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Article

Waterproofing materials by incorporating as grown carbon nanotubes into paint

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Abstract: We report a method for effectively and homogeneously incorporating carbon nanotubes (CNTs) in the form of double-wall (DWCNTs) and multi-wall (MWCNTs) structures into commercial paints without the use of additives, surfactants, or chemical processes. The process involves the physical mixing of the nanotubes and polymers using the cavitation energy of an ultrasonic bath. It is a simple, fast method that allows for uniform distribution of carbon nanotube bundles within the polymer for direct application. Due to the hydrophobic properties of the carbon nanotubes as grown, we used paint samples containing 0.3% by mass of both types of CNTs and observed an improvement in waterproofing through wettability and water absorption through immersion tests on the samples. Different solvents such as water, formaldehyde, and glycerin were used, and the results showed an increase in paint impermeability of 30% and 25% with the introduction of DWCNTs and MWCNTs, respectively. This indicates a promising, economically viable, and revolutionary method for applying nanotechnology in the polymer industry.

Keywords: paint; carbon nanotubes; dispersion method; impermeability; nanotechnology

1. Introduction

Nanoparticles, also known as particles with nanoscale dimensions, have been incorporated into polymeric matrices to produce materials with different chemical and physical properties [1–4]. Several industries worldwide are using these composites in various applications to reduce the weight of certain components and improve the mechanical and chemical properties of materials. In paints, the use of carbon nanotubes (CNTs) is widely employed to enhance properties such as porosity, corrosion resistance, thermal resistance, and impermeability. Typically, these nanoparticle incorporation processes involve surfactants, additives, and functionalization, making them small-scale and expensive [5].

Carbon nanotubes are known for their excellent properties [6,7] such as mechanical strength and electrical and thermal conductivity. For example, a CNT's Young's modulus of 1.28 ± 0.5 TPa [8] is five times larger than that of commercial steel. There are several papers involving CNTs that report studies and applications in various areas, from theoretical modeling to experimental analysis and a combination of both, such as beam, plate, and sheel structures [9–14].

However, when dispersed in polymers, due to their high aspect ratio and hydrophobicity, they tend to agglomerate over time, potentially leading to a deterioration in the properties of the polymer composite. CNTs as grown are naturally hydrophobic materials, and their uniform dispersion within the polymer matrix has traditionally required surfactants/additives or sophisticated chemical processes involving some form of chemical modification [7,8,15–20]. CNTs show real promise in the processing of polymer composites to provide mechanical reinforcement as well as enhance thermal and electrical conductivity, thereby enabling the development of lighter materials.

Thus, several studies have been carried out on composites, primarily cementitious matrices, using the "in situ" methodology, where CNTs are grown directly on other materials and their dispersion in the matrix occurs naturally, without chemical processes [21–25]. However, due to the chemical reactivity of polymers and the synthesis temperature of CNTs, the direct growth of carbon nanotubes on polymers has not yet been reported. Furthermore, when dispersed in polymer without chemical treatment, in addition to the cost, the material retains its hydrophobicity within the polymer matrix, contributing to the impermeability of the composite [5].

In this work, we report a simple, additive-free, and non-sophisticated chemical process for incorporating CNTs into polymeric matrices, such as commercial paints. This new incorporation method is based on the physical mixing of these materials (carbon nanotubes) into polymers using an ultrasonic bath. The synthesis of CNTs is carried out by chemical vapor deposition (CVD) using ethylene as the carbon source. Two types of CNTs were used: double-wall (DWCNTs) and multi-wall (MWCNTs) carbon nanotubes, and they were dispersed in commercial paint.

Wettability tests were conducted on mortar samples painted with both reference paint and nanostructured paint in order to analyze whether the incorporation of carbon nanotubes would positively influence the impermeability of the polymer (paint). It was observed that the effect of these nanomaterials on the wettability of the samples, using three types of solvents (water, formaldehyde, and glycerin), rendered the polymer more impermeable in all cases, highlighting the efficiency of the dispersion method. Thus, this work presents new perspectives for the practical application of nanostructured polymers in industry, improving the impermeability property of paints in a simple and cost-effective manner.

2. Materials and methods

2.1. Catalyst preparation and carbon nanotube synthesis

For the preparation of multi-walled carbon nanotubes (MWCNTs), a catalyst based on iron and cobalt supported on magnesium oxide (MgO) was developed [23–25]. The ionic solution of Fe and Co salts is impregnated into MgO by dry impregnation and then calcined at 500 ℃ for 2 h in an oxidizing atmosphere. The catalyst used for the synthesis of DWCNTs was prepared similarly using iron and cobalt, but now supported by aluminum oxide (Al_2O_3), as previously described [26]. The synthesis of the CNTs was performed by Chemical Vapor Deposition (CVD) using argon as the carrier gas (500 sccm) and ethylene as the carbon source (300 sccm). Both catalysts were used in the synthesis, resulting in a yield increase of 2300% for MWCNTs and approximately 800% for DWCNTs.

2.2. Dispersion CNT in commercial paint

The process of obtaining nanostructured paint described herein is achieved in a simple manner, free from additives, surfactants, and chemical processes such as functionalization for the incorporation of carbon nanotubes into polymeric matrices. The novel incorporation method involves the use of bath ultrasonics, utilizing cavitation energy at room temperature. **Figure 1** shows optical photos of the methodology and dispersion used.

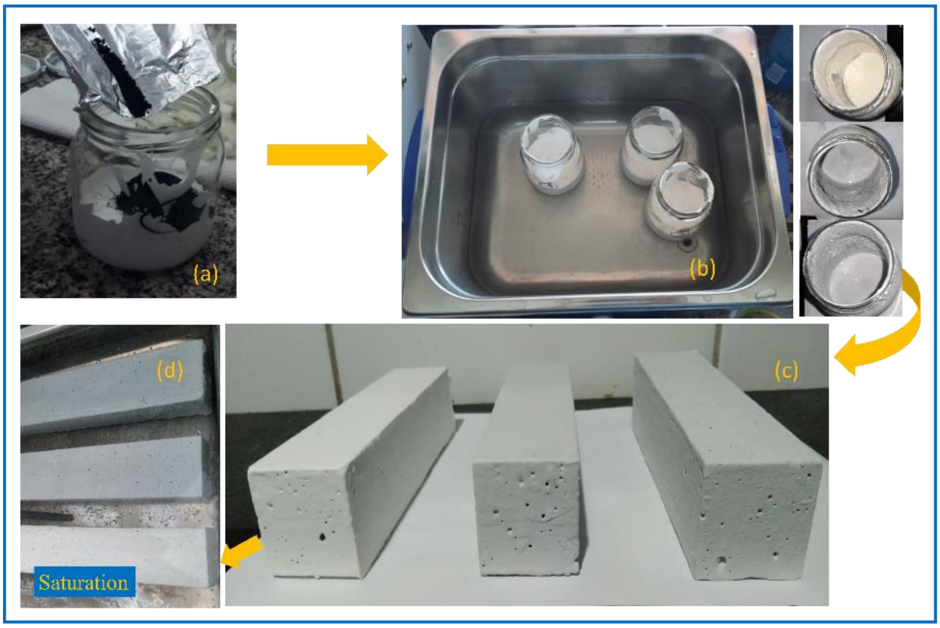

Figure 1. (a) Optical photos showing CNTs and paint mixture; **(b)** nanostructured paints at 0.3% of CNT and dispersion of the material with US; **(c)** appearance of mortar painted with nanostructured paints; **(d)** the samples of the mortar into water at 90 ℃ to saturation and impermeability measurements.

The as-grown DWCNTs and MWCNTs are incorporated into the polymer paint at 0.3% by weight (**Figure 1a**) by physical mixing and subjected to ultrasonic (US) treatment at a frequency of 40 Hz for 30 min using cavitation energy (**Figure 1b**). Cavitation occurs when millions of tiny, microscopic bubbles (cavities) collide in a liquid. Thus, cavitation occurs when there is an alternation of high- and low-pressure areas that diffuse through the liquid. The entire process takes place at room temperature. The same ultrasonic bath treatment is applied to the reference paint to expose it to the same cavitation energy. Subsequently, nanostructured paints suitable for direct application on mortar are obtained (**Figure 1c**).

Using standardized measurements (NBR 9978), the paint-coated mortar specimens are immersed in water at room temperature, and the volume of the specimen is periodically measured, then heated to saturation at 90 ℃ (**Figure 1d**) for impermeability measurements. In addition, the nanostructured paint samples are applied to glass slides (with a 0.38 mm spacer) for wettability measurements. In these experiments, 3 mL of fluids of different polarities and densities, namely water, glycerin, and formaldehyde, are added. Photographs of the bubbles formed on each surface are taken for contact angle measurements.

2.3. Procedures and equipment

The following procedures and equipment were used for the characterization of the materials and the paint samples:

Morphological analyses by Scanning Electron Microscopy (SEM) were performed using a Vega3-TESCAN microscope. Voltage ranges of 2–5 kV and magnifications ranging from 5000 X to 100,000 X were employed.

Transmission electron microscopy (TEM) was carried out at CNT using a FEI-Tecnai G2-20 SuperTwin microscope operating at a voltage of 200 kV.

Measurements of the impermeability are performed by NBR 9978 using samples of the mortar and absorption by immersion.

3. Results and discussion

3.1. Carbon nanotube types

Figure 2 shows SEM images (**Figure 2a**) and TEM images (**Figure 2b**) of the MWCNTs produced, revealing the presence of slender CNTs with an outer diameter of about 12–20 nm and lengths of several microns, along with the absence of amorphous carbon. In **Figure 2c** and **Figure 2d**, similar analyses are performed on DWCNT. The main difference between the two types, apart from the number of walls, is the length of the tubes. DWCNTs are arranged in bundles with lengths of about 300 μm, whereas MWCNTs have lengths on the order of 50 μm.

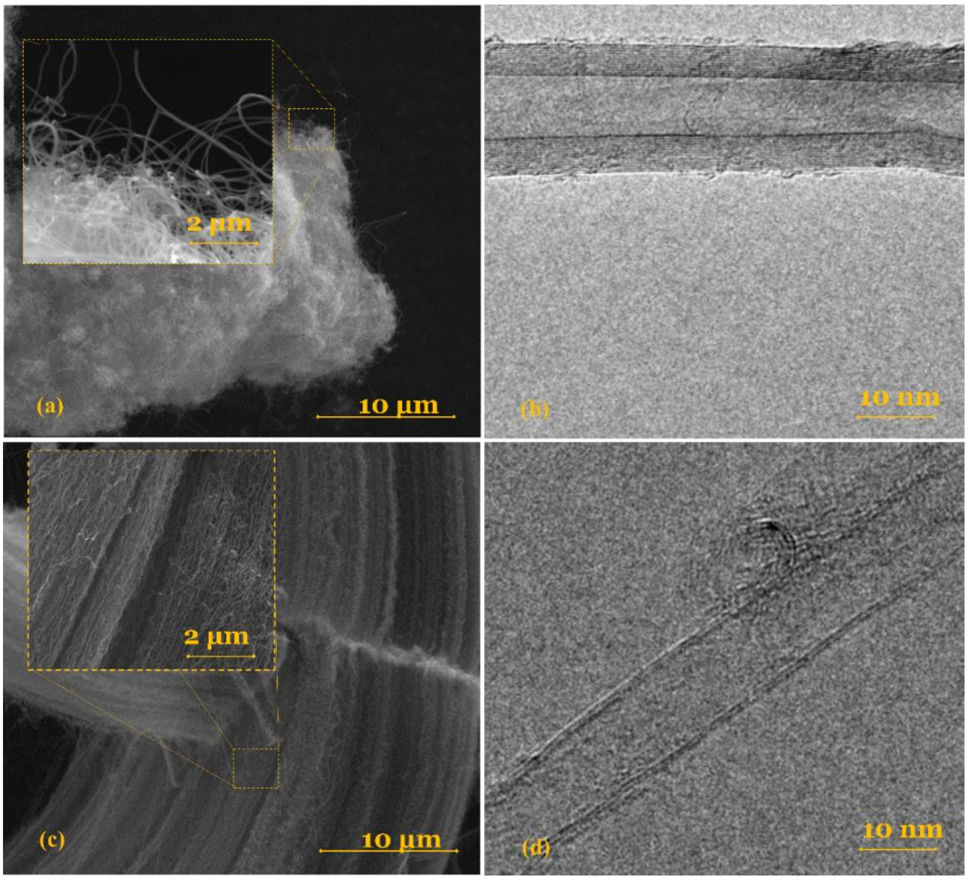

Figure 2. (a) and **(c)** SEM imagens and TEM images; **(b)** and **(d)** at types of the Carbon Nanotubes synthesized, MWCNTs and DWCNTs.

3.2. Nanostructured paint

To characterize the nanostructured paints, initial UV-vis absorbance measurements were performed on reference paste paints (without CNTs) and those with 0.3% DWCNTs and MWCNTs. UV-vis spectroscopy is a technique commonly used to evaluate the dispersion of CNTs in polymers. [20]. During UV-vis experiments, CNTs are activated and show characteristic bands. However, CNT aggregates are hardly sensitized even when analyzed in the UV-vis region between 200 and 800 nm, probably due to charge transfer between the individual nanotubes, which minimizes translational, rotational, and vibrational effects. Nevertheless, it is possible to establish a relationship between the individually dispersed nanotubes in solution and the corresponding absorption spectrum intensity. In this way, UV-vis spectroscopy can be used to monitor the dynamics of the CNT dispersion process.

The results shown in **Figure 3a** demonstrate the presence of CNTs, indicated by changes in the curve behavior and peaks in the region around 255 nm, associated with dispersion. In the case of the DWCNTs sample, the change in signal is more pronounced, probably due to the length of the CNTs bundles (approximately 300 μm), while for MWCNTs, the bundles are four times shorter.

To further demonstrate the temporal stability effect of cavitation dispersion of CNTs, the inset of **Figure 3b** shows an optical photograph of the paints dispersed in 1 L of water after ultrasonic dispersion with only mechanical agitation and a new UV-Vis spectroscopy measurement on diluted paints. In the spectrum in **Figure 3b**, peaks at 235 nm (not marquet) and 350 nm were observed for nanostructured paints. The absorption can be attributed to the π–π* transition of aromatic C=C bonds and the n–π* transition of surface functional groups of the polymers, such as C = O [27]. The higher intensity and peak shift from 350 nm to 375 nm in the pure paint indicate a variation in the optical path length traveled by the beam in the UV-vis spectrometry analyses due to the presence of dispersed CNTs.

The spectrum exhibits higher absorbance intensity in the nanostructured paints (indicating good dispersion), along with specific CNT bands.

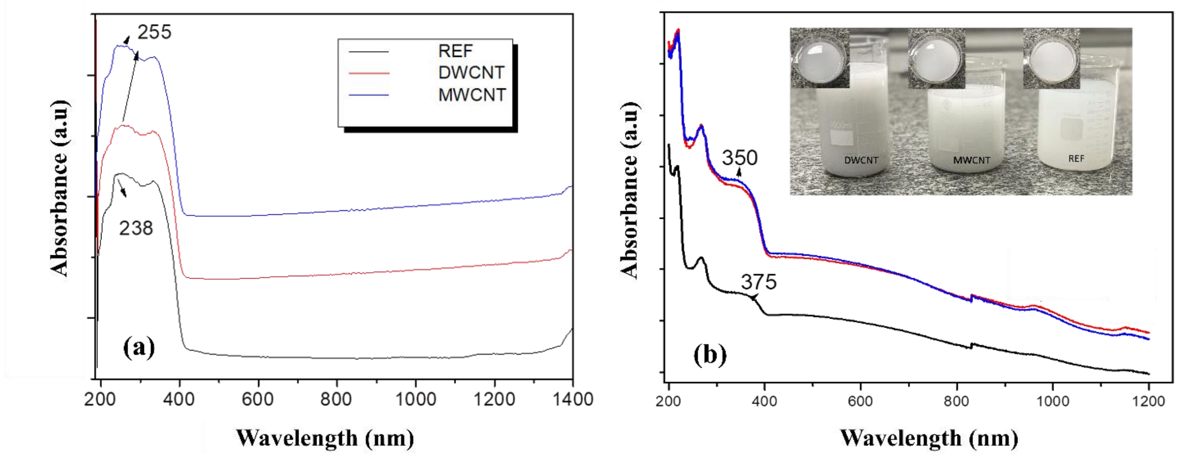

Figure 3. (a) Absorbance in UV-vis (200–1200 nm) for paints after US; **(b)** after dilution in water.

3.3. Impermeability by immersion

After preparing the paints, three mortar test specimens were painted with standardized thickness. The comparative results of all the prepared samples are shown in **Figure 4**. A significant difference in color can be observed between the reference sample (without nanotubes) and the samples with nanostructured paint containing DWCNTs and MWCNTs. **Table 1** shows the dry density data of the painted mortar samples before the water immersion experiment.

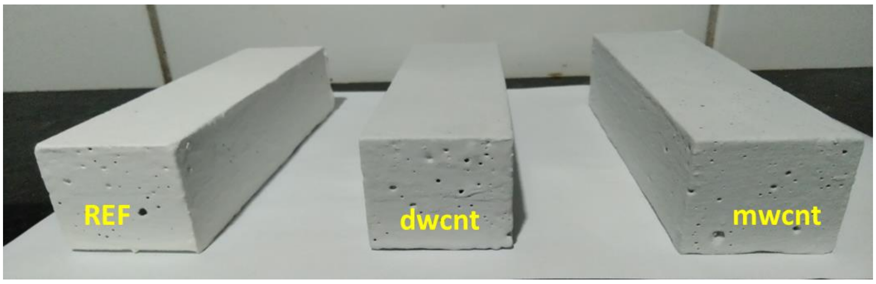

Figure 4. Optical photograph of mortar test specimens painted with paint without CNTs and nanostructured paint.

Table 1. Data of the density of the mortar test specimens painted with the prepared paints.

Samples	Dry mass (g)	Volume (cm^3)	Dry density (g/cm^3)
REF	551.91	224.64	2.46
DWCNT	566.65	230.40	2.46
MWCNT	582.61	237.12	2.46

After painting the three mortar test specimens, and due to the hydrophobic nature of carbon nanotubes as they grow, an expected result would be an improvement in paint impermeability with the introduction of CNTs. According to NBR9978 for mortar, the samples must be immersed in water for a minimum of 24 h to assess water absorption by immersion. Subsequently, the samples are boiled and saturated, and the absorption and impermeability are calculated. **Figure 5a** presents the data obtained for water absorption by immersion before boiling over 48 h, showing that the nanostructured samples exhibit lower water absorption throughout the analyzed period, with the sample containing DWCNT having even lower absorption than the one with MWCNT, mainly due to the significantly greater length of the CNTs.

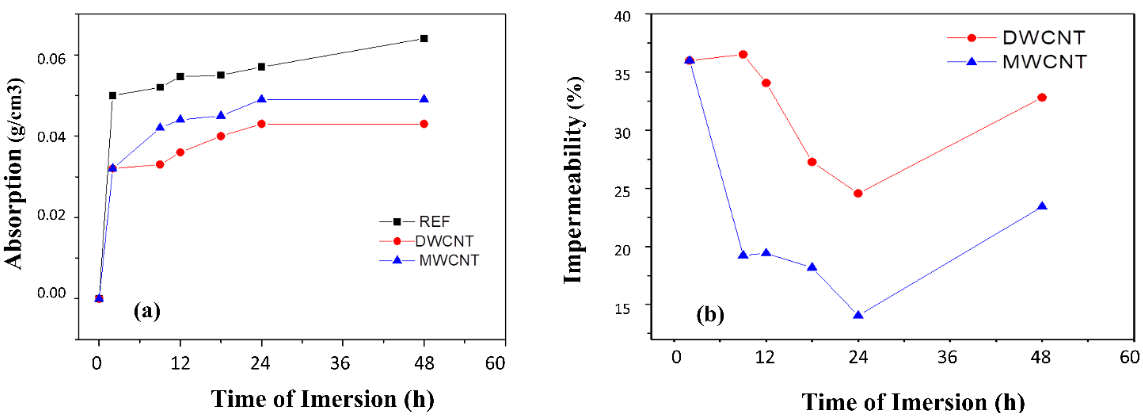

Figure 5. (a) Absorption by immersion in water by 48 h; **(b)** impermeability analyses after boiling at 5 h in relation to reference sample.

Following the boiling (at 90 ℃) for 5 h and complete saturation of the samples, **Figure 5b** confirms the previous data regarding lower absorption, or, as shown, higher impermeability (compared to the reference sample), with the sample with nanostructured paint containing DWCNTs being up to 30% more impermeable and with MWCNTs being approximately 25% more impermeable, compared to the reference paint without carbon nanotubes after 48 h. And **Figure 6** shows the absorption and impermeability measurements after saturation for all samples, confirming the results.

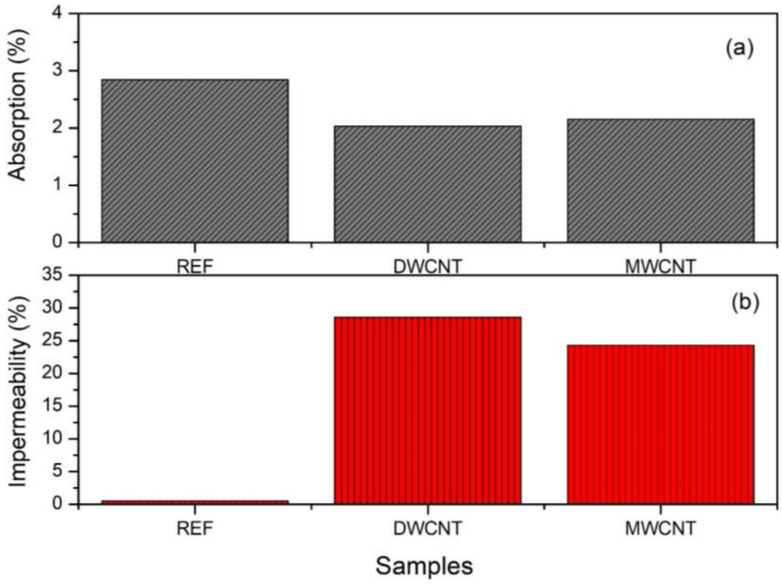

Figure 6. Absorption and impermeability at samples after saturation for 48 h.

These results demonstrate the effective dispersion of as-grown CNTs in paints and maintain the hydrophobic properties of the CNTs (dispersed without external treatment), thereby improving the impermeability of the polymer.

3.4. Wettability

With the introduction and dispersion of CNTs in the paints, there has been an increase in the impermeability of the test specimens, as CNTs are known to be hydrophobic. The interaction between a surface and a particular liquid can be studied by measuring the so-called contact angle (θ) [28]. This is defined as the angle between a plane tangent to a drop of liquid and the plane containing the surface on which the liquid is deposited. The nanostructured paint samples are applied to glass slides, and the determination of the angle was made from images taken with a CCD camera. The experiment was conducted in an unrefrigerated environment, and different reagents (water, formaldehyde, and glycerin) were used. The results obtained for the three coatings analyzed, REF, DWCNT, and MWCNT, are shown in **Figure 7**, and the wettability (or gain in impermeability) is summarized in **Table 2**.

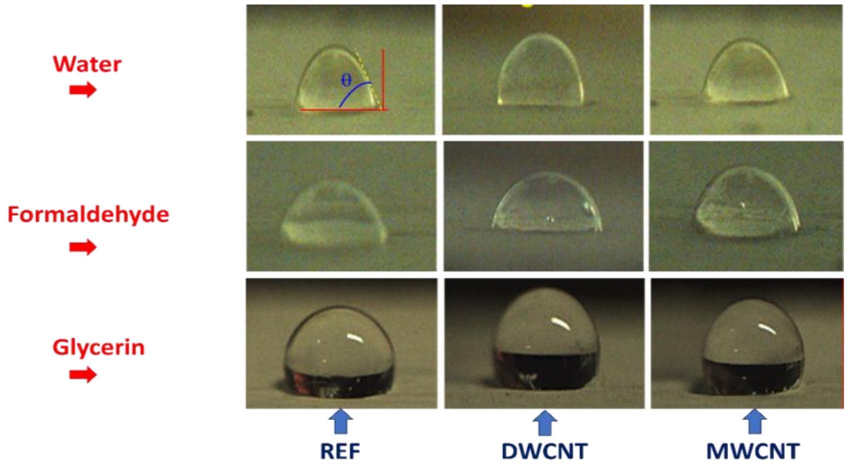

Figure 7. Photos obtained in the wettability experiment with different solvents for the REF, DWCNT, and MWCNT paints analyzed, showing the contact angle.

Table 2. Wettability data at contact angle of REF paints, with 0.3% DWCNT and with 0.3% MWCNT, in addition to the gain compared to the reference (in red).

Solvent	**Reference**	**DWCNT**	**MWCNT**
Water	60.0°	78.4° (+31%)	69.1° (+15%)
Formaldehyde	54.4°	66.6° (+22%)	61.9° (+14%)
Glycerin	99.0°	138.4° (+40%)	120.4° (+22%)

From **Table 2,** it can be observed that the presence of CNTs, as they are produced in the paints, promotes a lower gain in impermeability or wettability, regardless of the solvent polarity. Furthermore, this imperviousness effect is greater for the sample with DWCNTs than with MWCNTs, probably due to the way the CNT bundles are dispersed, where DWCNTs are four times longer.

4. Conclusion

This work presents prospects for the direct application of carbon nanotubes as produced in polymers, indicating a path towards an economically viable and environmentally sustainable application (without chemical functionalization processes) of nanotechnology in polymer composites. The main contributions are:

1) The method of dispersing CNT bundles in paint by Us-Bath is simple, effective, and demonstrates temporal stability with no additional cost to CNT synthesis.
2) Impermeability and wettability measurements showed that 0.3% of grown CNTs can improve the waterproof layer of exterior paint by up to 30%.

Author contributions: Conceptualization, VG; methodology, VG and IAMdS; formal analysis, EAdM; investigation, VG, IAMdS and EAdM; writing—original draft preparation, VG; writing—review and editing, VG, IAMdS and EAdM; visualization, EAdM; supervision, VG; project administration, VG. All authors have read and agreed to the published version of the manuscript.

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