



## THE INFLUENCE OF WATER ABSORPTION ON REINFORCED POLYMERS (FRP) USING MWCNT AND HGB

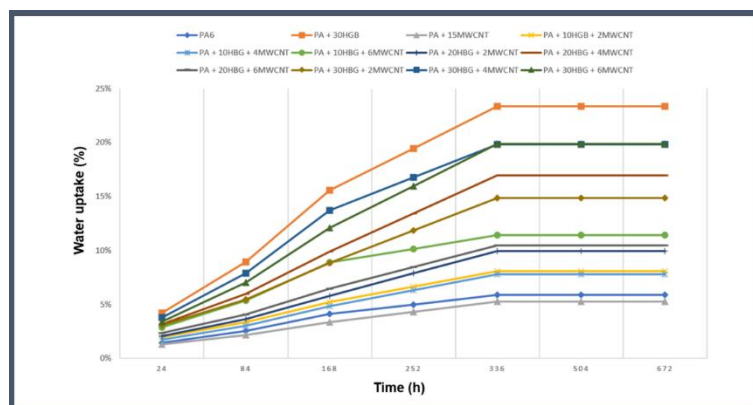
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In the current paper, different MWCNTs filler amounts, containing PA6 and HGBs were prepared by injection moulded. The water uptake at saturation, normalized to the polyamide mass, decreases; hence the diffusion rate in both MWCNTs is slower, respectively HGBs, which is faster. Injected moulded polymer samples can take less (6%) water uptake than neat polymer granules (11%). The addition of 15 wt% of multi-walled carbon nanotubes (sample 3) led to a minimum water absorption rate of 5%; this value is 15% less than the majority of the polymer composite mixtures and 1% less than pure PA6, mainly because other polymer composites which contained the HGB filler, absorbed more water.

The best results highlight the improved water resistance of polyamide composite (sample 3), which reduces the impact of water on the component and expresses better applicability in the water environment than other polymer composites or even pure PA6.



### INTRODUCTION

The reduction of weight in the transportation industry has become controversial in the last decade. More and more legislations and regulations have been implemented lately, to achieve climate-neutral by 2050, sustaining an economy with net-zero greenhouse gas emissions. This “wake-up” call has been made by the European Commission<sup>1</sup> as an urgent climate-neutral transition which urges companies and industries to produce sustainable products, reduce pollution and become more environmentally friendly by using green energy powered by wind turbines or solar panels. In the transportation industry progressively, the manufacturing side started to use daily, smart

materials, with the same or even better properties offered by the conventional materials produced from steel or aluminium. The polymer based composites reinforced with fillers, such as multi-walled carbon nanotubes (MWCNT) or hollow glass bubbles (HGB) are suitable substitutes for metals in the transportation parts. The injection moulding process explored the combination of affordable prices and enhanced properties such as low density, good mechanical properties or low water absorption.

Composite parts were investigated by other authors in their studies which used smart materials such as multi-walled carbon nanotubes<sup>2-5</sup> or hollow glass bubbles<sup>6-8</sup> and fillers. Materials’ usage depends on the applicability side and the

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performance a composite part needs to offer. Some parts need to meet certain requirements such as corrosion resistance or mechanical performance, whereas others need to offer good water absorption resistance. The usage of a plastic component in a wet environment or exposed to moisture is a real consideration and challenge sometimes in certain industries.

Water absorption represents the capacity of a polymer or a composite material to absorb or intake moisture from its environment.<sup>9</sup> The absorbed moisture of a composite component sometimes affects its properties by reducing the glass transition temperature and strength properties. Historically, research studies<sup>10-12</sup> explored the effect on water absorption for plastics and polymer composites when different fillers are used in the mixture. Sengupta *et al.*<sup>13</sup> observed that water uptake decreases significantly with increasing the concentration of carbon nanotubes in PA66/MWCNT films. However, another article<sup>14</sup> studied the structure-properties relationships of a PA12/PA6 containing MWCNT. The paper explored a substantial improvement concerning the water absorption behaviour of the polyamide and carbon nanotube composites, expanding the potential applications of materials. For example, neat granular Polyamide 6 intake has the highest water absorption and can go up to 11%, which could reach the maximum water uptake limit in less time.<sup>15</sup> Viktor Baukh *et al.*<sup>15</sup> researched water uptake by multilayer films and discovered that initially water was attracted by hydrophilic areas of the polymer matrix. In some cases, plasticization and swelling were caused when the water content increased, and the liquid was located in the hydrophilic part of the dispersant. The existence of water molecules in the polymers sometimes can be extremely difficult due to their high mobility and preference to form a bond cluster.<sup>16</sup>

In other cases, water uptake was evaluated on the mechanical properties and its effect on the blended polymer films.<sup>17</sup> Injection moulding samples from polyamide 6 (PA6) composites blended with 30 wt % of sustainable bamboo-based biochar (BC), can sometimes increase the strength of the final composite material and provide low water uptake.<sup>18,19</sup> Nevertheless, the high load of PA6/BC composites can decrease water absorption by 46% after a certain point. In a separate study, A. K.

Bajpai *et al.*<sup>20</sup> investigated the effect of water absorption on the ionizable interpenetrating polymer networks (IPN) of carboxymethyl cellulose and polyacrylic acid. Further studies<sup>21</sup> were made to determine the numerical solution of the approximated form for the diffusion coefficient and the equilibrium solvent uptake based on Fick's equation. By using the Fickian diffusion model<sup>22,23</sup> the description of the sample behaviour can be found and predicted. However, the prediction contradiction has been shown in the measurements of water uptake values for 24 polymers in the polyacrylate library. This became evident when Bozena *et al.*<sup>24</sup> found that neither initial nor equilibration water uptake could be predicted by merely looking at each polymer's hydrophobic character and/or T<sub>g</sub> of each polymer. Other studies<sup>25,26</sup> reflected how the mass increases, even with a few percentages from the original mass<sup>27,28</sup> when the polymer was used in liquids. The main aim of this paper is to assess the influence of multi-walled carbon nanotubes and hollow glass bubbles content in PA6-based hybrids on water diffusion; the study is focused on highlighting the influence of the amounts of filler loading MWCNT and HGB on the water uptake.

## RESULTS AND DISCUSSION

Table 2 shows the increased weight of composites after immersion treatment; the addition of MWCNT led to a reduction in water absorption and an improvement in the water resistance of sample 3. The addition of 15 wt% of multi-walled carbon nanotubes led to a minimum water absorption rate of 5%; this value is 15% less than the majority of the polymer composite mixtures and 1% less than pure PA6, mainly because other polymer composites which contained the HGB filler, absorbed more water. As can be seen in Figure 1, in all cases, the weight of the polyamide composite samples increased due to the water uptake load. The weight of the tested samples after test completion has substantially changed due to various factors. In some cases, the weight of the samples (*e.g.* sample 2 or sample 12) increased by up to 23%, directly proportional to the amount of water uptake accumulated.

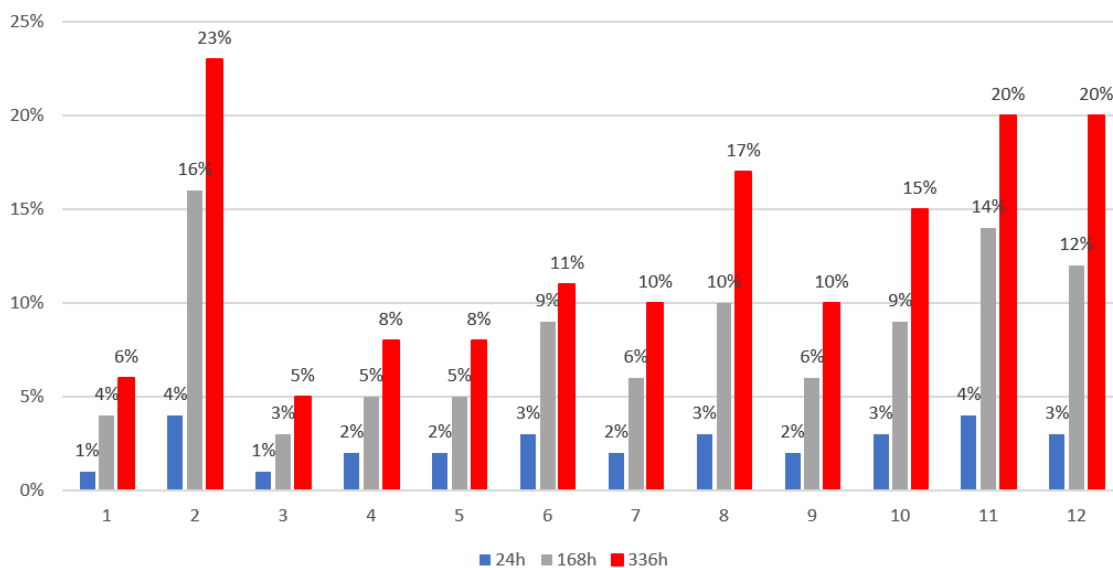


Fig. 1 – Water uptake percentage at different hours.

It is assumed the reason for the high amount of water uptake on the samples with the high HGBs load is that the filler was treated before with the coupling agent for better adhesion in the mixture. Therefore, the samples with the coupling agent could be affected if the agent was not entirely dried in the initial composition.

#### Effect of HGB and MWCNT contents on water uptake

The water absorption behaviour is displayed in Figure 2 for the different hollow glass bubbles and multi-walled carbon nanotubes composite. As shown in the attached graphic, all samples present a pattern of growth-shaped curves. In the first part of the curves (until about 336 h), the water uptake is directly proportional to the time, wherein in the other half of the curves (until about 504 h) the conditioned specimens are at the saturation limit. In other studies,<sup>29</sup> was observed that Fick's diffusion equation could be used to determine moisture diffusion curves for the studied materials.

The equation can be applied equally to hot/humid and water immersion data. There is also a possibility to directly relate changes in glass transition temperature with moisture content. Figure 2 revealed that with the increase in immersion treatment time, the water absorption of polymer composite samples gradually increased. It can be also observed that on the samples with HGB filler, the amount of the load is directly proportional to the time immersed under the water and the % of

the water, which has been taken during the investigation.

After 14 days (336h) of water immersion, samples touched the maximum water absorption limit and can be seen in Figure 2 that even if the study continued another 14 days (up to 672 h) the amount of water uptake has not changed and constantly mentioned the same amount of maximum limit.<sup>30</sup> This result further indicated that the addition of MWCNT load leads to the improved water resistance of polyamide composite (sample 3), reduces the impact of water on the component and expresses better applicability in the water environment than other polymer composites or even pure PA6. Normalized water uptake (Figure 3) represents the saturation of liquid intake for each polymer composite sample. As expected, the PA6 injection moulded water absorption at saturation of the composite sample is lower (6%) than the neat polyamide granules, which have the highest water absorption and can go up to 11% and could reach the maximum water uptake limit in less time.<sup>15</sup>

The supplier data sheet acknowledged that neat granules of polyamide 6 have a water absorption (saturation value of water at 23°C) of 10%, using *ISO 62*.<sup>31-33</sup> However, when the multi-walled carbon nanotubes are included in the polymer matrix, the normalized water contact at equilibrium is slightly reduced from 2 wt% MWCNT. The only disadvantage in composite polymers that contain multi-walled carbon nanotubes is when the hollow glass bubbles were used as a filler in the composite mixture. Hence, the high amount of water intake for the mixtures that contain HGBs in the composition. In the presented case, the diminution of the water

absorbed by polyamides is linked with several factors. As it is already known, water is absorbed only in the amorphous phase of materials, this is because the crystalline part is inaccessible to the liquid.<sup>34</sup> As stated above, the overall crystallinity enhances as multi-walled carbon nanotubes increase except for the nanocomposite with 2/ 4/ 6 wt% nanotubes and the hollow glass bubbles. Eventually, this happens because a denser network of MWCNTs

and HGBs could hinder the movement of water molecules through the material, decreasing the diffusion coefficient and the liquid content at equilibrium.<sup>10</sup> Therefore, it should not be forgotten that MWCNTs tend to have a reduced water absorption than the PA6, even when used in injected moulded parts, and, as a result, the overall water absorption of the nanocomposite that contains only MWCNTs tend to be slightly better.

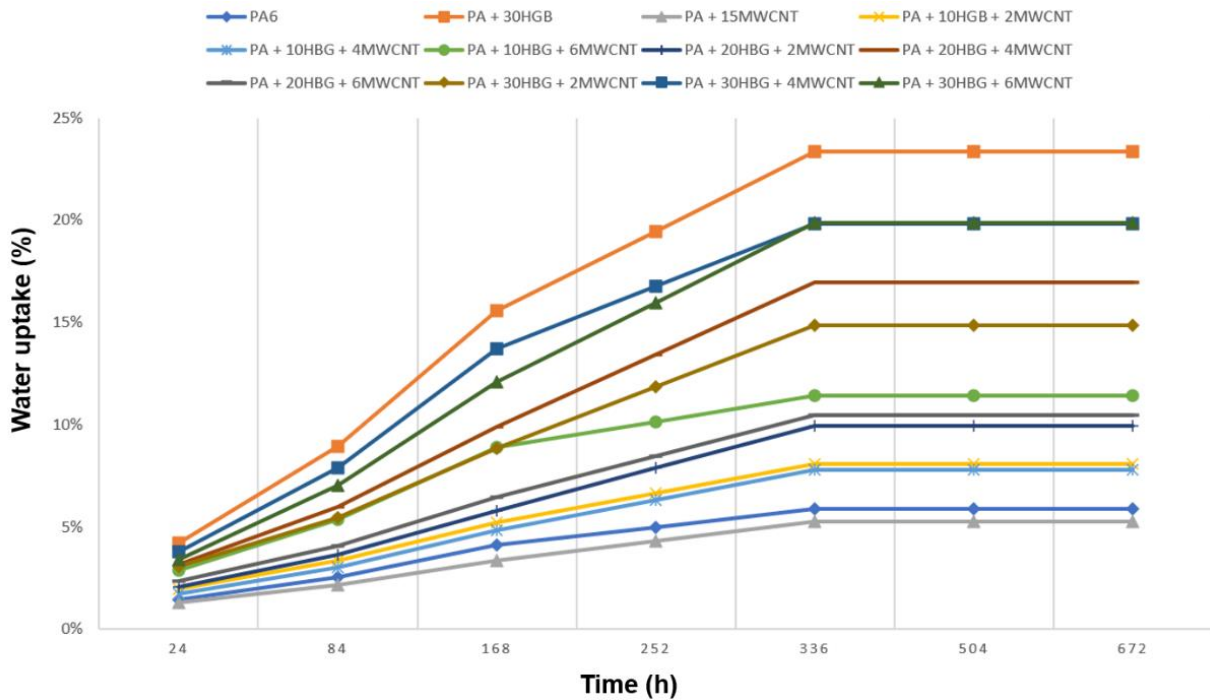


Fig. 2 – Moisture absorption curves measured by mass uptake.

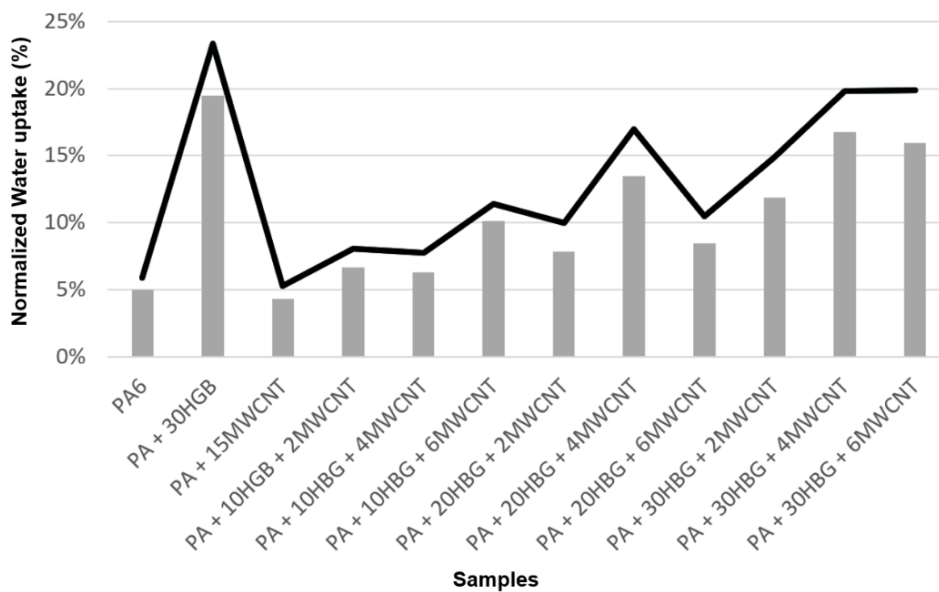


Fig. 3 – Normalized water uptake at saturation of PA6 blend, HGB and MWCNT composites measured at room temperature.

Table 1  
Formulations of PA6/HGM/MWCNT

Sample	PA6 (wt.%)	HGB (wt.%)	MWCNT (wt.%)
1) PA6	100	0	0
2) PA + 30HGB	70	30	0
3) PA + 15MWCNT	85	0	15
4) PA + 10HGB + 2MWCNT	88	10	2
5) PA + 10HGB + 4MWCNT	86	10	4
6) PA + 10HGB + 6MWCNT	84	10	6
7) PA + 20HGB + 2MWCNT	88	20	2
8) PA + 20HGB + 4MWCNT	86	20	4
9) PA + 20HGB + 6MWCNT	84	20	6
10) PA + 30HGB + 2MWCNT	88	30	2
11) PA + 30HGB + 4MWCNT	86	30	4
12) PA + 30HGB + 6MWCNT	84	30	6

### Materials

A blend of Polyamide 6 (PA6 Lanxess – Durethan B30S)<sup>38</sup> density 1140 kg/m<sup>3</sup> supplied by Mobi Stil Prod, Hollow Glass Bubbles compound of soda-lime borosilicate (grade iM16K),<sup>39</sup> density 0.46 g/cm<sup>3</sup> was obtained from 3M, Zwijndrecht, Belgium and the Multi-walled Carbon Nanotubes (NC7000),<sup>40</sup> average diameter 10–9 nm, length of 1.5 μm, a carbon purity of 90%, and a surface area of 250–300 m<sup>2</sup> g<sup>-1</sup> were supplied by Nanocyl Belgium.

### Preparation of composites

Composites of PA6 blend and different HGM/MWCNT contents were prepared by mixing the masterbatch and then via injection moulding at different loading, as used in (Table 1). The different composites were extruded using a corotating twin-screw extruder operating at 40 rpm, with a temperature profile between 220–240 °C. All the components were premixed by tumbling and fed simultaneously into the extruder. After that,

samples (ISO 527 and ASTM D790)<sup>34-35</sup> were prepared by injection moulded using a Haake Minijet Pro<sup>36</sup> from Thermo Fisher Scientific at 250 °C applying a pressure of 650 bar for 15 seconds; the resulting parts were used eventually for the water absorption test as well.

Before starting the Water Uptake test, the samples were carefully inspected for any damage to the surface (e.g injection moulding failure parts, chipping or cracking surface).

### EXPERIMENTAL

The prepared specimens were carefully dried in an oven for 24 h at 50 ± 3 °C, cooled in a desiccator, and immediately weighed with a precise laboratory analytical balance scale (0.0001 g) as per the American Society for Testing and Materials Standard ASTM D570,<sup>37,38</sup> eventually, this represents samples conditioning; procedures for weighting good practice were followed.<sup>39</sup> For the 24 h immersion, the conditioned specimens were placed in a container of distilled water, maintained at room temperature (23 °C) and let rest on the edge, entirely immersed. After 24 h (±1 h), the specimens were removed from the water, one at a time, all surfaces of each sample were wiped off with a dry cloth and then were immediately weighed with the laboratory scale and the results were recorded as per (Table 2).

Table 2  
Weight increase after water immersion at different hours

Samples	24h	84h	168h	252h	336h
1) PA6	1%	3%	4%	5%	6%
2) PA + 30HGB	4%	9%	16%	19%	23%
3) PA + 15MWCNT	1%	2%	3%	4%	5%
4) PA + 10HGB + 2MWCNT	2%	3%	5%	7%	8%
5) PA + 10HGB + 4MWCNT	2%	3%	5%	6%	8%
6) PA + 10HGB + 6MWCNT	3%	5%	9%	10%	11%
7) PA + 20HGB + 2MWCNT	2%	4%	6%	8%	10%

Table 2 (continued)

8) PA + 20HBG + 4MWCNT	3%	6%	10%	13%	17%
9) PA + 20HBG + 6MWCNT	2%	4%	6%	8%	10%
10) PA + 30HBG + 2MWCNT	3%	5%	9%	12%	15%
11) PA + 30HBG + 4MWCNT	4%	8%	14%	17%	20%
12) PA + 30HBG + 6MWCNT	3%	7%	12%	16%	20%

Considering that only at 3 specific hours (24/ 168/ 336h) the measuring of the samples' water intake weight was conducted; for the rest of the hours the predicted percentage (%) of water absorption was calculated with the high-low method for semi-variable stepped values (1)

$m_0$  – conditioned mass

$m_{h(\max)}$  – conditioned mass at the “max” time (in hours)

$m_{h(\min)}$  – conditioned mass at the “min” time (in hours)

$m_{h(x)}$  – conditioned mass at “x” amount of hours

$h_x$  – “x” time of the samples immersed in the water

$k$  – variable intake per unit

$$m_{h(x)} = m_{h(\min)} - \frac{m_{h(\max)} - m_{h(\min)}}{(h_{\max} - h_{\min})} \times h_{\min} + k \quad (1)$$

$$k = \frac{m_{h(\max)} - m_{h(\min)}}{h_{\max} - h_{\min}} \times h_x \quad (2)$$

As the thickness of the specimens was not affected, the samples were not weighed in the bottle. For the long-term immersion (84/ 168/ 252/ 336/ 504/ 672h) the conditioned specimens were tested as described at 24 h immersion, except that were removed at the specified hours, and followed the same procedure. The completion of tests was defined by the saturation mass,  $M_\infty$ , and it was the repeated weightings at the end of every week until the weight gains of the last three consecutive weightings (336/ 504/ 672h) were less than 1% of the overall weight gain.

Eventually, the samples were considered  $C_s$  substantially saturated, based on the formula:

$$C_s = \frac{(M_\infty - M_0)}{M_0} \quad (3)$$

Not to be forgotten that the loss of water-soluble matter from test samples may also affect the final test results. This was checked by reconditioning (drying) the samples back to constant reconditioned mass  $M_c$  and then comparing it against the initial mass  $M_0$ .<sup>41</sup>

## CONCLUSIONS

The usage of polymer composites with smart materials is an especially attractive target, as it can improve the present literature, and allows the unique properties of multi-walled carbon nanotubes to be dispersed to those of other types of materials. In the current paper, different MWCNTs filler amounts, containing PA6 and HGBs were prepared by injection moulded. Based on current literature, the

use of multi-walled carbon nanotubes and hollow glass bubbles with polyamide 6 was less studied.

The main conclusions from the present work are outlined below:

Water uptake tests are important to be conducted on samples that will be exposed to moisture or used in a water environment.

Based on the PA6 supplier data sheet<sup>28</sup> and other water absorption conducted studies on PA6<sup>15</sup> the water uptake on injected moulded polymer samples can take less (6%) water uptake than neat polymer granules (11%).

The addition of hollow glass bubbles substantially increased the weight of the tested samples. In some cases, the weight of the samples (e.g sample 2 / 10/ 11/ 12) increased by up to 15–23%, directly proportional to the amount of water uptake accumulated.

The addition of 15 wt% of multi-walled carbon nanotubes (e.g. sample 3) led to a minimum water absorption rate of 5%; this value is 15% less than most of the polymer composite mixtures and 1% less than pure PA6, mainly because other polymer composites which contained the HGB filler, absorbed more water until reached higher saturation point (336 h).

The best results highlighted in sample 3 show an improved water resistance of polyamide composite, reduces the impact of water on the component, and expresses better applicability in the water environment than other polymer composites or even pure PA6.

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