

Water-Based Processing of Fiberboard of Acrylic Resin Composites Reinforced With Cellulose Wood Pulp and Cellulose Nanofibrils

Emanoele Maria Santos Chiromito¹, Eliane Trovatti² and Antonio Jose Felix Carvalho^{1,*}

¹Department of Materials Engineering, São Carlos School of Engineering, University of São Paulo, Av. João Dagnone, 1100, 13563-120, São Carlos-SP-Brazil.

²University of Araraquara-UNIARA, R. Carlos Gomes, 1217, CEP 14801-320, Araraquara, SP, Brazil.

*Corresponding Author: Antonio Jose Felix Carvalho. Email: toni@sc.usp.br.

Abstract: Despite the great potential of cellulose wood pulp and cellulose nanofibrils as reinforcing filler in thermoplastics, its use is limited due to its tendency to form agglomerates and due to its high hydrophilic character. Here we describe fiberboard composites with high contents of wood pulp or cellulose nanofibrils, and a resin of poly (styrene-methyl-methacrylate-acrylic acid) used as water-based emulsion. Cellulose wood pulp and cellulose nanofibrils were used directly in the form of water suspensions. The method is based on the flocculation of the polymer emulsion followed by agglomeration of a mixture of the polymer emulsion and cellulose suspension, leading to the co-precipitation of the composite material, which can be easily separated from the water phase. Composites with acrylic polymer/cellulose fibers in the proportions of 75:25, 50:50 and 25:75 wt% were prepared. Composites were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and water absorption tests. SEM analysis revealed a very good dispersion of the fibers without evidence of agglomeration, which led to superior mechanical properties. These results showed the effectiveness of the methodology and the potential of cellulose wood pulp and CNF as reinforcement fillers in fiberboard composites and any other high fiber-content materials.

Keywords: Cellulose wood pulp; cellulose nanofibrils; composites; acrylic resin emulsion; fiberboard

1 Introduction

The development of composites reinforced with materials derived from renewable resources is of great interest nowadays. This approach opens the possibility of technological innovation since new materials and new processing strategies can be developed. Cellulose nanofibrils (CNF) and bleached cellulose wood pulp are interesting examples of renewable materials for composite reinforcement purpose. These materials have low cost since bleached cellulose pulp is a commodity and CNF is produced from wood pulp and interesting properties, such as low density, low coefficient of thermal expansion, high surface area, high specific strength, high Young's modulus [1], besides the advantages of the nanometric nature of CNF [2].

Cellulose fibers are high hydrophilic materials forming strong agglomerates, especially when dried, and this feature makes it very difficult to disperse them in the majority of commercial thermoplastic polymers, which are predominantly hydrophobic. [3,4] This is the main reason why cellulose wood pulp and CNF are not used more extensively as reinforcement in non-water soluble matrices [5-7].

Several studies have been published regarding to the preparation and characterization of composites of diverse polymer resins with cellulose such as phenolic [8], epoxy [9], acrylic [10], polyester [11] and a variety acrylic copolymer emulsions [11-13]. In general, these methods are laborious and involve the use

of organic solvents and complex chemical reactions and/or expensive processes, which generally modifies the cellulose properties. [12,14,15].

The process described in this paper is based on a previous research in our group, in which composites with low fiber content (5 to 15 wt%) were prepared by an all-aqueous process based on the quick destabilization of a mixture of polystyrene nanoemulsion and cellulose wood pulp or CNF suspension [16]. The principle of the method is based on the flocculation of a polymer nanoemulsion in the presence of a fiber or nanofiber suspension. Nanoemulsions are stable due to the repulsive ionic forces between the polymer particles and, when a coagulant is added, the particles are attracted one to each other leading to the coagulation. When the coagulation takes place in the presence of fibers, the fibers are coated by the polymer and it can be removed from the suspension after agglomeration as a composite mass.

Here we describe an alternative way for the preparation of fiberboard composites with high fiber content, up to 75%. This is a challenge since at high fiber loads the agglomeration will be favored, resulting in poor finishing and poor mechanical properties. The process is based on the flocculation of a nanoemulsion of an acrylic resin in the presence of cellulose wood pulp or CNF suspension. The focus of this work was the control of the process aiming to avoid fiber segregation and agglomeration. The material generated using the method was processed as thermoplastic composites with fiber content of 25, 50 and 75 wt%.

2 Experimental

2.1 Materials

Commercial acrylic resin based on styrene, methyl methacrylate and acrylic acid was supplied as emulsion by Hydronorth Brazil, with solid content of 13,9 wt%, pH 9 and $M_w = 175.000 \text{ g}\cdot\text{mol}^{-1}$. Aluminium potassium sulphate salt ($\text{KAl}_3(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) solution (alum) used as flocculation agent was supplied by Synth (Brazil). Bleached Kraft wood pulp (CP) from Eucalyptus was supplied by Suzano Papel e Celulose S.A. Cellulose nanofibrils (CNF) aqueous suspension at 3 wt% solid content produced from bleached Eucalyptus wood pulp was supplied by Suzano Papel e Celulose S.A.

2.2 Fiberboard Composites Preparation

Bleached pulp was dispersed in water for 24 h at a concentration of 8 wt%. This cellulose fibers suspension was homogenized with an Ultra-Turrax homogenizer (model T-25, IKA-Germany) operating at 10.000 rpm for 10 minutes. Then, cellulose pulp (CP) or cellulose nanofibrils (CNF) suspension was mixed with the acrylic resin emulsion (AR) and homogenized with the Ultra-Turrax for 2 min. The proportions of cellulose fibers suspension and acrylic resin emulsion were set to give composites with final polymer/cellulose proportions of 75:25, 50:50 and 25:75 wt%, named respectively as AR/CP 75:25, AR/CP 50:50 and AR/CP 25:75. Similar procedure was used to prepare the composites based on CNF, which were named AR/CNF 75:25, AR/CNF 50:50 and AR/CNF 25:75, respectively to their CNF/polymer proportions of 75:25, 50:50 and 25:75 wt%.

The flocculation and agglomeration were obtained adding 10 mL/L of a 1 wt% solution of alum under vigorous agitation. Flocculation took place after few minutes and was evidenced by the separation of a white mass from water, which was visible as a clear liquid layer at the top of the mixture. In the second step of the process, the water was removed by filtration and the material retained on the filter was washed with distilled water and then removed in the form of a plate. The plate was dried in an air-circulation oven at 60°C for 24 hours and hot-pressed at 160°C and 10 MPa for 3 minutes generating the plates of the composite material. The step in which the wet sheet is removed from the filter is critical once it should have uniform thickness to give a homogeneous fiberboard without voids or defects.

2.3 Characterization

FTIR spectra were obtained using a Perkin-Elmer Spectrum 100 FT-IR Spectrometer with attenuated total reflectance (ATR) device of diamond coated zinc selenide crystal. The measurements were performed with 4 cm^{-1} resolution being taken 32 scans for each run performed from 650 to 4000 cm^{-1} .

Thermogravimetric analysis (TGA) was assessed using a Perkin Elmer Thermogravimetric Analyzer Pyris 1 TGA equipped with a platinum crucible using samples with 3-10 mg at constant heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ from room temperature to 850°C , under nitrogen flow at $20\text{ mL}\cdot\text{min}^{-1}$.

Water absorption experiment was carried out by the immersion of small plates with $40 \times 4 \times 1\text{ mm}$ in distilled water at room temperature for 72 hours, and the mass gain were measured in intervals of 2 hours. For weighing, the samples were removed and the excess water was carefully removed with an absorbent tissue.

DMA measurements were carried out in a Perkin Elmer DMA 8000 Dynamic Mechanical Analyzer equipment working in three-point bending mode. Samples were analysed at temperature range from -20 to 150°C , heating rate of $3\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, and oscillation frequency of 1 Hz.

Tensile Tests were carried out in an Instron 5969 Universal Testing Machine equipped with a 5 kN load cell, at a deformation rate of $100\text{ mm}\cdot\text{min}^{-1}$ according to ASTM D 638. Specimens were $108\text{ mm} \times 10\text{ mm}$ and were kept at 23°C and 50% RH for 72 hours before tests.

Scanning Electron Microscopy (SEM) of fragile fractured surface obtained in liquid nitrogen were examined using an Inspect F50 scanning electron microscope from FEI, the Netherlands.

3 Results and Discussions

3.1 Composites Fiberboard Preparation

Fig. 1 shows the dried composites before hot-pressing prepared with CNF (1A) and cellulose wood pulp (1B).

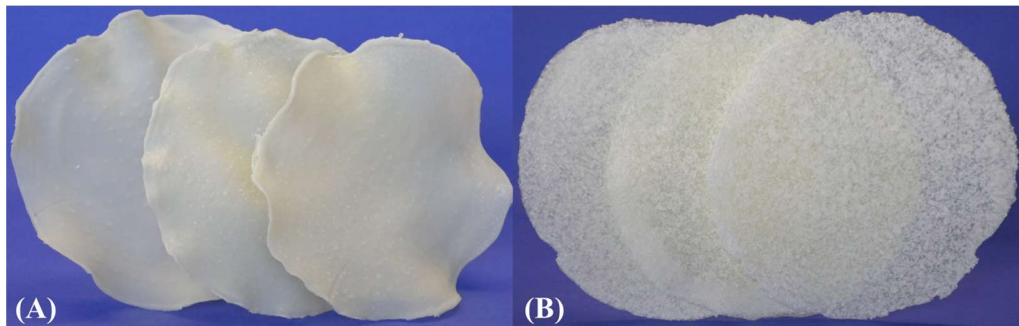


Figure 1: Photographs of the dried fiberboard composites before pressing, prepared with A) CNF and B) cellulose wood pulp (CP)

It is possible to observe that AR/CNF samples (Fig. 1(A)) are very homogeneous material, and the AR/CP samples (Fig. 1(B)) shows less homogeneous aspect with agglomerates of wood pulp and regions of voids.

Fig. 2 shows the fiberboard composites after hot-pressing. As observed, before the hot-pressing process the CNF composites are more homogeneous while CP composites show agglomerates with an irregular surface evidenced in AR/CP 25:75 (Fig. 2(F)).

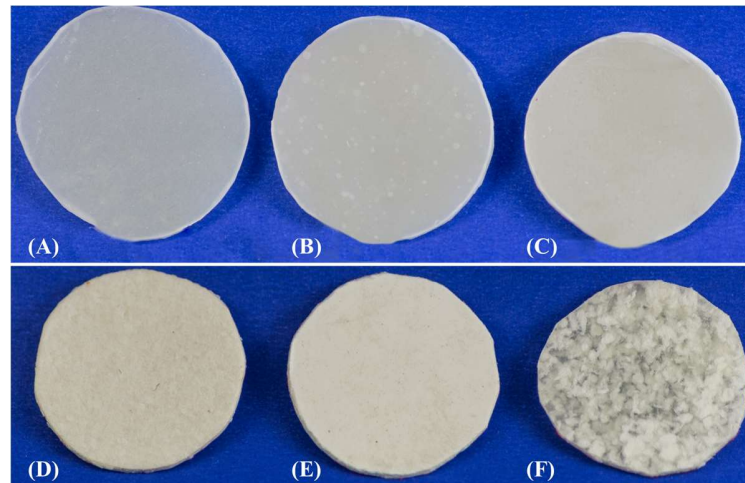


Figure 2: Fiberboard composites obtained by co-precipitation process and hot pressing (a) AR/CNF 75:25, (b) AR/CNF 50:50, (c) AR/CNF 25:75, (d) AR/CP 75:25, (e) AR/CP 50:50 and (f) AR/CP 25:75

As already mentioned, the method used is based on the flocculation and coagulation of a polymer nanoemulsion in the presence of the fiber in water suspension [16]. The nanoemulsion stability is due to the repulsion between the negatively charged particles prepared with an anionic surfactant. When the stability of the nanoemulsion is broken by the addition of divalent or trivalent ions, such as Al^{3+} , the repulsion between particles is replaced by attraction forces leading to the flocculation and then coagulation of the polymer particles [17,18]. The flocculation occurs due to the van der Waals attraction forces among the components, once the repulsion of the charged particles is shielded by the flocculant agent, which neutralizes the particle charge. The destabilized particles and fiber mixture agglomerate into larger aggregates that can be separated from the water, giving rise, directly, to the composite. When the coagulation takes place the fiber in suspension are coated with the polymer emulsion, followed by the composite mass formation, in which the fiber/matrix dispersion is high homogeneous.

3.2 Fourier Transform Infrared Spectroscopy

The typical spectrum of the cellulosic substrate (Figs. 3(A) and 3(B)) showed bands at 3300 , 2880 and 1100 cm^{-1} , associated with the vibration of the O-H, C-H, and C-O-C bonds, respectively [19]. The bands at 1730 cm^{-1} and 2900 in acrylic resin spectrum is associated to C=O ester and CH_2 , typical of the methyl methacrylate [20], and those at 700 and 750 cm^{-1} corresponded to the vibration of the mono substituted polystyrene ring. FTIR spectra of the fiberboard composites of AR based on CNF or cellulose wood pulp resulted in a combination of their typical peaks, and no shifting in vibrational bands were observed. A gradual increase in peak intensity at 1730 cm^{-1} indicated the increase in the acrylic resin concentration in the fiberboards composites.

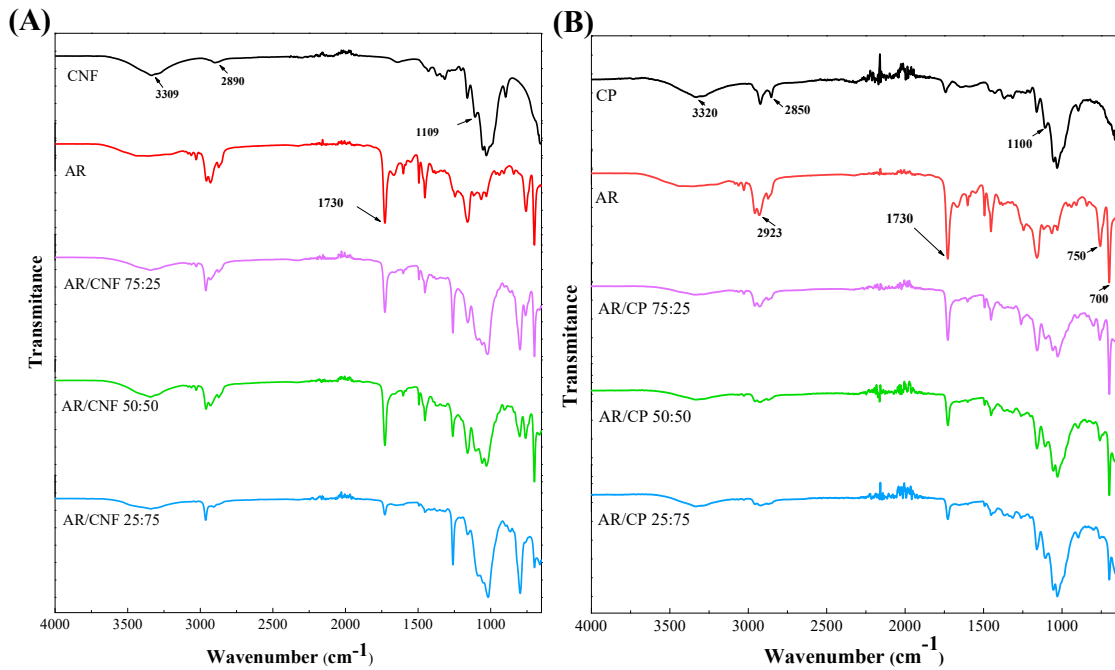


Figure 3: FTIR spectra of fiberboard composites, polymer resin, CNF and cellulose wood pulp

3.3 Thermogravimetric Analysis (TGA)

Fig. 4 shows the TGA tracing of AR/CNF and AR/CP in which is possible to observe two weight-loss events, one due to the degradation of the acrylic resin and the other corresponding to cellulose degradation. The onset of weight loss was observed at 350°C (Fig. 4(A)) for CNF, 350°C for cellulose pulp (Fig. 4(B)) and 460°C for the acrylic resin. The content of AR and fibers in the fiberboards composites were estimated by the area of the TGA derivative peaks, and showed in Tab. 1. The results revealed, in general, that the content of fibers and AR agrees with the theoretical amounts estimated from the quantity of materials used in the composites preparation.

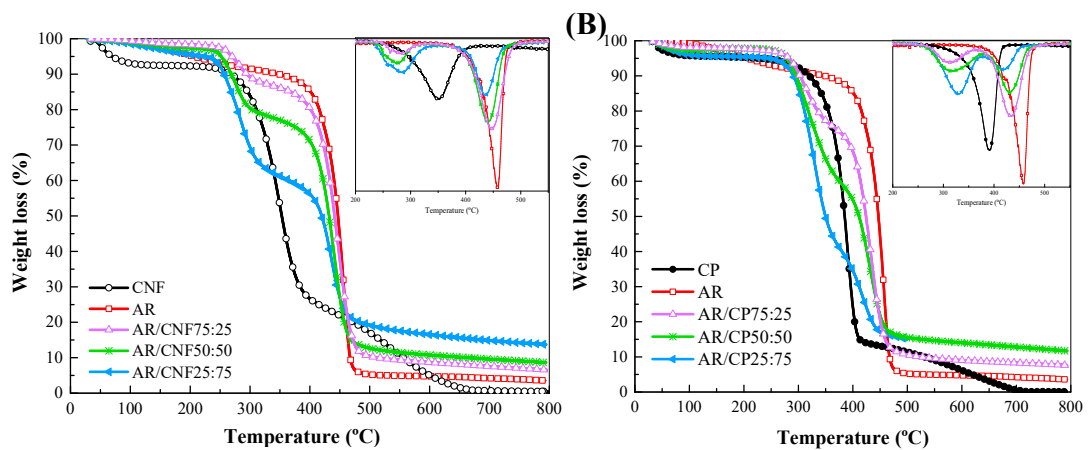


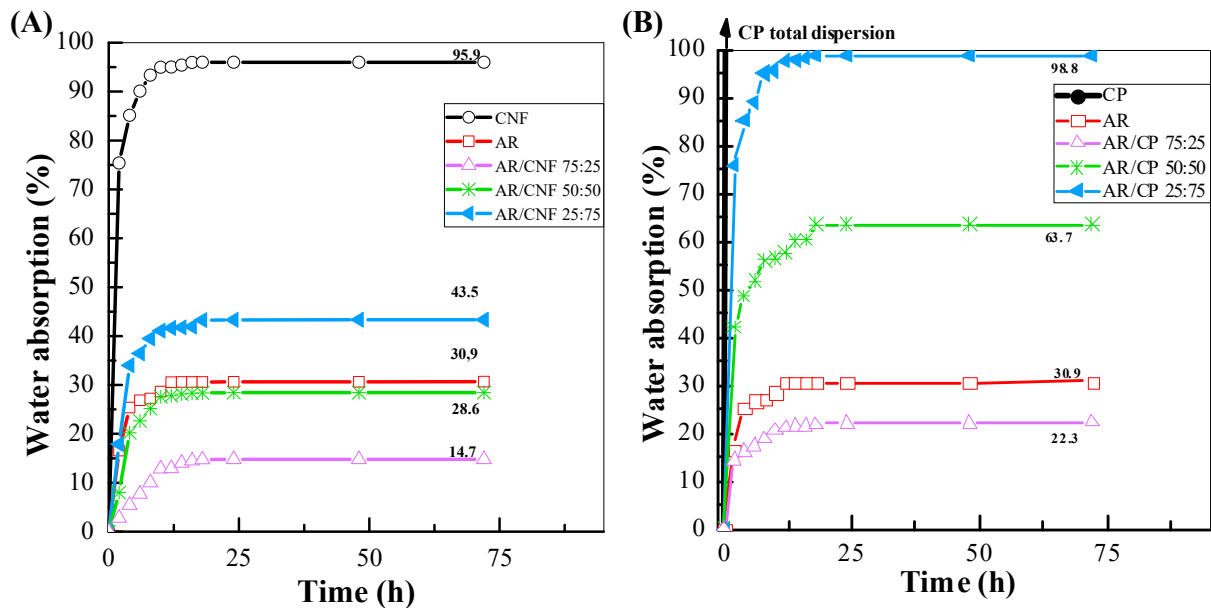
Figure 4: Thermogravimetric curves of a) AR/CNF fiberboards, b) AR/CP fiberboards

Table 1: Compositions of AR/CNF and AR/CP composites, calculated from the peak areas according to DTGA curves

Fiberboard	Composition determined by DTGA area	
	AR (%)	Cellulose fibers (%)
AR/CNF 75:25	77	23
AR/CNF 50:50	49	51
AR/CNF 25:75	24	76
AR/CP 75:25	71	29
AR/CP 50:50	45	55
AR/CP 25:75	26	74

3.4 Water Absorption

Fig. 5 shows the results of the water absorption tests. In general, the CNF composites showed lower water absorption than wood pulp composites. It is interesting to observe that the composites with 25 wt% of cellulose pulp or CNF show water absorptions lower than the acrylic resin. It suggests a synergic effect that avoids water absorption when cellulose fibers and the resin are used in combination. It is also possible to observe that CNF absorbs almost 100% of its weight in water, wood pulp disintegrates. The high-water absorption of the acrylic resin is due to its hydrophilic character probable due to the presence of acrylic acid in its structure.

**Figure 5:** Water absorption curves of a) AR/CNF and b) AR/CP fiberboards

3.5 Dynamic Mechanical Measurements

Fig. 6 shows the data of DMA measurements for (A and B) storage modulus and (C and D) loss tangent ($\tan \delta$). Figs. 6(A) and 6(B) shows the storage modulus as function of temperature for the CNF and CP composites, respectively. It is possible to see that glass transition was about 38°C for the acrylic resin and that fiber addition increases the glass transition temperature. It leads to an increase in the

modulus of the rubbery plateau above glass transition, as expected for fiber reinforced composites. For the composite with 75% fiber (CNF and CP) the rubbery plateau is almost suppressed. The $\tan \delta$ curves for the composites with CNF and pulp are showed in Figs. 6(C) and 6(D), respectively. Fiber load causes a very relevant decrease in damping. $\tan \delta$ peak shift to higher temperatures with increase in fiber content. $\tan \delta$ peak shows a slight shift from 33°C for neat matrix to about 35°C for the composites with CNF and CP. The strong reinforcement effect can be attributed to the percolation effect and to the strong interaction between fibers due to hydrogen bonding [21].

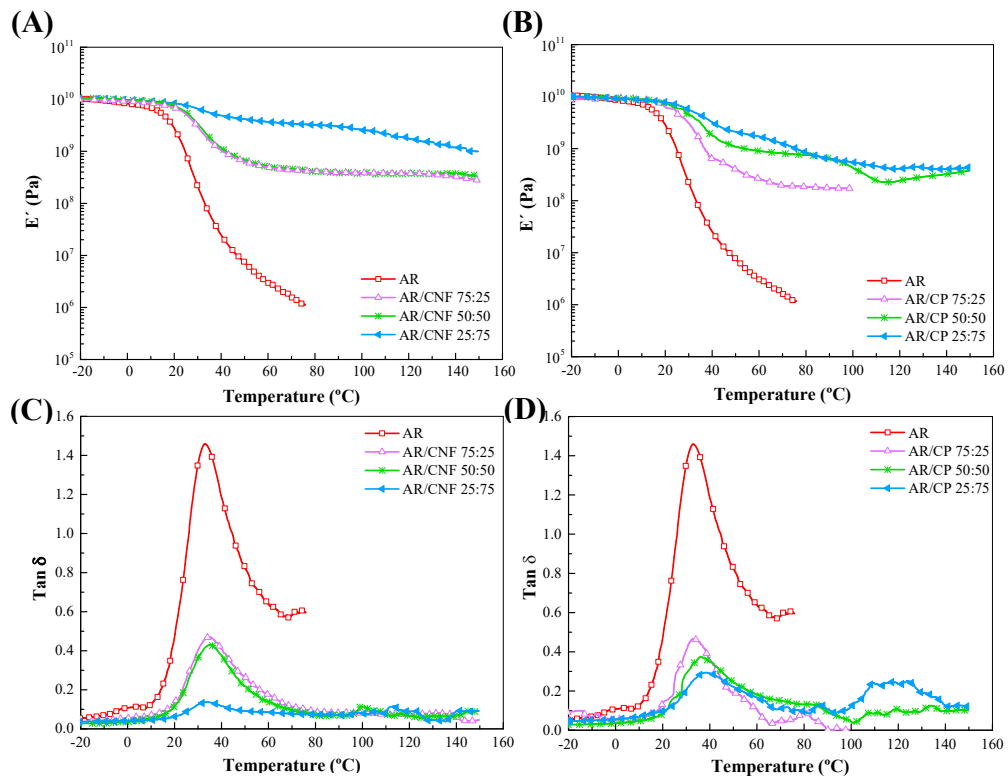


Figure 6: Storage modulus (E') vs. temperature of a) AR/CNF and b) AR/CP. $\tan \delta$ of c) AR/CNF and d) AR/CP

3.6 Tensile Tests

The results of tensile tests are showed in Fig. 7 and the data obtained for Young's modulus, tensile stress and elongation at break are presented in Tab. 2. Fiber load improves the modulus and tensile strength and decreases elongation at break, as expected for composites. The reinforcement effect is much more pronounced for CNF composites due to its high aspect ratio when compared to cellulose pulp. It is interesting to observe that even with high reinforcement effect the elongation remains relatively high, especially for CNF composites.

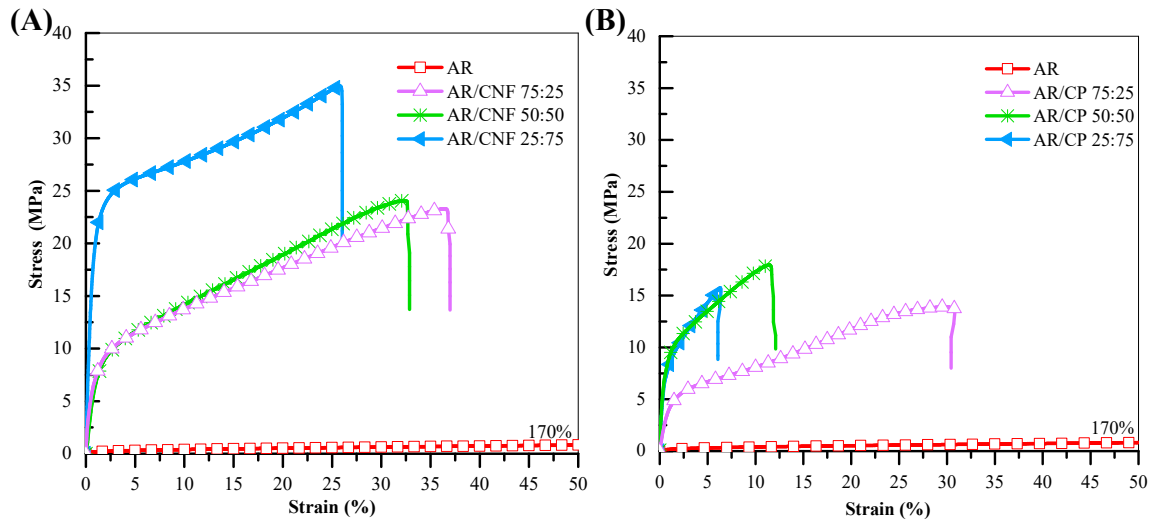


Figure 7: Stress-strain curves of a) AR/CNF and b) AR/CP fiberboards

Table 2: Values for Young's modulus, tensile stress and elongation at break obtained from mechanical tests for the composites with CNF and pulp

Samples	E modulus (GPa)	*SD	Tensile strength (MPa)	*SD	Elongation at break (%)	*SD
AR	0.02	0.01	1.7	0.4	155.2	20.2
AR/CNF 75:25	0.80	0.27	23.3	1.7	36.6	8.6
AR/CNF 50:50	1.29	0.09	24.1	2.8	32.6	0.8
AR/CNF 25:75	2.75	0.50	35.0	5.2	25.8	9.7
AR/CP 75:25	0.58	0.11	14.0	3.1	30.0	10.5
AR/CP 50:50	1.38	0.42	18.0	4.0	11.6	2.2
AR/CP 25:75	1.73	0.37	15.7	3.0	6.3	1.1

*Standard Deviation

3.7 Scanning Electron Microscopy (SEM)

Scanning electron microscopy images of the starting materials, nanofibrilated cellulose and wood pulp, are shown in Fig. 8.

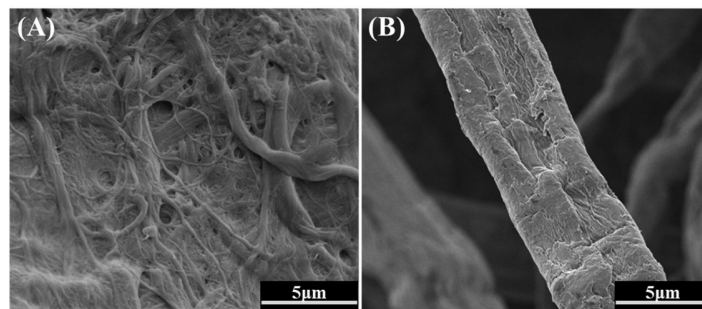


Figure 8: SEM micrographs of a) CNF and b) cellulose wood pulp

Fig. 9 shows the fragile fracture surface of composites reinforced with CNF with two magnifications. Fiber dispersion and fiber adhesion are very good in all the samples. No cluster or agglomerates are observed, confirming the high efficiency of the method used for composite preparation.

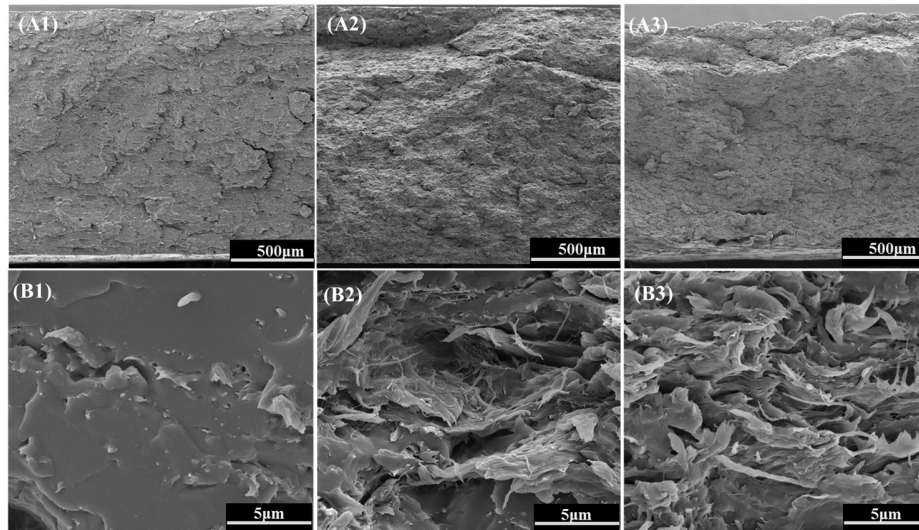


Figure 9: SEM micrographs of fractured surfaces of composites reinforced with cellulose nanofibers: A1-B1) AR/CNF 75:25, A2-B2) AR/CNF 50:50 and A3-B3) AR/CNF 25:75

Fig. 10 shows the fragile fracture surface of the pulp reinforced composites. Here we can also observe a good fiber dispersion of the fiber in the matrix. However, some fiber debonding can be observed. This effect is related to the low adhesion between the matrix and the fiber. This result can be explained by the low aspect ratio of pulp which decreases fiber adhesion, probably because pulp has an average length lower than the critical fiber length for the matrix/reinforcement pair. This result corroborate with the results of the mechanical tests in which a low degree of reinforcement was observed for the pulp composites.

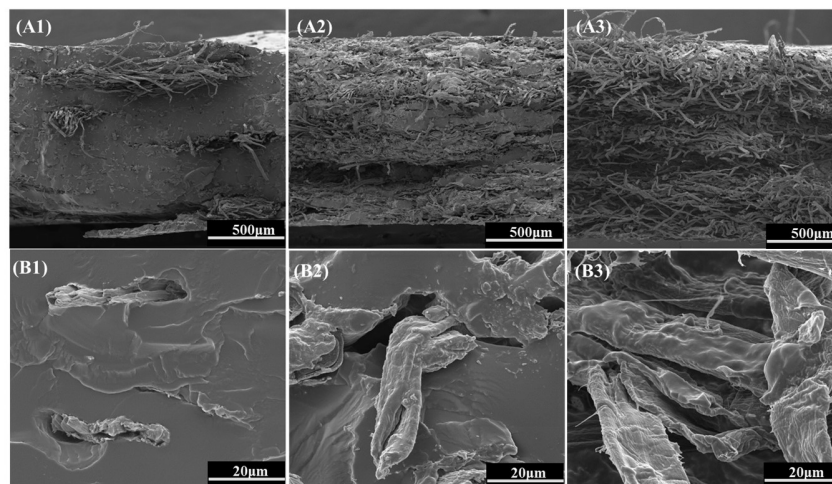


Figure 10: SEM micrographs of fractured surface of composites reinforce with cellulose pulp: A1-B1) AR/CNF 75:25, A2-B2) AR/CNF 50:50 and A3-B3) AR/CNF 25:75. The results obtained showed the method used for composite preparation is very efficient and can lead to very homogeneous composites

4 Conclusions

Fiberboard composites of CNF and cellulose wood pulp were prepared by flocculation/coagulation of a mixture of fiber or nanofibers in suspension and an acrylic resin nanoemulsion. The use of aqueous media for the processing is one of the advantages of the process, which is a green approach and gives exceptional result for fiber dispersion, avoiding fiber agglomeration. Fiber dispersion was confirmed by scanning electron microscopy of fragile fracture surfaces of the composites. Water absorption of the composites increases, as fibers content of the composites was increased, except for the composites with 25 wt% of fiber. The tensile tests showed the additive reinforcing effect of fiber and nanofibers with an appreciable increase in the modulus of elasticity and in tensile strength, while elongation at break decreases less than it is expected for composites. DMA data also indicated the strong reinforcing effect since the rubber plateau shows a very high level of modulus.

Acknowledgements: This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior-Brasil (CAPES)-Finance Code 001. E. C. thanks CAPES for a MsC. Scholarship. The authors also acknowledge the National Council for Scientific and Technological Development (CNPq) for financial support (476709/2013-0 and 307124/2015-0) and for São Paulo Research Foundation (FAPESP).

References

1. Klemm, D., Schumann, D., Kramer, F., Heßler, N., Hornung, M. et al. (2006). Nanocelluloses as innovative polymers in research and application. *Advances in Polymer Science*, 205, 49-96.
2. Carvalho, A. J. F. (2014). Nanocelluloses from eucalyptus wood pulp: a morphological comparison. *Journal of Renewable Materials*, 2, 118-122
3. Eichhorn, S. J. , Dufresne, A., Aranguren, M., Marcovich, N. E., Capadona, J. R. et al. (2010). Review: current international research into cellulose nanofibres and composites. *Journal of Materials Science*, 45, 1-33.
4. Oksman, K., Aitomaki, Y., Mathew, A. P., Siqueira, G., Zhou, Q. et al. (2016). Review of the recent developments in cellulose nanocomposite processing. *Composites Part A: Applied Science and Manufacturing*, 83, 2-18.
5. Kalra, V., Escobedo, F., Joo, Y. L. (2010). Effect of shear on nanoparticle dispersion in polymer melts: A coarse-grained molecular dynamics study. *Journal of Chemical Physics*, 132, 1-11.
6. Volk, N., He, R., Magniez, K. (2015). Enhanced homogeneity and interfacial compatibility in melt-extruded cellulose nano-fibers reinforced polyethylene via surface adsorption of poly(ethylene glycol)-block-poly(ethylene) amphiphiles. *European Polymer Journal*, 72, 270-281.
7. Nechita, P., Panaitescu, D. M. (2013). Improving the dispersibility of cellulose microfibrillated structures in polymer matrix by controlling drying conditions and chemical surface modifications. *Cellulose Chemistry and Technology*, 47, 711-719.
8. Nakagaito, A. N., Yano, H. (2008). The effect of fiber content on the mechanical and thermal expansion properties of biocomposites based on microfibrillated cellulose. *Cellulose*, 15, 555-559.
9. Omrani, A., Simon, L. C., Rostami, A. A. (2008). Influences of cellulose nanofiber on the epoxy network formation. *Materials Science and Engineering A*, 490, 131-137.
10. Kumar, V., Kumari, M. (2014). Processing and characterization of natural cellulose fibers/thermoset polymer composites. *Carbohydrate Polymers*, 109, 102-117.
11. Faruk, O., Bledzki, A. K., Fink, H. P., Sain, M. (2012). Biocomposites reinforced with natural fibers: 2000-2010. *Progress in Polymer Science*, 37, 1552-1596.
12. Trovatti, E., Oliveira, L., Freire, C. S. R., Silvestre, A. J. D., Pascoal Neto, C. (2010). Novel bacterial cellulose-acrylic resin nanocomposites. *Composites Science and Technology*, 70, 1148-1153
13. Manfredi, L. B., Rodriguez, E. S., Wladyka-Przybylak, M., Vazquez, A. (2006). Thermal degradation and fire resistance of unsaturated polyester, modified acrylic resins and their composites with natural fibres. *Polymer Degradation and Stability*, 91, 255-261.
14. Kalia, S., Boufi, S., Celli, A., Kango, S. (2014). Nanofibrillated cellulose: surface modification and potential applications. *Colloid and Polymer Science*, 292, 5-31.

15. Gandini, A., Belgacem, M. N. (2007). Surface and in-depth modification of cellulose fibers. *Materials, Chemicals and Energy from Forest Biomass*, 954, 93-106.
16. Carvalho, A. J. F., Trovatti, E., Casale, C. (2018). Polystyrene/cellulose nanofibril composites: fiber dispersion driven by nanoemulsion flocculation. *Journal of Molecular Liquids*, 272, 387-394.
17. Israelachvili, J. (2011). *Intermolecular and surface forces*. Elsevier.
18. Hiemenz, P. C., Rajagopalan, R. (1997). *Principles of colloid and surface chemistry*. CRC Press.
19. Grande, R., Trovatti, E., Pimenta, M. T. B., Carvalho, A. J. F. (2018). Microfibrillated cellulose from sugarcane bagasse as a biorefinery product for ethanol production. *Journal of Renewable Material*, 6, 195-202.
20. Ghorbel, E., Hadriche, I., Casalino, G., Masmoudi, N. (2014). Characterization of thermo-mechanical and fracture behaviors of thermoplastic polymers. *Materials (Basel)*, 7, 375-398.
21. Favier, V., Cavaille, J. Y., Canova, G. R., Shrivastava, S. C. (1997). Mechanical percolation in cellulose whisker nanocomposites. *Polymer Engineering and Science*, 37, 1732-1739.