



Poly 2-ethyl-2-oxazoline/microcrystalline cellulose composites for cultural heritage conservation: Mechanical characterization in dry and wet state and application as lining adhesives of canvas

Annalisa Cataldi*, Flavio Deflorian, Alessandro Pegoretti

University of Trento, Department of Industrial Engineering and INSTM Unit, Via Sommarive 9, 38123 Trento, Italy

ARTICLE INFO

Article history:

Accepted 22 June 2015

Available online 21 July 2015

Keywords:

Cellulose

Composites

Moisture

Mechanical properties

Adhesion

Canvas

ABSTRACT

The aim of this work is the investigation of the stabilizing effect of microcrystalline cellulose powder (MCC) on the mechanical performance of two commercial thermoplastic resins (Aquazol[®] 200 and Aquazol[®] 500) used as adhesives in the conservation of artworks. The two polymers, having different molecular weights, were melt-compounded and compression molded with various amounts of MCC (5–30 wt%). The mechanical response of the microcomposites under dry and wet (equilibrium at 23 °C and a R.H. 55%) conditions, was investigated. DMTA analysis showed an increase of the dynamic moduli and the glass transition temperature with the microfiller content more pronounced for conditioned samples over the dried ones, and a concurrent decrease of the thermal expansion coefficient. Creep tests showed that MCC caused an improvement of the creep stability (i.e. a reduction of the creep compliance) for both dried and conditioned samples. For wet samples, the simultaneous enhancement of the elastic modulus and the stress at break limited the embrittling effect detected for dried composites. These materials were applied as lining adhesive for oil paintings between two kinds of canvas an English linen and a woven polyester under environmental conditions at temperature of 23 °C and a relative humidity of 55%. Single-lap shear tests both in quasi-static and creep conditions confirmed the improvement of the dimensional stability provided by MCC with a reduction of the joint displacement and an increase of the adhesive strength as the filler content increases. Additionally, *post-fracture* optical microscope observations of the cross-sections of the adhesive area proved how MCC introduction did not change the fracture behavior of the neat adhesives.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Aquazol, a poly(2-ethyl-2-oxazoline), has been used in the field of cultural heritage conservation since the early 1990s [1], but scientific studies on this synthetic resin have been carried out since the 1980s [2–4]. Its reported high flexibility even at low humidity level [5,6], ability to make protective film, good capability to penetrate into fine cracks and easy removability, being a water soluble polymer, represents the main reasons that led to the introduction of this polymer in the conservation of works of art. Aquazol, generally called PEOX, is a versatile polymer soluble in a wide range of organic solvents. Aliphatic tertiary amides present a chemically stable form of nitrogen, therefore PEOXs tend to guarantee a good aging behavior [7,8]. Additionally, it has a good thermal stability and bonds to a broad range of materials [7]. The most common use of this thermoplastic resin is in coating

formulations [9], as pigment dispersants in inks [10] and as adhesive for various types of artworks [7,11]. Its refractive index is close to that of soda-lime glass and therefore Aquazol was originally applied as consolidant for glass objects [4]. Since 1930s, synthetic resins have been introduced in the lining of paintings in order to replace natural glue/paste adhesives that may suffer of embrittlement and are stiff [12]. In the 1990s Aquazol was introduced as adhesive to the restoration of easel paintings [4]. The results of accelerated aging studies demonstrated how Aquazol polymers are able to maintain both their neutral pH and their stability with aging [4,13]. Nowadays, conservators utilize this polymer also as adhesive on friable paint films and cracked gilding in order to readhere the paint film onto the preparation layers and original canvas [11,13].

On the other hand, Aquazol is very sensitive to water sorption especially at elevated humidity levels. Conditioning levels over 50% of relative humidity significantly affect its mechanical behavior. The plasticizing action due to the moisture content emphasizes its rubber-like behavior leading to a decrease of its

* Corresponding author. Tel.: +39 0461 282411; fax: +39 0461 281977.

E-mail address: annalisa.cataldi@ing.unitn.it (A. Cataldi).

dimensional stability. This loss of tension can produce a distortion of the canvas thus impairing a coherent reading of the artwork [14].

In the last years, microcrystalline cellulose (MCC) has attracted the attention as a potential interesting reinforcing filler for polymeric materials [15,16], because of its low density, high specific strength and stiffness [17]. MCC can be produced from a variety of natural plants by the reaction of cellulose with a water solution of strong mineral acids at boiling temperature. The hydrolysis reaction removes the amorphous fraction and reduces the degree of polymerization of the cellulose chains and in this way fibers with a high degree of crystallinity can be obtained [18]. Moreover, microcrystalline cellulose has a good water swelling resistance and thermo-chemical stability [19,20].

In the present work, the investigation of the possible stabilizing effect of the MCC introduction on the mechanical performance of Aquazol/microcrystalline cellulose composites at temperature of 23 °C and a relative humidity of 55% and a comparison with the mechanical behavior of the corresponding dried materials was performed. The final goal is the limitation of the plasticizing action of the moisture content on the neat Aquazol to be applied as a canvas lining adhesive through the introduction of a natural microfiller. The assessment of the role of MCC on the consolidation of the paint-shear and the lining adhesive shear through a deep mechanical characterization was conducted.

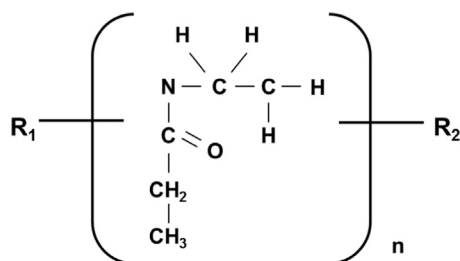
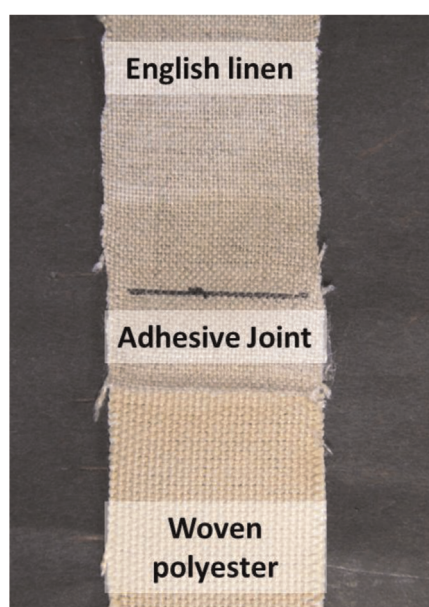


Fig. 1. Structure of the repeat unit of Poly 2-ethyl-2-oxazoline.



2. Experimental

Two different molecular weights of the same water soluble poly 2-ethyl-2-oxazoline, commercially called Aquazol[®] 200 (AQ200) and Aquazol[®] 500 (AQ500) supplied by Polymer Chemistry Innovation (USA) (Fig. 1), were selected as polymeric matrices. Microcrystalline cellulose powder (MCC) was purchased from Sigma Aldrich (USA). Materials were melt compounded in a Haake Rheomix[®] internal mixer ($T=160$ °C, rotor speed=60 rpm, residence time=5 min) and compression molded at 170 °C in a Carver hydraulic press under a pressure of 4 MPa for 5 min. Microcomposites with a MCC content of 5 wt% and 30 wt% were obtained in form of square sheets with an average thickness of 1.3 mm. Some samples were dried at 50 °C for 24 h and other samples were conditioned at a temperature of 23 °C and 55% of relative humidity in a chamber with a saturated solution of $Mg(NO_3)_2 \cdot 6H_2O$ for 30 days. This is the humidity level recommended in museums, churches and historical buildings in order to guarantee the optimal artwork conservation and protection [21]. Thin films 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. Samples were denoted identifying the matrix (AQ200), the filler (MCC), its weight concentration and its conditioning level. For instance, AQ200-MCC-30_w indicates the conditioned formulation with a MCC amount of 30 wt%, while AQ200-MCC-30_d refers to the same formulation in the dry state.

The moisture content M%, was determined by monitoring the change of weight of at least five specimens for each formulation, by using a Gibertini E42 electronic balance with an accuracy of 10^{-4} g. According to ASTM D570 standard, M% was calculated by the comparison between the initial weight of the samples (w_0) and the weight at the equilibrium point (w_t) according to Eq. (1)

$$M(t) = 100 \frac{(w_t - w_0)}{w_0} \quad (1)$$

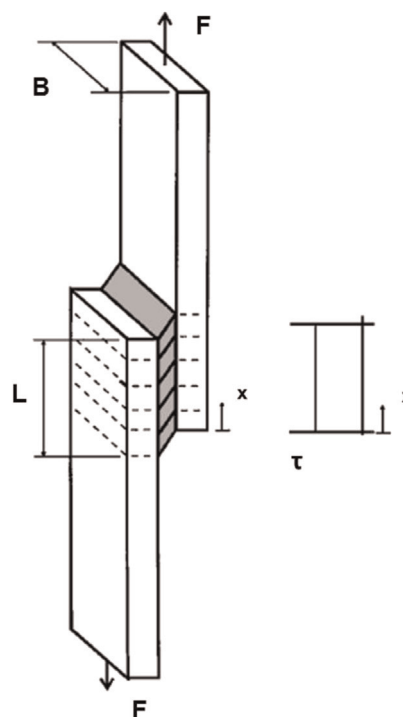


Fig. 2. (a) Representation of a single-lap adhesive joint with textile adherends. (b) Schematic of testing parameters.

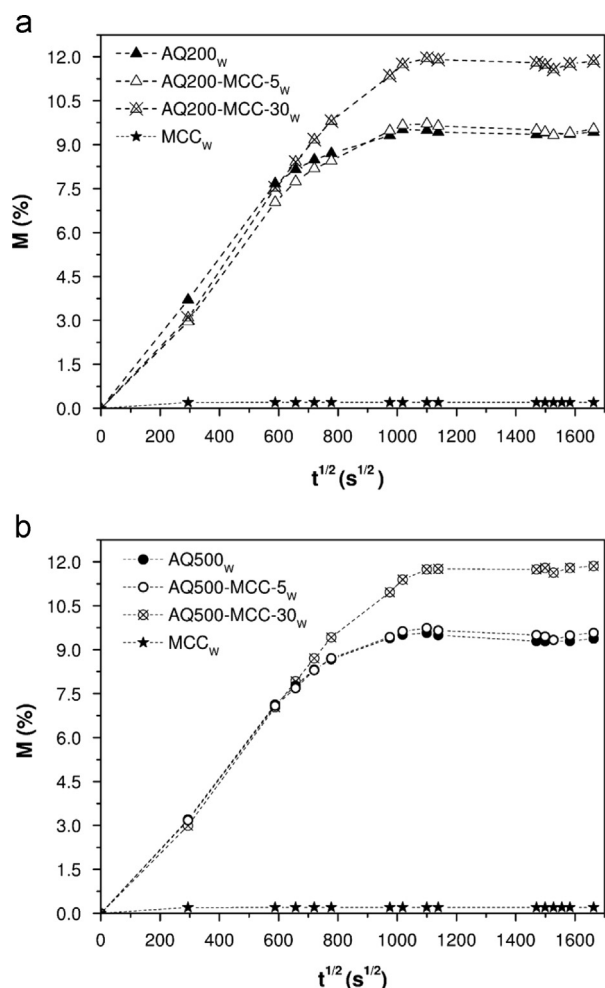


Fig. 3. Water uptake of MCC powder, neat matrices and relative composites conditioned at RH=55% and $T=23\text{ }^{\circ}\text{C}$ for 30 days. (a) AQ200 based composites, (b) AQ500 based composites.

Table 1

Results of water absorption kinetics of neat AQ200 and AQ500 and resulting composites (conditioned samples).

Sample	M_{MAX} (wt%)	t_s (h)
MCC _w	0.20	24
AQ200 _w	9.37	264
AQ200-MCC-5 _w	9.51	264
AQ200-MCC-30 _w	11.91	336
AQ500 _w	9.35	264
AQ500-MCC-5 _w	9.56	264
AQ500-MCC-30 _w	11.77	336

M_{MAX} : maximum moisture content at the equilibrium point.
 t_s : time to reach the equilibrium point.

Moreover, the final moisture content (M_{max}) and the time required to reach the equilibrium water content (t_s) were evaluated.

Dynamic mechanical thermal analysis (DMTA) measurements were performed through a TA Instrument DMA Q800 apparatus under tensile configuration. Rectangular specimens 15 mm long, 5 mm wide and 1.3 mm thick were tested in a temperature range between $-10\text{ }^{\circ}\text{C}$ and $150\text{ }^{\circ}\text{C}$ at a heating rate of $3\text{ }^{\circ}\text{C min}^{-1}$ and a frequency of 1 Hz. Storage modulus (E') loss modulus (E'') and loss tangent ($\tan \delta$) trends were registered as a function of the temperature. Coefficients of linear thermal expansion (CLTE) were determined from the evaluation of the slope of thermal strain

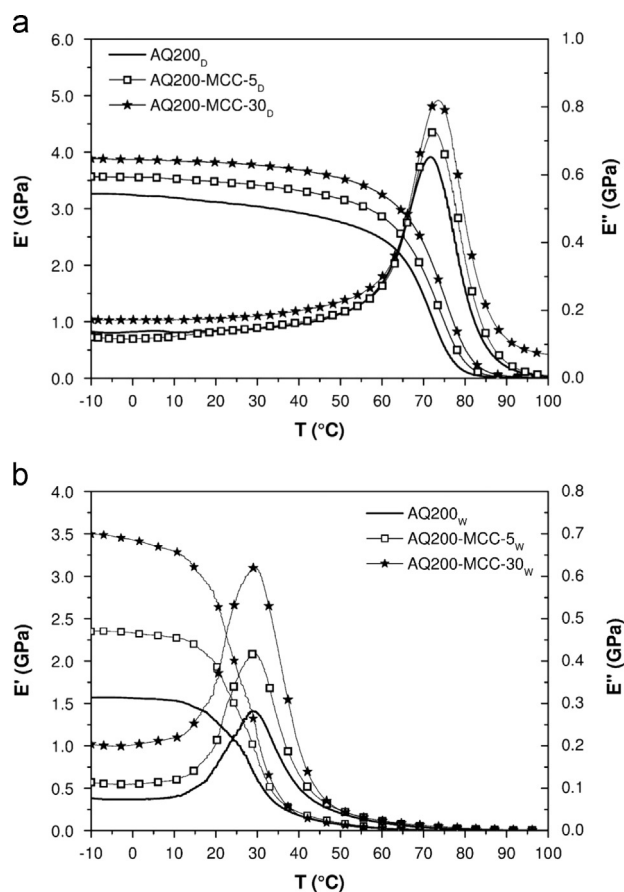


Fig. 4. DMTA thermograms of neat AQ200 and relative composites under (a) dry and (b) wet conditions.

Table 2

Results of DMTA tests on neat AQ200 and AQ500 and resulting composites in dry and conditioned state.

Sample	E' at $25\text{ }^{\circ}\text{C}$ (GPa)	E'' peak value (GPa)	$\tan \delta$ peak value	T_g at E'' peak ($^{\circ}\text{C}$)	CLTE_g (K^{-1})	CLTE_r (K^{-1})
AQ200 _d	3.08	0.65	3.25	71.6	$9.3\text{E}-05$	$10.1\text{E}-03$
AQ200-MCC-5 _d	3.45	0.67	3.18	72.5	$8.0\text{E}-05$	$8.8\text{E}-03$
AQ200-MCC-30 _d	3.80	0.80	2.52	73.5	$5.8\text{E}-05$	$6.9\text{E}-03$
AQ200 _w	1.56	0.28	0.60	28.9	$10.2\text{E}-05$	$3.8\text{E}-04$
AQ200-MCC-5 _w	2.33	0.42	0.69	29.1	$9.4\text{E}-05$	$3.7\text{E}-04$
AQ200-MCC-30 _w	3.43	0.62	1.09	29.9	$7.7\text{E}-05$	$3.4\text{E}-04$
AQ500 _d	3.41	0.69	3.23	73.9	$8.9\text{E}-05$	$8.4\text{E}-03$
AQ500-MCC-5 _d	3.53	0.70	3.17	74.4	$7.1\text{E}-05$	$7.0\text{E}-03$
AQ500-MCC-30 _d	4.00	0.84	2.54	75.0	$4.8\text{E}-05$	$4.8\text{E}-03$
AQ500 _w	1.92	0.33	0.67	31.6	$10.1\text{E}-05$	$4.5\text{E}-04$
AQ500-MCC-5 _w	2.70	0.48	0.72	31.6	$9.2\text{E}-05$	$4.3\text{E}-04$
AQ500-MCC-30 _w	3.90	0.64	0.80	32.9	$6.5\text{E}-05$	$4.1\text{E}-04$

CLTE_g : coefficient of linear thermal expansion in the glassy state (interval $0\text{--}35\text{ }^{\circ}\text{C}$, for dried samples and interval $0\text{--}25\text{ }^{\circ}\text{C}$ for conditioned samples).

CLTE_r : coefficient of linear thermal expansion in the rubbery state (interval $50\text{--}55\text{ }^{\circ}\text{C}$, for dried samples and interval $30\text{--}35\text{ }^{\circ}\text{C}$ for conditioned samples).

curves below T_g (between $0\text{ }^{\circ}\text{C}$ and $55\text{ }^{\circ}\text{C}$ for dried samples, and between $0\text{ }^{\circ}\text{C}$ and $25\text{ }^{\circ}\text{C}$ for conditioned samples) and above T_g (i.e. between $65\text{ }^{\circ}\text{C}$ and $75\text{ }^{\circ}\text{C}$ for dried samples, and between $30\text{ }^{\circ}\text{C}$ and $35\text{ }^{\circ}\text{C}$ for conditioned samples). Additionally, the ratios between the values of E' , E'' and CLTE in the glassy and rubbery state were normalized over the corresponding properties of the neat matrices in order to estimated relative properties (E'/E'_0 , E''/E''_0 , $\text{CLTE}_g/\text{CLTE}_{g0}$ and $\text{CLTE}_r/\text{CLTE}_{r0}$) as a function of the filler content.

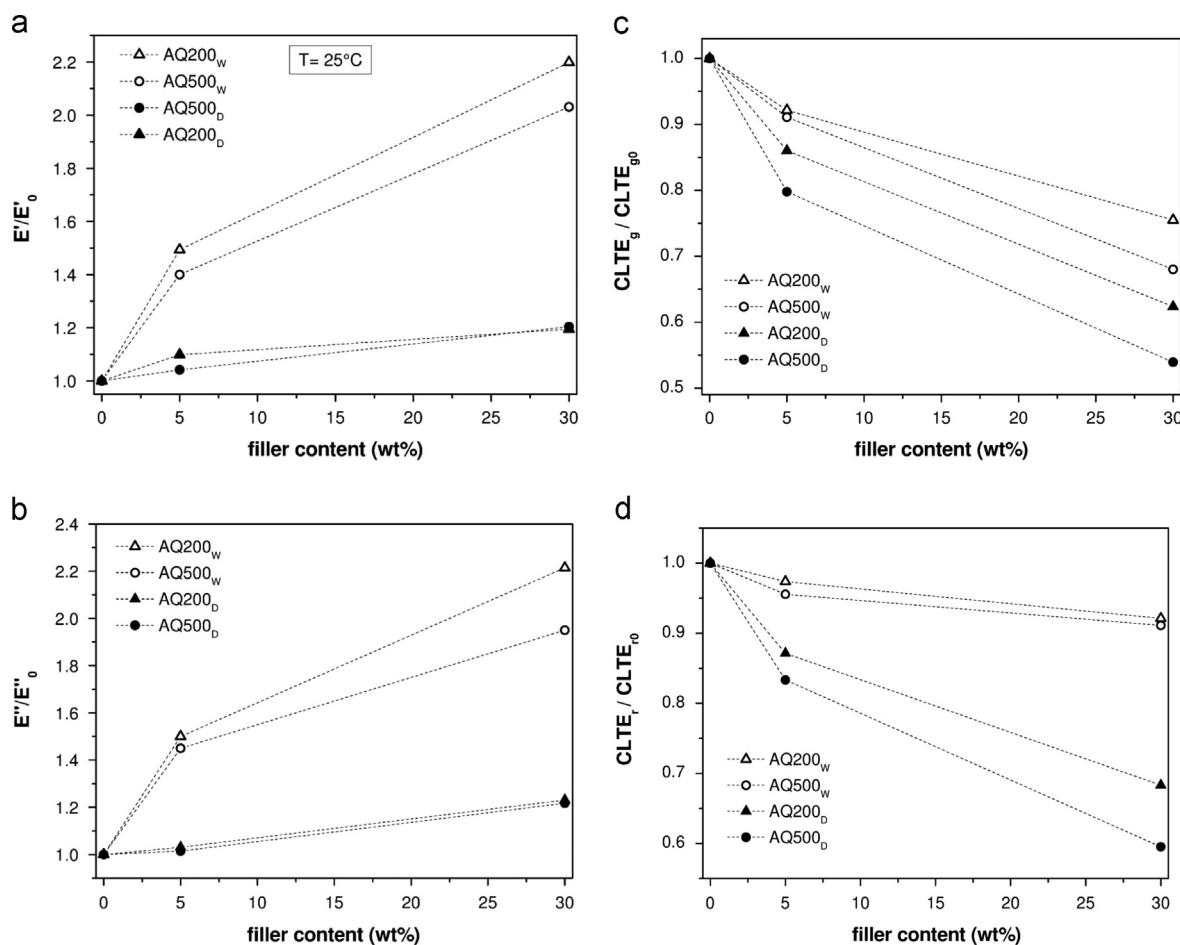


Fig. 5. DMTA relative properties trends of neat AQ200 and AQ500 and resulting composites in dry and wet state. (a) Storage modulus, (b) loss modulus, (c, d) coefficient of linear thermal expansion below and above T_g .

Quasi-static tensile tests were performed on ISO 527 type 1BA samples (gauge length 30 mm, width 5 mm, distance between the grips 55 mm, thickness 1.3 mm) by using an Instron[®] 4502 universal testing machine, equipped with a 1 kN load cell. For dried samples, the evaluation of the elastic modulus E , was performed at a crosshead speed of 0.25 mm min^{-1} (strain rate equal to 0.02 min^{-1}) and a maximum axial deformation level of 1%. The strain was recorded by using a resistance extensometer Instron[®] model 2620-601 (gauge length of 12.5 mm). According to ISO 527 standard, the elastic modulus was determined as a secant value between deformation levels of 0.05% and 0.25%. For wet samples having a rubber-like behavior, a secant elastic modulus at 10% strain was determined. Tensile properties at break (stress at break σ_B , and strain at break ϵ_B) were performed at a crosshead speed of 10 mm/min, without using the extensometer. A tensile energy to break (TEB) was calculated by integration of the area under the stress-strain curve corresponding to the total energy absorbed per unit volume of each specimen up to fracture. Additionally, relative values of E , σ_B and TEB (i.e. E/E_0 , σ_B/σ_{B0} and TEB/TEB_0) were estimated as a ratio between the values of composites over that of neat matrices.

Creep tests were conducted with a TA Instrument DMA Q800 apparatus under tensile configuration at 30°C . Each sample was tested applying a constant stress (σ_0) of about 10% of the stress at break of the corresponding unfilled matrix, for a total time of 3600 s. Rectangular specimens (15 mm long, 5 mm wide and 1.2 mm thick) were tested and the creep compliance $D(t)$, was determined as the ratio between the time dependent deformation $\epsilon(t)$ and the applied stress (σ_0). At least five specimens of each

sample were tested for each test. The ratio between the composites values and the neat matrix values of D (i.e. the relative property trend D/D_0) as the function of the filler content was examined.

Single-lap adhesive joints (12.7 mm long and 25 mm wide) bonding two kinds of canvas, were obtained by applying a pressure of 1 MPa for 5 min at 60° . A value of pressure higher than the standard normally used in lining works, was utilized in order to allow the reproducibility of tests. The two canvases used for this application were a pure linen fabric, English canvas, made of boiled and wet spun flax yarn, with a weight of 170 g/m^2 , a yarn count of 22×20 threads per cm and a plain weave pattern, representing the original oil painting canvas, and a uncoated woven polyester, Sintel, with a weight of 260 g/m^2 , a yarn count of 22×22 threads per cm and a plain weave pattern, utilized as the lining textile. The English canvas had an average thickness of 0.35 mm, while, the average thickness of the woven polyester was of 0.45 mm. In this way rectangular samples 200 mm long and 25 mm wide were produced to be tested under single-lap shear configuration (Fig. 2).

Single-lap shear tests in quasi-static conditions were performed by an Instron[®] 4502 universal testing machine, equipped with a 10 kN load cell, at crosshead speed of 10 mm/min. The adhesive shear strength (τ_B), was determined by dividing the maximum force by the overlapping area.

Observations of the fracture surface of adhesive joints were carried out by a Wild Heerbrugg Leica optical microscope at a magnification of $40\times$.

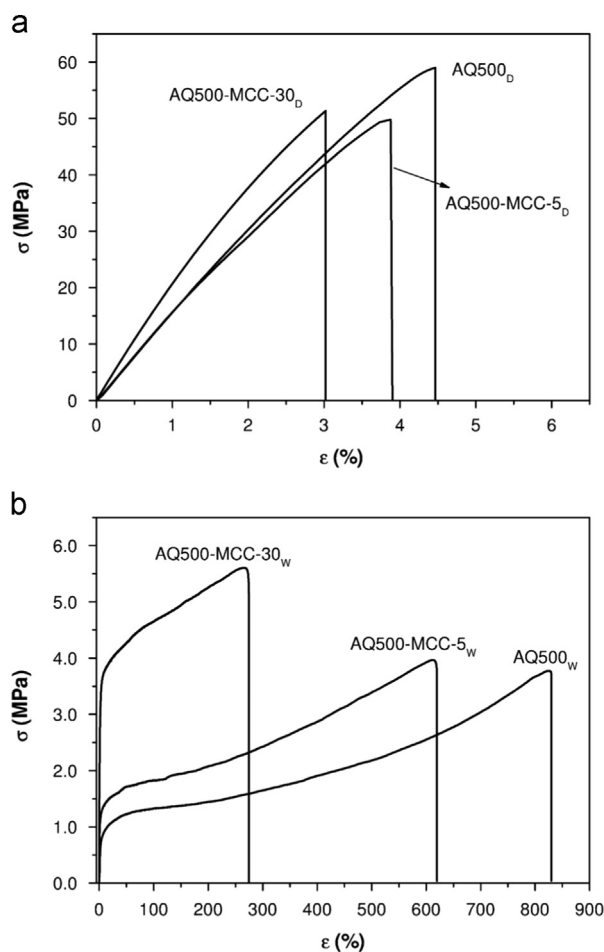


Fig. 6. Representative stress–strain curves of neat AQ500 and resulting composites under (a) dried and (b) wet conditions.

Single-lap shear tests under creep conditions were performed with an Instron® 4502 universal testing machine at a temperature of 30 °C and 55% of relative humidity, for 3600 s under a constant stress (τ_0), corresponding to about 50% of the shear stress at break (τ_B) of each neat matrix adhesive sample. The joint displacement (u) was investigated in the gauge length of each sample. At least five specimens were tested for each sample. Moreover, the ratios between the composites values and the neat matrices values of τ_B and u (i.e. the relative properties trends τ_B/τ_{B0} and u/u_0) as the function of the filler content were evaluated.

3. Results and discussion

The moisture sorption kinetics of unfilled and filled matrices are reported in Fig. 3(a) and (b). The maximum moisture content (M_{MAX}) and the time required to reach equilibrium conditions (t_s) are summarized in Table 1. Gravimetric curves of all formulations show a typical Fickian behavior, with a linear relationship between the humidity absorption and the square root of the time until the equilibrium point [22–24].

Even though MCC powder absorbs much less water than the two matrices, the introduction of this filler leads to an increase of the moisture content, more evident as its content increases. In fact, an important absorbing mechanism in composite materials is the capillarity and the flow of water through microcracks, voids and other defects along the filler–matrix interface [5]. Moreover, the time needed to reach an equilibrium point (t_s) increases with the

Table 3

Tensile properties of neat AQ200 and AQ500 and resulting composites in the dry state.

Sample	E (GPa)	σ_B (MPa)	ϵ_B (%)	TEB (MJ m ⁻³)
AQ200 _D	3.05 ± 0.15	52.26 ± 5.34	3.26 ± 0.27	1.13 ± 0.38
AQ200-MCC-5 _D	3.23 ± 0.33	29.07 ± 3.11	2.21 ± 0.22	0.43 ± 0.04
AQ200-MCC-30 _D	4.22 ± 0.30	40.16 ± 1.56	2.07 ± 0.09	0.43 ± 0.04
AQ500 _D	3.33 ± 0.44	59.80 ± 1.45	4.55 ± 0.11	1.44 ± 0.15
AQ500-MCC-5 _D	3.47 ± 0.10	47.88 ± 2.99	3.84 ± 0.32	0.99 ± 0.18
AQ500-MCC-30 _D	4.50 ± 0.63	52.05 ± 2.57	2.77 ± 0.28	0.84 ± 0.02

E : elastic modulus.

σ_B : stress at break.

ϵ_B : strain at break.

TEB: specific tensile energy to break.

Table 4

Tensile properties of neat AQ200 and AQ500 and resulting composites in the conditioned state.

Sample	$E_{10\%}$ (MPa)	σ_B (MPa)	ϵ_B (%)	TEB (MJ m ⁻³)
AQ200 _W	4.56 ± 0.06	1.86 ± 0.13	861 ± 28	9.46 ± 0.21
AQ200-MCC-5 _W	5.79 ± 0.14	2.44 ± 0.06	846 ± 25	12.75 ± 0.54
AQ200-MCC-30 _W	14.59 ± 0.79	3.77 ± 0.18	426 ± 21	12.18 ± 0.38
AQ500 _W	11.56 ± 0.20	3.90 ± 0.21	724 ± 29	17.80 ± 0.68
AQ500-MCC-5 _W	14.31 ± 0.70	4.13 ± 0.09	646 ± 14	17.01 ± 0.18
AQ500-MCC-30 _W	38.68 ± 1.44	5.90 ± 0.10	276 ± 8	14.50 ± 0.20

$E_{10\%}$: elastic modulus calculated at 10% of strain.

σ_B : stress at break.

ϵ_B : strain at break.

TEB: specific tensile energy to break.

filler amount. In fact, t_s increases from the 11 days observed for unfilled polymers and composites with 5 wt% of MCC up to 14 days measured for the two formulations with 30 wt% of MCC. This means that the total amount of moisture absorbed at the equilibrium increases with the filler content but a longer time is required to reach a stationary condition.

In order to study the synergetic effect of water sorption and MCC introduction on the viscoelastic properties of examined matrices, DMTA measurements were performed on dried and conditioned samples. Representative DMTA curves for dried and wet samples of AQ200 resin and relative composites are reported in Fig. 4(a) and (b). For sake of brevity the plots of the samples based on AQ500 resin are not reported since the curves are quite similar to that reported in Fig. 4(a) and (b). The stiffening effect in the glassy region provided by MCC particles is clearly evident on both the storage (E') and loss (E'') moduli curves. In Table 2 some relevant data emerging from DMTA analysis are shown. In Fig. 5 (a) and (b) the trends of relative storage modulus (E' at 25 °C), loss modulus (E'') peak are reported. The increase of the storage modulus with the content of MCC particles is more pronounced for the wet samples. Moreover, for both dried and conditioned composites the viscous part of the viscoelastic response (loss modulus) also increases with the MCC content, but, for wet samples, its ratio with the elastic component, represented by the loss tangent, increases as MCC content increases. In particular, AQ200/MCC wet composites show the highest increase of $\tan \delta$ in comparison to AQ500/MCC ones. Therefore, the peak value of $\tan \delta$ depends on the humidity content of the samples. From the position of the E'' peak it is possible to assess that the glass transition temperature is slightly affected by MCC addition. In fact, a slight increase of T_g is observed for samples in both dry and wet state (Table 2). As reported in Table 2 and in Fig. 5(c) and (d), the linear thermal expansion coefficient of the two matrices decreases proportionally to the MCC content in the glassy and in the rubbery state. In this

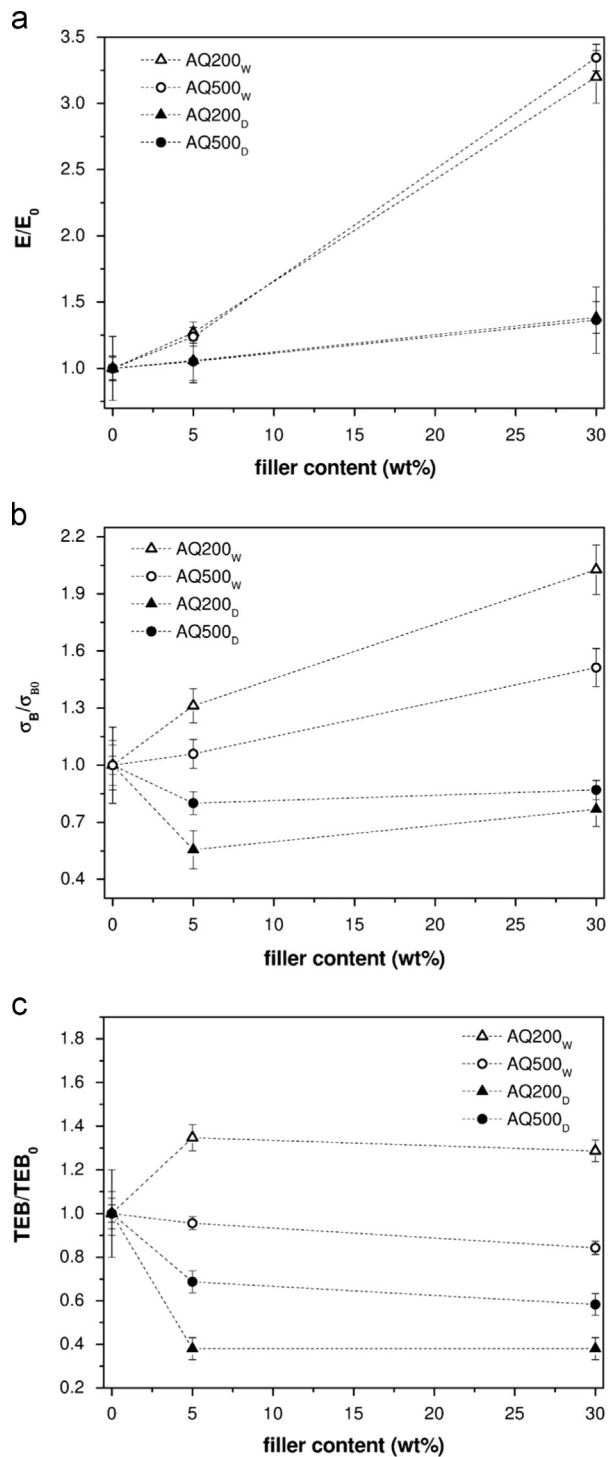


Fig. 7. Comparison between relative tensile properties of dried and wet composites: (a) elastic modulus, (b) stress at break, (c) tensile energy to break.

case, dried composites register a more significant reduction of this property. Interestingly, the plasticizing effect promoted by the water content increase is largely over ridden by the stiffening action of MCC. A similar behavior was reported in our previous work on a commercial acrylic matrix widely used in the field of art protection and restoration (Paraloid B72) reinforced with microcrystalline cellulose powder [25].

Representative stress/strain curves of dried and conditioned AQ500 composite samples obtained from quasi-static tensile tests are reported in Fig. 6(a) and (b). The stress–strain curves of AQ200

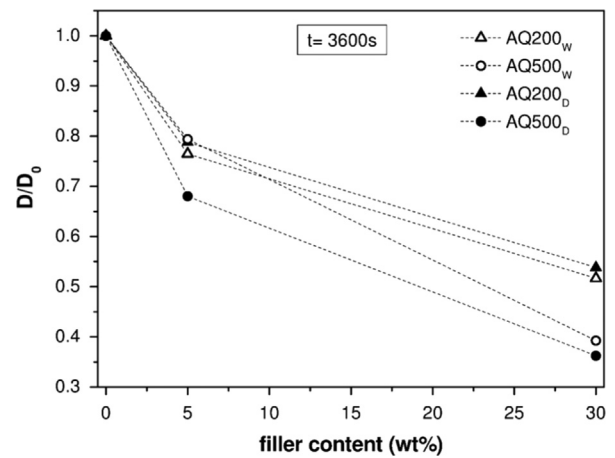


Fig. 8. Comparison of relative creep compliance values at 3600 s between dried and wet samples.

Table 5

Results of single-lap shear tests on neat matrices and resulting composites.

Sample	τ_B (MPa)	u at $t = 3600$ s (mm)
AQ200	1.04 ± 0.02	22.90 ± 0.03
AQ200-MCC-5	1.26 ± 0.02	14.33 ± 0.03
AQ200-MCC-30	1.17 ± 0.01	11.90 ± 0.02
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

τ_B : shear strength.

u : joint displacement.

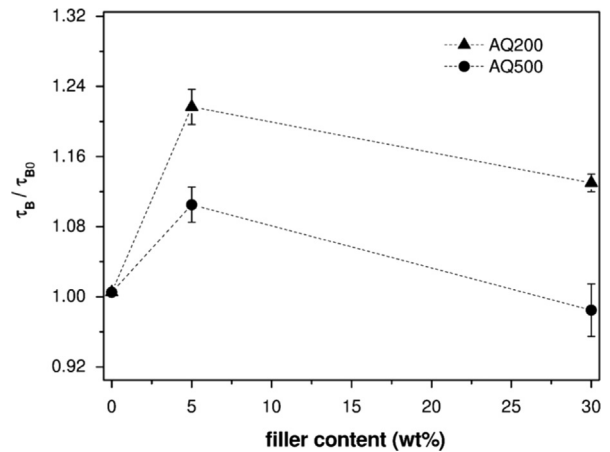


Fig. 9. Relative shear strength values for adhesive joints based on MCC polymer composites.

are omitted since the tensile behavior of this matrix is similar to that of AQ500. Tables 3 and 4 provide the main parameters obtained from tensile tests. It is evident how the presence of moisture changes the mechanical response of these polymer matrices and their corresponding composites, passing from brittle to ductile behavior. As one can see in Fig. 5(a) and (b) dried composites samples deform to a much smaller amount and then fracture in comparison to wet samples. This experimental evidence can be also observed by the direct comparison between the relative tensile properties of conditioned and dried formulations presented in Fig. 7(a)–(c). As clearly shown in Fig. 7a, an increase of the elastic modulus (E) with the filler loading can be observed with relative values much higher for wet samples. For both types of polymer matrices, an embrittling effect due to the MCC

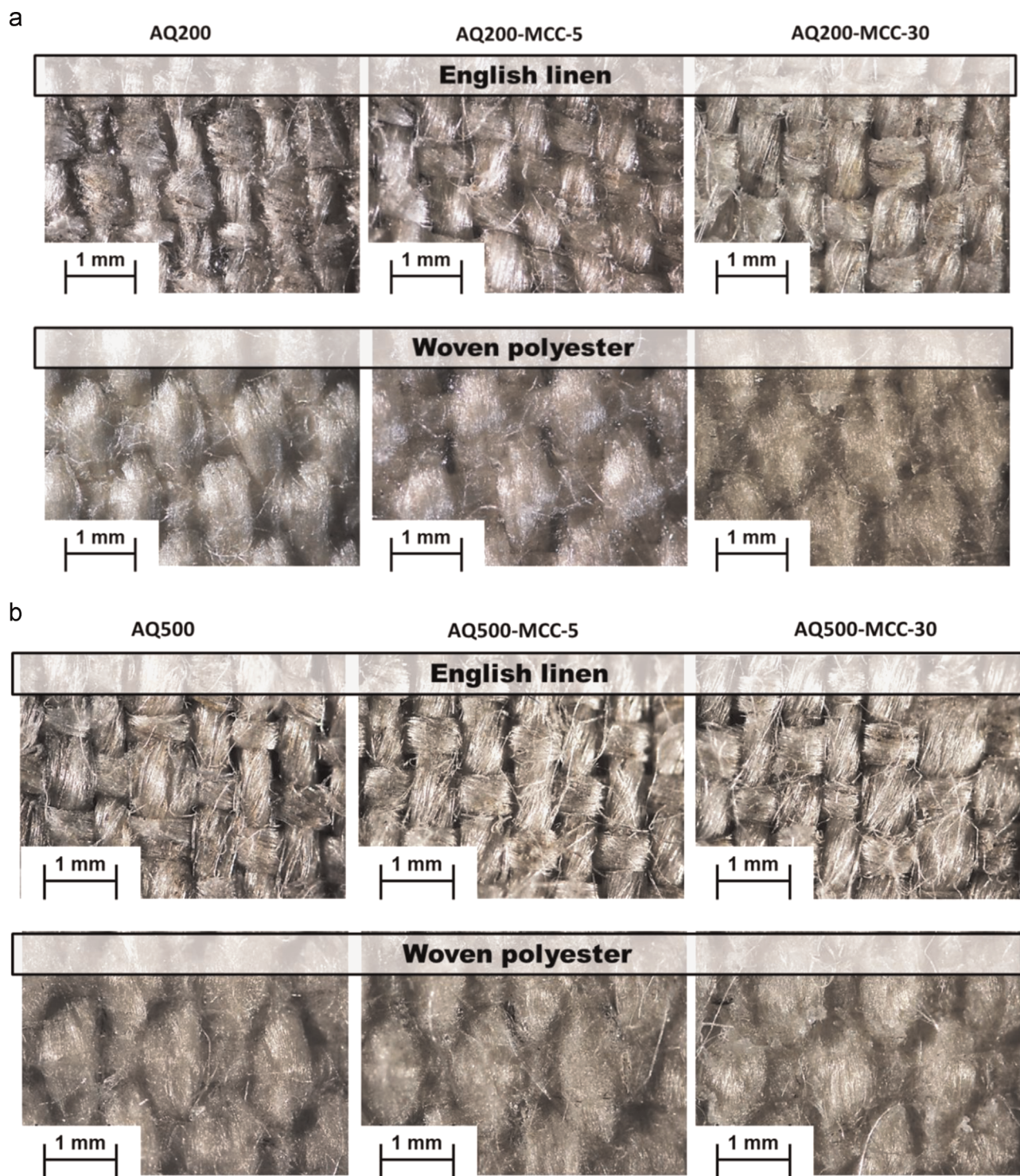


Fig. 10. Optical microscope images of overlap adhesive area of MCC based polymer composites. (a) Neat AQ200 and resulting composites, (b) neat AQ500 and resulting composites.

introduction can be detected under dry state with a decrease of the stress at break (σ_B), the ultimate strain (ϵ_B) and consequently of the specific tensile energy to break (TEB). On the other hand, wet samples do not present this drawback. In fact, the increase of the σ_B is proportional to the MCC content thus avoiding the drop in TEB values. For AQ200 based composites a remarkable increase of the tensile toughness (TEB) can be observed. For instance, AQ200-MCC-30_w manifests an increase of σ_B and TEB values of about 100% and 35%, respectively, in comparison to neat matrix. These results highlight the reinforcing and stabilizing effect of this

natural plant-based microfiller on the investigated polymer matrices under equilibrium conditions at the humidity level typical of a museum environment.

Finally, creep tests evidence the stabilizing effect induced by MCC addition, with an important reduction of the creep compliance values regardless to the matrices and the moisture content, especially for long creep times (Fig. 8).

On the basis of these results, it was decided to test the materials as lining adhesives for easel paintings canvas. During the application, a lining adhesive has to guarantee an optimal degree

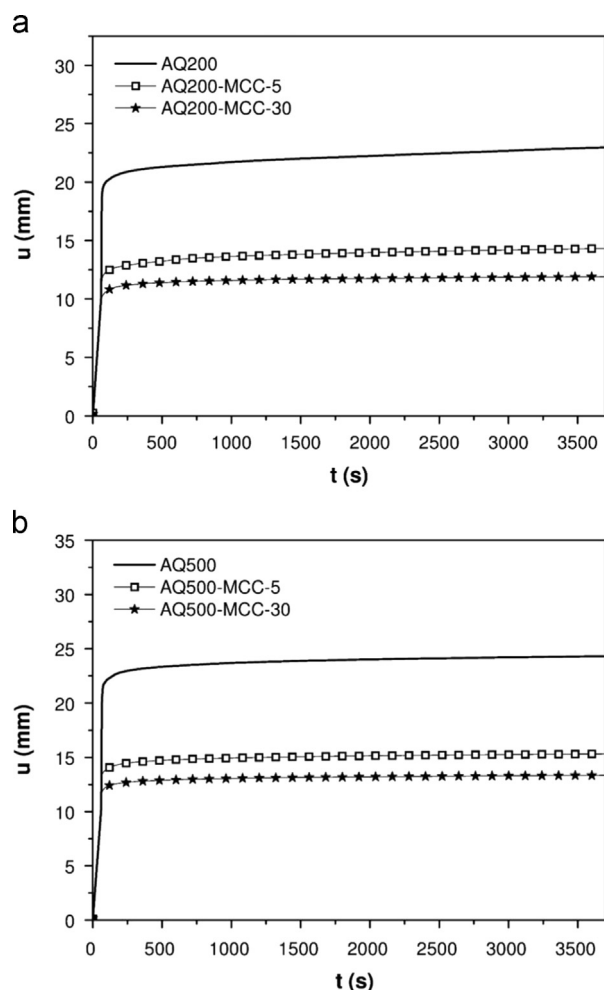


Fig. 11. Displacement curves from tensile creep tests on adhesive joints based on MCC polymer composites. (a) Neat AQ200 and resulting composites, (b) neat AQ500 and resulting composites.

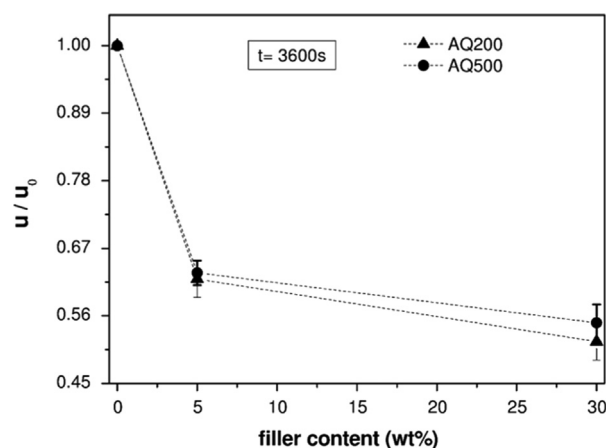


Fig. 12. Relative displacement at 3600 s for adhesive joints based on MCC polymer composites.

of viscosity, a good wettability and a high durability. After the application the adhesive joint needs to satisfy other mechanical properties, such as an appropriate adhesive strength to keep connected to different surfaces (the old canvas and the new lining textile), good viscoelastic and creep strength and relaxation resistance [26]. This is because easel paintings being fixed to a stretcher are subjected to constant long-lasting stresses. Therefore,

for this specific application an improved dimensional stability is highly desirable. Single-lap shear tests in quasi-static and creep configuration were performed on canvas samples lined with thin MCC adhesive films. In Table 5 the most important results from single lap shear tests are collected; while, in Fig. 9 the relative shear strength (τ_B) values, as a function of filler loading are reported. The results show that the introduction of MCC particles to AQ200 and AQ500 leads to an increase of τ_B for formulations with 5 wt% of microfiller. While, adhesive joints with the highest MCC content manifest a value of τ_B close to that of the neat matrices. As previously seen, also during application it is possible to appreciate the synergistic effects of both moisture content and MCC within these materials. The higher percentage of water in samples with 5 wt% of MCC in comparison to the pure polymers could be the cause of the τ_B increase, while, in the composite with 30 wt% of MCC, the filler action is predominant, but the presence of moisture limits the τ_B loss. Since the introduction of a reinforcing agent in adhesive systems could impair their fracture behavior, optical microscope observations of the fracture surfaces were performed. Fig. 10(a) and (b) shows the two cross-sections of each joint (the neat polymers and their corresponding composites) after fracture, with the English linen canvas in the upper part of the samples and the woven polyester in the bottom parts. The images show that all formulations, even with the highest amount of MCC, manifest the same fracture mode of the neat matrices, i.e. an adhesive fracture. In fact, the adhesive joints fail at the linen/glue interface and the main part of the adhesive layers remain on the woven polyester. This could be explained through a different penetration degree of adhesive films into the two kinds of canvas due to a difference in the inter-yarn porosity of the two selected textiles. The woven polyester has a lower inter-yarn porosity in comparison to the linen canvas and maybe this affects the penetration of adhesive films, allowing a higher penetration of these materials into the lining textile.

Adhesive displacement curves of the filled and unfilled matrices, shown in Fig. 11(a) and (b), prove the higher creep stability upon a constant stress of filled adhesive joints in comparison to the corresponding neat matrices. In fact, displacement values of the microcomposites adhesive joints are lower than the unfilled polymers ones, especially for long time of testing. From Fig. 12 it is possible to observe that an MCC addition of 30 wt% in AQ200 and AQ500 matrices is able to lead to a reduction of joint displacement of about 50%. Considering the end use of easel paintings that, fixed to a stretcher, are subjected to long lasting stresses and thus the viscoelastic-creep properties required to a lining adhesive, this is a very promising result in view of a real application of filled Aquazol as lining adhesive for paintings on canvas.

4. Conclusions

Microcrystalline cellulose was added to two commercial matrices to prepare innovative thermoplastic adhesives for artwork restoration. The mechanical response of the resulting materials in dry and conditioned states was investigated. The water diffusion through the filler/matrix interface led to an increase of the equilibrium moisture content of composites samples in comparison to the neat matrices. Nevertheless, MCC addition produced on both dried and conditioned samples a noticeable stabilizing effect. In fact, an increase of the dynamic storage and loss moduli, more pronounced for wet samples, and a decrease of the thermal expansion coefficient as the filler loading increases were observed. The presence of absorbed water led to a change in the tensile behavior of the two neat matrices, with a transition from a brittle to a ductile failure mode. Additionally, MCC introduction in wet formulations determined a remarkable increase in

the stiffness associated to an enhancement of the tensile properties at break. In contrast, the ultimate mechanical properties of dried microcomposites were reduced by MCC. Moreover, both dried and wet formulations highlighted a similar stabilizing effect induced by MCC addition under constant long-lasting (creep) stresses, regardless to the moisture content. Also during application of these materials as canvas lining adhesives the positive effect of MCC on the dimensional stability of the neat matrices was not limited by the moisture content. All dried and conditioned microcomposites reported a reduction up to 50% of the adhesive joint elongation. It is assumed that the higher amount of moisture within samples with 5 wt% of MCC led to an increase of the adhesive strength. Finally, MCC introduction was able to balance the plasticizing action of the water even during the application of these materials at a temperature of 23 °C and a relative humidity of 55%. This is very important, especially for Aquazol polymers which have a very high tendency to moisture sorption.

Acknowledgments

The support of conservators Mrs Lilia Gianotti and Mr Lorenzo Pontalti for supplying canvas textiles utilized in this work is kindly acknowledged.

References

- [1] Friend S Aquazol. One conservator's empirical evaluations, technical exchange in WAAC, vol. 18; 1996.
- [2] Chiu TT, Fairchock WJ. Poly (2-ethyl-2-oxazoline): a new water- and organic-soluble adhesive. In: Glass JE, editor. Ater-soluble polymers: beauty with performance. Washington, D.C: American Chemical Society; 1986. p. 425–33.
- [3] Wolbers RC. Short term mechanical properties of adhesives: solvent and plasticizer effects, third congress on color and conservation, materials and methods of restoration of movable polychrome works, Milan; 2006. p. 111–8.
- [4] Wolbers RC, McGinn M, Duerbeck D. Poly(2-Ethyl-2-Oxazoline): a new conservation consolidant. In: AIC-WAG Proceedings: Painted Wood: history and conservation; 1994. p. 514–27.
- [5] Chen CH, Wilson JE, Davis RM, Chen W, Riffle JS. Measurement of the segmental adsorption energy of poly(2-ethyl-2-oxazoline) on silica in water and ethanol. *Macromolecules* 1994;27:6376–82.
- [6] Mirderikvand G, Dautre M, Murray A, Fuster-López L, Yusà-Marco DJ, Mecklenburg MF. Adhesives in the formulation of filling materials for easel paintings: requirements, suitability, and stability. *Adhesives and consolidants for conservation*. Ottawa, Canada; 2011.
- [7] Arslanoglu J, Gallent C. Evaluation of the use of Aquazol as an adhesive in paintings conservation. *WAAC Newslett* 2003;25:12–8.
- [8] Meaurio E, Cesteros LC, Katime I. Study of the solvent role on complexation in systems poly(mono malkyl itaconate)/tertiary polyamide. *Polymer* 1998;39:379–85.
- [9] Walton CD, Warchol JF. Creping adhesives containing oxazoline polymers and methods of use thereof. Wilmington, US: Hercules Incorporated; 1998.
- [10] Brinkhuis R. Hyperbranched Esteroxazoline Polymers, US Patent US 20030144457 A1; 2003.
- [11] Arslanoglu J. Aquazol as used in conservation practise. *WAAC Newslett* 2004;26:10–5.
- [12] Bria CF. The history of the use of synthetic consolidants and lining adhesives. *WAAC Newslett* 1986;8:7–11.
- [13] Shelton C. The use of Aquazol-based gilding preparations. In: WAG sessions of the AIC annual meetings. Norfolk (Virginia); 1996.
- [14] Ackroyd P. The structural conservation of canvas paintings: changes in attitude and practice since the early 1970s. *Rev Conserv* 2002;3:3–14.
- [15] Spoljaric S, Genovese A, Shanks RA. Polypropylene–microcrystalline cellulose composites with enhanced compatibility and properties. *Composites Part A* 2009;40:791–9.
- [16] Shanks RA, Hodzi CA, Ridderhof D. Composites of poly (lactic acid) with flax fibers modified by interstitial polymerization. *J Appl Polym Sci* 2006;99:5–13.
- [17] Qui W, Endo T, Hirotsu T. Interfacial interaction, morphology and tensile properties of a composite of highly crystalline cellulose and maleated polypropylene. *J Appl Polym Sci* 2006;102:30–41.
- [18] Thummanukitcharoen P, Limpanart S, Srikulkit K. Preparation of organosilane treated microcrystalline cellulose (Simcc) and the polypropylene/Simcc composite. In: Proceedings of the 18th international conference on composite materials. Jeju Island (Korea); 2011.
- [19] Chauhan YP, Sapkal RS, Sapkal VS, Zamre GS. Microcrystalline cellulose from cotton rags (waste from garment and hosiery industries). *Int J Chem Sci* 2009;7:681–8.
- [20] Das K, Ray D, Bandyopadhyay NR, Sengupta S. Study of the properties of microcrystalline cellulose particles from different renewable resources by XRD, FTIR, nanoindentation, TGA and SEM. *J Polym Environ* 2010;18:355–63.
- [21] Van Grieken R, Janssens K. Cultural heritage conservation and environmental impact assessment by non-destructive testing and micro-analysis. London: CRC Press; 2004.
- [22] Cui YH, Wang XX, Xu Q, Xia ZZ. Research on moisture absorption behavior of recycled polypropylene matrix wood plastic composites. *J Thermoplast Compos Mater* 2010;24:65–82.
- [23] Harper BD, Staab GH, Chen RS. A note on the effects of voids upon the hygral and mechanical properties of AS4/3502 graphite/epoxy. *J Compos Mater* 1987;21:280–9.
- [24] Ishai O. Environmental effects on deformation, strength, and degradation of unidirectional glass fiber reinforced plastics, II experimental study. *Polym Eng Sci* 1975;15:491–9.
- [25] Cataldi A, Dorigato A, Deflorian F, Pegoretti A. Effect of the water sorption on the mechanical response of microcrystalline cellulose based composites for art protection and restoration. *J Appl Polym Sci* 2014;131:40741.
- [26] Hill Stoner J, Rushfield R. Conservation of easel paintings. United States: Routledge; 2012.