Polymer composite with micro- and nanocellulose for artwork protection and restoration

A. Cataldi[a]*, A. Dorigato[a], F. Deflorian[a], L. Berglund[b], A. Pegoretti[a]

[a] *Department of Industrial Engineering and INSTM Research Unit , University of Trento, Via Mesiano 77, 38123, Trento*
[b] *KTH, Department of Fibre & Polymer Technology, Wallenberg Wood Science Center 10044 Stockholm, Sweden*
* *annalisa.cataldi@ing.unitn.it*

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Abstract
Micro- and nanocomposites were prepared using Aquazol® 500 as a polymeric matrix and a microcrystalline cellulose (MCC), and suspensions of cellulose nanocrystals (CNC), as reinforcing agents. After a preliminary thermo-mechanical characterization that highlighted a stabilizing effect due to the micro- and nanofiller introduction, with an increase of the elastic modulus and a decrease of the thermal expansion coefficient and the creep compliance [1], these materials were applied as canvas lining adhesives. Single–lap shear tests both in quasi-static and creep conditions confirmed the dimensional stability provided by cellulose micro- and nanoparticles, with an important reduction of the adhesives compliance proportional to the filler content. Interestingly, MCC and CNC introduction did not impair the fracture behavior of the neat matrix.

1. Introduction

Thermoplastic resins are used in a broad range of applications to preserve and restore artworks. An important use segment of these materials is related to their adhesive capacity. Among thermoplastic products, a versatile polymer, applied as adhesive material for many classes of artworks, is Aquazol, a poly (2-ethyl-2-oxazoline), generally called PEOX, soluble in water and in a wide range of other organic solvents. Aquazol has been used in the field of conservation since the early of 90's, but scientific studies on this synthetic resin have been carried out since the 80's [2-4]. Natural fillers present several advantages in comparison to the corresponding synthetic agents. They are non-toxic, biodegradable and recyclable. Natural plant derived particles have generally lower density and high specific strength and elevated stiffness . Microcrystalline cellulose MCC, is one of the most used reinforcing fillers, it can be easily prepared through the reaction of cellulose with water solution of strong mineral acid at boiling temperature. The hydrolysis reaction removes the amorphous fraction and reduces the degree of polymerization of the cellulose chains [5]. Cellulose nanocrystals, CNC, are produced by the acid hydrolysis of natural cellulose sources [6]. Still and rod-like CNC particles have interesting properties, in terms of biocompatibility, anisotropy, good optical transparency, low thermal expansion coefficient and, especially, high elastic modulus, similar to steel [7]. These features guarantee to nanocellulose a wild range of applications and promising results in the composite technology. The final aim of this research is the

improvement of the mechanical performance of a commercial resin (i.e. Aquazol 500), especially in terms of dimensional stability, strength and elastic modulus [8-9], developing new micro/nanocomposites with a lower environmental impact and interesting functional properties, to be applied as lining adhesive on oil paintings substrate, without impairing their good handling properties.

2. Experimental section

2.1 Materials

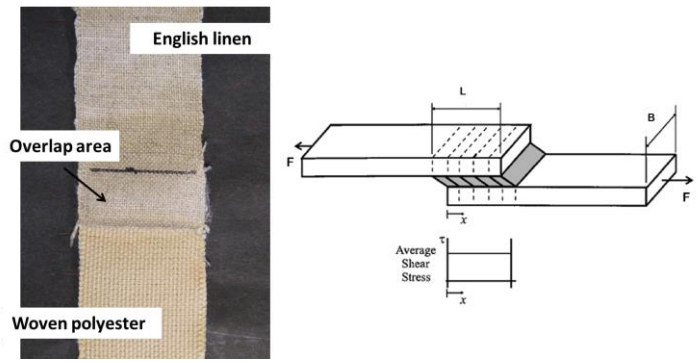
A poly (2-ethyl-2-oxazoline), Aquazol 500 (AQ500), with a specific density of 1.07 $g \cdot cm^{-3}$ and a melt flow index at 190 °C and 2.16 kg of 2.45 $g \cdot 10min^{-1}$ was supplied by Polymer Chemistry Innovation (USA). A microcrystalline cellulose (MCC), in form of fine powder, supplied by Sigma Aldrich (USA), with a specific gravity of 1.56 $g \cdot cm^{-3}$ and average aspect ratio of 2.5 was selected as reinforcing agent. Aqueous suspensions at 5.5 wt% and 8.7 wt% of cellulose nanocrystals (CNC), with average aspect ratio of 50, were produced by acid hydrolysis of MCC powder and used as nanofillers.

2.2 Micro- and nanocomposites preparation

Aquazol 500 was melt-compounded in a Haake Rheomix® internal mixer (T= 160°C, rotor speed= 60 rpm, residence time= 5 min) and compression molded in a Carver hydraulic press (T= 160°C, P= 4 MPa time= 5 min), with 5 wt% and 30 wt% of microcrystalline cellulose powder. Thin films of MCC composites with an average thickness of 100 μm were obtained by a further compression molding at 150 °C under a pressure of 4 MPa for 10 min. Using an aqueous solution at 5 wt% of the same polymeric matrix and aqueous suspensions at 5.5 wt% and 8.7 wt% of cellulose nanocrystals as fillers, composites with a CNC content of 5 wt% and 30 wt% were produced by solution mixing and film casting. All CNC formulations were dried at 40 °C in a vacuum oven until the complete cleaning of the solvent. In this way films with an average thickness of 250 μm were obtained. Before testing, samples were dried at 50 °C for 24 h in a vacuum oven. Samples were denoted indicating the matrix (AQ500), the filler (MCC or CNC) and its weight amount. For instance, AQ500-MCC-5 represents a sample with a MCC content of 5 wt%. While, AQ500-5.5CNC-5 identifies a composite made of an aqueous suspension at 5.5 wt% of CNC and a CNC amount of 5 wt%.

2.3 Adhesive joints production

Adhesive joints (12.7 mm long and 25 mm wide) connecting two kinds of canvas, an English linen (170 g/m2), representing the original oil painting substrate, and a woven polyester (260 g/ m2) utilized as lining textile, were obtained by using a temperature of 65°C and a pressure of 1MPa for 5 min. In this way rectangular samples 200 mm long and 25 mm wide were produced to be tested by single-lap shear test (Figure 1). Before testing, samples were conditioned at 23°C and 55% of relative humidity in a chamber with a super-saturated solution of $Mg(NO_3)_2 \cdot 6H_2O$ for 48 hours.



(a) (b)

Figure 1. (a) Representation of an adhesive joint with textile adherends for single-lap shear tests. (b) Schematic of testing conditions.

2.4 Experimental techniques

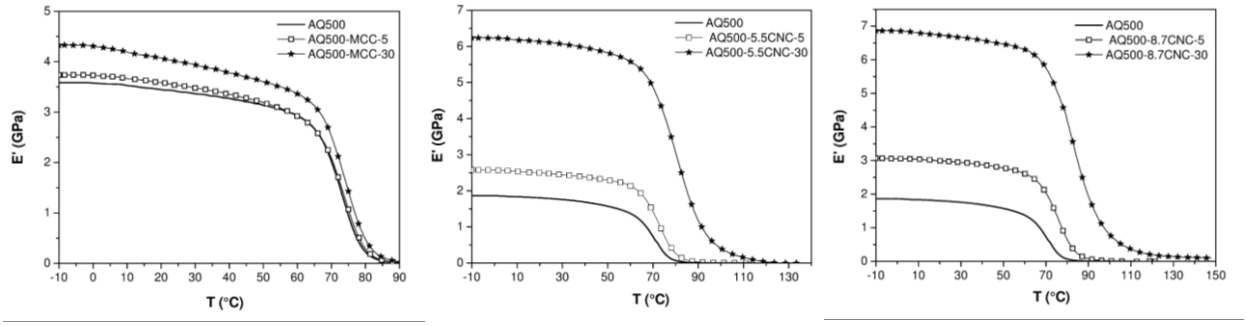
Dynamic mechanical thermal analysis (DMTA) and Creep tests were performed by using DMA Q800 device by TA Instruments under tensile configuration. Rectangular specimens 15 mm long, 5 mm wide and 1.3 mm thick were tested in a temperature range between -10 °C and 150 °C at a heating rate of 3 °C·min-1 and a frequency of 1 Hz to determine the trends of the storage modulus (E'), loss modulus (E'') and loss tangent (tanδ) as a function of the temperature. Moreover, through the evaluation of the thermal strain it was possible to determine the coefficients of linear thermal expansion (CLTE) below Tg (i.e. in a temperature interval between 0 °C and 55 °C for MCC based composites and between 0 °C and 40 °C for CNC based samples) and above Tg (between 70 °C and 75 °C for MCC based composites and between 70 °C and 80 °C for CNC based samples). While, applying a constant stress (σ_0= 10% of the stress at break of the neat matrix) at 30 °C for a total time of 3600s the creep compliance D(t), calculated as the ratio between the time dependent deformation ε(t) and the applied stress (σ_0= 10% of the stress at break of the neat matrix), was evaluated.
Single-lap shear tests in quasi-static and creep conditions were performed on rectangular canvas samples (gage length 130 mm, width 25 mm) by using an Instron® 4502 universal testing machine, equipped with a 10kN load cell, at crosshead speed of 10 mm/min to determine the adhesive shear strength (τ_B), by dividing the maximum force for the overlapping area. While the time depending joint displacement (u), was obtained applied a constant stress (τ_0), corresponding to about 50% of the shear stress at break (τ_B) of the neat matrix for 3600 s. At least five specimens of each formulation were tested for each test. Microstructural analysis of fracture overlap adhesive area of MCC and CNC based polymer composites were carried out by a Wild Heerbrugg Leica optical microscope at a magnification of 40X.

3. Results and Discussions

3.1 DMTA

Mono-frequency DMTA tests were conducted on micro and nano formulations. In Figure 2 the representative storage modulus curves of MCC and CNC filled composites are reported. Micro- and nanocellulose play similar interesting effects on AQ500. In fact, the progressive

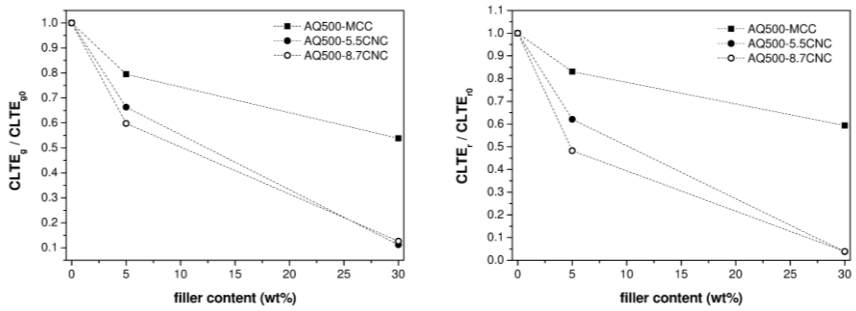
enhancement of the dynamic modulus E', evidences a stiffening action produced by micro and nanofillers.



(a) (b) (c)

Figure 2. Representative storage modulus curves of neat matrix and relative micro- and nanocomposites. (a) MCC filled composites, (b) CNC at 5.5 wt% filled composites, (c) CNC at 8.7 wt% filled composites.

While, the determination of the coefficient of linear thermal expansion (CLTE), calculated, as the slope of the secant line of thermal strain curves in the glassy ($CLTE_g$) and rubbery ($CLTE_r$) states (Figure 3(a-b)), highlights how the introduction of MCC and CNC leads to the improvement of the dimensional stability of the neat matrix with a decrease of CLTE proportional to the filler amount under and above the glass transition temperature. As one can see, the effect played by CNC nanoparticles on the viscoelastic behavior of the resulting materials is much more pronounced than that obtained for MCC filled composites. Moreover, the aqueous suspensions at different concentrations of CNC reported similar values of CLTE in both glassy and rubber states at highest CNC amount.

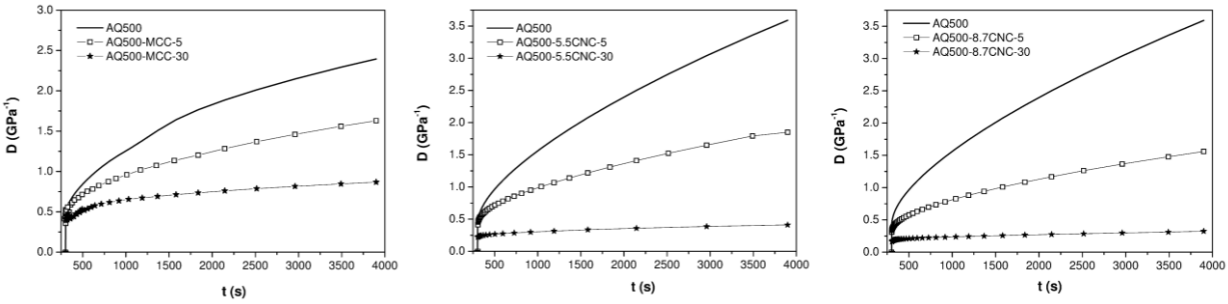


(a) (b)

Figure 3. Comparison between relative coefficient of linear thermal expansion trends of MCC and CNC polymer composites. (a) coefficient of linear thermal expansion below T_g, $CLTE_g$, (b) coefficient of linear thermal expansion above T_g, $CLTE_r$.

3.2 Creep tests

The stabilizing effect provided by MCC and CNC particles is confirmed by creep test. In fact, as reported in Figure 4(a-c), the creep compliance of the neat AQ500 is significantly reduced at elevated filler contents, especially for long creep times.



(a) (b) (c)

Figure 4. Representative creep compliance D, curves of neat matrix and relative micro- and nanocomposites. (a) MCC filled composites, (b) CNC at 5.5 wt% filled composites, (c) CNC at 8.7 wt% filled composites.

It is interesting to note that also in this analysis CNC filled composites registered the highest enhancement of the dimensional stability with respect to MCC formulations and the two suspensions at different concentration of CNC show a similar creep behavior at highest amount of CNC (Figure 5).

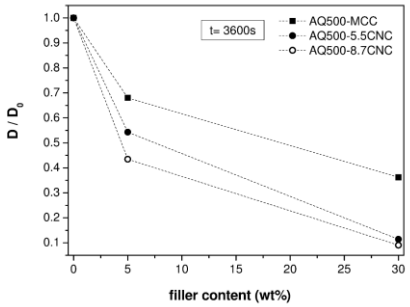


Figure 5. Comparison between the relative creep compliance trends of MCC and CNC polymer composites.

3.3 Single-lap shear test

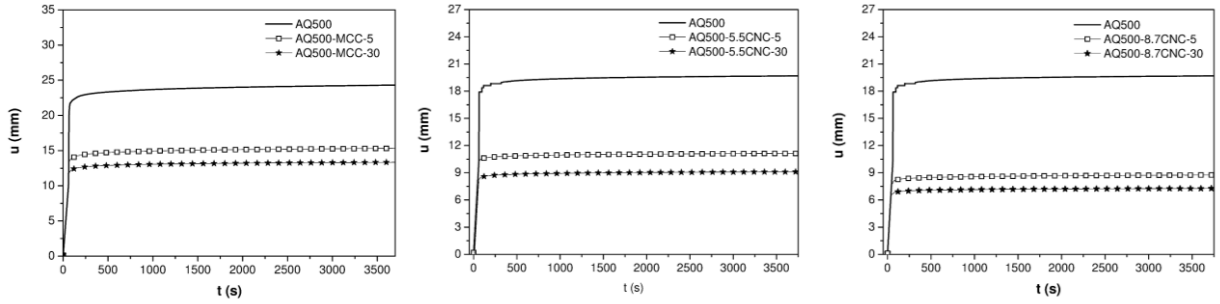
Single-lap shear tests in quasi-static and creep configuration were performed on canvas samples lined by thin MCC and CNC films. In Table 1 and 2 the most important results from single-lap shear tests are collected. While, in Figure 6 (a-c) representative joint displacement curves of MCC and CNC filled composites are presented.

Sample	τ_B [MPa]	u at t= 3600s [mm]
AQ500	1.76 ± 0.01	24.29 ± 0.05
AQ500-MCC-5	1.87 ± 0.01	15.25 ± 0.02
AQ500-MCC-30	1.70 ± 0.02	13.35 ± 0.03

Table 1. Results of single-lap shear tests on neat matrix and relative MCC filled composites

Sample	τ_B [MPa]	u at t= 3600s [mm]
AQ500	3.41 ± 0.02	19.68 ± 0.04
AQ500-5.5CNC-5	3.21 ± 0.01	11.10 ± 0.02
AQ500-5.5CNC-30	2.70 ± 0.02	9.07 ± 0.03
AQ500-8.7CNC-5	3.04 ± 0.04	8.78 ± 0.03
AQ500-8.7CNC-30	2.35 ± 0.02	7.25 ± 0.02

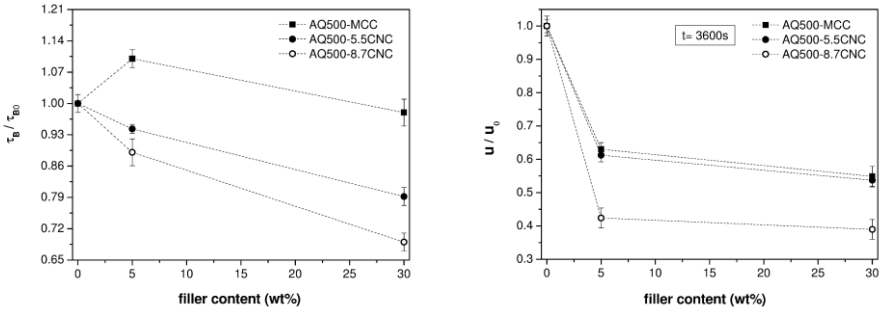
Table 2. Results of single-lap shear tests on neat matrix and relative CNC filled composites



(a) (b) (c)

Figure 6. Representative joint displacement curves of neat matrix and relative micro- and nanocomposites. (a) MCC filled composites, (b) CNC at 5.5 wt% filled composites, (c) CNC at 8.7 wt% filled composites.

As one can see, the introduction of MCC particles does not negatively affect the adhesive strength of the neat AQ500, even at highest amount of this microfiller. Actually, the formulation with 5 wt% of MCC reports an increase of this property. While, for CNC composites the increase of the filler loading leads to a progressive decrease of the adhesive strength in both suspensions. On the other hand, all the examined natural fillers are able to confirm the improvement of the dimensional stability even during their application as lining adhesives, reporting a decrease of the joint displacement as the filler amount increases. In order to better assess these evidences, in figure 7(a-b) the relative trends of the adhesive strength (τ_B) and the joint displacement, as a function of fillers loading are reported.



(a) (b)

Figure 7. Comparison between the main single-lap shear test results of MCC and CNC polymer composites. (a) Relative adhesive strength trends, (b) relative joint displacement trends.

It is evident how MCC and CNC, applied on canvas, produce opposite effects on the adhesive strength of the neat Aquazol, while show a similar stabilizing action, except those formulations made of the most concentrated CNC suspension that report the highest reduction of the joint displacement.

3.4 Microstructural analysis

Since the introduction of a reinforcing agent in adhesive systems could change their fracture behavior, microstructural analysis of overlap bonded area were performed. Figure 8(a) evidences how the presence of MCC does not change the failure mode of the neat matri**x**, even at higher filler amounts. In fact, all the MCC based samples report an adhesive fracture,

where adhesive joints fail at the textile/adherend interface and the main part of the adhesive layer remains on the woven polyester. This could be related to a higher chemical affinity between examined composites and this synthetic textile.

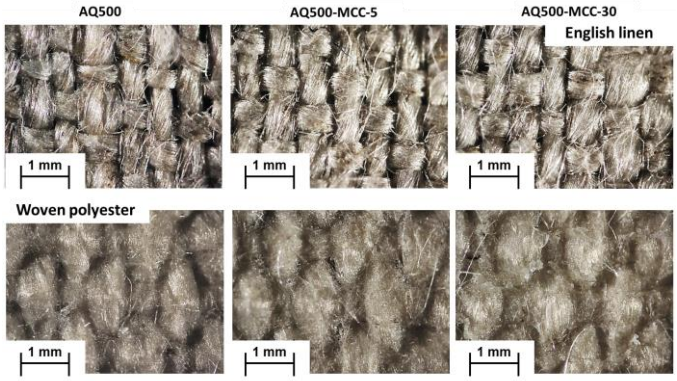
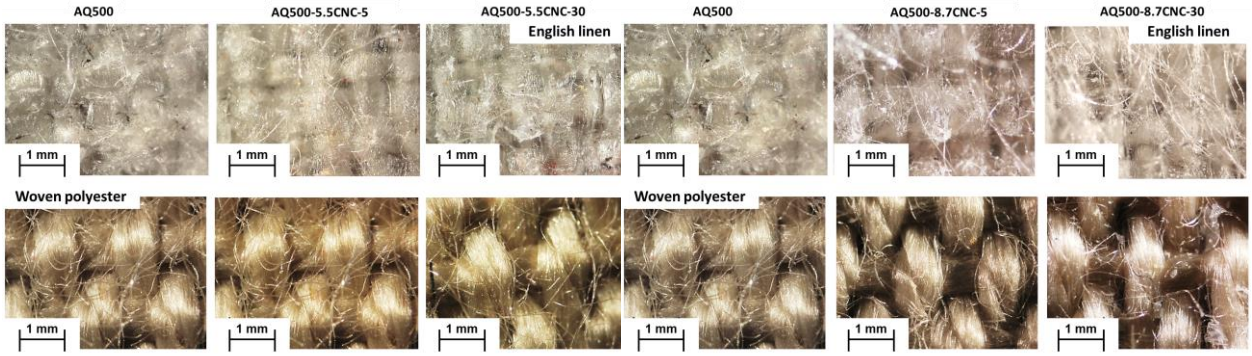


Figure 8. Microstructural analysis of overlap adhesive area of MCC based polymer composites.

Also the introduction of CNC does not change the fracture mode of AQ500 that remains an adhesive fracture, but this time the adhesive layers show a higher affinity with the natural linen (Figure 9(a-b)).



(a) (b)

Figure 9. Microstructural analysis of overlap adhesive area of CNC based polymer composites. (a) CNC at 5.5wt% filled samples, (b) CNC at 8.7 wt% filled samples.

4. CONCLUSION

Innovative micro- and nanocomposites were prepared starting from a thermoplastic resin, widely used in the artwork restoration, and adding a microcrystalline cellulose (MCC), and suspensions of cellulose nanocrystals (CNC), as reinforcing agents. The thermo-mechanical analysis evidenced how the introduction of both micro- and nanofillers led to a stabilizing effect on the neat matrix, with an increase of the elastic modulus and a decrease of the thermal expansion coefficient and the creep compliance. These positive response oriented the application of these materials as canvas lining adhesives. Single–lap shear tests both in quasi-static and creep conditions highlighted the dimensional stability produced by micro- and nanocellulose, with an important decrease of the joint displacement as the filler content increases. Moreover, MCC and CNC introduction did not affect the fracture behavior of the neat matrix, while a decrease of the adhesive strength as CNC content increases was detected.

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