Effect of the Water Sorption on the Mechanical Response of Microcrystalline Cellulose-Based Composites for Art Protection and Restoration

Annalisa Cataldi, Andrea Dorigato, Flavio Deflorian, Alessandro Pegoretti

Department of Industrial Engineering and INSTM Research Unit, University of Trento, 38123 Trento, Italy
Correspondence to: A. Cataldi (E-mail: annalisa.cataldi@ing.unitn.it)

ABSTRACT: Thermoplastic composites based on a commercial acrylic matrix widely used in the field of art protection and restoration (Paraloid B72) and various concentrations (up to 30 wt %) of microcrystalline cellulose powder (MCC) were prepared by melt-compounding and compression molding. The mechanical behavior of the resulting materials conditioned at a temperature of 23°C and a relative humidity level of 55% was compared to that of the corresponding dried materials. Even though the moisture absorption of the filler was lower than the neat matrix, the maximum moisture content increased with the MCC amount, probably due to the preferential water diffusion path through the microvoids and/or the filler-matrix interface. Although the increase of moisture content for filled samples, DMTA analysis evidenced a stabilization upon MCC introduction, with an increase of the storage modulus and a decrease of the thermal expansion coefficient proportional to the filler loading. A similar trend was displayed by the corresponding dried materials. The tensile elastic modulus and the ultimate properties such as the stress at break and the tensile energy to break (TEB) of conditioned samples increased proportionally to the filler amount. On the contrary, the failure properties of dried composites were negatively affected by the presence of the microcellulose. It is worthwhile to report that a significant improvement of the creep stability was induced by MCC introduction both for dried and conditioned samples. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40741.

INTRODUCTION

Acrylic resins are commonly used in the field of cultural heritage restoration for the treatment of artworks. Among thermoplastic polymers, Paraloid B72®, a methyl-acrylate/ethylene methyl-acrylate (MA/EMA) copolymer, is one of the most used. Thanks to its good optical features and the possibility to be easily removed in case of need, this resin is applied as a protective layer for compact surfaces, as a consolidant of porous materials, and as an adhesive.[1–4]

Generally speaking, the long-term efficiency of polymers used in conservation treatments is strictly related to their durability in terms of chemical and photo-thermal oxidation stability, yellowing resistance, preservation of mechanical properties, water resistance and gas permeability. The synergistic action of sunlight, atmospheric pollution, temperature, and moisture may induce a certain degradation of the polymer structure with a reduction of the consolidative/protective capabilities of the artwork preservative materials.[5,6] Moreover, if the artwork is subjected to chemical, biological, and/or physical attack, the degradation reactions are strongly promoted by the presence of

water inside materials. If compared to commonly used acrylics resins for art conservation, Paraloid B72 presents a lower tendency to water sorption and a good chemical and photo-thermal oxidation stability.[7–9]

Because of its low density, high specific strength and elevated stiffness,[10] microcrystalline cellulose (MCC) is an interesting reinforcing filler for polymeric matrices.[11,12] Due to the production process based on the reaction of cellulose with a water solution of strong mineral acids at boiling temperature, these natural fibers present a high degree of crystallinity. In fact, the hydrolysis reaction destroys the amorphous fraction and reduces the degree of polymerization of the cellulose chains.[13] Therefore, microcrystalline cellulose has a good water swelling resistance and thermochemical stability.[14,15] Moreover, microcrystalline cellulose is non-toxic, biodegradable and recyclable.

In a previous work of this group,[16] the improvements of the thermomechanical properties of Paraloid B72 through the introduction of various amounts of a commercial microcrystalline cellulose powder have been investigated. In that work both the matrix and the filler were dried under vacuum, and the
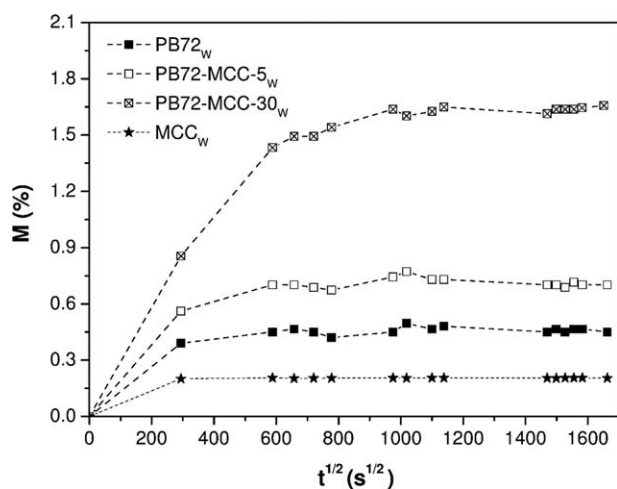
Figure 1. Water uptake of MCC powder, neat PB72, and relative composites conditioned at RH = 55% and $T = 23°C$ for 30 days.

prepared samples were sealed in vacuum bags till testing. Due to the uniform dispersion of the microfiller within the matrix, the tested composites displayed a remarkable improvement of thermomechanical behavior in comparison to the neat matrix, especially in terms of dimensional stability and stiffness.

Nevertheless, in real-life application the material is exposed to environmental conditions and tends to reach an equilibrium moisture content.

In the present article a careful investigation has been conducted on the effects of the moisture content on the mechanical performances of Paraloid B72/microcrystalline cellulose composites. A comparison with the mechanical behavior of the corresponding dried materials was also presented. The final goal is the assessment of the mechanical response of the prepared composites under recommended hydro-thermal conditions for artworks conservation.

EXPERIMENTAL

Microcrystalline cellulose powder (Sigma Aldrich), with a specific gravity of 1.56 g cm^{-3}, was selected as reinforcing filler. Paraloid B72 (PB72) resin (Rohm and Haas, Germany) with a specific gravity of 1.15 g cm^{-3} and a mean molecular weight (M_w) of 90,000 g/mol, was used as polymer matrix. MCC powder and matrix pellets were dried under vacuum at 105°C for 24 h. Both 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. Square sheets of neat PB72 and composite samples with a filler amount of 5 wt % and 30 wt %, 150 mm long and 1.4 mm thick, were obtained. After drying at 50°C for 24 h, the samples were conditioned at 23°C and 55% of relative humidity in a chamber with a supersaturated solution of Mg(NO$_3$)$_2$·6H$_2$O for 30 days. This is the humidity level recommended in museums, churches and historical buildings in order to guarantee the optimal artwork conservation and fruition. Samples were denoted indicating the matrix (PB72), the filler (MCC), its weight concentration and its conditioning level (W = conditioned at

$T = 23°C$ and RH = 55%, D = dry state). For instance, PB72-MCC-30$_D$ identifies a composite sample with a MCC amount of 30 wt % in the dry state.

The moisture absorption was evaluated by monitoring the change of weight of five specimens for each formulation, by using a Gibertini E42 electronic balance with a resolution of 10^{-4} g. According to ASTM D570 standard, the moisture content of a sample was calculated comparing its initial weight (w_0) and the weight at the equilibrium point (w_t) according to eq. (1):

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

Moreover, according to ASTM D5229 standard, 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) were performed by a TA Instrument DMA Q800 machine under tensile configuration. Rectangular specimens 15 mm long, 5 mm wide, and 1.4 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. The thermograms of the storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) were registered. Moreover, through the evaluation of the thermal strain it was possible to determine the coefficients of linear thermal expansion (CLTE) below T_g (i.e. in a temperature interval between 0°C and 35°C) and above T_g (i.e. between 50°C and 55°C).

Quasi-static tensile tests were carried out on ISO 527 type 1BA samples (gage length 30 mm, width 5 mm, distance between the grips 55 mm, thickness 1.4 mm) by using an Instron® 4502 universal testing machine, equipped with a 1 kN load cell. Tensile tests for the evaluation of the elastic modulus were performed at a crosshead speed of 0.25 mm min^{-1} (strain rate equal to 0.02 min^{-1}) imposing a maximum axial deformation level of 1%. The strain was recorded by using a resistance extensometer Instron® model 2620-601 (gage length of 12.5 mm). According to ISO 527 standard, the elastic modulus was evaluated as a secant value between deformation levels of 0.05% and 0.25%. Ultimate tensile properties were evaluated at a crosshead speed of 10 mm/min, without using the extensometer. At least five specimens were tested for each sample.

Creep tests were performed at 30°C by a TA Instrument DMA Q800 machine under tensile configuration, applying a constant stress (σ_0) of 2.35 MPa, corresponding to about 10% of the

Table I. Results of Water Absorption Kinetics of Neat PB72 and Relative Composites (Conditioned Samples)

Sample	M_{MAX} (wt %)	t_s (h)
MCC$_W$	0.20	24
PB72$_W$	0.45	96
PB72-MCC-5$_W$	0.70	96
PB72-MCC-30$_W$	1.63	240

M_{MAX}: maximum moisture content at the equilibrium point; t_s: time to reach the equilibrium point.
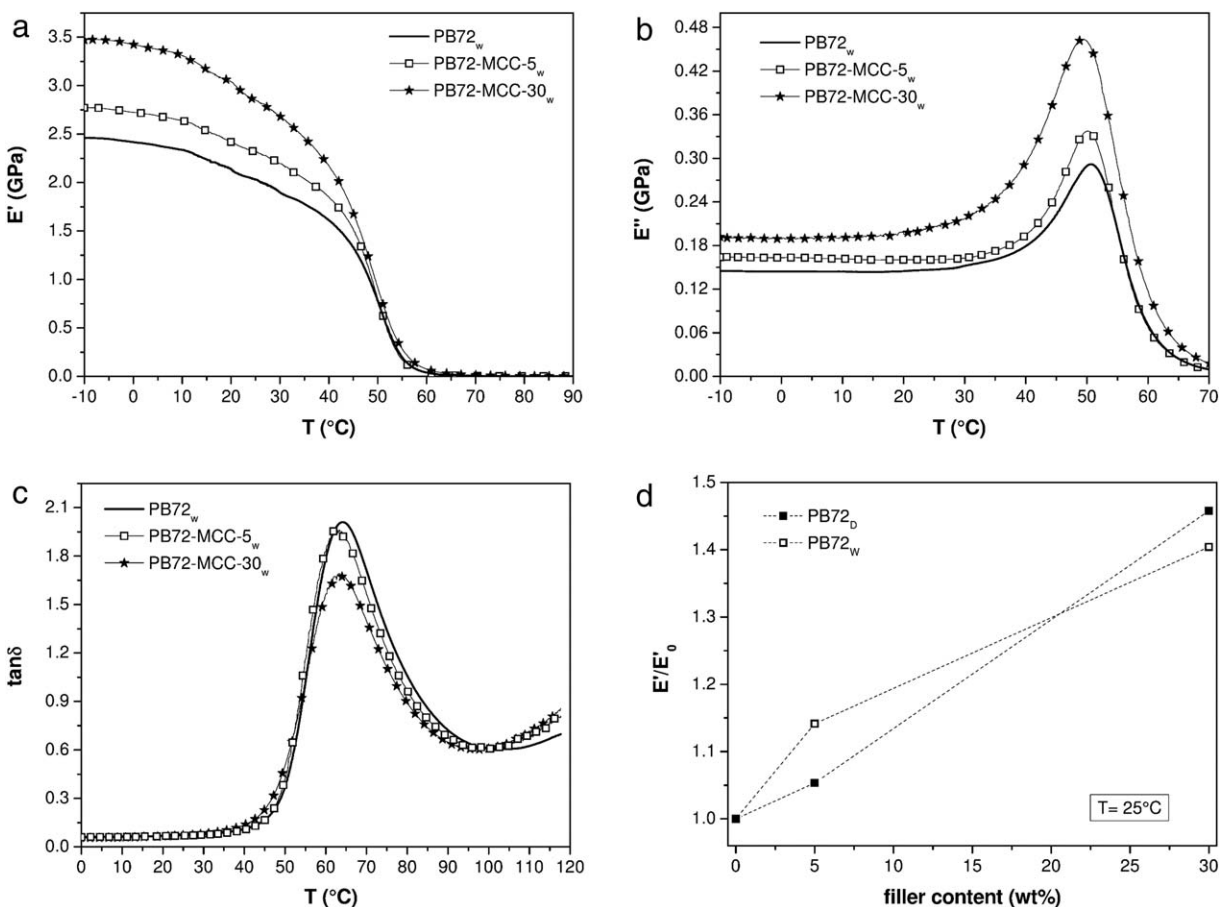
Figure 2. DMTA curves of neat PB72 and relative composites. (a) Storage modulus, (b) loss modulus and (c) loss factor of conditioned samples. (d) Relative elastic modulus at $T = 25°C$ of dried and conditioned composites.

stress at break of neat conditioned PB72. Rectangular specimens 15 mm long, 5 mm wide, and 1.4 mm thick were tested for 3600 s, and the creep compliance $D(t)$, determined as the ratio between the time dependent deformation $\varepsilon(t)$ and the applied stress (σ_0).

RESULTS AND DISCUSSION

The water uptake tests allowed the determination of the moisture absorption kinetics of the neat matrix and the relative composites (Figure 1). The maximum moisture content (M_{MAX}) and the time taken to reach the equilibrium conditions (t_s) are summarized in Table I. In the initial part of the curves reported in Figure 1, it is possible to observe a linear relationship between the humidity sorption and the square root of the time, typical of a Fickian diffusion. After this step, the water sorption rate decreases until an equilibrium point. Similar behavior is widely documented in the scientific literature on the hygrothermal aging of polymer composites.[17] Although MCC powder sorbs less water than the neat polymer, the introduction of this filler in the composites leads to an increase of the moisture content in comparison to the unfilled sample. Moreover, the increase in the moisture content is proportional to the MCC content of the composites. In fact, the equilibrium moisture content of PB72-W is 0.45 wt %, while, PB72-MCC-5$_W$ and

PB72-MCC-30$_W$ samples present an equilibrium value of 0.70 wt % and 1.60 wt %, respectively. Moreover, the time needed to reach the equilibrium level (t_s) increases with the filler amount, passing from 4 days for the PB72-MCC-5$_W$ sample up to 10 days for the PB72-MCC-30$_W$ composite. Moisture absorption in polymeric materials is generally governed by the Fick's diffusion law. It is known that water molecules may rapidly diffuse within the matrix, while moisture diffusion through filler particles is considerably slower. Another important mechanism in composite materials is the capillarity and the flow of water through

Table II. Results of DMTA Tests on Neat PB72 and Relative Composites

Sample	T_g (°C)	$CLTE_g$ (K^{-1})	$CLTE_r$ (K^{-1})
PB72$_D$	50.5	6.3E-05	6.2E-03
PB72-MCC-5$_D$	51.3	6.7E-05	5.7E-03
PB72-MCC-30$_D$	52.9	4.8E-05	3.6E-03
PB72$_W$	50.5	8.0E-05	4.5E-03
PB72-MCC-5$_W$	50.1	7.3E-05	5.1E-03
PB72-MCC-30$_W$	49.3	5.8E-05	3.4E-03

T_g: glass transition temperature (evaluated as E'' peak); $CLTE_g$: coefficient of linear thermal expansion in the glassy state (interval 0°C–35°C); $CLTE_r$: coefficient of linear thermal expansion in the rubbery state (interval 50°C–55°C).
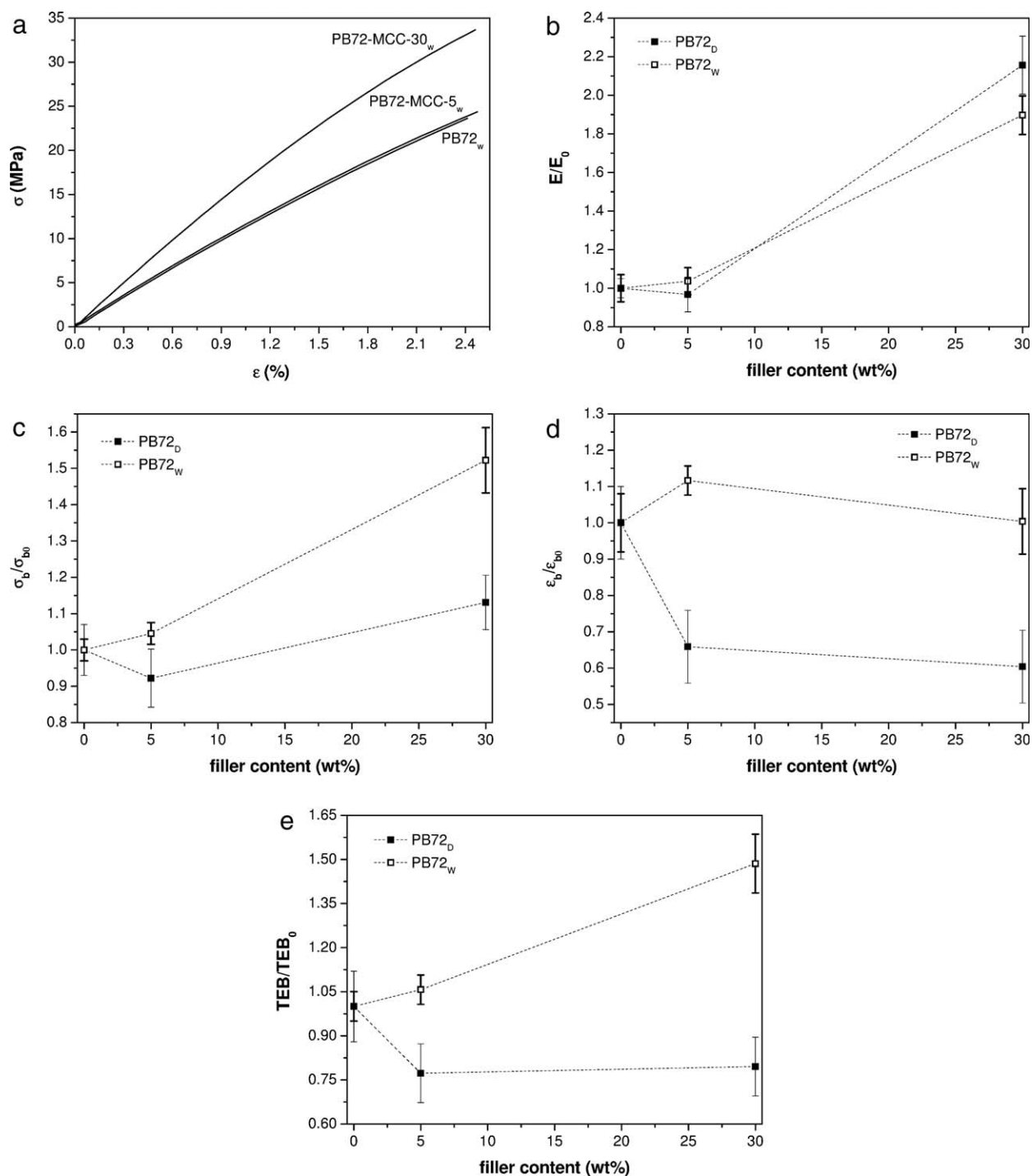
Figure 3. Quasi-static tensile properties of neat PB72 and relative composites. (a) Representative stress-strain curves of conditioned samples. Comparison between dried and conditioned composites: (b) relative elastic modulus, (c) relative stress at break, (d) relative strain at break, and (e) relative tensile energy to break.

microcraks, voids and other defects, including the filler-matrix interface.[18–22] Therefore, the higher tendency of MCC based composites to absorb water in comparison to the neat polymer matrix could be explained considering the capillary water diffusion through the filler/matrix interface. The effect of water uptake on viscoelastic properties of conditioned samples were investigated by DMTA analysis. In Figure 2(a–c) the tempera-

ture dependence of the storage modulus (E'), loss modulus (E''), and loss factor (tan δ) of neat PB72 and relative composites are reported, while in Table II some parameters, such as glass transition temperature evaluated as E'' peak and the coefficient of linear thermal expansion in the glassy (CLTEg) and in rubbery (CLTEr) states are reported. Interestingly, both the storage (E') and the loss (E'') moduli increase proportionally to the

Table III. Tensile Properties of Neat PB72 and Relative Composites

Sample	E (GPa)	σ_b (MPa)	ε_b (%)	TEB (MJ m^{-3})
PB72$_D$	1.54 ± 0.08	23.01 ± 1.51	3.46 ± 0.19	0.44 ± 0.08
PB72-MCC-5$_D$	1.49 ± 0.22	21.22 ± 2.37	2.28 ± 0.43	0.34 ± 0.11
PB72-MCC-30$_D$	3.32 ± 0.40	26.02 ± 2.44	2.09 ± 0.33	0.35 ± 0.09
PB72$_W$	1.65 ± 0.06	23.53 ± 0.39	2.49 ± 0.11	0.35 ± 0.02
PB72-MCC-5$_W$	1.71 ± 0.06	24.60 ± 0.38	2.78 ± 0.01	0.37 ± 0.02
PB72-MCC-30$_W$	3.13 ± 0.09	35.82 ± 1.88	2.50 ± 0.13	0.52 ± 0.07

E: elastic modulus; σ_b: stress at break; ε_b: strain at break; TEB: specific tensile energy to break.

filler loading. Correspondingly, tan δ values decrease with the MCC amount. Considering that loss factor is calculated as the ratio between E'' and E', the detected tan δ trend can be explained by the fact that the positive contribution of the MCC addition on the E' is higher than the E'' enhancement. Therefore, MCC has a more relevant action on the elastic components rather than on the dissipative behaviour of the neat matrix. A similar stabilizing effect has been already reported in literature for MCC filled polymer composites.[11,23,24] Through the comparison between the relative storage modulus values of conditioned and dried composites [Figure 2(d)], it is possible to conclude that the stabilizing effect provided by the MCC introduction does not markedly depend on the moisture content. As reported in Table II, the coefficient of linear thermal expansion decreases proportionally to the MCC content both in the glassy and in the rubbery state, regardless to the presence of moisture in the materials. Therefore, it is interesting to observe how the plasticizing effect promoted by the sorbed water is largely overcompensated by the stiffening action due to the microfiller addition. Moreover, the glass transition temperature, evaluated in correspondence to the E'' peak, increases with the MCC amount for dried samples, while in conditioned samples the presence of moisture at elevated filler amount leads to a slight decrease of the T_g values (Table II). However, it can be concluded that the effects of both the MCC introduction and the moisture content on the glass transition temperature are very limited.

Representative stress/strain curves obtained from quasi-static tensile tests of conditioned samples are reported in Figure 3(a), while in Figure 3(b–e) a direct comparison between the relative (i.e. normalized over the value corresponding to neat polymer matrix) parameters detected from tensile test of conditioned and dried formulations are presented. In Table III the most important results from tensile tests are summarized. Tensile tests evidenced a progressive increase of the elastic modulus (E) with the filler loading for both dried and conditioned samples. Considering standard deviation values associated to these measurements, stress at break (σ_b) of dried samples is practically unaffected by MCC addition, while for conditioned composites a noticeable increase of σ_b can be observed. The reinforcing effect of this natural plant-based microfiller on polymer matrices is therefore confirmed.[25] Interestingly, while both ultimate strain (ε_b) and specific tensile energy to break (TEB), of dried materials are negatively affected by MCC introduction, conditioned samples show an increase of TEB as the filler loading

increases. For instance, a TEB enhancement of 20% in comparison to the neat PB72 matrix was registered for the PB72-MCC-30W sample.

Also creep tests confirmed the stabilizing effect induced by MCC addition, with an important reduction of the creep compliance values, especially at long creep times [Figure 4(a)]. In this case, for dried materials a more pronounced creep compliance
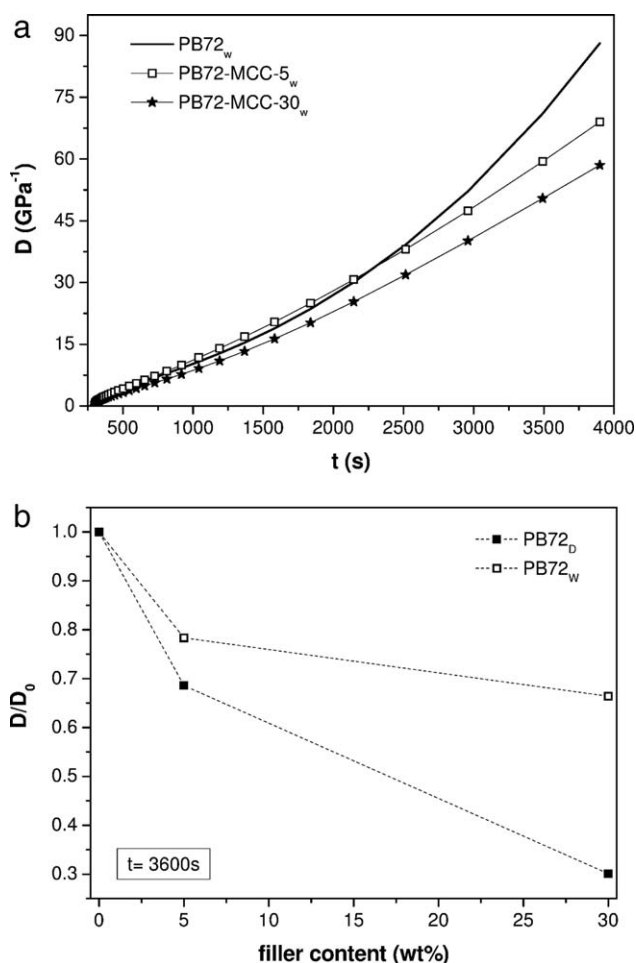

Figure 4. Creep behavior of neat PB72 and relative composites. (a) Representative creep compliance curves of conditioned samples and (b) comparison of relative creep compliance values at 3600 s between dried and conditioned samples.

reduction was observed in comparison to the corresponding conditioned samples [Figure 4(b)].

On the basis of the collected results it can be concluded that the concurrent action of a natural reinforcing microfiller, like MCC, and a limited moisture content leads to an improvement of filled materials showing better mechanical performance than the PB72 matrix. This demonstrates how MCC has a predominant role on the mechanical response of PB72 composites over the action of water absorbed by these materials under standard hydro-thermal service conditions.

CONCLUSIONS

Different amounts of a microcrystalline cellulose powder were added to a commercial MA/EMA acrylate matrix to prepare innovative thermoplastic polymer composites to be applied as consolidant and/or protective materials for the artwork restoration. In order to investigate the combined effects of the introduction of a natural reinforcing filler and the water uptake on the thermo-mechanical behavior of the resulting materials, conditioned samples were compared to the corresponding dried materials. The water diffusion through the filler/matrix interface led to an increase of the equilibrium moisture content with respect to the neat polymer matrix. Nevertheless, MCC addition produced an interesting stabilizing effect on the matrix, with an increase of the dynamic moduli (E', E'') and a decrease of the thermal expansion coefficient, proportional to the filler amount. Moreover, MCC introduction in conditioned formulations determined an increase of the stiffness associated to an enhancement of the tensile properties at break, in contrast to the mechanical behavior of dried microcomposites that reported a slight drop in these properties. Therefore, under hydrothermal service conditions recommended for artwork conservation, the moisture content did not impair the stabilizing effect provided by MCC introduction. In fact, PB72/MCC conditioned composites showed better mechanical performance in comparison to the corresponding dried materials, demonstrating how MCC has a role on the mechanical response of these polymers predominant over the action of absorbed water.

REFERENCES

1. Amoroso, G. G.; Fassina, V. Stone Decay and Conservation; Elsevier: Amsterdam, **1973**.

2. Down, J. L.; MacDonald, M. A.; Tétreault, J.; Williams, R. S. Stud. Conserv. **1996**, *41*, 19.

3. Paul, S. Surface Coatings Science and Technology; Wiley: Chichester, **1996**.

4. Taylor, T. H. In Situ Repair of Architectural Glass, Adhesives and Consolidants; International Institute for Conservation: London, **1984**.

5. Wypich, G. Handbook of Material Weathering; ChemTec Publishing: Toronto, **1995**.

6. Davis, A.; Sims, D. Weathering of Polymers; Applied Science Publishers: London, **1983**.

7. Chiantore, O.; Lazzari, M. *Polymer* **2001**, *42*, 17.

8. Lazzari, M.; Chiantore, O. *Polymer* **2000**, *41*, 6447.

9. Sale, D. Adhesives and Consolidants for Conservation Ottawa; Ottawa, Ont.: Canadian Conservation institute, **2011**.

10. Qui, W.; Endo, T.; Hirotsu, T. *J. Appl. Polym. Sci.* **2006**, *102*, 30.

11. Spoljaric, S.; Genovese, A.; Shanks, R. A. *Compos. A* **2009**, *40*, 791.

12. Shanks, R. A.; Hodzi, c. A.; Ridderhof, D. *J. Appl. Polym. Sci.* **2006**, *99*, 5.

13. Thummanukitcharoen, P.; Limpanart, S.; Srikulkit, K. In 18th International Conference On Composite Materials; Jeju Island, Korea, **2011**. 21-26 August 2011.

14. Chauhan, Y. P.; Sapkal, R. S.; Sapkal, V. S.; Zamre, G. S. *Int. J. Chem. Sci.* **2009**, *7*, 681.

15. Das, K.; Ray, D.; Bandyopadhyay, N. R.; Sengupta, S. *J. Polym. Environ.* **2010**, *18*, 355.

16. Cataldi, A.; Dorigato, A.; Deflorian, F.; Pegoretti, A. *J. Mater. Sci.* **2014**, *49*, 2035.

17. Springer, G. In Environmental Effects on Composite Materials, Vol. 1; Springer, G., Ed.; Technomic Publishing Inc: Wesport, CT, **1981**, Chap. 6.

18. Paplham, W. P.; Brown, R. A.; Salin, I. M.; Seferis, J. C. *J. Appl. Polym. Sci.* **1995**, *57*, 133.

19. Thomason, J. L. *Composites* **1995**, *26*, 467.

20. Thomason, J. L. *Composites* **1995**, *26*, 477.

21. Pegoretti, A.; Migliaresi, C., *Polym. Comp.* **2002**, *23*, 342.

22. Pegoretti, A. In Wiley Encyclopedia of Composites; Nicolais, L.; Borzacchiello, A., Eds.; John Wiley & Sons: Hoboken, NJ, USA, **2012**.

23. Kiziltas, A.; Gardner, D. J.; Han, Y.; Yang, H. S. *Thermochim. Acta* **2011**, *519*, 38.

24. Mathew, A. P.; Oksman, K.; Sain, M. M. *J. Appl. Polym. Sci.* **2005**, *97*, 2014.

25. Wu, Q.; Henriksson, M.; Liu, X.; Berglund, L. A. *Biomacromolecules* **2007**, *8*, 3687.