Combined effect of water uptake and temperature on Wood Polymer Composites

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Abstract

Wood polymer composites are materials frequently used for outdoor applications, since they can operate under a large range of temperature and moisture conditions. The present work investigates the combined effect of water soaking and temperature (ranging from 10 °C up to 40 °C) on wood flour filled high density polyethylene. Water soaking tests have revealed that the percentage of absorbed water at the saturation plateau increases with temperature due to the induced stiffness reduction of the polymeric matrix. This hypothesis has been confirmed by Scanning Electron Microscopy (SEM) analyses, which has allowed to observe the filler-matrix interface and to measure the wood flour particle size. In addition, instrumented Charpy impact tests have shown a strong toughness reduction as a consequence of fiber-matrix debonding induced by particle swelling, which worsens with temperature.

1. Introduction

Wood Polymer Composites (WPCs) are materials made of wood fibers or flour, a thermoplastic matrix and a small amount of additives. In the last few years, these materials have attracted more and more interest in research and industry because of some important advantages over natural wood and polymers reinforced with traditional fillers.^{1,2}

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In general, these composites have a reduced environmental impact and low cost thanks to natural fibers coming from industrial or agricultural waste. In particular, natural fibers improve strength and stiffness and the presence of the hydrophobic polymeric matrix enables the composite to perform in wet environments better than natural wood.³⁻ ⁶ Thus, WPC profiles can be successfully employed in outdoor decking and furniture, or even structural applications in close contact with water, such as dock walkways or piers. Nevertheless, wood fibers are hydrophilic as they are composed of cellulose, lignin and hemicellulose. These molecules are rich in hydroxyl functional groups that bind water easily by hydrogen bonding. This induces a relatively high moisture absorption that leads to swelling, distortion, biological degradation and reduction of stiffness and strength until fracture.^{7,8}

A comprehensive analysis of various factors influencing the performance of WPCs has been recently reported by Olakanmi et al.⁹ In addition, several studies have correlated the effects of moisture, or water uptake, to the reduction of mechanical properties, e.g. bending, tension, impact and creep.¹⁰⁻¹⁷ Properties decay has been attributed to the degradation of the natural filler as a result of long-term water exposition, development of internal stress due to filler swelling and matrix-reinforcement interface failure.^{7,10,13,18} For these reasons, many papers have evaluated the influence of different types of filler, fiber chemical treatments and composite composition on the amount of water absorbed by WPCs.^{7,10,19-22} In particular, the presence of an adequate coupling agent is the parameter that affects water resistance most remarkably. As it improves the interfacial adhesion between the hydrophobic matrix and the hydrophilic fibers, not only mechanical properties are improved but also water absorption is significantly reduced.²³ One of the most common techniques used to investigate composite materials morphology is Scanning Electron Microscopy (SEM).²⁴ This analysis is often used to investigate the fracture behavior depending on many factors such as the chemical nature of fiber and matrix, fiber-matrix interface and fiber distribution and orientation.^{9,19,25}

Owing to high depth of field, SEM observations can qualitatively evaluate and quantify the relative importance of all these factors. In the specific case of WPCs, this analysis is particularly useful to observe the fiber-matrix interface directly and to evaluate the adhesion quality. However, it should be pointed out that this analysis gives partial information about environmental conditioning: since observations are necessarily performed in the microscope observation chamber after a certain time, one is only able to visualize the permanent consequences of conditioning.

The reduction of the filler-matrix adhesion can also be evaluated by mechanical testing such as Charpy impact test. This three-point dynamic measurement provides easy-to-get information on fracture toughness, impact resistance and it is often used for assessing improvements in the experimental composite formulation. In particular, some studies have shown that impact properties can benefit from coupling agents in the WPC formulation.^{25,26} For this reason, impact tests can be used to evaluate the filler-matrix interface adhesion, also in saturation and thermal conditioning.

The dependency of mechanical properties of WPC on moisture absorption has been widely investigated ^{11-21,27,28,30} while, to the authors' knowledge, not enough attention has been paid to the influence of water soaking in conjunction with thermal conditioning.¹⁰ Since WPCs are mainly used in outdoor applications, where temperature can vary in a quite large range, understanding the complex interplay between these two factors is very important to predict the performance reduction. Only a few papers have studied the effect of temperature and water absorption on the mechanical properties of WPC. For example, Bledzky et al.¹⁰ have measured the reduction of bending properties of wood flour filled polypropylene due to a complex environmental conditioning comprising static and cyclic water absorption at two different temperatures. The authors have observed that thermal conditioning increases the reduction has not yet been fully explored. Thus, the combined effect of water sorption and temperature on the

mechanical performance reduction needs to be studied in greater detail, in particular concerning the interaction between wood particles and polymer at the interface, in order to better understand the mechanisms that produce the decrease in mechanical properties. The present study investigates the influence of water soaking at various operating temperatures (from 10 °C up to 40 °C) on the properties of a high density polyethylene based WPC, filled with 50 wt.% wood flour. The morphology of the composite and of the filler-matrix interface have been analyzed with SEM after environmental conditioning and Charpy impact tests have also been performed to quantify the combined effect of temperature and water soaking.

2. Materials and methods

2.1 Materials

High density polyethylene (Eraclene BC-82) with a density of 0.954 g/cm³, MFR equal to 0.25 g/10 min at 190 °C with 2.16 kg weight, flexural elastic modulus of 1.2 GPa and strain at break of 30 MPa, has been obtained in pellets from Versalis S.p.A. The wood flour filler has been obtained from softwood (spruce) planning residues with a particle size between 100-300 μ m. A commercial maleic anhydride grafted polyethylene (Licocene PE MA 4351 by Clariant) has been used as a coupling agent to improve compatibility and adhesion between matrix and fibers.

2.2 Sample preparation

Wood flour has been dried overnight at 80 °C in an air-circulation oven before compounding to reduce moisture amount to less than 1 wt.%. The HDPE granules with 50 wt.% wood flour and the coupling agent in the amount of 4 wt.% have been then mixed together using a compounding-extrusion system (SKY WIN Technology Co. Ltd., Nanjing, China) composed of a twin screw co-rotating intermeshing extruder (50

mm diameter screw and length over diameter ratio of 25), directly feeding into a water cooled single screw extruder (80 mm screw and length over diameter ratio of 30) for profile extrusion. The transition zone between twin screw and single screw is equipped with a vacuum venting zone to help degasification of water vapor. The thermal profiles have been as follows: flat 175 °C in the twin screw extruder, flat 150 °C in the single screw extruder and 160 °C in the die. The system has been operated with a feed rate of 40 kg/h. Specimens have been obtained in bars of 10×15 mm rectangular cross section, along the extrusion direction.

2.3 Water absorption tests

Before testing, all samples have been dried overnight at 80 °C in an air-circulation oven (reaching 0.22 % moisture content) and subsequently weighed with a Mettler Toledo AE240 analytical digital balance (with a resolution of 0.1 mg). The water soaking has been measured as a function of time on WPC samples (10×15×60 mm) put in thermostatically controlled water baths (Julabo MD GmbH, Germany) kept at 10 °C, 20 °C, 30 °C and 40 °C, respectively. Absorption tests have been conducted in accordance with the test procedures recommended by ASTM D570.²⁹

The weight gained by the samples has been used as a measure of the water uptake: the conditioned specimens have been removed from the bath, wiped free of surface moisture with a dry paper, weighed and immediately put back into the water bath. Now, one can define M_t to be the mass of the sample at time t and M_0 its initial mass, measured prior to immersion, so that the water content in the sample at time t is

$$\bar{M}_t = M_t - M_0 \tag{1}$$

while, letting M_{∞} be the mass saturation value of the specimen, the water content at saturation is

$$\overline{M}_{\infty} = M_{\infty} - M_0 \tag{2}$$

The percentage of water absorption μ at any time, t, has been calculated by using the following equation:

$$\mu(\%) = \frac{100 \,\overline{M_t}}{M_0},\tag{3}$$

The weight has been monitored to determine the absorption of water up to saturation and this has been defined as the first point at which the water content difference with respect to the following one is less or equal to 1%.

2.4 Mechanical characterization

Impact properties have been evaluated using a CEAST Resil Impactor device with a 50 J hammer. The 15×10 mm unnotched WPC specimens have been tested in flatwise direction with a length span of 40 mm. The three-point dynamic impact tests have been performed in two different conditions: (i) after 4 hours of soaking in water at 10 °C, 20 °C, 30 °C and 40 °C and (ii) after saturation in water at the same temperatures. To make sure that test conditions are kept equal to those described, sample positioning and test time lasted less than 5 s after sample extraction from the thermostatic bath. In all cases, five samples have been tested for each water temperature.

The instrumented impact test layout used in the present study is depicted in Fig. 1. The samples positioned on the supports have been broken by the pendulum with a force that has been measured by a load cell positioned directly on the hammer, while the displacement has been evaluated through an encoder. Data have been acquired by CEAST DAS 64 K and the Visual IMPACT software has calculated the total absorbed energy during impact as the area under the force-displacement curve. The total energy W has been split into initiation W_i and propagation W_p energies. In particular, initiation energy refers to the energy measured up to the load maximum, i.e. the peak point, while

propagation energy refers to the energy portion from the peak to full rupture of the specimen. The detailed description of Charpy impact test can be found in the ISO 179-2 standard. ³¹



Fig. 1 – Instrumented impact test layout.

Three-point static bending tests have been performed according to ISO 178 using a length span of 100 mm at a crosshead speed of 1 mm/min. Before testing, the specimens $(15 \times 10 \text{ mm})$ have been preconditioned for 4 hours in water kept at 10 °C, 20 °C, 30 °C and 40 °C. A dynamometer (INSTRON 4467, Norwood, MA, USA) with a 500 N load cell has been used to measure the stiffness and strength of the samples. At least five specimens for each condition have been tested.

2.5 Scanning Electron Microscopy observations

Specimen impact fractured surfaces have been observed by a ZEISS Evo EVO M15 Scanning Electron Microscope in order to analyze the mechanisms of failure, the composite morphology and the wood/HDPE interface quality. SEM images have been acquired on gold-sputtered impact fracture surfaces of specimens at an accelerating voltage of 15 kV. Before sputtering, the samples have been equilibrated at room temperature and relative humidity. For each fracture surface analyzed, at least 15 micrographs for each magnitude have been evaluated to be sure of considering a significant portion of the sample.

3. Results and discussion

3.1 Effect of temperature on water absorption

The results of water absorption as a function of soaking time at each tested temperature are summarized in Fig. 2: all curves have the same qualitative trend, independently of water temperature. In agreement with the literature, water absorption increases with immersion time with a rate that is initially higher and gradually slows down until a plateau is reached.²⁷ Here the sample achieves the saturation condition and the maximum water concentration. By observing Fig. 2 and recalling our definition of saturation, such a point is reached at 549 hours at 10 °C, 715 hours at 20 and 30 °C and at 880 hours at 40 °C. The most interesting aspect is that saturation occurs at different values, which increase with water temperature (Tab. 1). This behavior has been already observed in a previous work.³¹



Fig. 2 – Water absorption curves as a function of time at different water temperatures.

Tab. 1 – Diffusion parameters.

Water temperature (°C)	n	k (h^{-n})	μ_{∞}
10	0.475	5.14E.2	2.52
10	0.475	5.14E-2	3.52
20	0.458	5.76E-2	4.65
30	0.445	6.25E-2	6.13
40	0.470	4.74E-2	9.73

The water diffusion mechanism can be analyzed by observing the shape of the sorption curves in a log-log plot of $\overline{M}_t/\overline{M}_\infty$ versus time, which can be fitted by an equation such as:

$$\frac{\overline{M}_t}{\overline{M}_{\infty}} = \frac{\mu}{\mu_{\infty}} = kt^n \tag{4}$$

where k and n are constants, in particular k is a parameter that depends on filler geometry and the affinity between the material and water molecules ⁷, while n is an indication of how diffusive is the transport mechanism: the closer is n to 0.5 the more Fick's law is respected.³² These constants and the percentage of water absorption at saturation μ_{∞} for each water temperature are listed in Tab. 1.

The values of *n* are slightly below 0.5, indicating moderately diffusive behavior. Some authors have already observed that water transport in natural fiber filled polymers is controlled by Fick's law, consisting in a diffusion of water molecules within the natural fibers between polymer chains.^{7,33}

On the other hand, it is important to point out that the water content at saturation is not the same value at each temperature: μ_{∞} is always increasing with temperature, but from 10 up to 30 °C such an increase is linear, while the saturation value at 40 °C is not aligned with the previous three points and is about 30 % higher. Generally speaking, it would be expected that the amount of water that is absorbed at saturation depends on the amount of wood filler, in particular it would increase with filler content.³² This is reasonable because water absorption of HDPE matrix is negligible and the hydrophilic nature of wood flour is the only responsible for water absorption. In the present study all specimens had the same wood flour content (50 wt.%), thus it should have been expected that temperature only acted on the kinetics of diffusion. The fact that saturation values are strongly influenced by temperature indicates that phenomena other than simple diffusion must be occurring, such as some kind of degradation, fracture of the fiber-matrix interfaces or temperature dependent particles swelling.

The behavior of k is consistent with μ_{∞} in that the first three values increase linearly with temperature while the value at 40 °C decreases of about 30 %. This behavior can be easily justified on mathematical grounds by looking at Eq. 4.

3.2 Morphological evaluations of wood flour

With the aim of investigating the effects of both water temperature and soaking time on the WPC morphology, detailed SEM observations have been conducted on impact fractured WPCs samples that have been conditioned at 10 °C and 40 °C in two different ways: (i) soaked in water for 4 hours and (ii) after reaching the saturation condition. It should be noted that SEM analyses have been carried out at room temperature in high vacuum and not during conditioning, therefore one can only observe the permanent outcome of the environmental conditioning after re-equilibrating the samples at room temperature and relative humidity. This has been measured to be about 1.27 % according to ASTM D4442 standard method A.

In Fig. 3, a typical set of microstructures of WPCs at low magnification is presented, so that the size of the wood particles can be easily observed. In particular, Figs. 3(a) and 3(b) show the sample surfaces after 4 hours soaking in water at 10 °C and 40 °C,

respectively, while Figs. 3(c) and 3(d) after saturation at the same temperatures. Notice that after 4 hours soaking all samples have reached thermal equilibrium, yet only a negligible amount of water (below 1 %) has been absorbed, thus only thermal conditioning effects can be appreciated. Comparing Fig. 3(a) with Fig. 3(c) and Fig. 3(b) with Fig. 3(d), it is evident that wood particles of saturated samples are larger: water absorption induces a rather stable swelling. Moreover, from the comparison between Fig. 3(a) and Fig. 3(b), one can conclude that temperature alone is not sufficient to modify wood particles morphology permanently.



Fig. 3 – SEM images of impact fracture surfaces of WPC at low magnification on different soaking time and temperature conditions: unsaturated at (a) 10 °C, (b) 40 °C, saturated at (c) 10 °C and (d) at 40 °C. Superimposed yellow lines indicate the main axes of the ellipse.

In order to provide a quantitative evaluation of the dimensional change caused by saturation effect, particle size measurements have been conducted on SEM images. The

shape of each wood particle has been approximated to an ellipse, as indicated by the yellow lines in Fig. 3, which represent the main axes of each ellipse. Average minor and major axes values have been measured by considering both the surface and the core regions of the samples. At least 100 wood particles per sample have been selected and the resulting measurements are summarized in Fig. 4. As qualitatively observed in Fig. 3, the data of Fig. 4 confirm that saturated particles are larger than unsaturated ones by approximately 35-45 %. On the other hand, the particle size of unsaturated samples soaked in water at 40 °C is comparable to those soaked at 10 °C revealing that the single effect of temperature does not permanently affect the size of the unsaturated particles. A further consideration can be made by comparing the particle size of the saturated samples at 40 °C to the 10 °C ones, with the former that appear to be slightly larger than the latter, even if the measurements are affected by a high standard deviation. The rather high dispersion in the size of the saturated particles can be explained on the basis of the anisotropy of the wood particles, whose orientation is random within the observed samples and varies from particle to particle.



Fig. 4 – Particle size measurements as a function of the environment condition. Major (full colour bar) and minor (striped colour bar) axis of the ellipse.

It is well known that wood-polymer interface of WPC is weak. Although coupling agents can be used to improve its properties, it remains the weakest part of the composite and therefore the most susceptible to stress-induced damage of the interface.^{10,22} In Fig. 5 typical examples of wood-HDPE interfaces, in saturated and unsaturated conditions at 10 °C and 40 °C, are shown at higher magnifications. In Fig. 5, red arrows indicate wood-polymer interfaces. In all cases, fracture surfaces are rough with some wood flour pull-out, as suggested by the presence of voids. Figs. 5(a) and 5(b) show that the interface in unsaturated conditions is overall good, thus temperature alone is not sufficient to produce permanent damage of the interface. On the other hand, the interface appears damaged in Figs. 5(c) and 5(d) as a consequence of the combined effect of temperature and water sorption.



Fig. 5 – SEM images of impact fracture surfaces of WPC at high magnification on different soaking time and temperature conditions: unsaturated at (a) 10 °C, at (b) 40 °C, and saturated at (c) 10 °C and (d) 40 °C. Superimposed red arrows indicate the wood-polymer interfaces.

Debonding can be explained as an effect of considerable particle swelling during saturation. Particles, initially unstressed in dry condition, swell during water soaking and fill up all of the volume that is allowed by the large deformation of the compliant matrix. However, unlike HDPE, wood particles are anisotropic and their swelling is not the same in all directions. For this reason, the anisotropy mismatch between matrix and particles gives rise to shear stresses at the interface, whose properties are already reduced due to the presence of absorbed water.^{28,34} These stresses can cause the fracture of the interface. Since SEM observations have not been taken during saturation but only after drying and re-equilibrating the sample, particles tend to recover their initial volume due to water loss, while the matrix remains deformed plastically. The result is the formation of large gaps around the particles.

This mechanism can also explain the temperature dependent saturation values (Fig. 2). Assuming that the available volume for water absorption is the sum of the particles volume plus the gaps around the particles, it is reasonable that the conditioning at 40 °C allows a greater absorption of water and thus a higher saturation value. This dependence between particle volume and temperature could be explained by the effect of temperature on the matrix compliance. It is well known that HDPE stiffness decreases with temperature and that the soaked particles tend to expand until the stiffness of the matrix allows it. For these reasons, a higher temperature could make the polymer matrix more compliant to particle swelling: the stiffness of the matrix decreases, particles can expand more and absorb more water.

3.3 Effect of temperature and water absorption on mechanical properties

In order to measure the weakening effect of hygrothermal stresses on the wood-HDPE interface, instrumented Charpy impact tests have been performed after 4 hours of water soaking and in saturated condition at all four temperatures. The results are shown in Fig.

6. A temperature independent behavior is evident in unsaturated WPC samples, while changes in impact properties due to water soaking are remarkable in saturated WPC samples: as can be seen, all saturated samples show a greater resilience than unsaturated ones. This behavior can be explained by the presence of water that increases the mass to be displaced during the test and has a plasticizing effect on the wood particles.¹⁸ In addition, the resilience of saturated samples has a slight increase with temperature, which is consistent with higher saturation values (see Fig. 2). This trend is valid for all temperatures except for 40 °C, at which impact strength significantly decreases. This behavior is similar to the trend of the *k* parameter (Tab. 1), which was previously explained on the basis of the behavior of μ_{∞} .



Fig. 6 – Charpy impact strength for unsaturated and saturated WPCs samples.

Moreover, a greater value of μ_{∞} at 40 °C corresponds to a larger average particles size, as reported in Fig. 4, and it produces higher shear stresses at the interface due to the anisotropy mismatch between filler and matrix and possible biological degradation effects on wood due to the long-time exposure to water at relatively high temperature.³⁵ This induces a more extensive failure of the interfaces between the polymer and wood particles. This can be observed in SEM images and can be appreciated by comparing, for example, Fig 3(c) with Fig. 3(d).

In fact, Stark and Rowlands investigated the influence of wood flour size on impact properties of WPCs using different particle sizes and observed that larger particles showed lower impact energy as a result of higher stress concentrations in the material.³⁶ This result is consistent with the present study, where lower impact strength values have been obtained for saturated samples at 40 °C (see Fig. 6), where wood particles are the largest.

In Fig. 7, the dynamic response of the fractured sample in saturated and unsaturated conditions at 40 °C has been also investigated by considering the force-displacement curves obtained from instrumented Charpy impact tests. Hristov et al. have used an analogous impact test layout with a similar system (polypropylene filled with pine wood fibers)²⁵. The 40 °C saturated and unsaturated are comparable and the same trend has been observed for all temperatures tested. As can be seen, force increases until reaching a peak corresponding to the maximum force that defines the crack initiation region. Beyond this value, the crack propagates with decreasing force values. The peak of the force is higher for unsaturated samples, while saturated samples have shown the greatest displacement.



Fig. 7 – Force -displacement curves obtained from instrumented impact tests for WPC samples soaked at 40 °C in saturated and unsaturated conditions.

A complete analysis of the impact behavior can be conducted by considering the two principal phases of the fracture process, i.e. crack initiation W_i and propagation energies W_p .²⁵ Figs. 8 and 9 report the comparison between initiation and propagation energies for unsaturated and saturated samples, for all temperature tested. Fig. 8 shows that the energies for unsaturated samples are substantially the same and temperature independent, while, as reported in Fig. 9, initiation energy is greater than propagation energy for saturated samples. This can be explained by the wood particles softening effect due to water uptake.²⁸ Although with high standard deviations, the lowest propagation values for the saturated sample tested at 40 °C may be a further indication that the interface has failed and the sample does not require high propagation energy to reach complete failure.

In Fig. 8, we have shown that initiation and propagation energies for unsaturated samples maintain the same value for all temperatures tested. This result could be compared and discussed in relation to static bending tests results, shown in Tab. 2, although the two tests are performed at very different velocities. The comparison can be made with particular reference to toughness, i.e. the amount of energy per unit volume that a material can absorb before fracture, at all tested temperatures. In Fig. 10 a representative stress-strain curve for each temperature is shown. Despite stiffness and strength decrease with temperature, ductility increases and this makes toughness weakly temperature dependent, in agreement with the impact results for unsaturated samples. In addition, thanks to bending tests, the effect of the sole temperature on WPC properties can be evaluated. As expected, stiffness and strength decrease with temperature and WPC becomes more ductile. In particular, at 40 °C the loss in stiffness, which is comparable with the loss in strength, decreases by a factor of two. This trend can justify the increase in particle size at 40 °C, because the matrix is more compliant and allows the particles to swell and absorb more water.



Fig. 8 – Initiation and propagation energy for unsaturated samples at 10 °C, 20 °C, 30

°C and 40 °C.



Fig. 9 – Initiation and propagation energy for saturated samples at 10 °C, 20 °C, 30 °C

and 40 °C.

Tab. 2 – Three point flexural tests. Number in parentheses are the standard deviations.

	10 °C	20 °C	30 °C	40 °C
Stiffness (GPa)	3.42 (0.89)	2.89 (0.86)	2.19 (0.15)	1.78 (0.12)
Strength (MPa)	21.23 (0.77)	18.65 (0.44)	16.83 (1.40)	12.18 (1.49)
Toughness (kJ/mm ³)	25.21 (2.21)	22.36 (1.84)	22.00 (2.24)	25.97 (3.02)



Fig. 10 – Flexural properties for each temperature.

4. Conclusions

In this article a 50 wt.% wood flour filled HDPE has been studied after conditioning in water at different temperatures. The results have shown that the percentage of absorbed water at the saturation plateau occurs at different values, which increase with temperature due to the induced stiffness reduction of the polymeric matrix and possible wood particles degradation.

In this respect, SEM, impact and bending analyses have shown that this temperature dependence seems to be due to particle swelling that is allowed by the increasing matrix compliance. As the swelling increases, the anisotropy mismatch driven shear stresses at the filler-matrix interface increase until debonding. This critical situation has been

reached at 40 °C under saturation condition, where the material showed a strong reduction of toughness.

These results have important consequences on the use of WPCs in outdoor applications. These materials can be properly used in wet environment at different operating temperatures, but it is important to underline that WPCs can be strongly sensitive to water soaking in conjunction with relatively high temperatures. This type of environment can lead to complete filler-matrix debonding and thus to a consistent reduction in mechanical properties. For this reason, it is important to evaluate the environmental conditions of WPC installation and to avoid the concurrent presence of high temperature and water soaking in structural applications.

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