

The effect of cellulose fibres in an epoxy adhesive for bonding wooden load-bearing elements

Petra Lacikova^{1*}, Jan Vanerek¹, and Adam Betak¹

¹Brno University of Technology, Faculty of Civil Engineering, Veveri 331/95, Brno, Czech Republic

Abstract. The work deals with the modification of the properties of epoxy adhesive. The modification consists of reinforcing this adhesive with cellulose fibres. In the field of wood glued elements, the current research focuses on the possibility of increasing the ductile behaviour of the epoxy adhesive, which would significantly increase the ability of the adhesive to transfer the stresses induced by the volumetric changes of the wood adherend. For this purpose, the adhesive was modified with fibres having a reinforcing character, which may include cellulose fibres. Due to the epoxy resin's non-polar nature and the cellulose fibre's hydrophilic nature, which inhibits the fibre's homogeneous dispersion, the fibres have been modified with silanes. This paper describes the effect of adhesive modification by determination of tensile and shear strength at different amounts of filling and different types of silane pre-treatment of cellulose fibres. The optimum filling amount can be considered as 1.0% filling of nanofibrillated cellulose (NFC) with epoxy-functional silane pre-treatment.

1 Introduction

Epoxy resins possess versatility due to their ability to react with various substrates, making them widely used in industry for both protective coatings and structural applications, including laminates and composites. They are also commonly used for casting and bonding a variety of materials, such as metals, hard plastics, ceramics, and glass, with a particular emphasis on bonding wood [1-2].

These are two-component systems with extremely strong adhesive properties, allowing for the bonding of materials with high tensile and compressive strength. Epoxide resins are compounds that typically contain more than one epoxy (oxirane) group per molecule. This group is highly reactive, and its reactivity with a variety of substances (resulting in cross-linking of macromolecular products) is the basis for the applications of these resins as adhesives, laminates, and more. During the curing process, no by-products are released, and there is only slight shrinkage. These important thermosetting polymers exhibit high resistance to corrosion, a high modulus of elasticity, and are thermally stable. However, due to the highly cross-linked nature of epoxy resins, they tend to be brittle, limiting their use in many critical areas [1-5].

* Corresponding author: lacikova.p@fec.vutbr.cz

In today's world, where there is an increasing focus on producing high-quality products and constructions, epoxy adhesives are frequently modified in a variety of ways. One such method of modifying epoxy adhesives is filling them with fibre fillers to reinforce them [5-9].

The production of synthetic fibres requires large amounts of energy and threatens the quality of the environment, during production and recycling. Meanwhile, the processing of natural fibres is gaining popularity again due to their lower cost in comparison to synthetic fibres. Natural fibres have various benefits such as their lightweight, non-abrasive, and non-toxic nature, low acquisition costs, and biodegradability. Examples of natural fibres include flax, bamboo, sisal, hemp, jute, and especially cellulose fibres [7, 10-12].

Cellulose is the most abundant and important biopolymer on Earth. The potential uses of cellulose have developed and increased since the beginning of nanocellulose preparation. Nanocellulose has very good physical, mechanical, biological, and chemical properties. Nanocellulose can be divided into three groups, nanocrystalline cellulose (NCC), microfibrillated cellulose (MFC) and nanofibrillated cellulose (NFC) [10].

Cellulose is usually obtained by pulping from trees suitable for producing high-quality pulp. One of the disadvantages of cellulose fibres for their industrial applications is the strong hydrophilic character of their surface, which inhibits the homogeneous dispersion of these fibres in non-polar polymers. Because of the hydrophilic nature of the fibres, the adhesion is weakened, which in turn reduces the mechanical properties of such filled composites. Therefore, ways are being sought to chemically modify the natural fibres to make them compatible with the hydrophobic polymer matrix [7, 10].

The main objective of this research was to mitigate the brittle behaviour of the epoxy adhesive that was used by the addition of reinforcing fibres. The improvement of mechanical and other properties of composite materials depends mainly on the filler content, shape and size, surface properties and degree of dispersion [5]. Cellulose fibres were used to create a more flexible bonded joint. To ensure good dispersion of the fibres in the adhesive matrix, silane pre-treatment of the fibres was chosen. The silane pre-treatment was chosen to change the hydrophilic nature of the cellulose fibres to a hydrophobic nature, thereby providing better bonding to the epoxy adhesive matrix, which is non-polar in nature. The effects of the reinforcing fibres were verified by the resulting strength parameters and microscopic observation of filler dispersion. The bonded lap joints were exposed to hygrothermal stress. Epoxies, due to their brittle behaviour, are unable to accommodate the stresses induced by the volumetric changes in the wood adherend. The effect of modification with cellulose fibres was verified based on the tensile shear strength of the bonded samples after hygrothermal stress.

2 Materials and methods

2.1 Materials

A two-component epoxy system (Spolchemie, Czech Republic) was used for the experiment. The epoxy system consists of component A (epoxy resin: CHS-EPOXY 531) and component B (hardener: TELALIT 0492). The mass ratio of epoxy resin to hardener is 100:27. After curing, the manufacturer recommends post-curing at elevated temperature to achieve maximum final properties, specifically for 72 hours of exposure at 85°C. Post-curing will allow maximum mechanical and chemical properties to be achieved. The selected properties of the epoxy resin and hardener are shown in Table 1.

The surface silane pre-treatment of the fibres to improve the dispersion of cellulose in the non-polar polymer matrix and increase the interfacial bonding was used. For the silane

treatment, the epoxy-functional silanes Silquest A-187 and Coatosil MP 200, amino-functional silanes Silquest A 1170, Silquest Y-1699 and Silquest A-1100 (Momentive, Grolman Group, Germany) were used.

Table 1: The selected properties of the components of the epoxy system.

Epoxy resin CHS-EPOXY 531	
Epoxy index [eg/kg]	5.5 – 5.7
Epoxy mass equivalent [g/mol]	175 - 182
Viscosity at 25 °C [Pa.s]	1.5 – 2.3
Free epichlorohydrin [ppm]	max 10
Hardener TELALIT 0492	
Amino number [mgKOH/g]	550 - 600
Viscosity at 23 °C [mPa.s]	15 - 30

Fibrous cellulose powder TENCEL FCP 9/300 (Lenzing Fibers, Austria) was used as a reinforcing filler. The cellulose filler is white in colour, 100% pure and has a density of 0.35-0.60 g/cm³. The sieve analysis (according to DIN EN ISO 4610) for fibrous cellulose powder is summarized in Table 2. To fill the epoxy adhesive for lap joints, microfibrillated cellulose (MFC) was transformed into nanofibrillated (NFC) cellulose. After microscopic analysis, the length of the NFC fibres was determined to be 180 µm with a diameter of 10 µm. For the shear-stressed glued lap joints, beech planks (*Fagus sylvatica* L.) with a density of (700 ± 50) kg/m³ at a wood moisture content of (12 ± 1) % were selected.

Table 2: Sieve analysis by air jet sieve of fibrous cellulose powder (sieve analysis was obtained from TENCEL® FCP 9/300 material data sheet from Lenzing Fibers company, Austria).

Sieve [mm]	Remain [%]
0.200	max. 3
0.100	max. 40
0.032	max. 85

2.2 Preparation of samples for tensile properties

Test samples of modified epoxy blends were prepared using a mechanical homogenizer with a constant filling amount of 1.0% MFC fibres with 0.6% and 2.4% silanes. A mechanical homogenizer was also used to disperse the epoxy adhesive with 1.0% MFC without silane and the reference mixture (epoxy resin + hardener). This procedure was chosen to determine the type and optimum amount of silane treatment of cellulose fibres for the next stages.

The amount of epoxy was heated to approximately 55°C. The silane was then poured into epoxy and MFC cellulose in the proper amount was added. The homogenizer (ULTRA-TURRAX T25, IKA, Germany) was set for 12,000 rpm for 20 minutes (Fig. 1). The hardener was added and the mixture was poured into the mould, where the mixtures were left to harden for 24 hours. After curing, the mixtures were consequently exposed to 80°C for 72 h for the post-curing process.

An ultrasonic homogenizer (SONOPULS, Bandelin, Germany) was used to defibre MFC to NFC (Fig. 2). The use of the ultrasonic homogenizer was intended to prevent the formation of air pores in the epoxy matrix and better dispersion of the fibres. A description of the pulping of the MFC to NFC and preparation of the modified adhesive by the ultrasonic homogenizer is given in the following subsection 2.3. For tensile strength, the epoxy resin with 1.0% NFC was prepared by the ultrasonic homogenizer. Test samples were subjected to a tensile strength test according to standard EN ISO 527-1 (type 1B) [13].

2.3 Preparation of test samples for tensile shear strength of bonded joints

After selecting the optimum amount and type of silane, the amount of cellulose fibre filling was optimized. The mixtures for lap joints are summarized in Table 3. MFC was diluted with ethanol at a certain fibre content. Selected silane (Coatosil MP 200) was added to the mixture (MFC in ethanol) in selected amounts of 2.4%. The mixture was stirred by the ultrasonic homogenizer (Fig. 2) at 50 Hz in 10 cycles for 2 min, with a 1 min delay between cycles to lower the probe temperature. After this pulping process, MFC becomes NFC.

Then the mixture is added to the heated epoxy resin at about 55 °C, which is mixed by the ultrasonic homogenizer at 50 Hz also in 10 cycles for 2 min, with a 1 min delay between cycles to lower the probe temperature. The mixture was stored for 2 hours in a vacuum oven at 50°C where the volatile ethanol was removed from the epoxy mixture. After two hours, a quantity of hardener was added to the mixture.

Table 3: Mixtures to optimise the amount of cellulose.

Designation	Epoxy resin	Hardener	Silane/Amount	Cellulose/Amount of epoxy	Mixing
EP1	CHS-EPOXY 531	Telalit 0492	-	-	Ultrasonic
EP2			-	NFC 1.0 %	
EP3			Coatosil MP 200/2.4 %	NFC/0.5 %	
EP4			NFC/1.0 %		
EP5			NFC/2.0 %		
EP6			NFC/5.0 %		

The epoxy adhesive was applied to the rounded beech boards (150×130 ×5 mm) at a rate of 300 g/m². The adhesive was applied evenly to both the surfaces of the beech boards, which were glued together to form a 10 mm thick panel. The panel was then placed in a pressing assembly where a pressure of approximately 0.8 N/mm² was applied for 24 hours. Post-curing was not included in the preparation of these wood assemblies.

After three days, five 20 mm wide strips were cut from the bonded panels with close contact in the direction of the fibres. The test samples were prepared according to standard EN 302-1 [14]. Grooves were cut in the glued panel, transverse to the grain of the wood, to create a shear surface (20×20 mm) in the central part. The cuts separated the wood and glue layers but did not extend beyond the glue layer (Fig. 3).



Fig. 1: Homogenizer ULTRA-TURRAX T25, IKA during homogenization of the mixture with MFC.



Fig. 2: Ultrasonic homogenizer Bandelin SONOPULS during homogenization of the mixture with NFC.

The specimens (Fig. 3 (c)) were stressed in hygrothermal exposure environments (A4, A5) defined in EN 302-1. The test samples were placed horizontally into the water for soaking at all the sides. The standard climatic environment 20°C/65% (A1) was created by mixing NH_4NO_3 salt with water (63.9 g of salt per 100 ml of distilled water).

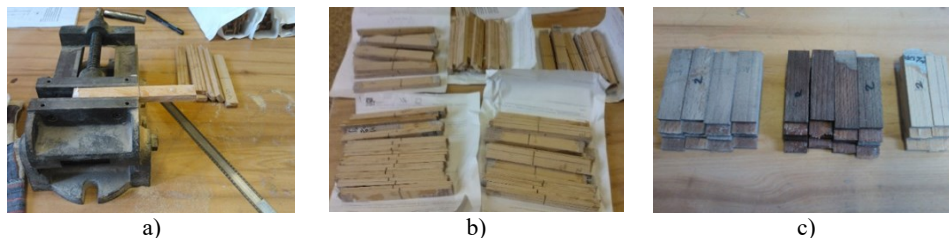


Fig. 3: a) cutting grooves, b) notched samples, c) samples with 2.0% NFC (right A1, A4, A5) after the test.

2.4 Experimental procedures

2.4.1 Determination of tensile properties of epoxy

The determination of the tensile properties was performed according to the standard EN ISO 527-1 [13]. From each mixture with different types of silane pre-treatment, six specimens were prepared. The Testometric M350-20CT press device was used to determine the tensile strengths. A strain gauge (of 50 mm length) was placed on the working part of the samples, crosshead constant rate of 1 mm/min was set until the test specimen broke. The maximum applied force was recorded and then the tensile strength of the material was calculated.

2.4.2 Determination of the tensile shear strength of lap joints

The tensile shear strength of lap joints of beech wood was performed according to standard EN 302-1 [14]. The test specimen was symmetrically clamped in the jaws of a press device Testometric M350-20CT. The rate of force increase of the tensile testing machine was 1mm/min. The resulting value of shear strength was calculated as the average strength of ten valid measurements from each mixture of lap joints. The percentage of failure in the wood was visually estimated for each test body.

2.4.3 Microscopic analysis

Microscopic analysis of NFC dispersion in the adhesive matrix was carried out using a desktop scanning electron microscope MIRA3 (Tescan, Czech Republic). The instrument was set to an acceleration voltage of 20 kV, a magnification range of 200-5000 \times , and a secondary electron detector was used.

3 Results and discussion

3.1 Tensile strength

Different functional silanes and homogenization technologies were selected to verify which type of modified epoxy adhesive to use for application to wood lap joints. Based on the tensile

strength results (Fig. 4), the homogenization technology, filler form and silane type were optimized.

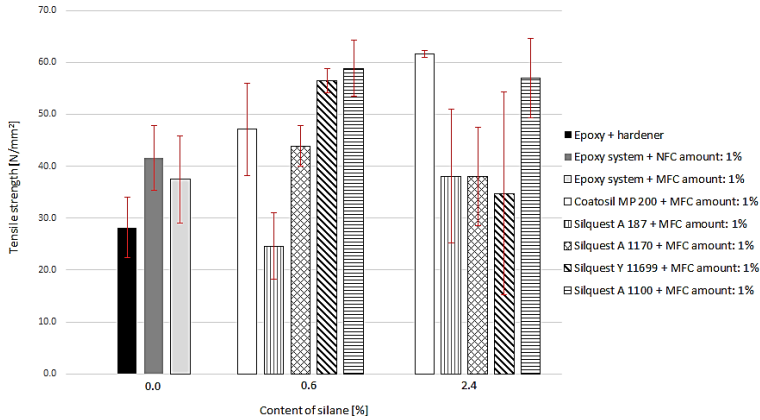


Fig. 4: Effect of type, amount of silane and filling in the epoxy adhesive on tensile strength.

For a silane content of 0.6%, the highest tensile strength was 58.9 N/mm^2 for Silquest A 1100 (amino-functional silane); in general, epoxy-functional groups achieved the lowest strengths. For a silane content of 2.4%, Coatosil MP 200 (epoxy-functional) had the highest tensile strength of 61.6 N/mm^2 and Silquest A 1100 (amino-functional silane) with a strength of 57.0 N/mm^2 . It should be noted that high strengths were achieved even when the mixture (epoxy with MFC) was mixed with a mechanical homogenizer and the cured samples contained air voids (Fig. 6). The assumption that the strength increases with higher amounts of silane was confirmed identically for the epoxy-functional silanes (Coatosil MP 200 and Silquest A 187). Considering the assessment of the variance of the values, Coatosil MP 200 silane at 2.4% was chosen for further experimental purposes.

3.2 Tensile shear strength of glued joints

The wood glued specimens were exposed to hygrothermal stress (A4 and A5). All specimens showed a visible decrease in strength compared to reference environment A1. The results of the tensile shear strengths are shown graphically in Fig. 5. After determining the tensile shear strength, the degree of cohesive failure of the wood was visually assessed (the higher the value, the more stable the glued joint was).

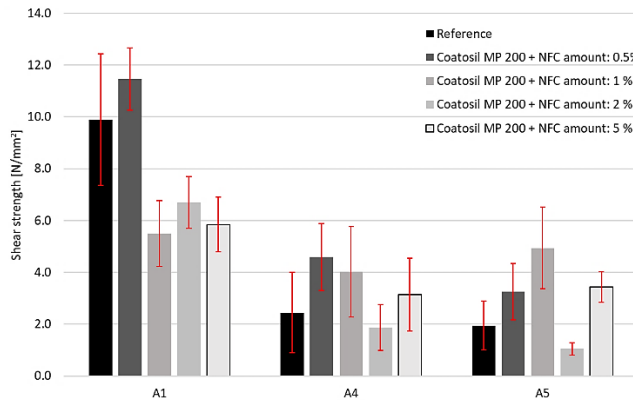


Fig. 5: Results of the performed shear strength depending on the adhesive modification and sample treatment.

The highest tensile shear strength was obtained in the acclimation environment (A1) at 0.5% NFC filling of 12.5 N/mm², which corresponded to 50% cohesive failure in wood. The reference specimens showed the highest cohesive failure rate in wood in A1. When the epoxy was filled with 1.0% NFC, the tensile shear strength in all three exposures (A1, A4 and A5) showed almost the same values, and the highest values of cohesive failure (70%) were obtained in exposures A4 and A5, indicating a stable bonded joint. In the reference case, there was almost a fourfold decrease in strengths after hygrothermal stress (A4 and A5) compared to the A1. In all cases, it was confirmed that the application of NFC fibres to the adhesive increased the stability of the bonded joint in exposures A4 and A5.

3.3 Microscopic analysis (SEM)

Fracture surface analysis (samples after shear strength determination and in the case of 1.0% MFC filling, samples after tensile strength determination) was carried out to assess the difference in mixing technology and to assess the dispersion of NFC filler in the epoxy adhesive matrix. Fig. 6 a) and Fig. 6 b) are micrographs of the mixtures that were processed by the mechanical homogenizer (MFC fibres). Air pores and cracks are observed in these images. In the fracture surface images of mixtures prepared by an ultrasonic homogenizer (NFC fibres) – see Fig. 6 c) to f), the presence of air pores was not evident. The use of different amounts of filling is visible in Fig. 6 c) and d). All the micrographs in Fig. 6 demonstrate that the dispersion of the fibres in the epoxy matrix was orderly.

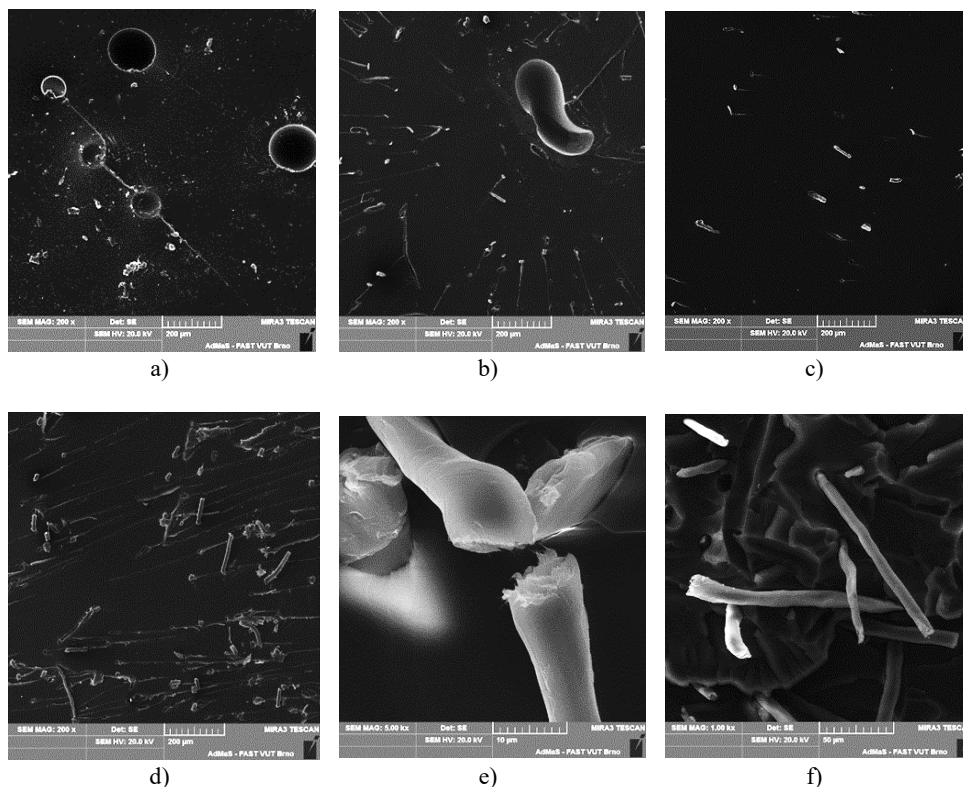


Fig. 6: Micrographs from SEM - a) reference epoxy (200x), b) epoxy with 1.0% MFC (200x), c) fibre dispersion at 0.5% NFC filling (200x), d) fibre dispersion at 1.0% NFC filling, e) detail of broken NFC fibre at 2.0% filling (5000x), f) fibre distribution at 5.0% filling (1000x).

4 Conclusion

The experiment evaluated the effect of pre-treatment of cellulose fibres with different types of silanes. Based on the tensile properties of the modified epoxy system (modification by 1.0% of MFC cellulose fibres), the amount of silane pre-treatment by 2.4 wt% appears to be the optimum amount for proper dispersion of the two-phase system. Coatosil MP 200 epoxy-functional silane had the most positive impact on this epoxy system. Based on the assessment of the influence of cellulose fibre size effect in epoxy adhesive, pulping cellulose into the NFC showed better strengths than MFC- filled epoxy specimens.

Due to the change in filler dimensions, an ultrasonic homogenizer was chosen for better dispersion. Based on SEM analysis, it fulfilled the assumption of avoiding the formation of air pores in the adhesive matrix. The micrographs from the SEM analysis also confirmed good dispersion of the NFC cellulose fibres in the adhesive, no clumps were observed, hence the silane pre-treatment was an appropriate step. Proper dispersion was also observed even at the highest amount of NFC at 5.0% using the same amount of silane coupling agent.

In all cases, it was confirmed that the application of NFC fibres to the epoxy adhesive increased the stability of the bonded joint under hygrothermal stress. Such modified adhesive can better adapt to the volume changes of the wood adherend. From the determined properties, 1.0% of NFC filling with silane pre-treatment of cellulosic fibres (Coatosil MP 200) appears to be the optimum filling rate for wood glued materials. The adhesive treated in this way can transfer the stresses in the glued joint induced by the volumetric changes of the wood adherend.

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