14.2; 21.1; 271.6%, respectively.

Table 4 Mechanical properties of blended handsheets in 45:55 proportion

Variation	Tensile strength (N/m)	Tensile index (N·m/g)	Stretch (mm)	Bursting index (kPa·m²/g)	Tear index (mN·m²/g)	Fold endurance (number)
45E 55S	1525	24.72	3.506	2.4	16.69	22
45E 55 P	2015	28.87	3.627	2.14	11.52	25
55E 45 S	1889	28.68	3.158	2.09	15.72	21
45S 55P	1832	30.99	4.148	3.19	19.83	112
55E 45P	1893	27.62	3.117	2.3	11.97	23
55S 45 P	1969	30.75	3.335	3.55	18.06	114
Mean	1853.8	28.61	3.482	2.61	15.63	52.8

Where: E (Eucalyptus pulp), S (Sisal pulp) and P (Pine pulp)

The increase in mechanical properties with nanocellulose addition is explained by nanocellulose properties (nanometric scale) and influence of these components in paper structure. According to Viana et al. (2017), nanofibrillated cellulose presents large specific surface area and ability to generate strong intermolecular hydrogen bonds which improve mechanical properties of materials. Also, the length diameter ratio is high, forming a rigid, homogeneous network with low porosity (Lavoine et al. 2012). Nanocellulose addition in papers improve fibers interaction in paper structure (interfiber bonding) since the stress transfer is enhanced due to higher fiber-fiber contact links and increase in the number of bonds, causing improvement in strength property during certain mechanical request (Charani et al. 2013).

Some authors reported similar tendency of increasing strength properties with addition of nanocellulose in paper. Fathi and Kasmani (2019) reinforced blended papers with nanocellulose and obtained significant improvement in tensile, bursting, tear resistance and fold endurance of 33, 33.5, 6.6 and 63.2 by adding just 1% of nanocellulose. Guan et al. (2019) reported increase of 32.4% in tensile index by adding up to 10% of nanocellulose in bamboo pulps. Balea et al. (2019) obtained increase of 60 and 15% in tensile and bursting index by adding up to 3% of nanocellulose. According to authors, nanocellulose content did not caused significant increase in tear index.

Huge improvement of mechanical property despite inexpressive increase in grammage is another amazing property of nanofibrillated cellulose we observed in this study. By just increasing handsheet grammage in 10%, we have got substantial improvement in mechanical properties. The addition of nanocellulose allows to reduce paper grammage for a given strength requirement. Then, papers with low grammage and addition of small quantity of nanocellulose tend to present similar strength properties than high grammage papers. This could lead nanocellulose to a promising material that can be used in many applications such as composites, packaging, electron devices, coatings, pharmacy, biomedicine and chemical industries, thanks to their high strength and stiffness along with low weight (Klemm et al. 2018).

Strength properties are very important in pulp and paper industries and impact many applications. Table 5 shows values obtained for mechanical properties of blending papers with nanocellulose in the two reinforcement methods. The Figure 2 also shows the same results, but presented in graphic form (bar chart) for better comprehension of results.

The variations of mechanical properties between the blending proportion can be related to ranges in morphologic and chemical properties between the three fibers or even factors associated to the handsheet forming, such as fibers accommodation, interfiber bonding, variations in volume mensuration, among others.

An increasing tendency is observed in all strength properties as nanocellulose content is enhanced in mixture method. Results shown in this study agrees with Viana et al. (2017), Lavoine et al. (2012), Balea et al. (2019) and other authors. Same explanation given in previous paragraph about increase in mechanical properties when nanocellulose is added in paper structure can be addressed for such behavior in mixture method.

In contrast, coating method presented lowest values for all strength properties. In some cases, strength was even fewer than those obtained in virgin handsheet, with no nanocellulose added. These results disagree with majority of authors. Charani et al. (2013) reported that coating method lead to a to significant enhancement of the strength properties. According to authors strength properties were similar to those obtained in blending with pulp suspension (mixture method), differently from results reported in this study. Differences between these two surveys can be related to methodology (coating pattern) performed in each study. For example, the dispersion of nanocellulose can strongly affect mechanical and rheological properties. Pour dispersion can have no improvement or even decline some property due to agglomeration problems through hydrogen bonding (Campano et al., 2018). The dispersion (methodology) could be one of the reasons why coating method presented results significatively fewer than in mixture method and also practically did not differ from the paper without nanocellulose reinforcement.

Table 5 Physical properties of blended handsheets with nanocellulose reinforcement

Treatment	Tensile strength (N/m)	Tensile index (N·m/g)	Stretch (mm)	Bursting index (kPa·m^2/g)	Tear index (mN·m^2/g)	Fold endurance (number)
MT1 (45E 55S 3)	2633 cdefghi	38.4 abcdef	3.896 abcd	3.11 abcd	21.62 abcde	54 d
MT2 (45E 55P 3)	2535 cdefghi	36.93 abcdefgh	4.138 abcd	2.60 cde	15.32 fghi	54 d
MT3 (55E 45S 3)	2377 efghi	34.6 bcdefgh	3.846 abcd	2.92 abcde	17.22 defghi	45 d
MT4 (45S 55P 3)	3244 abcd	45.77 ab	4.931 abcd	3.27 abcd	22.10 abcd	480 ab
MT5 (55E 45P 3)	2457 defghi	34.71 bcdefgh	3.663 abcd	2.74 bcde	13.44 hi	51 d
MT6 (55S 45P 3)	2748 abcdefgh	38.6 abcdef	4.153 abcd	3.59 abc	26.29 a	257 abcd
Mean	2665.67	38.17	4.10	3.04	19.33	156.83
MT7 (45E 55S 5)	2668 cdefghi	37.91 abcdefg	4.258 abcd	2.82 abcde	22.18 abcd	97 cd
MT8 (45E 55P 5)	2204 fghi	33.25 cdefgh	3.679 abcd	2.51 cde	15.62 fghi	74 d
MT9 (55E 45S 5)	2784 abcdefg	40.23 abcde	4.520 abcd	3.28 abcd	20.51 bcdef	66 d
MT10 (45S 55P 5)	3117 abcde	44.54 abc	5.452 a	3.53 abc	23.21 abc	406 abc
MT11 (55E 45P 5)	2701 bcdefghi	37.7 abcdefg	3.016 bcd	2.43 cde	14.82 ghi	60 d
MT12 (55S 45P 5)	3115 abcde	43.83 abcd	5.135 abc	3.29 abcd	24.11 ab	274 abcd
Mean	2764.83	39.58	4.34	2.98	20.08	162.83
MT13 (45E 55S 10)	3549 a	46.58 a	5.478 a	3.59 abc	23.32 abc	424 abc
MT14 (45E 55P 10)	3215 abcd	43.53 abcd	4.681 abcd	3.06 abcd	16.79 efghi	307 abcd
MT15 (55E 45S 10)	3110 abcde	40.86 abcd	4.288 abcd	3.32 abcd	18.58 cdefgh	346 abcd
MT16 (45S 55P 10)	3510 ab	47.57 a	5.421 ab	4.09 a	26.00 a	590 a
MT17 (55E 45P 10)	2965 abcdef	42.55 abcd	4.367 abcd	2.90 abcde	15.91 fghi	144 bcd
MT18 (55S 45P 10)	3362 abc	47.08 a	5.627 a	3.92 ab	22.23 abcd	541 a
Mean	3285.17	44.70	4.98	3.48	20.47	392.00
CT19 (45E 55S 10)	2100 ghi	28.77 efgh	3.752 abcd	2.15 de	14.91 ghi	18 d
CT20 (45E 55P 10)	1878 i	25.61 h	2.576 d	2.19 de	13.83 hi	17 d
CT21 (55E 45S 10)	2121 ghi	28.76 efgh	2.796 cd	2.21 de	15.04 ghi	18 d
CT22 (45S 55P 10)	2525 defghi	32.51 defgh	3.537 abcd	2.96 abcd	19.36 bcdefg	49 d
CT23 (55E 45P 10)	1915 hi	26.52 gh	3.331 abcd	1.65 e	12.37 i	33 d
CT24 (55S 45P 10)	2009 ghi	28.48 fgh	3.771 abcd	3.44 abcd	19.59 bcdefg	40 d
Mean	2091.33	28.44	3.294	2.43	15.85	29.17
Pooled Mean	2701.73	37.72	4.180	2.98	18.93	196.2
CV (%)	9.85	9.87	18.34	13.85	11.62	28.35

Means followed by same letter in column do not differ statistically from each other by Tukey test at 5% de probability level.

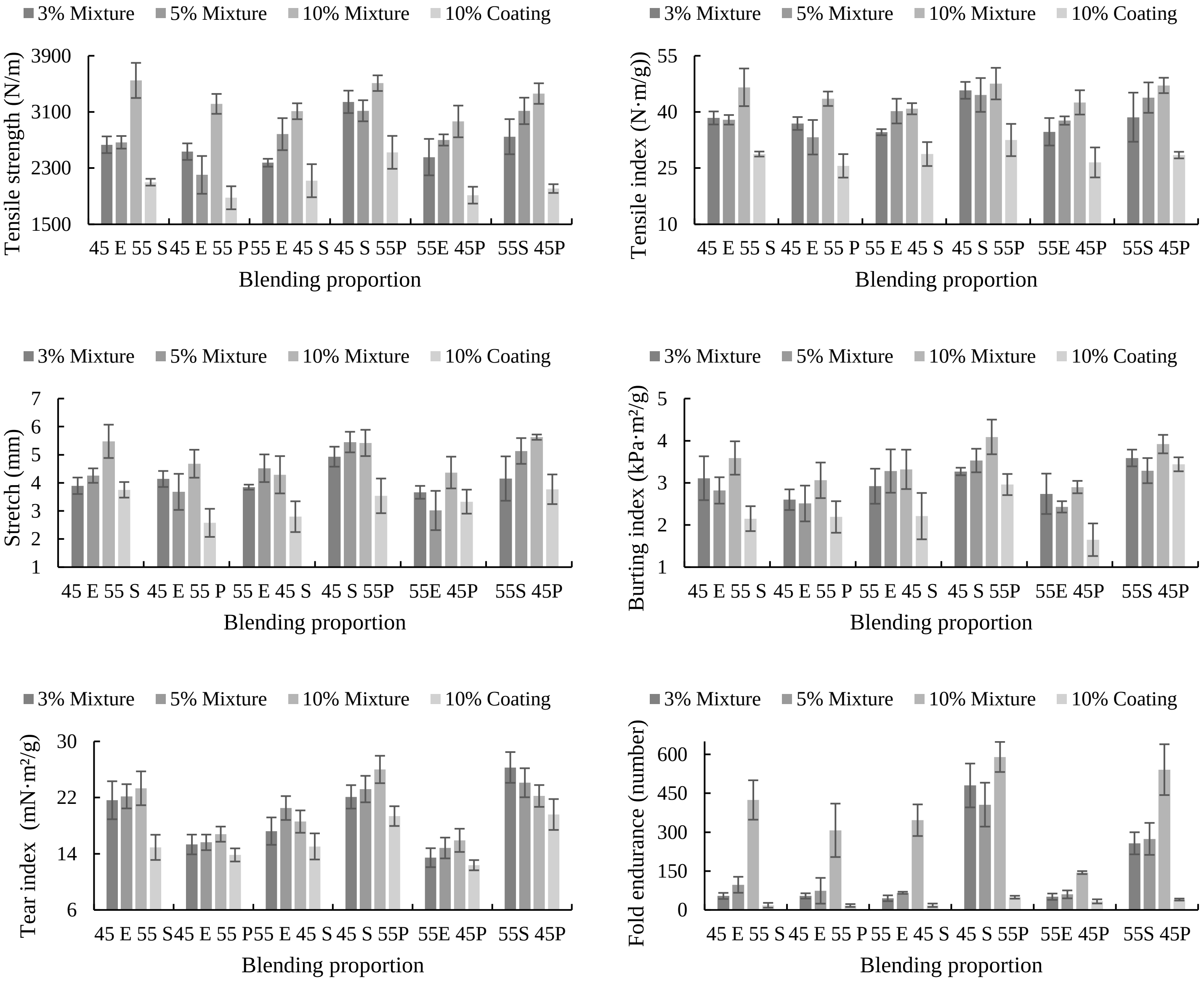

Figure 2. Mechanical properties behavior due to blending proportion and nanocellulose and reinforced method.

Generally, the highest values for all strength properties were obtained in 45S:55P blending proportion, mainly represented by MT16 (45S 55P 10) treatment. These results can be due to strength properties of this fibers, thanks to their morphological properties such as huge fiber length. Additionally, nanocellulose may have had remarkable influence on strength properties. Nanocellulose could have acted like fine between the long and resistant fibers on paper structure and contributed to upgrading interfiber bonding and consequently mechanical properties. According to Verdejo and Bismarck (2017) nanofibrils form a three-dimensional network structure by wrapping, interlacing or linking fibers, enhancing strength properties.

Tensile properties can be divided in many other properties, such as tensile strength, stretch, tensile energy absorption, tensile stiffness, breaking length and tensile index. These properties give us different and important information about paper strength. Table 5 and Figure 2 presents results from tensile strength, stretch and tensile index from samples. Values from tensile properties are similar and presented same tendency. Statistical differences happened between treatments. Highest values were found in treatments from MT method and higher nanocellulose content MT13 (45E 55S 10), MT16 (45S 55P 10) and MT18 (55S 45P 10). Lowest values were found in treatments coating method represented by CT20 (45E 55P 10) and CT23 (55E 45P 10). An increasing tendency is observed when nanocellulose content is enhanced in mixture method. Figure 3 illustrates this tendency using tensile index.

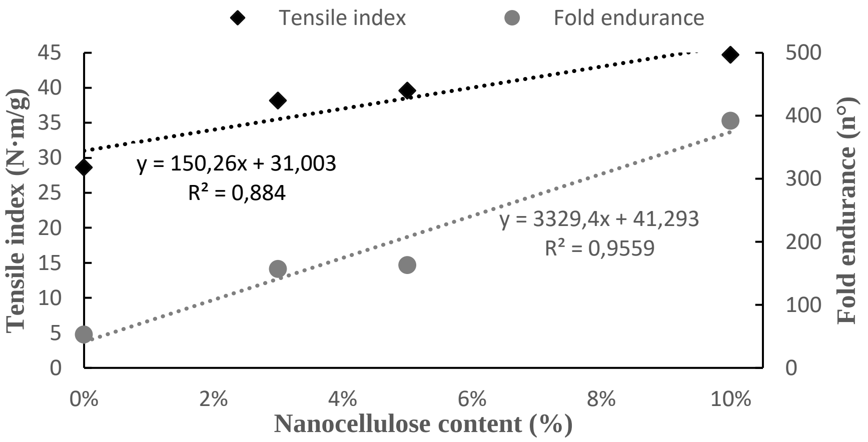

Fig. 3 Tensile index and fold endurance behavior according to nanocellulose content increase in mixture method

The other strength properties presented same tendency as observed in tensile properties. Statistical differences occurred between treatments. Highest values were found in treatments MT16 and MT18 for bursting index while lowest values were found in treatments CT23 and CT19 (45E 55S 10). In tear index, highest values were found in treatment MT16 and MT18 and lowest values in treatments CT23 and CT20. Fold endurance presented the biggest difference between mixture and coating method. Highest values were also represented by treatments MT16 and MT18 while lowest values were represented by treatments MT8 (45E 55P 5), MT9 (55E 45S 5), MT11 (55E 45P 5) and all treatments from coating method.

Conclusion

Nanocellulose addition in paper structure resulted in different and impressive paper properties. Nanocellulose addition affected both physical and mechanical properties of blended papers. In physical properties, nanocellulose resulted in increment of thickness, volume, grammage, apparent density, opacity and roughness and reduction of bulk, brightness and air permeance. All strength properties were dramatically increased by nanocellulose reinforcement. Higher increments were observed in tensile strength and fold endurance. Fiber blending of different fibers with nanocellulose addition also affected paper properties. The best proportion for mechanical properties was 45% sisal and 55% pine pulp. In physical properties, the best proportion varied depending on property.

The two-reinforcement methods were different regarded to physical and mechanical properties. There were statistically significant differences between treatments in all evaluated properties. In mixture method, increasing tendencies with of nanocellulose content were observed for thickness, grammage, apparent density and strength properties. A decreasing tendency was observed for bulk and air permeance. Other properties showed no trend. In general, coating method presented higher values in thickness, grammage, bulk and brightness compared to mixture method. However, coating method reduced apparent density, opacity and strength properties. All strength properties were dramatically affected by coating method. In this study, mixture of nanocellulose along with the cellulosic pulps during paper formation presented superior properties than superficial coating of dry formed papers for blended papers.

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