Innovative Microcrystalline Cellulose Composites as Lining Adhesives for Canvas

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Thin adhesive composite films were prepared by melt-compounding and compression molding of a thermoplastic resin (Paraloid® B72) widely used for art protection and restoration with a microcrystalline cellulose powder (MCC). To simulate an oil painting restoration work, MCC-based composites were applied as lining adhesives on two kinds of canvases (English linen and woven polyester). Interestingly, single–lap shear tests both in quasi-static and creep conditions showed a remarkable stabilizing effect provided by MCC addition. Post-mortem microstructural analysis of the overlap adhesive area proved how MCC introduction did not change the fracture behavior of the bonded joints. The visual assessment of transparency and color measurements evidenced a chromatic variation of MCC-based films with a filler amount of 30 wt%, while, UV-vis analysis showed a decrease of relative transmittance in proportion to the MCC content. Additionally, rheological tests highlighted a viscosity increase for Paraloid B72 in both dry and wet conditions ($T = 23$°C and RH = of 55%) as the MCC content increases. POLYM. ENG. SCI., 55:1349–1354, 2015. © 2015 Society of Plastics Engineers

INTRODUCTION

Thermoplastic resins are the most used preserve products to restore artworks, including applications as removable adhesives. Probably the first polymer used in conservation was polyvinyl acetate (PVA). From the 1930s to the 1950s, PVA was one of the few synthetic resins utilized for any general application in conservation [1]. Now, among the various thermoplastic polymers available, acrylic resins are the most frequently used adhesives for cultural heritage repair and conservation and, in particular, Paraloid B72, a methyl-acrylate/ethylene methyl-acrylate (MA/EMA) copolymer [2, 3]. The main reasons for its success are its good yellowing resistance, chemical stability even at high humidity levels, and its optical properties [4].

As far as paintings restoration is concerned, if the conservation state of the canvas-based substrate is critical, it is necessary to carry out a lining work in order to recover the original mechanical capabilities of canvas to support the painted film. The lining of paintings was introduced starting in the 18th century [1]. The first adhesives adopted for lining were animal glue and flour, applied by hot steel iron. Wax-resins, generally called hot-seal adhesives, were introduced in the 19th century in order to replace natural glue/paste adhesives which can suffer from degradative processes becoming hard and brittle. Lining processes were substantially improved by the introduction of hot-tables and low-pressure consolidation processes that guaranteed a better control of temperature and pressure parameters during treatment [5]. This change in technology led to the use of heat-seal adhesives, such as Paraloid B72. From the 1970s onward, conservators have tested different synthetic resins and various methods to improve the restoration of flax-based textiles including dispersions of acrylic polymers. The lining of oil paintings requires a combination of optical and chemical stability and specific mechanical properties. Despite this, the approach of conservators has always been to choose resins based solely on their optical and chemical properties and rarely on mechanical properties. The addition of additives creating a composite adhesive may be a solution for this issue, allowing for the maintenance of the optical and chemical properties while increasing mechanical insufficiencies and minimizing increases in cost. Considering the recent attention of composite scientists towards cellulose-based fillers reinforcements as a bio-based alternative to their synthetic equivalents [6, 7], and the similar chemical composition of this kind of fillers with the substrate of oil paintings that was investigated in this work, microcrystalline cellulose (MCC) was chosen as filler. The main aim of this research is the improvement of the thermo-mechanical performance of Paraloid, already used in restoration, by adding microcrystalline cellulose developing a new microcomposite which could be more suitable for applications for the linings of paintings, especially, in terms of dimensional stability and elongation resistance.

EXPERIMENTAL

A Paraloid B72 (PB72) acrylic resin (Rohm and Hass, Germany) was used as the thermoplastic matrix and microcrystalline cellulose powder (MCC) (Sigma Aldrich, USA) was selected as a filler. Composites with 5 wt% and 30 wt% MCC were prepared by melt-compounding in a Haake Rheomix® internal mixer ($T = 160$°C, rotor speed = 60 rpm, residence time = 5 min) and compression molding in a Carver hydraulic press ($T = 150$°C, $P = 4$ MPa, $t = 5$ min). 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 from the same preparation batches were then subject to one of two treatments: drying at 50°C for 24 h in a vacuum oven, or conditioning for 48 h at 23°C and 55% relative humidity in a chamber with a super-saturated solution of $Mg(NO_3)_2 \cdot 6H_2O$. Samples were denoted indicating the matrix (PB72), the filler (MCC), its weight amount and their conditioning level (W = conditioned at $T = 23$°C and RH = 55%, D = dry state). For instance, $PB72_W$ represents the neat matrix sample in the conditioned state, while, $PB72\text{-}MCC\text{-}30_D$ identifies a Paraloid sample in the dry state containing a MCC amount of 30 wt%.

Optical transparency of thin MCC adhesive films with an average thickness of 100 μm was evaluated through digital pictures taken by a professional Canon EOS 550D digital camera equipped with a zoom lens EF-S 18–135 mm, at a distance of 20 cm from the specimens.

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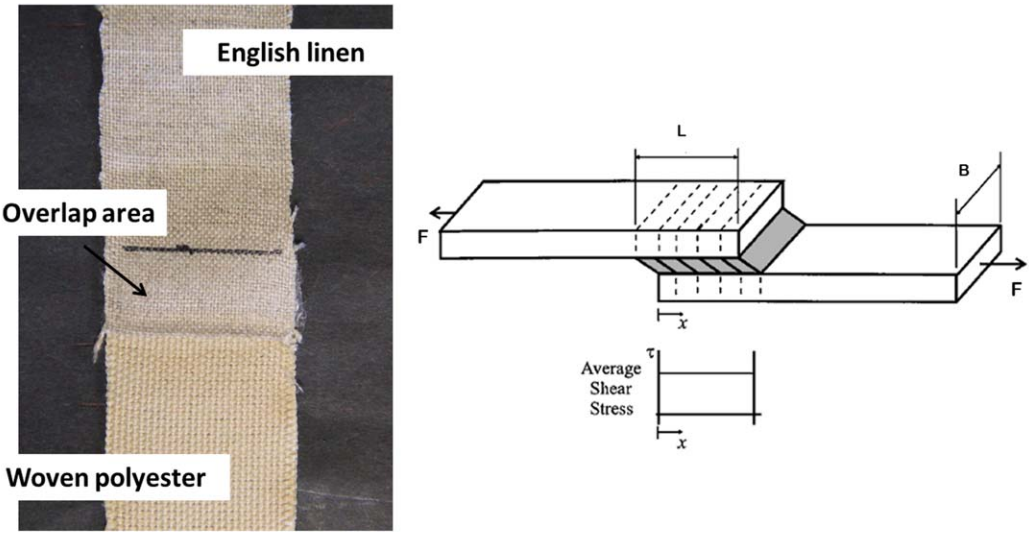


FIG. 1. (a) Representation of a single-lap adhesive joint with textile adherents. (b) Schematic of testing parameters. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The color of the samples was quantified by a portable spectrophotometer (Konica Minolta® model CM-2600d) with a diameter target area of 8 mm and CM-S100w (SpectraMagicTM NX) software. Three readings were performed in different zones of each specimen placed on a white sheet. Color measurements were analyzed by considering the CIELAB color system [8]. Each color is described trough three Cartesian coordinates: *L**, lightness or luminosity of color, from 0 (absolute black) to 100 (absolute white); *a**, variation in redness–greenness (positive *a** is red and negative *a** is green); and *b**, change in yellowness–blueness (positive *b** is yellow and negative *b** is blue). Another important value is *dE·ab*, the total color difference between a target and different samples, in this case each of the three neat matrices and the relative MCC composites, respectively. *dE·ab* values were provided by the CM-S100w software.

Relative transmittance spectra of thin adhesive films of neat matrices and corresponding composites were recorded with a Jasco570 UV-Vis-NIR spectrophotometer, at a spectral wavelength range of 250−800 nm.

Dynamic rheological tests were performed by using an Anton Paar MCR 301 rheometer in plate-cone configuration, imposing a maximum shear strain (γ_0) of 1%. An angular frequency range between 0.05 and 300 s^{-1} was used. Dried plates with an average diameter of 25 mm and an average thickness of 0.8 mm were tested at 160°C, the temperature used to produce the MCC composites. Conditioned samples with the same geometry were examined at 60°C, the temperature generally used to apply the lining adhesive on canvases [3, 9, 10].

Single-lap adhesive joints (12.7 mm long and 25 mm wide) connecting two kinds of canvas, an English linen (170 g/m^2), representing the original oil painting substrate, and a woven polyester (260 g/m^2), utilized as lining textile, were obtained by applying a pressure of 1 MPa for 5 min at 60°C. A value of pressure higher than the standard normally used in lining works, was utilized in order to allow the reproducibility of experimental data. In this way rectangular specimens 200 mm long and 25 mm wide were produced to be tested under single-lap shear configuration (Fig. 1).

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 a crosshead speed of 10 mm/min until failure. The adhesive shear strength (τ_B) was determined dividing the maximum force by the overlapping area.

Microstructural analysis of the fracture surface of adhesive joints was carried out with a Wild Heerbrugg Leica optical microscope at a magnification of 40×.

Single-lap shear tests under creep conditions were performed with an Instron® 4502 universal testing machine at a temperature of 30°C, for 3600 s under a constant stress (τ_0), corresponding to about 50% of the shear stress at break (τ_B) of each neat sample. The change in gauge length for each sample was taken as the joint displacement (*u*). The compliance of the English canvas and woven polyester were not calculated, but five specimens with the same overlap area and fabric lengths were tested for each sample to allow for direct comparison of *u*.

RESULTS AND DISCUSSION

In Fig. 2, optical pictures of thin films of the neat matrix and relative composites are shown. Formulations with the highest MCC amount show a chromatic change, ranging from a colorless material to a light yellow/brown one, without a substantial change in transparency. This evidence was quantified by color measurements and the main color parameters are listed in Table 1. In the CIELAB 1976 system, the Cartesian coordinates, *L**, *a**, and *b**, describe a three-dimensional space useful to identify colors. *L**, *a**, and *b** values correspond to CIE XYZ tristimulus values *X, Y, Z*, by following equations:

$$\mathrm{L}{*}=116\left(\frac{Y}{Y_n}\right)^{1/3}-16 \tag{1}$$

$$\mathrm{a}{*}=500\left[\left(\frac{X}{X_n}\right)^{1/3}-\left(\frac{Y}{Y_n}\right)^{1/3}\right] \tag{2}$$

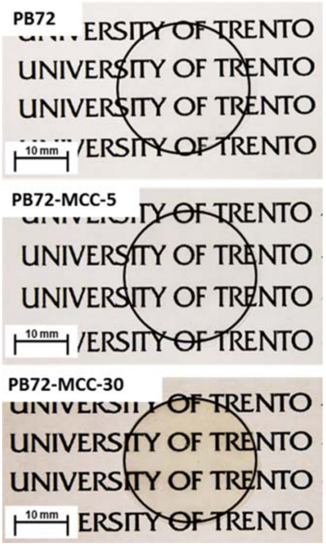


FIG. 2. Optical images of thin adhesive composite films showing the effect of the addition of 5 wt% and 30 wt% MCC on the optical properties of the PB72 matrix. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$b* = 200\left[\left(\frac{Y}{Y_n}\right)^{1/3} - \left(\frac{Z}{Z_n}\right)^{1/3}\right] \qquad (3)$$

where X_n, Y_n, and Z_n are the tristimulus values of the white stimulus, which is typically the brightest stimulus in the view field [11]. All the tested films have similar lightness value (L^*), while report a decrease of redness–greenness value (a^*), and an enhancement of yellowness−blueness value (b^*) as MCC loading increases. These variations are related to a chromatic shift of the neat matrix toward yellow tones with a slight decrease of brightness, especially for those formulations with 30 wt% of MCC. In order to quantify the color difference between the examined samples, the Euclidean distance between the dE^*ab values of the neat matrix (L_s, a_s, b_s) and the color values of the MCC loaded matrices (L_2, a_2, b_2) was estimated according to *Eq. 4*. [12]:

$$dE* \cdot ab = \left[\left(L_2^* - L_s^*\right)^2 + \left(a_2^* - a_s^*\right)^2 + \left(b_2^* - b_s^*\right)^2\right]^{1/2} \qquad (4)$$

The just noticeable difference (JND) is the minimum dE^*ab value that can be perceived by the human eye. The accepted dE^*ab value for a barely perceivable difference is 2.3 and is given a unit of 1 JND. Color differences below 1 JND, or 2.3 dE^*ab, are not easily detected by an observer [13]. Considering the dE^*ab values collected in Table 1, only PB72-MCC-30 samples result in a noticeable color difference, which is already seen in Fig. 2.

TABLE 1. Measured CIELAB color coordinate values.

Sample	L^*	a^*	b^*	$dE^* \cdot ab$
PB72	93.76 ± 0.07	2.70 ± 0.05	−10.51 ± 0.24	0
PB72-MCC-5	93.57 ± 0.71	2.65 ± 0.05	−10.06 ± 0.23	0.56 ± 0.07
PB72-MCC-30	92.57 ± 0.42	2.09 ± 0.04	−6.24 ± 0.27	4.36 ± 0.24

L^*, a^*, b^*: Color Cartesian coordinates.
$dE^* \cdot ab$: Total color difference.

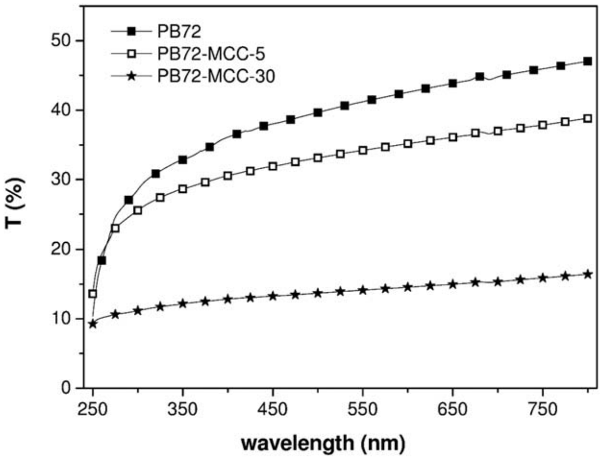
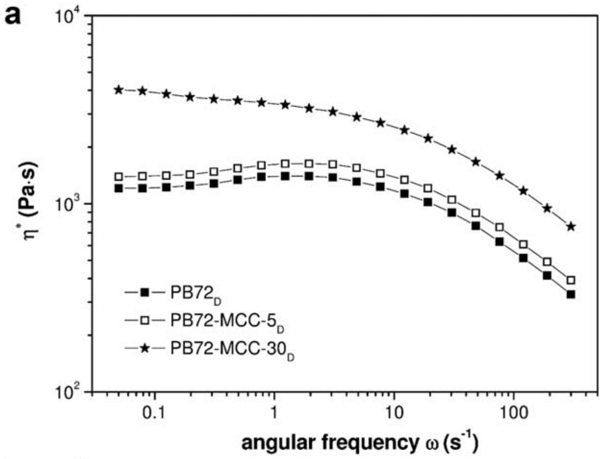


FIG. 3. Relative transparency of PB72/MCC-based polymer composites from UV-vis spectroscopy measurements with respect to the neat matrix.

Relative transmittance ($T\%$) spectra, of neat matrix and MCC filled films are reported in Fig. 3. The addition of MCC leads to an increased drop in transmittance values with increasing filler content. In particular, PB72 loses about 15% and 70% of the transmittance after the introduction of 5 wt% and 30 wt% of MCC, respectively.

On the basis of these results and the mechanical properties of these materials reported in a previous work [14], it was decided to examine their use as candidates for lining adhesives used on canvas based artwork. A preliminary thermo-mechanical characterization highlighted a stabilizing effect due to the microfiller introduction with an increase of the elastic modulus and a decrease of the thermal expansion coefficient and the creep compliance, both desirable properties of lining adhesives. Additionally, for this type of restoration, and considering that oil paintings are subject to long-lasting stresses due to being stretched over the frame, an improved dimensional stability is desirable and is more important than the adhesive optical properties.

Another important parameter to be considered, for successful lining work of oil paintings is the product penetration into the canvas and is strictly related to viscosity of the resin. Rheological tests were conducted on dried and conditioned samples at different temperatures related to both the processing and lining cycles, in order to assess the possible effect of MCC introduction on the viscosity of the neat matrix. Figure 4a reports apparent viscosity curves of dried MCC composites tested at 160°C (i.e., the temperature of melt-compounding). As expected, all tested composites exhibit a pseudoplastic behavior typical of a thermoplastic polymer in the molten state, with a first Newtonian step at lower angular frequencies (ω) values, where apparent viscosity (η^*) is still not dependent on ω. This plateau was followed by a drop in viscosity due to molecular and/or particles orientation [15, 16]. Because of the instrument limitations it was not possible to reach the last Newtonian step. As one can see, PB72/MCC formulations show a viscosity increase at elevated filler amount, especially at low angular frequencies. Conditioned samples of PB72 and its relative MCC composites were tested at 60°C, the same temperature used to produce adhesive joints on canvas samples. In Fig. 4b rheological curves for conditioned samples show a similar solid-like behavior for all examined



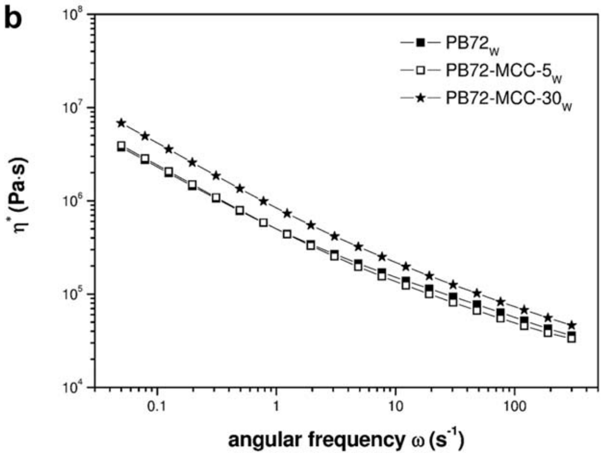


FIG. 4. Apparent viscosity of neat PB72 and its relative MCC composites. (a) dried polymer composites tested at 160°C, (b) conditioned polymer composites tested at 60°C.

formulations. The Newtonian plateau disappears and, in particular, η^*/ω curves of PB72/MCC composites highlight how the presence of moisture limits the η^* increase detected in dried samples tested at 160°C. These results confirm the slight increase of the matrix tendency to uptake water after the MCC introduction, as we have previously observed [17]. The rheological response of conditioned MCC polymer composites at 60°C is very important, considering the final application of these materials. In fact, the addition of MCC does not substantially change the viscosity of the neat matrix under lining conditions, thus avoiding relevant change in the product penetration degree within the textile that could affect their adhesion power. Single-lap shear tests in quasi-static and creep configuration were performed on canvas samples lined by thin MCC films. In Table 2, the most important results from single lap shear tests are collected. In Fig. 5, the relative shear strength (τ_B) values as a function of filler loading are reported. Compared with the neat PB72 results, it is possible to see that MCC introduction does not impair the adhesive strength. These results are in agreement with microstructural, physical and thermo-mechanical results collected in our previous studies, that demonstrated how uniformly dispersed MCC particles within this thermoplastic matrix do not lead to a decrease of their thermo-mechanical response, especially after conditioning. Even though in conditioned samples the MCC addition produces an enhancement of the moisture content, the presence of water does not limit the positive effects of this natural filler on the examined matrices and their thermoplastic behavior [14, 17].

TABLE 2. Results of single-lap shear tests on neat matrix and relative composites.

Sample	τ_B (MPa)	u at $t = 3600$ s (mm)
PB72	0.98 ± 0.05	13.78 ± 0.04
PB72-MCC-5	0.95 ± 0.01	10.94 ± 0.02
PB72-MCC-30	0.98 ± 0.02	8.92 ± 0.02

τ_B, shear strength; u, joint displacement.

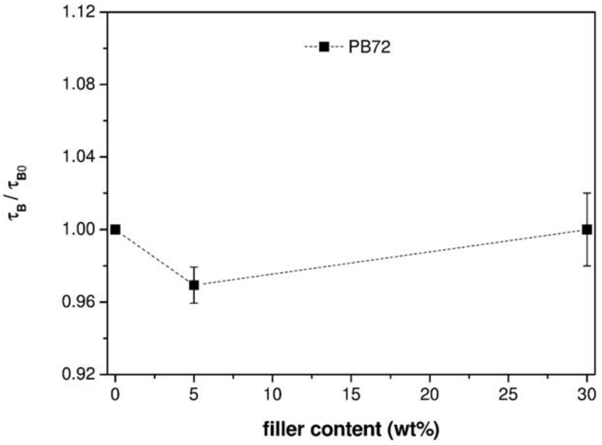


FIG. 5. Relative shear strength values of adhesive joints of PB72/MCC composites compared with the failure of the neat matrix.

Since the introduction of a reinforcing agent in adhesive systems could modify their fracture behavior, microstructural analysis of fracture surface were performed. Figure 6 shows the fracture surfaces of different joints (i.e., the neat PB72 and its relative microcomposites) after failure, for both the English linen in the upper part of the figure and the woven polyester below. These images highlight how the presence of MCC does not change the failure mode of the neat matrix, even at high filler content. All examined adhesives failed by adhesive fracture and all joints showed failure at the linen/adherend interface, where the main part of the adhesive layer remains on the woven polyester. At the same time some small differences among the adhesive film of the pure Paraloid and those filled with increasing amounts of MCC are noticeable. The appearance of these films slightly changes with the enhancement of the filler loading. In particular, the neat Paraloid film uniformly covers the polyester fabric, while PB72/MCC films, especially at highest amounts of MCC, present a not homogenous thickness with points where the microfiller, changing the path of the fracture, made an adhesive film more concentrated and others where the thickness of the adhesive is lower and the woven below is more visible.

Figure 7 highlights the higher dimensional stability under a constant applied stress of filled adhesive joints in comparison to the corresponding neat matrix. The joint displacement values of samples with MCC filler are systematically lower than those of the unfilled polymer over the whole range of tested period. From Fig. 8, it is possible to observe how an MCC addition of 30 wt% in PB72 matrix results in a reduction of joint displacement of about 40% after 1 h at 30°C. This is a very promising

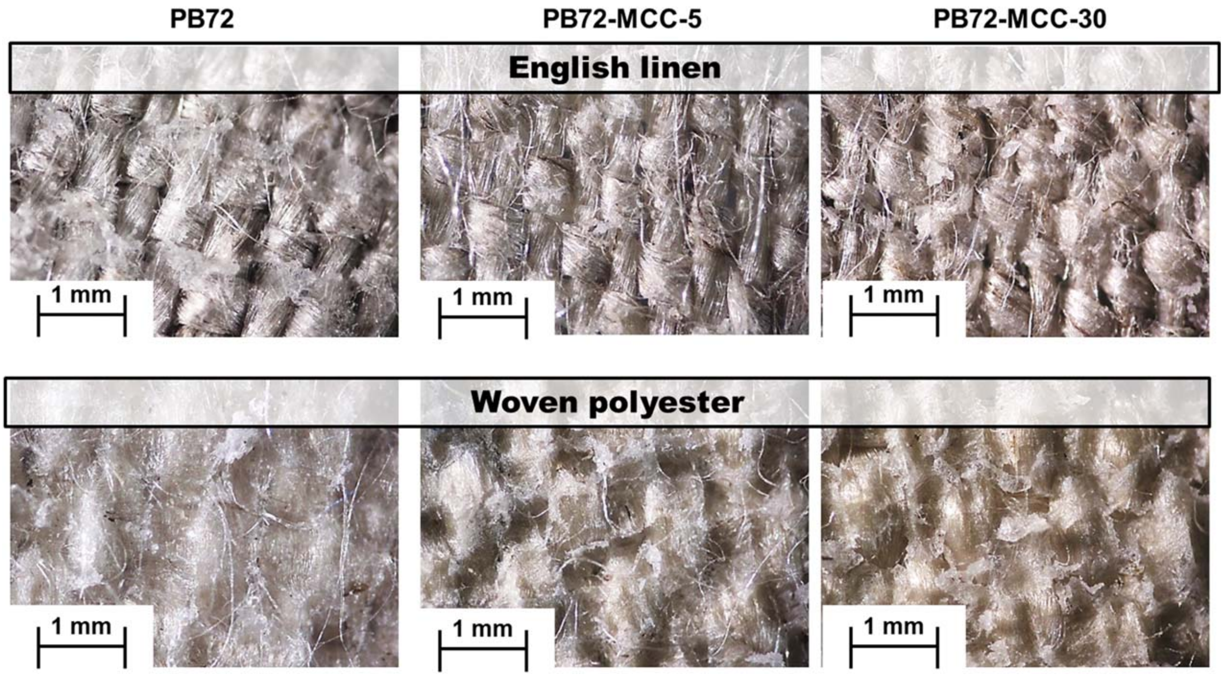


FIG. 6. Optical micrograph of the shear failure surface of overlap adhesive joints. Failure always occurred at the linen/adhesive interface. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

result, considering the service life of oil paintings, that being fixed to a frame, are subjected to long-lasting constant stresses.

CONCLUSIONS

Thin adhesive films to be used for artwork protection and restoration, were produced by melt-compounding and compression molding, adding 5 and 30 wt% of MCC to Paraloid B72, a commercially available and commonly used thermoplastic resin for this field. The transparency decrease, the chromatic change of these materials after the MCC introduction and the results of a preliminary thermo-mechanical characterization suggested their application as lining adhesives for canvas. For successful lining work of oil paintings a good dimensional stability of the adhesive joint is required, being that the substrate is exposed to long-lasting constant stresses due to frame fixing. Rheological tests on dried samples showed a viscosity increase proportional to the MCC content at processing temperature ($T = 160°C$), while variation of the viscosity was limited under lining conditions ($T = 60°C$ and $RH = 55\%$). Single–lap shear tests on adhesive joints under quasi-static and creep conditions confirmed the stabilizing effect provided by the addition of MCC, most importantly the reduction of the joint displacement as the filler loading increases without impairing the adhesive strength of the neat matrix. Additionally, microstructural analysis of the overlap adhesive area of MCC composites showed that MCC introduction did not change the fracture mode of the adhesive layer.

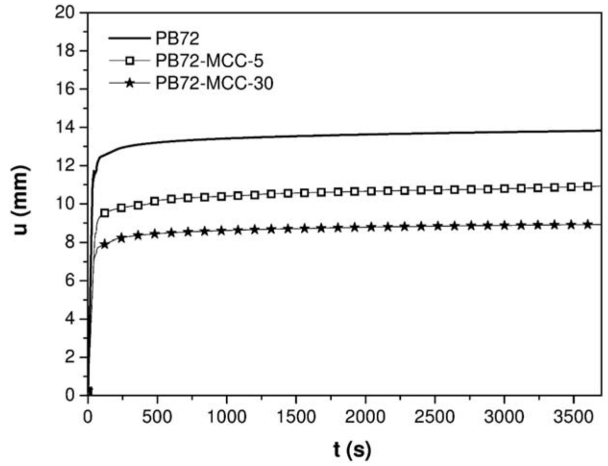


FIG. 7. Representative displacement curves from tensile creep tests on adhesive joints $T = 30°C$, total time = 3600 s, $\tau_0 = 50\%$ of the shear stress at break (τ_B), overlap area = 12.7 mm long and 25 mm wide.

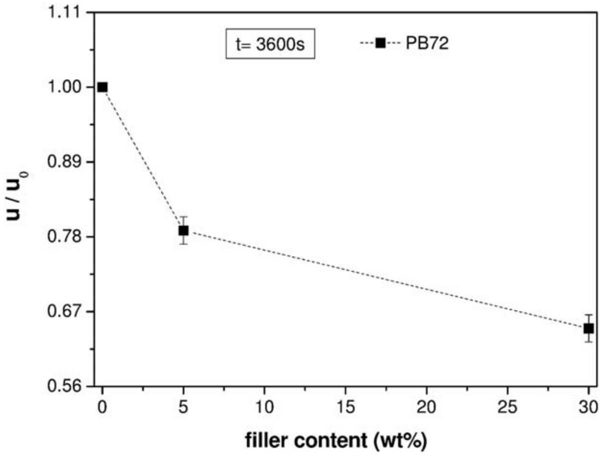


FIG. 8. Relative displacement at 3600 s for adhesive joints based on MCC-filled polymer with respect to the neat matrix.

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REFERENCES

1. C.F. Bria, *WAAC Newsletter*, **8**, 7 (1986).
2. J.L. Down, M.A. MacDonald, J. Tétreault, and R. S. Williams, *Stud. Conserv*., **41**, 19 (1996).
3. J. Podany, K.M. Garland, W.R. Freeman, and Joe Rogers, *J. Am. Inst. Conserv*., **40**, 15 (2001).
4. D. Sale, in: *Proceedings of the Adhesives and Consolidants for Conservation* Ottawa, Canada (2011).
5. G.A. Berger, *J. Am. Inst. Conserv*., **18**, 44 (1978).
6. S. Spoljaric, A. Genovese, and R.A. Shanks, *Compos. Part A*, **40**, 791 (2009).
7. R.A. Shanks, C.A. Hodzi, and D. Ridderhof, *J. Appl. Polym. Sci*., **99**, 5 (2006).
8. CIE, *Colorimetry*. CIE Publication No 15.2 CIE Central Bureau, Vienna, (1986).
9. D. Allard and K.B. Katz, *J. Am. Inst. Conserv*., **26**, 19 (1987).
10. K.B. Katz, *J. Am. Inst. Conserv*., **24**, 60 (1985).
11. R.W.G. Hunt and M.R. Pointer, *Measuring Colour*, 4th ed., Wiley, UK, (2011).
12. G. Sharma and R. Bala, Eds., *Digital Color Imaging Handbook*, CRC Press, London, UK (2002).
13. M. Mahy, L. Van Eycken, and A. Oosterlinck, *Color Res. Appl*., **19**, 105 (1994).
14. A. Cataldi, A. Dorigato, F. Deflorian, and A. Pegoretti, *J. Mater. Sci*., **49**, 2035 (2014).
15. S. Sinha Ray, *Clay-Containing Polymer Nanocomposites*, S.S. Ray, Ed., Elsevier, Amsterdam, 305 (2013).
16. J.R. Wagner Jr., E.M. Mount III, and H.F. Giles Jr., *Extrusion*, 2nd ed., J.R. Wagner, E.M. Mount, and H.F. Giles, Eds., William Andrew Publishing, Oxford, UK, 233 (2014).
17. A. Cataldi, A. Dorigato, F. Deflorian, and A. Pegoretti, *J. Appl. Polym. Sci*., **131**, 9070 (2014).