

The Lap Joint Shear Strength of Wood Materials Bonded by Cellulose Fiber-Reinforced Polyvinyl Acetate

Deniz Aydemir

Polyvinyl acetate (PVA) is commonly used to bond wood materials, but it generally exhibits poor performance when used in composites that require resistance to water and creep. However, it can be reinforced with different particles to improve its performance, making it useful for various applications. In this study, PVA was reinforced with cellulose fibers (CFs) at different loadings (1%, 2%, and 4%). A mixer was used to blend the PVA and CFs. Thermal properties and morphological structure of CF-reinforced PVA adhesive were studied by thermogravimetric analysis (TGA/DTG) and scanning electron microscopy (SEM). The lap joint shear strength of woods bonded by CF reinforced PVA adhesive was tested on poplar and Scots pine woods that had 12% moisture content. The addition of CFs to PVA increased the thermal stability of PVA to different extents depending on the degree of loading on the CFs. The results of morphological studies indicated that some fluctuations on the SEM pictures were observed due to the dispersion of the CFs in the PVA matrix. The results showed that lap joint shear strength of the two different species of wood increased in all states after CFs were added to the PVA.

Keywords: Polyvinyl acetate; Cellulose fibers (CFs); Thermal analysis; Morphological structure; Lap shear joint strength

Contact information: Bartin University, Faculty of Forestry, Forest Industrial Engineering, Turkey, Tel: +903782235077, Fax: +903782235062; E-mail: denizaydemir@bartin.edu.tr

INTRODUCTION

Cellulose is a natural polymer with the chemical formula $(C_6H_{10}O_5)_n$. It is a polysaccharide that consists of a linear chain of several hundred to over ten thousand β (1 \rightarrow 4) linked D-glucose units (Nishiyama *et al.* 2002; Klemm *et al.* 2005). Cellulose fibers (CFs) have a high strength, which is attributed to their spiral microfibrillar angle (Ichhaporia 2008). The linear chains have hydroxyl groups that form inter-molecular and intra-molecular hydrogen bonds with the macro-structure of cellulose. Therefore, CFs are hydrophilic biopolymers that have varying degrees of polymerization (DP). The mechanical properties of CFs depend on their DP. CFs are used as reinforcing agents in polymer composites because they provide many important advantages and they have strong mechanical properties (Mohnty *et al.* 2005). Cellulose and its derivatives have been used in many different applications such as for optical films, surface coating, biodegradable plastics, and for many composite materials (Fahmy and Mobarak 2009). CF reinforced polymer composites have received much attention because they provide many advantages, *i.e.*, they have low density and low cost, and they are non-abrasive, non-toxic, and biodegradable. Because of this, the current study has been conducted on composites that include CFs. These composites exhibit improved mechanical, thermal,

and morphological properties due to the good dispersion of CFs throughout the matrices of the composite materials (Kalia *et al.* 2011).

PVA is a biodegradable polymer with excellent chemical resistance, water solubility, hydrophilic properties, and excellent film-forming ability. The hydrophilic property of this matrix explains the enhanced interfacial compatibility between the fibers and the polymer matrix. PVA is non-toxic and eco-friendly; thus, it can be used in medical applications such as for wafers or capsules that contain medicine, yarn for surgery, and for drug delivery systems (Qua *et al.* 2009). Lee *et al.* (2009) evaluated the reinforcing effect of CFs in PVA. The composites obtained showed significantly improved tensile strength and thermal properties. In a similar paper, Zimmermann *et al.* (2004) also observed a good reinforcing effect of CFs in PVA composites. They found that the composites that were obtained had significantly improved mechanical and barrier properties. Leitner *et al.* (2007) studied nanocomposites with cellulose nanofibrils in the PVA matrix. The results showed that the tensile strength was improved as the content of nanofibrils was increased.

In this study, PVA was chosen as the matrix due to the above specified advantages and its compatibility with the hydroxyl groups of the CFs. The thermal and morphological properties of the adhesive obtained and the effect of the adhesive on the lap joint shear strength of woods were investigated.

EXPERIMENTAL

Materials

Bleached kraft cellulose fibers (CFs) were prepared by using Scotch pine wood in pulp and paper laboratory of our department. CFs obtained had a mean particle length of 1.75 mm and particle widths of 30 μm . The CFs were used to reinforce the PVA adhesive. PVA having a polymerization degree of 1200 and solids content of 50% was purchased from Chemical Enterprise Caparol. Poplar (*Populus tremula*) and Scots pine (*Pinus sylvestris* L.) woods were cut into 50 x 150 x 5 mm samples. Before bonding, the samples were placed in a conditioning chamber for a week at a temperature of 20 °C and a relative humidity of 65%.

Preparation of Cellulose Fiber-Reinforced Polyvinyl Acetate Adhesive

CF-reinforced PVA adhesive was prepared successfully by the solution method using various percentages of fiber concentrations. Before CFs was added to polymer, they were homogenously blended in pure water with use of a mechanical mixer for 5 min. So, CFs did not exhibit any agglomerates. The resulting suspensions of cellulose were blended with PVA by a mechanical mixing for 20 min, producing a viscous solution. The blending process was performed at 50 °C with the help of a cooler. The resulting mixture was degassed for approximately 30 min in an oven at 50 °C without any vacuum. Neat PVA films were prepared using a similar process and similar conditions. Some of the mixture obtained was applied to the surface of the wood samples. The rest of the mixture was cast on an aluminum plate (to keep a minimum level any agglomerates or downfall of cellulose fibers) and was kept for a week until it was completely dry (for SEM, TGA/DTG analysis).

Methods

The morphologies of the surfaces of the PVA films were observed with a Phillips Electroscan 2020 environmental scanning electron microscope (ESEM) with an accelerating voltage of 5 kV. The surfaces of all samples were sputter-coated with gold using a Denton sputter coater for enhanced conductivity. The thermal properties of PVA reinforced with CFs were investigated using thermogravimetric analysis (TGA/DTG) (Perkin Elmer, TA Instruments, USA). The samples were heated from 25 °C to 600 °C at a heating rate of 10 °C/min with a nitrogen flow of 100 mL/min. The lap joint shear strength test was performed using a Utest testing machine (load cell 1 kN, Utest Inc., Turkey) with a cross head speed of 5 mm/min. The wood samples were done with width of 10 mm and a length of 150 mm. The thicknesses of the samples were calculated before the test. Samples used for the tensile tests were prepared and tested according to TS EN 392:1999. The adhesive was applied to the radial surface of the samples with a brush at an application rate of 220 g/m². The samples were pressed for 90 min in a hydraulic press at room temperature (22 ± 2 °C) with a pressure of 1.0 MPa. For each tensile test condition, ten replicates were used.

RESULTS AND DISCUSSION

SEM analysis was conducted in order to examine the morphology and fiber dispersion within the adhesive. SEM photographs of the surfaces of CF-reinforced PVA are shown in Fig. 1.

As shown in the figure, the homogeneity degree of the dispersion was changed when the loadings of the CF was increased from 1% to 4%. This change was attributed to the strong hydrogen bonding affinity. Figures 1(a), (b), (c), and (d) show that the CFs were distributed well throughout the PVA matrix. This also indicated that the CFs had excellent adhesion and strong interfacial bonding with the matrix.

When the loading of cellulose was increased to 4% in the matrix, the structure of the dispersion in the composites changed. The cellulose fibers were aggregated together in one part of the matrix, as shown in Figs. 1(e) and (f), whereas the distance between the CFs increased in other parts of the matrix. These CF domains, because of low dispersion and poor bonding, mechanically cause weakness in the PVA that leads to reduction in the strength and strain of the PVA structure. Therefore, poor dispersion can result in inferior performance in tensile testing.

Qua *et al.* (2009) studied nanocomposites made of cellulose nanofibers (110 nm long) and PVA. SEM photographs showed that the CFs appeared as white dots on the fracture surface of the PVA nanocomposites. It was found that there is some cellulose aggregation in PVA as a result of the high level of compatibility and interaction between the hydrophilic crystalline cellulose nanofibers and the PVA matrix. Lopez-Suevos and Frazier (2012) investigated the properties of PVA composites with cellulose nanofibrils. The results showed that there were cellulose fibril aggregates in the matrix.

The thermal stabilities of the CFs reinforced PVA adhesive were determined by thermogravimetric analysis (TGA/DTG), where the mass loss of the sample due to volatilization of degraded by-products was determined as a function of increasing temperature. Figure 2 shows the TGA/DTG curves of pure PVA and its formulations with cellulose fibers.

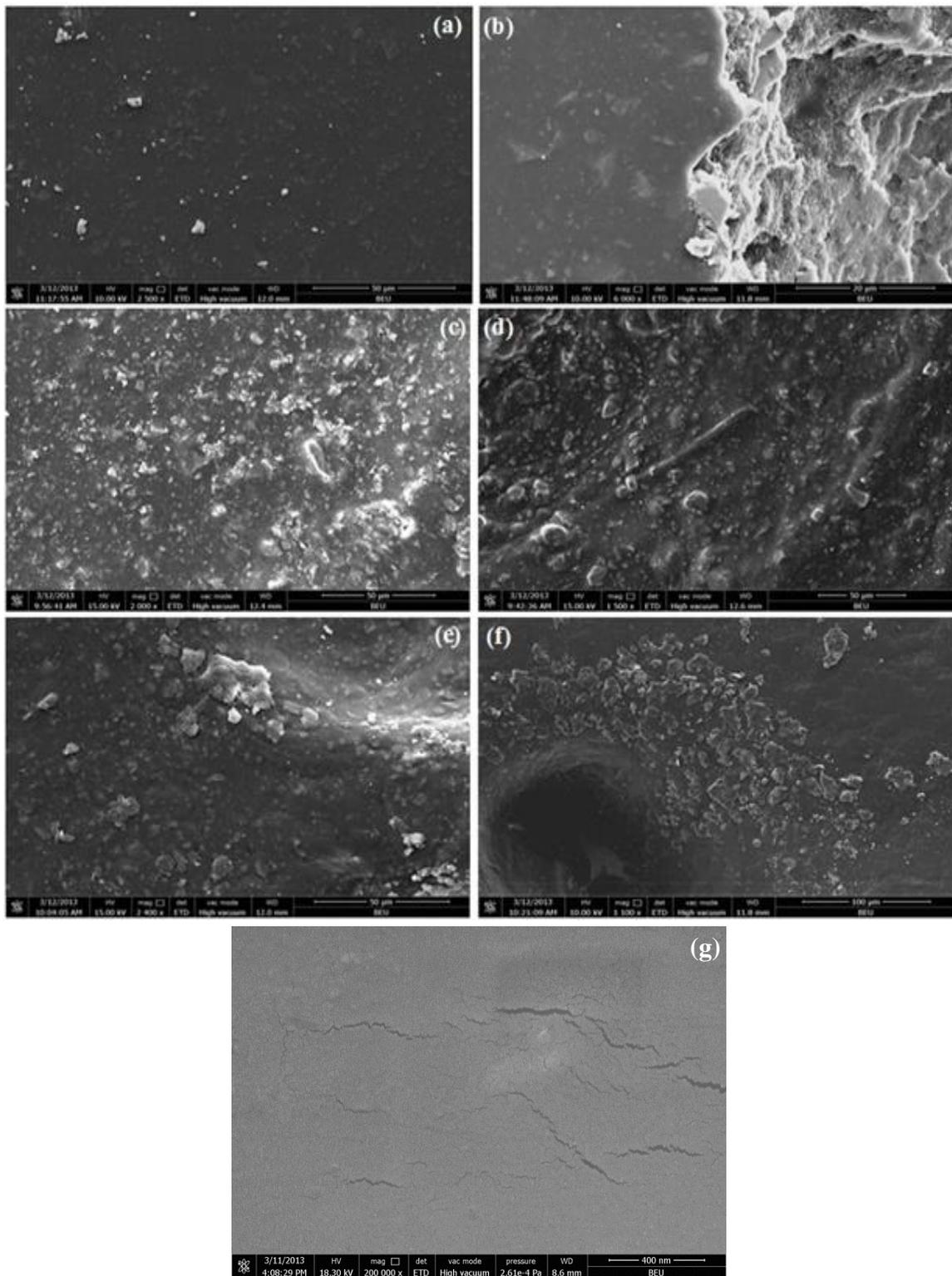


Fig. 1. SEM photographs of CF reinforced PVA adhesive for different loadings: (a and b) 1% CF; (c and d) 2% CF; (e and f) 4% CF; (g) pure PVA

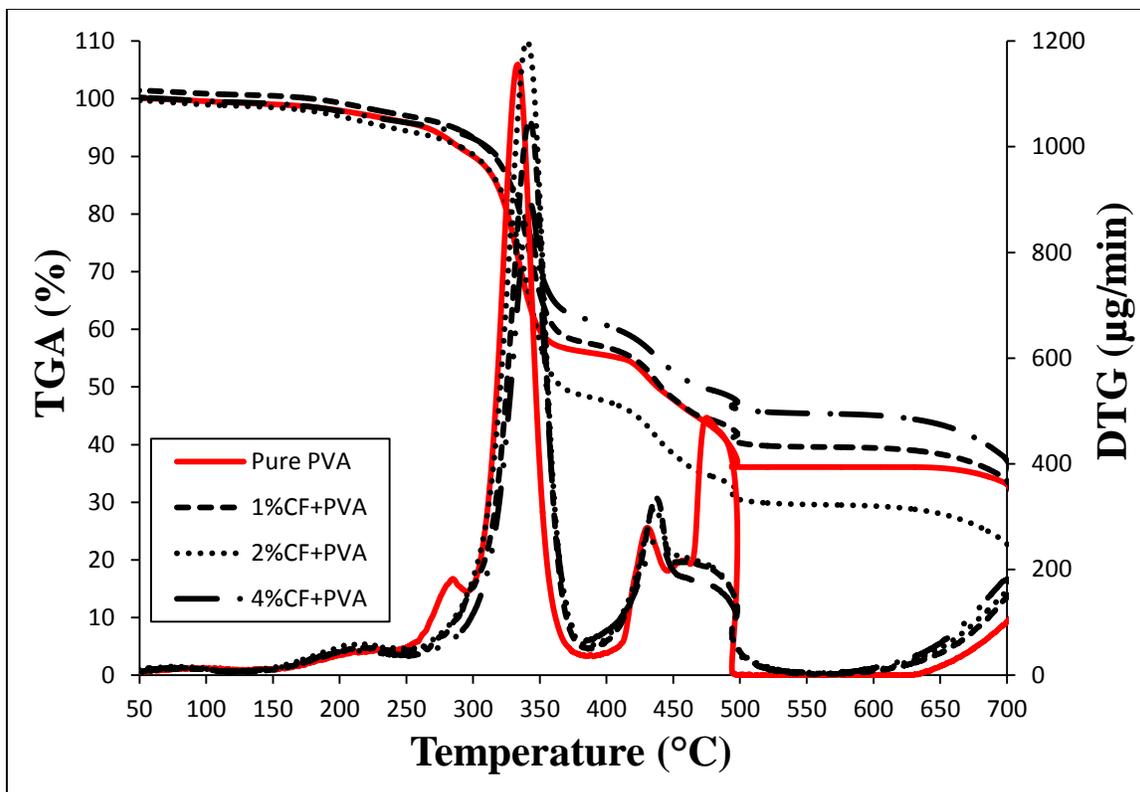


Fig. 2. Thermal stability of CF reinforced PVA composites

Thermogravimetric analysis was conducted under a nitrogen atmosphere to investigate the thermal stability of the materials obtained. The TGA curves showed that three degradation steps occurred in the samples. This was determined from the weight changes in TGA and the derivatives of the weight loss curves.

In the first step, pure PVA and the CF reinforced PVA exhibited a mass loss in the range of 50 °C to 100 °C. Qua *et al.* (2009) determined that PVA samples showed an initial weight loss around 75 °C, which resulted from the loss of moisture from the PVA upon heating. As shown by the mass loss in the first step, the pure PVA curve was close to that of the other composites up to a temperature of 270 °C. After this, the decomposition temperature of the PVA was found to increase with increasing fiber content. Hence, degradation ratios decreased as compared with pure PVA at the same temperature. This was due to the restriction of the mobility of the polymer chains and suppression of the decomposition as a result of the homogeneous distribution of cellulose nanofibers in the polymer (Qua *et al.* 2009).

Other decomposition steps were determined in the DTG curves. A different decomposition step was found due to the presence of CFs. Two decomposition stages were consistent with the generally accepted mechanism for the degradation of polymeric materials (Maruyama *et al.* 1989; Qua *et al.* 2009). Figure 2 shows that the second degradation temperature (T_d) of the PVA was at 298.8 °C and that T_d increased when CFs were added to the matrix. The T_d s of the 1%, 2%, and 4% CF reinforced PVA composites were at 307.4 °C, 308.8 °C, and 309.2 °C, respectively. Jia *et al.* (2007) and Tsuchiya and Sumi (1969) found that the second stage of degradation mainly involves dehydration

reactions and the formation of volatile products. Because of the increased difficulty in breaking hydrogen bonds between the matrix and the CFs, the T_d in the second step increased when CFs were present.

The third degradation step corresponds to the degradation of polyene residues at 450 °C to yield a mixture of carbon and hydrocarbons, *i.e.*, n-alkanes, n-alkenes, and aromatic hydrocarbons (Tubbs and Wu 1973). It was found that the T_{ds} of PVA and the composites were similar in this step. The third T_{ds} of the samples were found at 435.5 °C for pure PVA, 436.1 °C for 1% CF/PVA, 437.2 °C for 2% CF/PVA, and 437.8 °C for 4% CF/PVA. The details of TGA are given in Table 1.

Table 1. Summary Data of the Thermal Stability of CF Reinforced PVA Composites

Samples	DTG _{max} (°C)	T _{10%} (°C)	T _{50%} (°C)	Ash Content (%/min.)
Pure PVA	335.6	298.8	435.5	3.1
PVA+1%CF	337.4	307.4	436.1	2.9
PVA+2%CF	339.6	308.8	437.2	3.9
PVA+4%CF	340.9	309.2	437.8	2.4

Figure 3 shows the lap joint shear strength of the woods. Adding CFs to the matrix significantly increased the lap shear joint strength of the woods. However, this increasing trend was not found to be the same for both types of wood. Lap shear joint strength of Scots pine wood was found to increase when the CF loading increased from 1% to 4%. The strength of the poplar wood samples increased when the CF loading increased from 1% to 2%, but the strength decreased with 4% CF loading. Adding only 1% CF significantly enhanced lap shear strength, raising it from 5.93 MPa to 9.41 MPa for poplar wood and from 4.12 MPa to 10.28 MPa for Scots pine wood.

This increasing trend continued at 2% CF loading, calculated as 9.54 MPa for poplar wood and 10.74 MPa for Scots pine wood. Adding 1% and 2% CF resulted in a significant improvement in lap shear strength for both types of wood. In the highest loadings of CF, lap shear strength was found to be 7.07 MPa for poplar wood and 11.68 MPa for Scots pine wood. While the lap shear strength of poplar wood decreased at a CF loading of 4%, the strength value reached its maximum at 4% CF loading for Scots pine wood.

The anatomical structure of poplar was likely the reason for the decrease in strength and the failures in the wood because CFs cannot be mixed well with PVA at higher loadings due to their incompatibility with the matrix. This was confirmed in the SEM photographs in Figs. 1(e) and (f), which show poor dispersion of the CFs in some parts of the matrix. For Scots pine wood, the constant increase in the lap shear strength in the presence of CFs could be related to their compatibility with the matrix. Further morphological study is required to draw any clear conclusion regarding these phenomena.

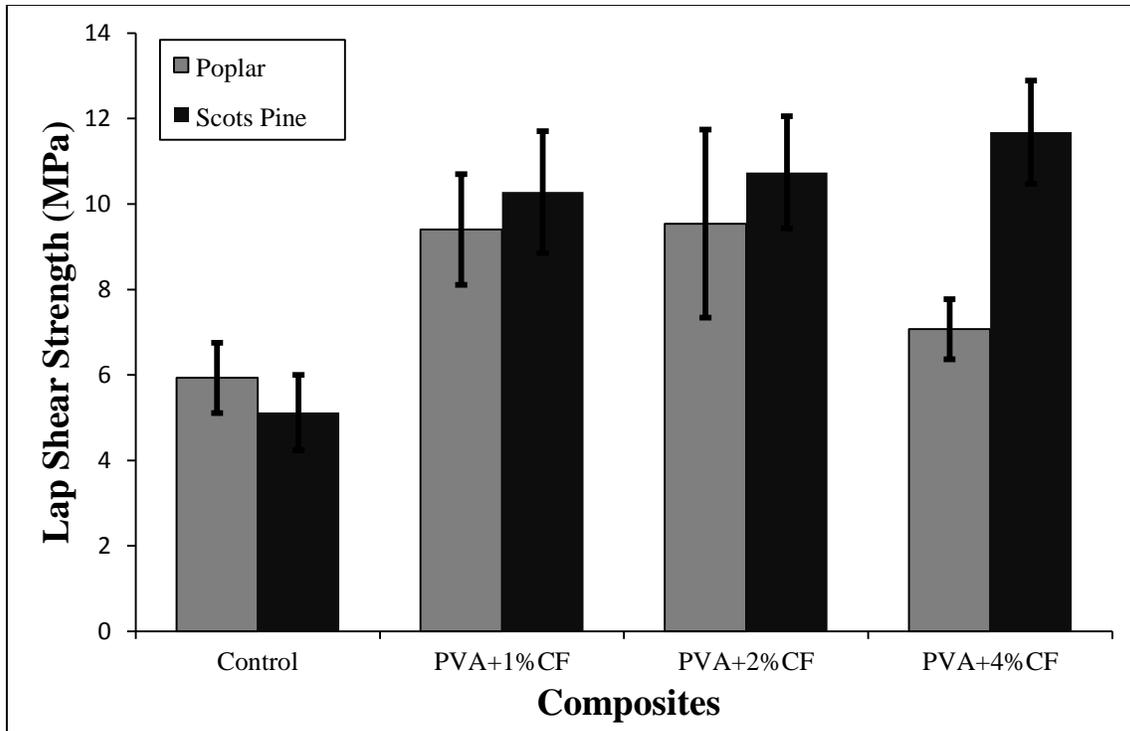


Fig. 3. Lap shear strength of the pine and poplar woods bonded by CFs reinforced PVA adhesive

During the shear test, all of the failures in the samples of both types of woods were due to breaking of the wood samples. Failures that occurred in the wood show a good bonding between wood and adhesive. Figure 4 shows the different failures in the wood samples.

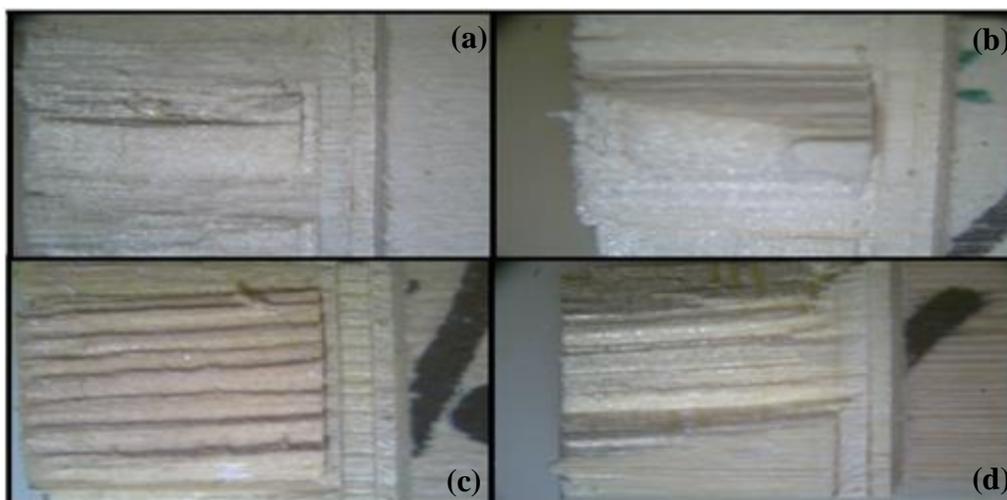


Fig. 4. Different failures of wood samples after lap joint shear strength test (a, b show to Poplar wood and c, d show to Scots wood)

Adhesion is the strength of the molecular layer of adhesive that is in contact with the surface layer of the substrate. The internal and applied energies may be dissipated at

other places in the bonded assemblies than the layer of molecular contact between the adhesive and the substrate. However, failure at the interface between the two is usually considered unacceptable. The occurrence of failure in wood or adhesive is due to their natural structures, and it has been shown to be a cause of weak internal strength of the wood or adhesive (Frihart 2005). In this study, the tensile test showed that all failures occurred in the internal structure of wood. Some interesting failures were given in Fig. 4.

Figure 5 shows the different failures in the wood samples. When the CF loading in the PVA was increased from 1% to 4%, the maximum force at break (F_{max}) and the deformation of the woods bonded by PVA composites increased significantly. F_{max} and deformation values were the same as the lap shear joint strength for both types of wood (Fig. 5).

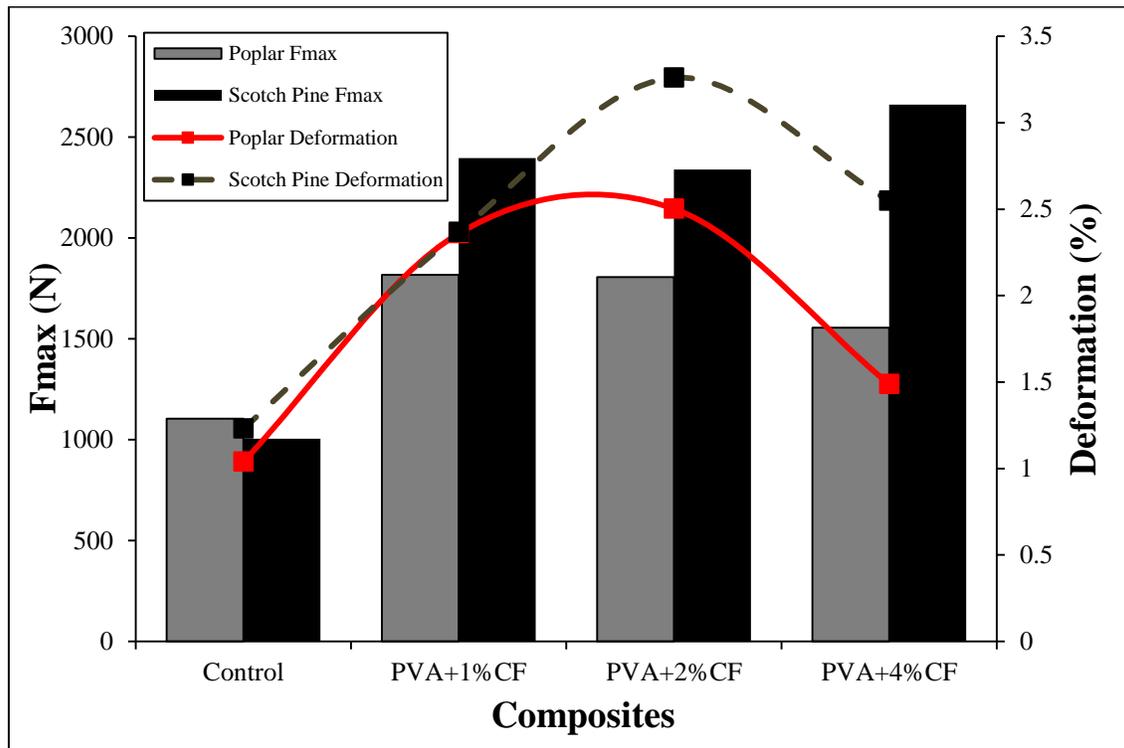


Fig. 5. F_{max} and deformation of CF reinforced PVA adhesive

Kaboorani and Riedl (2011) studied the effect of nano-clay on the bonding performance of PVA at wet and dry states. For the dry state, it was found that adding nano-clay to PVA clearly did not increase the shear strength of the joints bonded by the PVA significantly, although all strength values of the formulations with added nanoparticles were slightly greater than those of pure PVA. Adding only 1% of nano-clay (Lit.G-105-type) enhanced shear strength by 10%, but a further increase did not change the strength significantly. In contrast, a significant improvement in shear strength was achieved by Nanofil 116 as nano-clay loading increased. For the wet state at 1% loading, nano-clay did not change the strength considerably. However, as the loading of nano-clay was increased, marked improvements in shear strength were achieved as high as 53%. The changing ratio in the shear strength of wood was found to be the same for both Lit.G-105-type nano-clay and Nanofil 116-type nano-clay.

CONCLUSIONS

1. The results showed that adding CFs to the PVA matrix affected the properties of the matrix. CFs affected the bond strength of PVA and depended on the loading of the CFs. As CF loading increased in the PVA from 1% to 2%, a constant increase in the lap shear strength of both poplar wood and Scots pine wood occurred. A reduction in shear strength at 4% loading was detected, which could be the result of difficulty in achieving a uniform dispersion of the CFs at high loadings in the matrix.
2. The thermal stability of PVA was improved by adding CFs, and DTG_{max} was found in the 4% CF-reinforced PVA composites.
3. Evaluations conducted by SEM demonstrated that the quality of dispersion was a function of CF loading and that there was a direct link between the quality of dispersion and the properties of the PVA composites. At loadings of 1% and 2%, CFs were dispersed well in the matrix. However, at the high loading of 4% CFs, aggregates were observed in the SEM photographs.

REFERENCES CITED

- Fahmy, T. Y. A., and Mobarak, F. (2009). "Advanced nano-based manipulations of molasses in the cellulose and paper discipline: introducing a master cheap environmentally safe retention aid and strength promoter in papermaking," *Carbohydrate Polymers* 77(2), 316-319.
- Frihart, C. R. (2005). "Wood adhesion and adhesives," in, *Handbook of Wood Chemistry and Wood Composites*, Rowell, R. M. (ed.), CRC Press, New York, 703 p.
- Ichhaporia, P. K. (2008). *Composites from Natural Fibers*, North Carolina State University, Fiber and Polymer Science, Ph.D. Thesis, USA.
- Jia, X., Li, Y., Cheng, Q., Zhang, S., and Zhang, B. (2007). "Preparation and properties of poly(vinyl alcohol)/silica nano-composites derived from copolymerization of vinyl silica nanoparticles and vinyl acetate," *European Polymer Journal* 43(4), 1123-1131.
- Kaboorani, A., and Riedl, B. (2011). "Effects of adding nano-clay on performance of polyvinyl acetate (PVA) as a wood adhesive," *Cellulose* 14(5), 419-425.
- Kalia, S., Dufresne, A., Cherian, B. M., Kaith, B. S., Averous, L., Njuguna, J., and Nassiopoulos, E. (2011). "Cellulose-based bio- and nano-composites: A review," *International Journal of Polymer Science* Article ID 837875.
- Klemm, D., Heublen, B., Fink, H. P., and Bohn, A. (2005). "Cellulose: Fascinating biopolymer and sustainable raw material," *Angewandte Chemie International Edition* 44(22), 3358-3393.
- Lee, S. Y., Mohan, D. J., Kang, I. A., Doh, G. H., Lee, S., and Han, S. O. (2009). "Nanocellulose-reinforced PVA composite films: Effects of acid treatment and filler loading," *Fibers and Polymers* 10 (1), 77-82.
- Leitner, J., Hinterstoisser, B., Wastyn, M., Keckes, J., and Gindl, W. (2007). "Sugar beet cellulose nanofibril-reinforced composites," *Cellulose* 14(5), 419-425.
- Lopez-Suevos, F., and Frazier, C. E. (2012). "Fracture cleavage analysis of PVAc latex adhesives: Influence of phenolic additives," *Holzforschung* 60(3), 313-317.

- Maruyama, K., Takeuchi, K., and Tanizaki, Y. (1989). "Activation parameters for degradation of polyenes produced in heated poly(vinyl alcohol) film," *Polymer* 30 (3), 476-479.
- Mohnty, A. K., Misra, M., Drzal, L. T., Selke, S. E., Harte, B. R., and Hinrichsen, G. (2005). *Natural Fibers, Biopolymers, and Biocomposites: An Introduction*, CRC Press, USA.
- Nishiyama, Y., Langan, P., and Chanzy, H. (2002). "Crystal structure and hydrogen-bonding system in cellulose IB from synchrotron x-ray and neutron fiber diffraction," *Journal of American Chemical Society* 124(31), 9074-9082.
- Qua, E. H., Hornsby, P. R., Sharma, H. S. S., Lyons, G., and McCall, R. D. (2009). Preparation and characterization of poly(vinyl alcohol) nano-composites made from cellulose nanofibers," *Journal of Applied Polymer Science* 113, 2238-2247.
- TS EN 392 (1999). "Glued laminated timber - shear test of glue lines," Turkish Standardization Institute, Turkey.
- Tsuchiya, Y., and Sumi, K. J. (1969). "Thermal decomposition products of poly(vinyl alcohol)," *Journal of Polymer Science Part A* 7(11), 3151.
- Tubbs, R. K. and Wu, T. K. (1973). Thermal Properties of Polyvinyl Alcohol. In *Polyvinyl Alcohol: Properties and Applications*, Chapter 8, Wiley & Sons, New York, page 167.
- Zimmermann, T., Pohler, E., and Geiger, T. (2004). "Cellulose fibrils for polymer reinforcement," *Adv. Eng. Mater.* 6(9), 754-61.

Article submitted: September 27, 2013; Peer review completed: December 1, 2013;
Revised version received and accepted: January 5, 2014; Published: January 13, 2014.