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Research article

Development and evaluation of polyvinyl alcohol films reinforced with carbon nanotubes and alumina for manufacturing hybrid metal matrix composites by the sandwich technique

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Abstract: Metal matrix composites (MMCs) have been a fundamental element in the development of technologies related to the aerospace and automotive industries. This is because they have an excellent weight-to-strength ratio, i.e., they are light materials with a high mechanical resistance. In the manufacturing of MMCs, the incorporation and homogeneous dispersion of reinforcements in the matrix has been one of the biggest challenges. The issue has expanded to the manufacturing of materials reinforced with nano-scaled particles. This study is aimed at the manufacturing, optimization, and characterization of the polymeric matrix reinforced with carbon nanotubes and alumina (hybrid composites), in order to use the polymeric matrix as an inclusion vehicle of the nano-reinforcements in a metallic matrix.

The synthesis of the polymeric matrix composites was carried out by a solution mixing technique using polyvinyl alcohol as a matrix. For the reinforcement's dispersion, a magnetic stirring and sonication were used. Finally, the solution was put into a petri dish to allow its polymerization. The nano-reinforcement dispersion qualification and the quantification of the polymer matrix composite were carried out through the tension, nanoindentation, dynamical mechanical analysis test, elastic modulus mapping, and statistical model for dispersion. In addition, a preliminary study of the metallic composite was carried out and was fabricated by the sandwich technique. The initial characterization of the composites was performed through the nanoindentation test.

Keywords: hybrid composite materials; alumina; carbon nanotubes; polyvinyl alcohol; dispersion; mechanical properties

1. Introduction

Polymer and metal nanocomposites represent a new class of materials that offer an alternative to conventional filled materials. These materials have been increasingly studied due to their specific and interesting properties and potential for a wide range of applications as in aerospace, aeronautical, automotive, electronics, and sport industries [1–4]. In this new class of materials, nano-sized reinforcement offer a tremendous improvement in the materials's performance, however, manufacturing this kind of composites brings many challenges, and one of them is to achieve a good dispersion of the nano-reinforcements, this is difficult to achieve since their superficial area fosters cluster formation [5]. Different manufacturing techniques have been studied for producing polymer matrix nanocomposites (PMCs) such as the solution mixing [6] and the in situ polymerization [7], however, in some cases dispersion problems were reported. In the same way, metal matrix composites (MMCs) use different manufacturing techniques for producing the composites. These techniques are: powder metallurgical [8], stir casting [9], diffusion bonding [10], and thermal spray [11], however, MMCs present a major difficulty to achieve a good nano-reinforcement dispersion (respect to PMCs), because of this, an alternative technique such as the sandwich technique has been used [4,12].

The most commonly used reinforcements for the manufacturing composites are continuous fibers, whiskers, particles, and nano-reinforcements [13–16], which improve their mechanical properties due to two mechanisms: the good interaction between the matrix-reinforcement and the good dispersion. Extensive studies have shown that the incorporation of various types of nano-reinforcement in different polymer matrices allows to improve the mechanical performance of the polymer nanocomposites. Luo et al. [17] studied graphene incorporation in a polymeric hydrogel finding good mechanical properties, however, the elongation of the fabricated nanocomposites at break decreased as compared to the unreinforced hydrogel. In contrast, Salom et.al [18], found that the tensile properties of epoxy graphene nanocomposite decreased as the graphene was introduced to the epoxy matrix. Another author found the same behavior [19].

Due to the above, several authors have tried manufacturing hybrid composites in order to find a better combination for their mechanical properties. Hybrid nanocomposites can be prepared by combining more than one type of nanomaterial such as organic and inorganic nanomaterials together in a polymeric, metallic, or ceramic matrix. Generally, these hybrid nanocomposites are not simply physical mixtures of different nanomaterials, but they are intimately mixed and more homogenous mechanical properties are achieved. Some studies have been carried out about the incorporation of two nano-reinforcements. Karthikeyan et al. [20,21] studied the tribological and mechanical behavior of the hybrid nano-fillers of multi-walled carbon nanotubes (MWCNT) and alumina (Al_2O_3) epoxy nanocomposites for various weight fractions of 0.5, 1.0, 1.5, 2.0 and 2.5 wt% prepared by a sonication process. The authors found that the hybrid nanocomposite (1.5 wt% MWCNTs–Al_2O_3) leads to 85%, 82%, and 81% improved wear resistance; more than that of pure epoxy, however, the hybrid nanocomposites do not evidence considerable changes in their mechanical properties. Sameh Dabees et al. [22] studied the mechanical properties of high-density polyethylene reinforced

MWCNTs and Al_2O_3 in order to uses the hybrid composites in hip joint replacement. The author reported good mechanical properties and low toxicity for human cells. Other authors [23–25] have reported hybrid composites nano-reinforced with MWCNTs and silicon carbide (SiC) with promissory results for structural applications.

In this work, the hybrid polymer nanocomposite will be used as an inclusion vehicle for manufacturing hybrid metal matrix composites, and this previous step is very important because it defines the dispersion degree of the nano-reinforcements into the metallic matrix. Some studies have used several nano-reinforcements in order to improve the mechanical properties of some metals, such as aluminum, magnesium, and titanium. Padmavathi et al. [26] studied the tribological response of aluminum nano-reinforced with MWCNTs and SiC particles fabricated by stir casting. The author reported that the hybrid composites, under mild wear conditions, displayed a lower wear rate and friction coefficient compared to aluminum, however, for several load conditions, the hybrid composites increase their coefficient of friction. Kim et al. [27] studied (MWCNT)/Al_2O_3 preform-based aluminum hybrid composites fabricated using the infiltration method. The results evidence that the Al_2O_3 and MWCNTs were well-dispersed within the hybrid matrix. The array of the Al_2O_3 helped the well-dispersed MWCNT distribution within the matrix. This could also improve the infiltration behavior during the process. Paramsothy et al. [28] studied another kind of hybrid composites, in this case, the hybrid magnesium (AZ31/AZ91) alloy nanocomposite containing a TiC (titanium carbide) nanoparticle reinforcement was fabricated. The authors used the solidification processing followed by hot extrusion and they found that, compared to monolithic AZ31/AZ91, tensile (yield and ultimate) and compressive (only ultimate) strengths of AZ31/AZ91/1.5vol% TiC were each enhanced. This can be attributed to well-known factors related to reinforcement. Other researchers [29,30] have found an important increase in the tribological and mechanical properties of the hybrid magnesium composite reinforced with MWCNTs and SiC.

This research focuses on the manufacturing, evaluation, and characterization of a hybrid polymer composite nano-reinforced with (MWCNTs) and Al_2O_3, whose characterization is focused on the quantification of the dispersion of the nano-reinforcements in order to optimize the mechanical response of the hybrid composites. The hybrid polymer dispersion quantification was done by advanced techniques such as nanoindentation and statistical frequency analysis, whose dispersion quantification methodologies are not explored in literature. Finally, the hybrid polymer is used as an inclusion vehicle of nano-reinforcements for metal matrix composites manufacturing, using the novel sandwich technique [12,31]. This alternative technique for manufacturing MMCs consists of two steps: the first step is the pre-dispersion of the reinforcements in a polymeric matrix, which takes advantage of the ease of dispersing the reinforcements in a low-viscosity polymeric material. The second step is the hot compaction of the hybrid polymeric matrix with a metallic matrix, during this process the PVA is thermal degraded, and metallic matrix composites are obtained.

2. Materials and methods

2.1. Raw materials

Polyvinyl alcohol (PVA) is used as an inclusion vehicle for the nano-reinforcement in the metallic matrix. It was supplied by Sigma Aldrich with a molecular weight of 85000–124000 and

87–89% hydrolyzed. Table 1 shows the polyvinyl alcohol specifications.

Table 1. Sigma Aldrich material specifications [32].

Prod. number	Appearance (Form)	Assay % Hydrolized	Loss on drying	Residue on ignition (Ash)	Viscosity C = 4% H_2O	pH C = 4% H_2O
363081	Powder	87–89%	≤5%	≤5%	23–27cps	4.5 – 6.5

MWCNTs were supplied by Nanostructured & Amorphous Materials Inc. The MWCNTs have outer diameters of 10–40 nm and inner diameters of 5–10 nm as is shown in Figure 1a,b with a length of 30–50 µm. Figure 1c shows the Alumina (Al_2O_3) nanoparticle. Alumina nano-particles were supplied by Alpha Resources Inc. with a size of about 0.05 microns (50 nm).

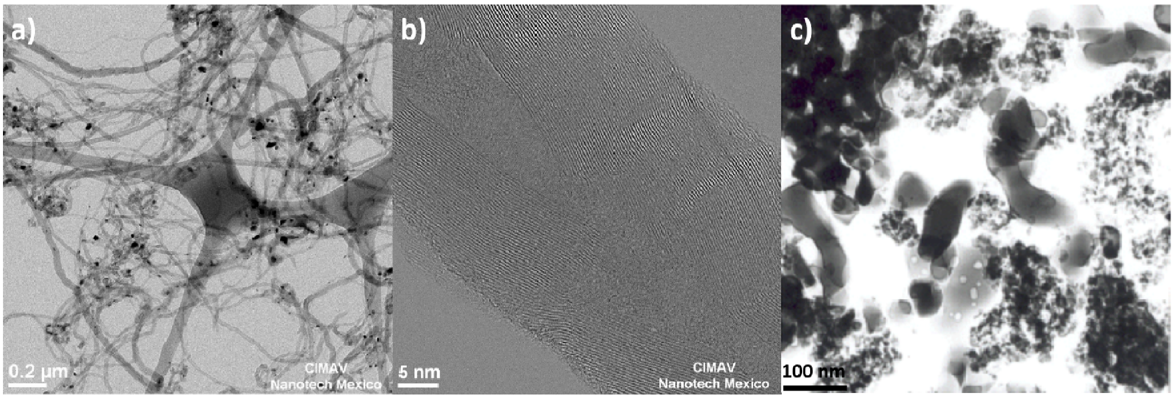

Figure 1. (a) TEM image of the MWCNTs, (b) HRTEM detail of MWCNT and (c) TEM-DF image of alumina used in this study.

For the preliminary metal matrix composite, a cold-rolled AA1100 aluminum alloy was used in the form of thin sheets with a thickness of 0.3 mm. Its nominal chemical composition is shown in Table 2 and the microstructural morphology is shown in Figure 2 with an optical microscope (OM) and scanning electron microscopy (SEM). The images show the phase formation for this alloy ($FeAl_3$ compounds).

Table 2. Nominal chemical composition (wt%) of the AA1100 aluminum.

Element	Si	Fe	Cu	Mn	Zn	Al
Balance	0.95% max	0.95% max	0.05–0.20%	0.05% max	0.10% max	99.0% min

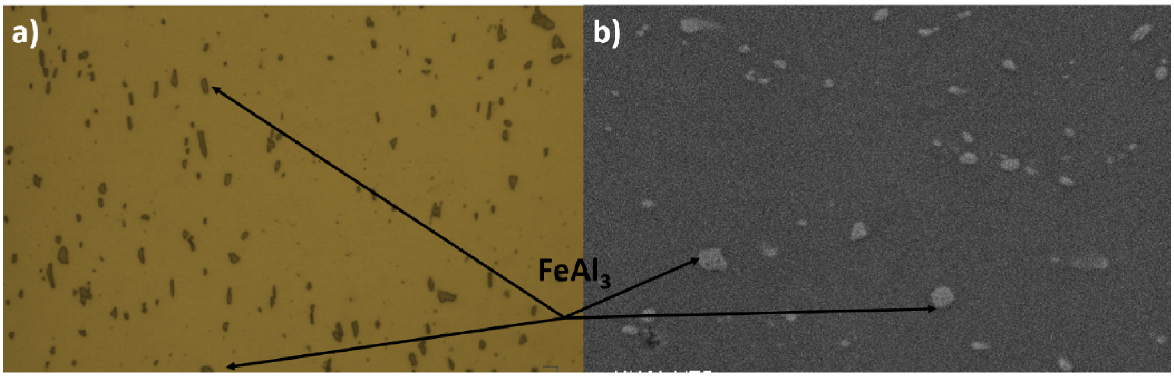

Figure 2. AA1100 aluminum microstructure (a) optical microscope and (b) scanning electron microscopy (SEM).

2.2. Synthesis of polymer matrix composites

Powder of fully hydrolyzed PVA was diluted in hot distilled water (4 wt% of PVA). MWCNTs were added into the PVA solution in percentages of 0.5 wt% and Al_2O_3 was introduced into the PVA solution in percentages of 1.0 and 2.0 wt%. The solution with the nano-reinforcements was dispersed by magnetic stirring for 1h at an average speed of 600–900 rpm followed by sonication, which was set to a power of 100 W and a probe's amplitude of 50%; the dispersion maximum energy was 60–70 kJ to prevent damage to the CNTs [33]. The polymer solution was poured into Petri acrylic dishes and dried for 1 week at room temperature for allowing the polymer to cure. The schematic process of the synthesis of polymer matrix composites reinforced with MWCNTs and Al_2O_3 is shown in Figure 3.

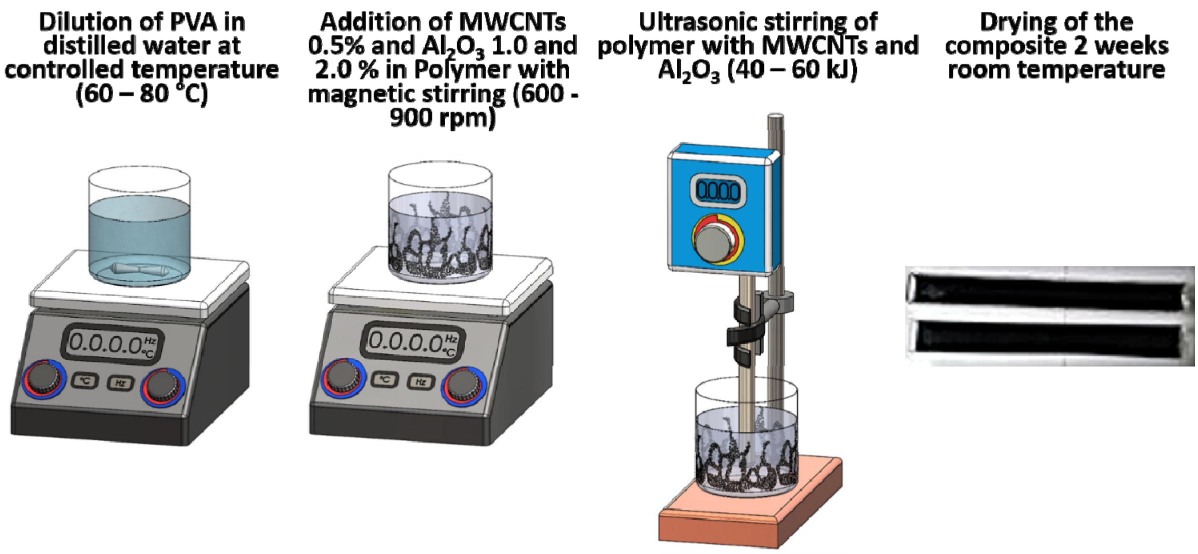

Figure 3. Synthesis of polymer matrix composites reinforced with MWCNTs and Alumina.

2.3. Dispersion qualification on polymer matrix composites nano-reinforced

For dispersion qualification, mechanical characterization was used. Tension test, DMA, and nanoindentation test were performed in order to identify the change and homogeneity of the nano-reinforcement in the polymeric matrix. Tensile samples were tested in a Shimadzu model AGS universal testing machine of 20 kN with 0.1% resolution on a speed of 0.5 mm/min, under the standard ASTM D882-02 [19]. Dynamic mechanical analysis (DMA) was carried out on a dynamic mechanical spectrometer (model DMA RSA3 from TA Instruments); the samples were subjected to tensile tests at room temperature, using a clamp speed of 0.005 mm/s [18]. The quasi-static nanoindentation tests were carried out using an IBIS Authority Fischer-Cripps nanoindenter with a Berkovich diamond indenter tip and a peak load of 5 mN. The nanoindenter was used to directly determine the nanomechanical properties, elastic modulus, and hardness of the bulk composites [17].

2.4. Dispersion quantification on polymer matrix composites nano-reinforced

For dispersion quantification, a modulus mapping was carried out by nanoindentation test. The tests were performed in a scanned area of 2.5 μm × 2.5 μm with a maximum load of 0.8 mN producing a maximum depth of about 50–200 nm. The separations between indentations were 250 nm. The mechanical properties were deconvoluted using the Oliver and Pharr method [34].

Representative images of modulus mapping were divided into 10 × 10 grid lines along with the horizontal and vertical directions. Then the spacing, both horizontal and vertical, between nearest changes of elastic modulus was measured at each grid intersection. These data were analyzed using the statistical distribution model [35] showed in Eqs 1 and 2.

$$f(x) = \frac{1}{xn\sqrt{2\pi}} exp\left[-\frac{1}{2}\left(\frac{lnx-m}{n}\right)^2\right], \text{for } x > 0, \text{and } f(x) = 0, \text{for } x \leq 0, \quad (1)$$

where $m = ln\frac{u^2}{\sqrt{u^2+\sigma^2}}$ and $n = \sqrt{ln\frac{u^2+\sigma^2}{u^2}}$, x is the free-path distance, u is the mean and σ is the standard deviation for the free-path distance measured.

A dispersion parameter, $D_{0.1}$, defined as the probability of the free-path distance distribution, was set in the range of 0.9–1.1 u. The distance distribution usually obeys a lognormal distribution model, in which $D_{0.1}$ is formularized as in Eq 2.

$$D_{0.1} = 1.1539 * 10^{-2} + 7.933 * 10^{-2} * \left(\frac{u}{\sigma}\right) + 6.6838 * 10^{-4} * \left(\frac{u}{\sigma}\right)^2 - 1.9169 * 10^{-4} * \left(\frac{u}{\sigma}\right)^3 + 3.9201 * 10^{-6} * \left(\frac{u}{\sigma}\right)^4 \quad (2)$$

Since in this method $D_{0.1}$ is deduced from the free-path distance distribution, a higher $D_{0.1}$ value indicates more spacing data close to the mean u. Dispersion of 100% signifies that all of the reinforcements are equally spaced, i.e., different percentages of the addition of nano-reinforcements can have the same values as the $D_{0.1}$ parameter. Moreover, $D_{0.1}$ measures the number of reinforcements that are at the same distance, regardless of their value. Actually, any value of $D_{0.1}$, $D_{0.2}$, $D_{0.3}$, etc., can be chosen in order to describe the dispersion of the nano-reinforcements into a matrix.

2.5. Synthesis of metal matrix composites

For the synthesis of MMCs, the first step was the pre-dispersion of the MWCNTs and Al_2O_3 reinforcements in the polymeric matrix (PVA) and the second step was the manufacturing of the metal matrix composites by the sandwich technique. Sheets of aluminum and polymer reinforced with MWCNTs and Al_2O_3 were stacked and hot compacted. The temperature was gradually raised for 1.5 h until 645 °C was reached; the pressure was also gradually raised to 40 MPa. This was followed by a holding period of 3.5 h for allowing the PVA to evaporate and the aluminum to diffuse between the sheets, to finally accomplish the composite consolidation. Figure 4 shows the synthesis route of Al–PVA/MWCNTs/Al_2O_3 composites: one composite sheet of PVA/MWCNTs/Al_2O_3 was alternately stacked with two aluminum sheets.

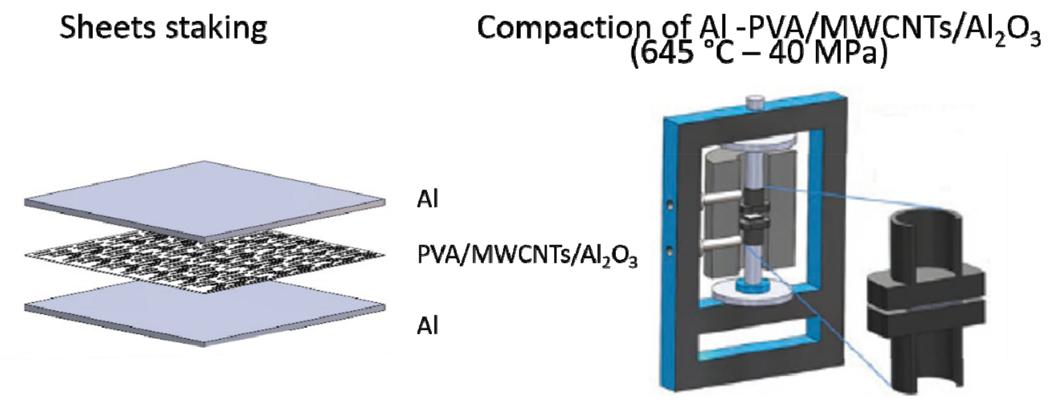

Figure 4. Synthesis route diagram of the Al–PVA/MWCNTs/Al_2O_3 composites.

Samples of the MMCs were cut and then were progressively polished using SiC emery papers and a finishing cloth loaded with 1 μm diamond paste. Finally, the samples were characterized by nanoindentation near the diffusion zone between the aluminum sheets.

3. Results and discussion

3.1. Raw materials characteristics

The characteristics of MWCNTs such as morphology and diameter are essential for their dispersion into the matrix. MWCNTs with a very large diameter have a small tendency to re-agglomerate after a dispersion process. Contrarily, a larger aspect ratio relationship promotes the MWCNTs tendency to agglomerate because of its large surface energy, allowing the formation of clusters, which in the composite causes an inefficient load transfer from the matrix to the reinforcement.

Figure 1a,b show TEM images of the as-received MWCNTs, as well as their outer and inner diameter distribution. Outer diameters of 10–40 nm and inner diameters of 5–10 nm were found; the presence of 30–50 walls in MWCNTs were observed. Although inner diameters of the MWCNTs have no direct influence on the dispersion of the CNTs in a material. Outer diameters of the MWCNTs used in this work are moderately small, which could increase the risk of agglomeration. Figure 1c shows the alumina reinforcement used in the hybrid composites manufacturing and the images evidence its morphology and its size is about 50 nm, however, it presents an irregular size in the image. Despite this, the use of the PVA solution allows having a very good dispersion of MWCNTs [36], as the interaction between CNTs and Al_2O_3 with the polymeric matrix. The dispersing effect of the polymer continued even after the polymerization and curing steps.

Finally, the aluminum alloy microstructure, which will be used for manufacturing MMCs, is shown in Figure 2a,b. It can be seen that α-Al, as a light color in the image and as a predominant phase in the aluminum alloy, and the darkest areas are the formation of Si-crystals and $FeAl_3$ phases, it was found in low proportions. Figure b) shows the same microstructure by SEM in which the $FeAl_3$ phase is identified as small clear islands. This validated that the alloy is aluminum AA1100.

3.2. Characterization of mechanical properties for PMCs

Conventional nanoindentation tests were performed in order to analyze the mechanical behavior of PVA, PVA/MWCNTs, and PVA/MWCNTs/Al_2O_3 composites, and the results are shown in Figure 5. Figure 5a shows the resulting load-displacement (P-h) for all composites studied. The results evidence the effect of the nano-reinforcements on mechanical properties of the composites. The composites experience an increase in stiffness with the nano-reinforcement content; it is evidenced by the lower penetration depths and lower initial unloading contact stiffness; in other words, the addition of nano-reinforcements notoriously influenced the PVA's stiffness increment.

Figure 5b,c show the results of elastic modulus and hardness for all the composites studied. For all composites, an increase in both properties is seen with the MWCNTs' and alumina content. The increment in elastic modulus and hardness for each composite are compared with unreinforced PVA. The increment in the elastic modulus was of 72%, 68%, 272%, 255%, and 394% for the composites PVA/MWCNTs, PVA/Al2O3-1%, PVA/Al2O3-2%, PVA/MWCNTs/Al2O3-1% and PVA/MWCNTs/Al_2O_3-2%, respectively. Whereas the hardness increased by 80%, 90%, 380%, 580% and 980% for the composites PVA/MWCNTs, PVA/Al_2O_3-1% PVA/Al_2O_3-2%, PVA/MWCNTs/Al_2O_3-1% and PVA/MWCNTs/Al_2O_3-2%, respectively. The relative high statistical dispersion of the properties may arise from the fact that the indenter is placed in areas that may differ in microstructure, and can even be placed directly onto an area that contains high local concentrations of alumina or MWCNTs during the nanoindentation test. Note also that the unreinforced PVA produces results with a small standard deviation and symmetrical confidence intervals, which is an indirect indication of the material's isotropy; such isotropy is lost with the addition of MWCNTs and Al_2O_3. Similar characterization of PVA reinforced with MWCNTs was performed by Cesar et al. [13]. The authors found that the composites increase their mechanical properties depending on the MWCNTs content, however, when high percentages in weigh of MWCNTs were added into the polymeric matrix, the mechanical properties decreased. The authors attribute this behavior to cluster formation during the manufacture process. Another work was presented by Shital More et al. [37]. They fabricated thin films of polyvinyl alcohol (PVA)–aluminium oxide(Al_2O_3) composite by solution casting method. The authors found a good dispersion by microscopes techniques, however, the quantification was not carried out. Shadpour

Mallakpour et al. [38] manufactured poly(vinyl alcohol)/surface modified Al_2O_3 nanocomposite and evidenced by FE-SEM and TEM characterization techniques a homogenous dispersion of nanoscale inorganic particles in the poly(vinyl alcohol) matrix.

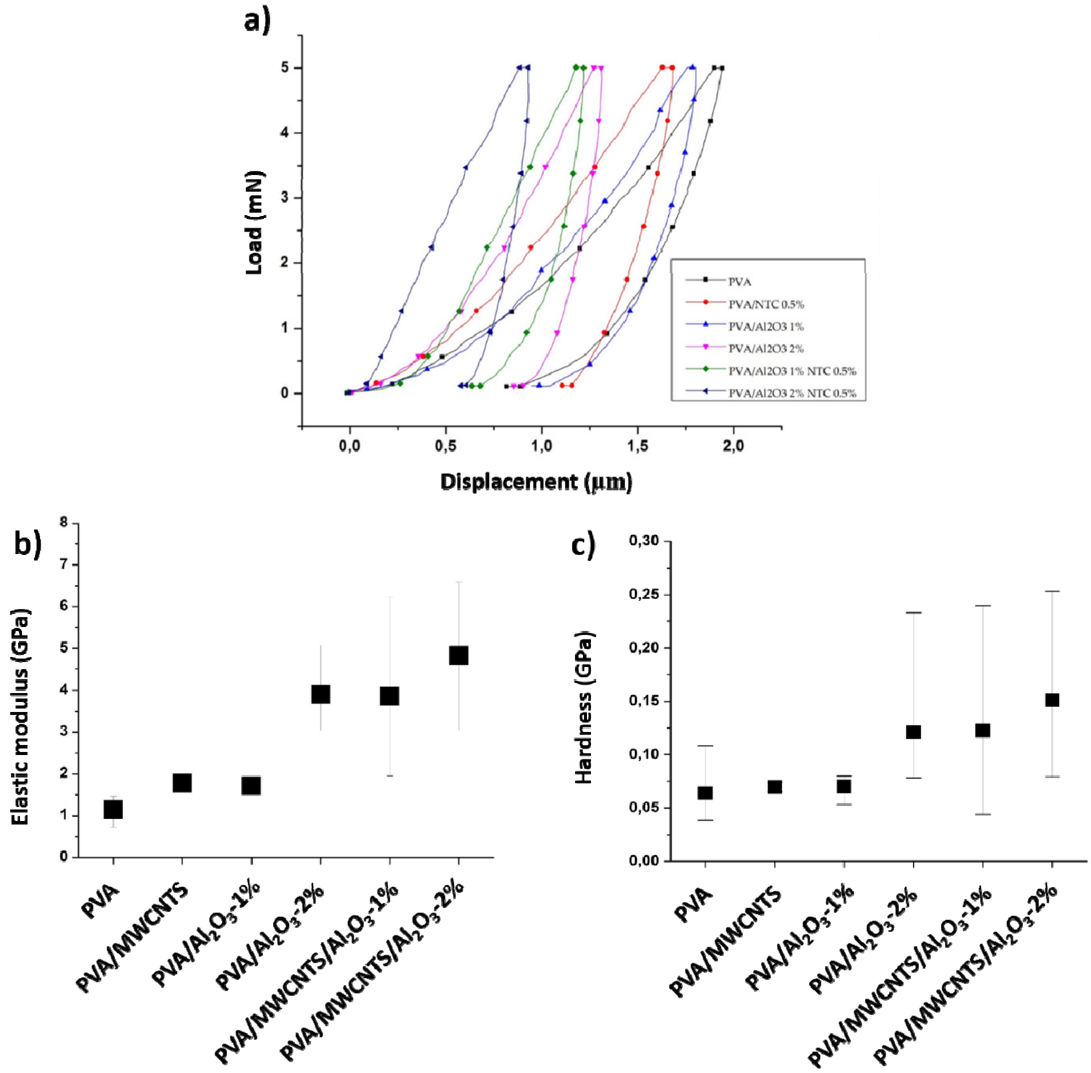

Figure 5. Nanoindentation results for all composites studied. (a) Load versus indenter displacement, (b) Elastic modulus, and (c) Hardness.

The bulk mechanical properties were measured by tension test and the behavior differs a bit from the nanoindentation results. The yield strength and the ultimate strength results are shown in Figure 6; the mechanical properties are dependent on the percentage of nano-reinforcement. It is observed that the PVA/Al_2O_3-1% and PVA/MWCNTs/Al_2O_3-1% composites show good behavior for both properties, yield strength and ultimate strength. However, a decreases in the mechanical proprieties is evidenced for the PVA/Al_2O_3-2% and PVA/MWCNTs/Al_2O_3-2% composites. These results may evidence a poor nano-reinforcement dispersion into the polymeric matrix. However, the dispersion results for nano-reinforcements show otherwise and are discussed later in this work. Therefore, a possible explanation for the decrease of the mechanical properties in the tension test could be attributed to defects in the manufacturing or curing process, i.e., during the polymeric composites synthesis some pores or lumps could be appear due to heterogeneous curing. The pores can appear or become trapped during the polymerization process. This process generates an exothermic reaction that allows the water evaporation that can be trapped. This is because the surface is the first zone to polymerize. Finally, due to atmospheric conditions, the polymer does not perform a homogeneous polymerization therefore the thickness of the composite can vary causing stress raising that will be noticed during mechanical tests. On the other hand, it must be clarified that the conditions for measuring properties by nanoindentation and tension are very different. In nanoindentation, the measurement volume is very small and the interaction with a volumetric defect is unlikely, contrary to what happens with the tension test where the sample volume for the test is considerably higher.

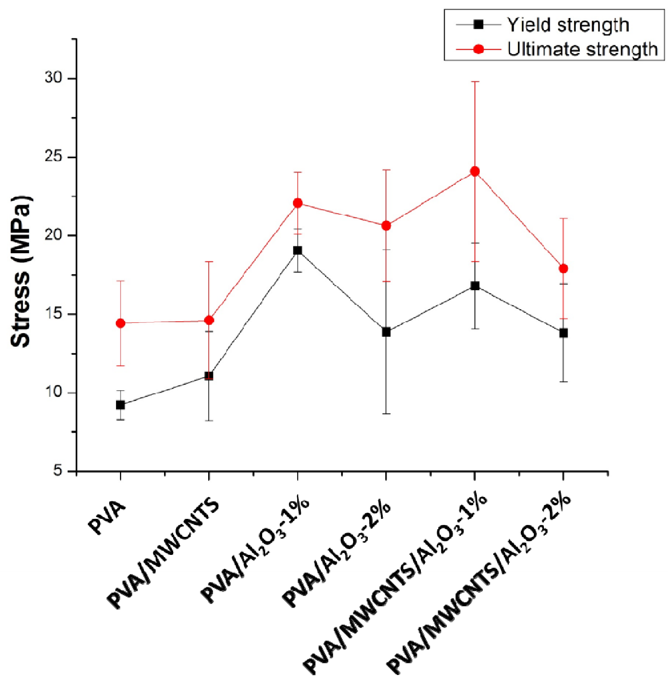

Figure 6. Ultimate and yield strength of the composites.

The DMA tests were conducted for PVA/MWCNTs/Al_2O_3-1% and PVA/MWCNTs/Al_2O_3-2% in order to evidence the effect of the hybrid nano-reinforcement in a polymeric matrix. Figure 7a,b show the stress-strain curve, the ultimate and yield strength for the composites tested. The results evidence that the best tensile mechanical properties of the composites were found for the PVA/MWCNTs/Al_2O_3-2% composite, and similar results were found in the nanoindentation test. This is because both tests were carried out in a small volume and their defects density decrease.

It is important to mention that the mechanical tests provide qualitative information about the dispersion of the nano-reinforcements in the polymer matrix, which is used in the metallic matrix. It should be noted that some works on hybridization with CNTs and Al_2O_3 have been carried out, focusing on studying the changes in their thermal properties for conductive polymers in functional applications. For example, Fan et al. [39] studied the evolution of conductive paths and interactions in the interfacial regions in epoxy-based composites reinforced with CNTs and Al_2O_3 micro-particles, although the authors did not measure the mechanical properties, they found a good dispersion for both, the CNTs and Al_2O_3 into the polymeric matrix. Finally, the authors concluded that there was a significant improvement in the dielectric properties of the hybrid composites, and these results were associated with the good dispersions achieved. Li et al. [40] studied multifunctional composites by hybrid fillers comprised of CNTs directly grown on alumina micro-spheres into epoxy matrix that was then reinforced with woven glass fibers. The authors evidenced an increase of their mechanical properties such as elastic modulus, flexural resistance, and interlaminar shear strength, additionally, the nano-reinforcement increased the thermal stability of the composite. In another study by Li et al. [41], the authors introduced into the woven glass-reinforced epoxy low percentages of CNTs and Al_2O_3, whose composites act as in situ sensors to monitor the damage initiation and propagation under mechanical loading. The dispersion qualification was observed by microscopy techniques.

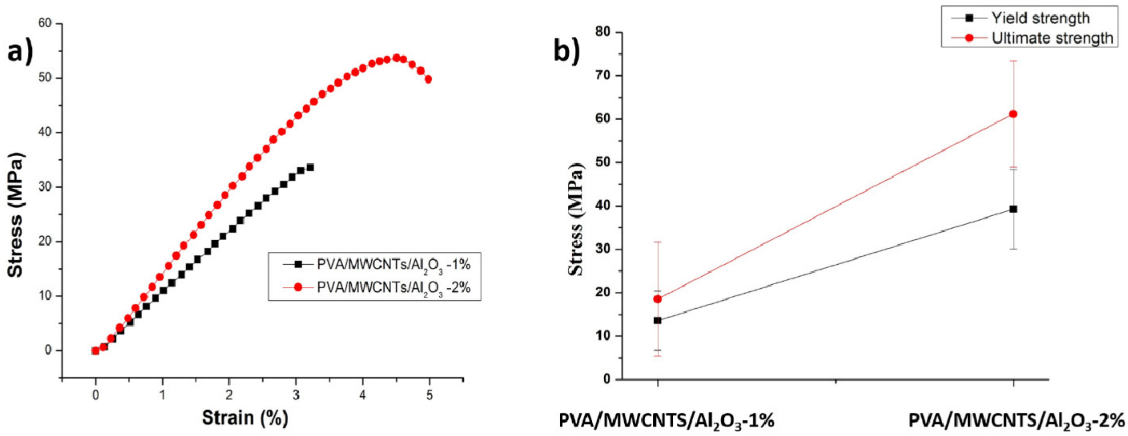

Figure 7. (a) Stress versus strain curves obtained by DMA, (b) Ultimate and yield strength.

3.3. Dispersion quantification of PMCs

For dispersion quantification, the modulus mappings were performed as described in section dispersion quantification on polymer matrix composites nano-reinforced. The mapping was carried out for the two-hybrid composites: PVA/MWCNTs/Al_2O_3-1% and PVA/MWCNTs/Al_2O_3-2%. Figure 8a shows that the elastic modulus mapping for the PVA/MWCNTs/Al_2O_3-1% composite, and it goes from 0.8 GPa for the base material up-to about 7 GPa in some zones where the indenter interacts with the nano-reinforcement Al_2O_3. The image evidences a good dispersion and the Al_2O_3 nano-reinforcement into the matrix without clusters. Those peaks of the nano-reinforcement with high mechanical properties are the values for quantifying the dispersion degree by the statistical model as described before. The results of the dispersion quantification are plotted below the modulus mapping as log-normal curve in Figure 8b. The results show an average spacing between MWCNTs of 0.58 µm and a dispersion degree $D_{0.1}$ of 12.09%. Therefore, about 12.09% spacing data are in the range of 0.48–0.59 µm, which corresponds to the range of 0.9–1.1 u. Additionally, the majority of measurements are at a value close to 0.4 µm, i.e., the Al_2O_3 nano-reinforcements are at this distance.

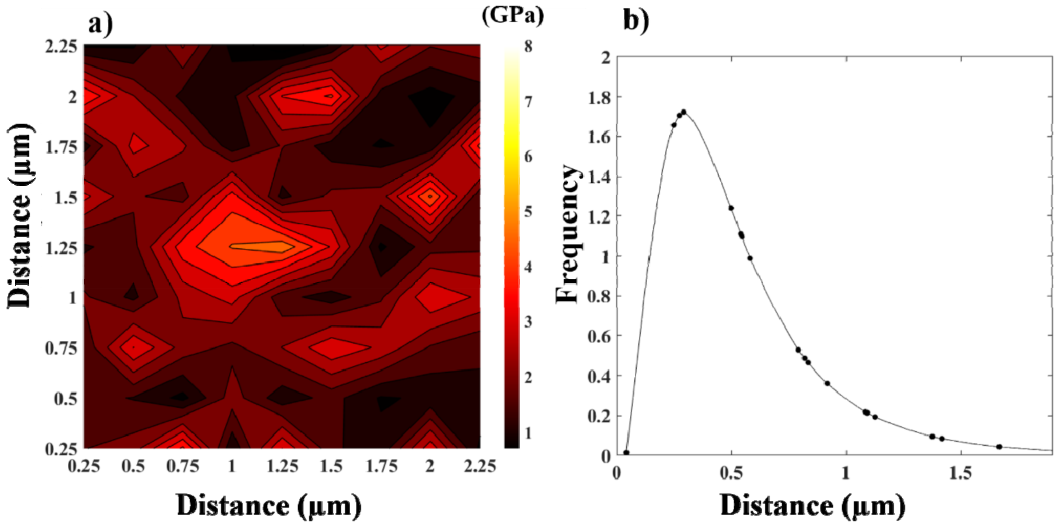

Figure 8. (a) Modulus mapping by nanoindentation and (b) frequency distribution for composite PVA/MWCNTs/Al_2O_3-1.

Finally, Figure 9a shows a similar trend for the PVA/MWCNTs/ Al_2O_3-2 composite, i.e., the elastic modulus changes from 0.8 GPa up-to about 8 GPa (Results obtained for a nanoindentation load of 0.8 mN). In addition, for these composites, there is a decrease in the dispersion in the reinforcing phase, but a greater elastic modulus with respect to the composite manufactured (PVA/MWCNTs/ Al_2O_3-1) was evidenced. This is consistent with the Al_2O_3 content; in other words, Al_2O_3 are closer and are present in more quantity for the hybrid composites with 2 wt% of alumina in the polymeric matrix. It is important to clarify that the Al_2O_3 elastic modulus is about 300–400 GPa, while the data obtained in the composites (even when the indenter tip is placed on top of an Al_2O_3) are influenced by the penetration depth of the indenter tip, i.e., by the volume of the sampled zone. A very shallow indentation (around 2–5 nm) is required to obtain values closer to the Al_2O_3 nano-reinforcement. The results for dispersion degree quantification are shown in Figure 9b; it also shows an average distance between Al_2O_3 of 0.27 µm and a dispersion degree of $D_{0.1}$ of 9.5%.

Therefore, about 9.5% of spacing data are in the range of 0.24–0.29 µm, which corresponds to the range of 0.9–1.1 u. Additionally, the majority of measurements are at a value close to 0.2 µm, i.e., the Al_2O_3 nano-reinforcements are at these distances.

The measurement of distribution uniformity of nano-reinforcements is useful for understanding the mechanical properties of the composites. There are two methodologies; one is through qualitative methods such as visual observation of images of composites, that do not produce numerical values that can be used for systematic comparison. Secondly, there are quantitative methods that can be used to predict the best achievable distribution uniformity of nano-reinforcements given the size and volume fractions of the composite constituents. For example, Haslam et al. [42] used a technique, which is partially based on a quadrat method, and considers the dispersion as well as agglomerate size distribution of the CNTs into the matrix. The methodology showed a good dispersion index of the nano-reinforcements, and the results were compared with the ASTM standard index for inclusion dispersion into the matrix, the results were similar. The stereology method proposed by Luo and Koo [43], which is used in this study, is based on the assumption that if all the inclusion particles are distributed at an equal free-path distance, the dispersion is perfect. The authors in their experiments found dispersion degree about 3–4% that compared with the results in this study are lower.

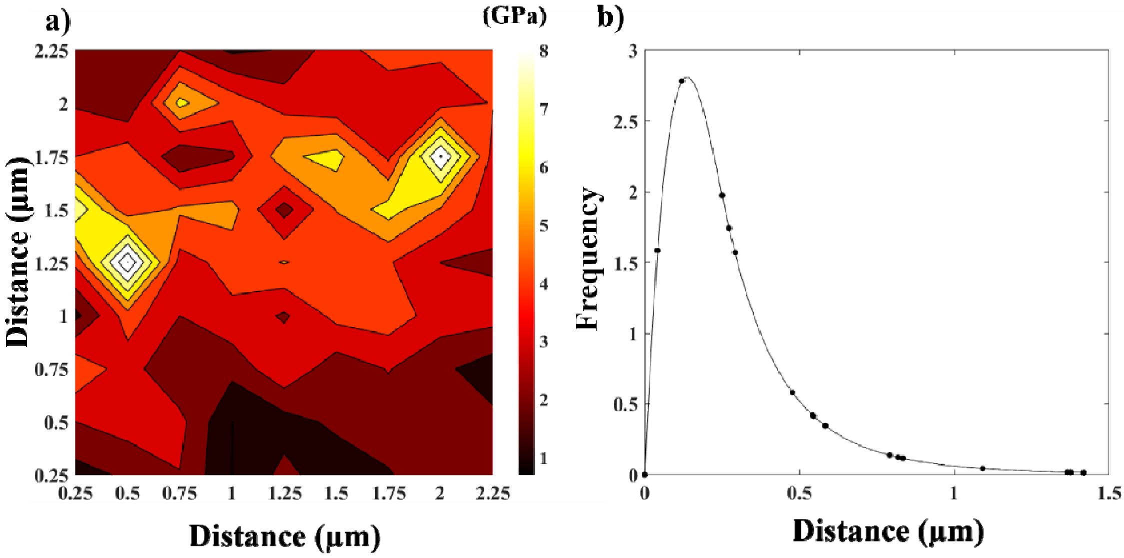

Figure 9. (a) Modulus mapping by nanoindentation and (b) frequency distribution for composite PVA/MWCNTs/Al_2O_3-2.

3.4. Preliminary mechanical characterization of MMCs

The preliminary MMCs characterization was carried out by nanoindentation and the results are shown in Figure 10. The elastic modulus and hardness were measured near the interfaces between the aluminum sheets; Figure 10a,b respectively show the variation of the elastic modulus and hardness as a distance function in the test, in the diffusion zone. All tests were conducted at the same load (5 mN), therefore no indentation size effect due to this factor is involved. Both the modulus and hardness were significantly increased close to the interface for the two hybrid metal matrix composites. The maximum increase in elastic modulus in the reinforced zone was 240% and 228% for the PVA/MWCNTs/Al_2O_3-1 and PVA/MWCNTs/Al_2O_3-2 composites, respectively (Figure 10a). The maximum increase in hardness in the reinforced zone was between 180% and 216% for the VA/MWCNTs/Al_2O_3-1 and PVA/MWCNTs/Al_2O_3-2 composites, respectively. This, in turn, indicates that the reinforcement is responsible for the enhancement of the mechanical properties. Figure 10c shows the zone (diffusion zone) where the nanoindentation tests were performed.

Several reinforcement mechanisms might explain the improvement in the mechanical properties of the synthesized MMCs composites. One mechanism is the dislocation generation by thermal expansion mismatch between the matrix MWCNTs and the Al_2O_3 nano-reinforcements. The dislocation stacking at the interface between the metal matrix and nano-reinforcements plays an important role in the strengthening of hybrid composites. Another important mechanism is the Hall-Petch strengthening, which improves the strength of MMCs due to the grain reduction close to the interface between the metallic matrix and nano-reinforcement. However, the metallic hybrid composites need more study in order to understand all the strengthening mechanisms.

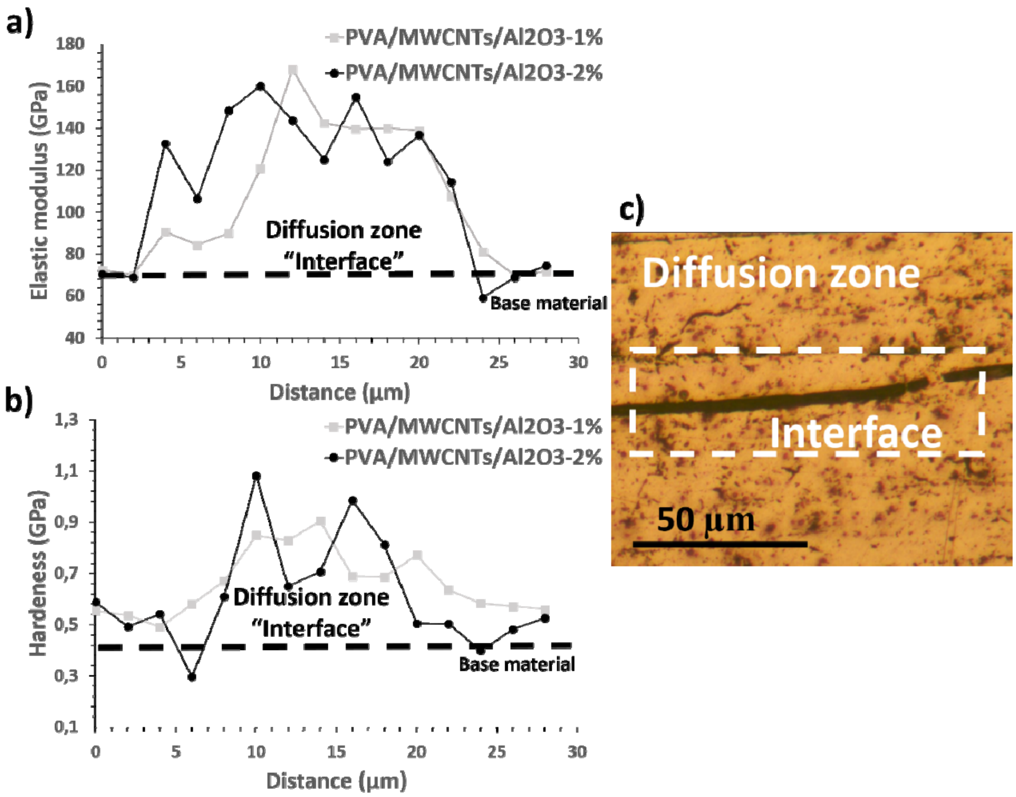

Figure 10. Nanoindentation tests for the hybrid metal matrix composites (a) Elastic modulus and (b) hardness.

4. Conclusions

In this research work, hybrid polymeric composites were synthesized and characterized in order to use the polymeric matrix as an inclusion vehicle of the nano-reinforcements into the metallic matrix. The obtained results for the hybrid polymer matrix composites show good dispersion degrees; this behavior explain the increase of the mechanical properties in all mechanical testing.

Using the statistical methodology through modulus mapping image analysis, the dispersion degree $D_{0.1}$ could be quantitatively compared among the different composites studied. This parameter is only related to the filler free path spacing distribution and is independent from the reinforcement size or type. It was shown that the free-path spacing decreases with the Al_2O_3 nano-reinforcement content and the mechanical properties in bulk composites presented a little decrease. This behavior could be caused by several situations: Nano-reinforcements agglomerations, manufacturing problems during the curing process, or some stress raiser during the tension test.

Finally, the manufacturing of MMCs by the sandwich technique was successful; the technique is particularly interesting because it produces a substantial increase in the mechanical properties of the hybrid metallic composites. Different strengthening mechanisms were identified that corroborate the improvement of the mechanical properties

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Conflict of interest

The authors declare no conflicts of interest.

References

1. Isaza MCA, Ledezma Sillas JE, Meza JM, et al. (2017) Mechanical properties and interfacial phenomena in aluminum reinforced with carbon nanotubes manufactured by the sandwich technique. *J Compos Mater* 51: 1619–1629.
2. Friedrich K, Almajid AA (2013) Manufacturing aspects of advanced polymer composites for automotive applications. *Appl Compos Mater* 20: 107–128.
3. Kessler MR (2012) Polymer matrix composites: A perspective for a special issue of polymer reviews. *Polym Rev* 52: 229–233.
4. Isaza C, Sierra G, Meza J (2016) A novel technique for production of metal matrix composites reinforced with carbon nanotubes. *J Manuf Sci E-T ASME* 138: 024501.
5. Alsharef JM, Taha MR, Khan TA (2017) Physical dispersion of nanocarbons in composites—A review. *Jurnal Teknologi* 79.
6. Xin F, Li L (2011) Decoration of carbon nanotubes with silver nanoparticles for advanced CNT/polymer nanocomposites. *Compos Part A-Appl S* 42: 961–967.
7. LaNasa JA, Torres VM, Hickey RJ (2020) In situ polymerization and polymer grafting to stabilize polymer-functionalized nanoparticles in polymer matrices. *J Appl Phys* 127: 134701.
8. Khodabakhshi F, Simchi A (2017) The role of microstructural features on the electrical resistivity and mechanical properties of powder metallurgy Al–SiC–Al_2O_3 nanocomposites. *Mater Design* 130: 26–36.
9. Khandelwal A, Mani K, Srivastava N, et al. (2017) Mechanical behavior of AZ31/Al_2O_3 magnesium alloy nanocomposites prepared using ultrasound assisted stir casting. *Compos Part B-Eng* 123: 64–73.
10. Kawasaki M, Han JK, Lee DH, et al. (2018) Fabrication of nanocomposites through diffusion bonding under high-pressure torsion. *J Mate Res* 33: 2700–2710.
11. Li Q, Yuan X, Xu H, et al. (2019) Microstructure and fracture toughness of in-situ nanocomposite coating by thermal spraying of Ti_3AlC_2/Cu powder. *Ceram Int* 45: 13119–13126.
12. Merino CAI, Sillas JL, Meza J, et al. (2017) Metal matrix composites reinforced with carbon nanotubes by an alternative technique. *J Alloys Compd* 707: 257–263.
13. Isaza MCA, Herrera Ramırez J, Ledezma Sillas J, et al. (2018) Dispersion and alignment quantification of carbon nanotubes in a polyvinyl alcohol matrix. *J Compos Mater* 52: 1617–1626.

14. Yuan W, Cui J, Xu S (2016) Mechanical properties and interfacial interaction of modified calcium sulfate whisker/poly(vinyl chloride) composites. *J Mater Sci Technol* 32: 1352–1360.
15. Srivatsan T, Lin Y, Chen F, et al. (2018) Synthesis and microstructural development of particulate reinforced metal-matrix composites using the technique of spray atomization and deposition, *TMS Annual Meeting & Exhibition*, Springer, Cham, 149–182.
16. Koli DK, Agnihotri G, Purohit R (2014) A review on properties, behaviour and processing methods for Al-nano Al_2O_3 composites. *Procedia Mater Sci* 6: 567–589.
17. Luo H, Dong J, Xu X, et al. (2018) Exploring excellent dispersion of graphene nanosheets in three-dimensional bacterial cellulose for ultra-strong nanocomposite hydrogels. *Compos Part A-Appl S* 109: 290–297.
18. Salom C, Prolongo M, Toribio A, et al. (2018) Mechanical properties and adhesive behavior of epoxy-graphene nanocomposites. *Int J Adhes Adhes* 84: 119–125.
19. Hu X, Ren N, Chao Y, et al. (2017) Highly aligned graphene oxide/poly(vinyl alcohol) nanocomposite fibers with high-strength, antiultraviolet and antibacterial properties. *Compos Part A-Appl S* 102: 297–304.
20. Karthikeyan P, Babu BG, Sabarinathan C, et al. (2015) Tribological performance of carbon nanotubes-alumina hybrid/epoxy composites. *Optoelectron Adv Mater-Rapid Commun* 9: 455–459.
21. Karthikeyan P, Babu B, Siva K, et al. (2016) Experimental investigation on mechanical behavior of carbon nanotubes-Alumina hybrid epoxy nanocomposites. *Dig J Nanomater Bios* 11: 625–632.
22. Dabees S, Kamel BM, Tirth V, et al. (2020) Experimental design of Al_2O_3/MWCNT/HDPE hybrid nanocomposites for hip joint replacement. *Bioengineered* 11: 679–692.
23. Jiang D, Zhang J, Lv Z (2012) Multi-wall carbon nanotubes (MWCNTs)–SiC composites by laminated technology. *J Eur Ceram Soc* 32: 1419–1425.
24. Ahmad I, Ahmed S, Subhani T, et al. (2016) Synergic influence of MWCNTs and SiC nanoparticles on the microstructure and properties of Al_2O_3 ceramic hybrid nanocomposites. *Curr Appl Phys* 16: 1649–1658.
25. Han D, Mei H, Xiao S, et al. (2018) A review on the processing technologies of carbon nanotube/silicon carbide composites. *J Eur Ceram Soc* 38: 3695–3708.
26. Padmavathi K, Ramakrishnan R (2014) Tribological behaviour of aluminium hybrid metal matrix composite. *Procedia Eng* 97: 660–667.
27. Kim H, Babu J, Kang C (2013) Fabrication of A356 aluminum alloy matrix composite with CNTs/Al_2O_3 hybrid reinforcements. *Mat Sci Eng A-Struct* 573: 92–99.
28. Paramsothy M, Chan J, Kwok R, et al. (2012) TiC nanoparticle addition to enhance the mechanical response of hybrid magnesium alloy. *J Nanotechnol* 2012: 401574.
29. Wei TZ, Shamsuri SRB, Yee CS, et al. (2013) Effect of sliding velocity on wear behavior of magnesium composite reinforced with SiC and MWCNT. *Procedia Eng* 68: 703–709.
30. Zhou X, Su D, Wu C, et al. (2012) Tensile mechanical properties and strengthening mechanism of hybrid carbon nanotube and silicon carbide nanoparticle-reinforced magnesium alloy composites. *J Nanomater* 2012: 851862.
31. Ramirez JMH, Bustamante RP, Merino CAI, et al. (2020) *Unconventional Techniques for the Production of Light Alloys and Composites*, Springer, Cham.

32. SIGMA-ALDRICH Products: Poly(vinyl alcohol) (363081), 2021. Available from: https://www.sigmaaldrich.com/.
33. Rossell MD, Kuebel C, Ilari G, et al. (2013) Impact of sonication pretreatment on carbon nanotubes: A transmission electron microscopy study. *Carbon* 61: 404–411.
34. Chen J, Bull S (2006) On the relationship between plastic zone radius and maximum depth during nanoindentation. *Surf Coat Tech* 201: 4289–4293.
35. Luo Z, Koo JH (2007) Quantifying the dispersion of mixture microstructures. *J Microsc 225*: 118–125.
36. Olayo R, Garcıa E, Garcıa-Corichi B, et al. (1998) Poly(vinyl alcohol) as a stabilizer in the suspension polymerization of styrene: The effect of the molecular weight. *J Appl Polym Sci* 67: 71–77.
37. More S, Dhokne R, Moharil S (2018) Structural properties and temperature dependence dielectric properties of PVA-Al_2O_3 composite thin films. *Polym Bull* 75: 909–923.
38. Mallakpour S, Dinari M (2013) Nanocomposites of poly(vinyl alcohol) reinforced with chemically modified Al_2O_3: Synthesis and characterization. *J Macromol Sci B* 52: 1651–1661.
39. Fan B, He D, Liu Y, et al. (2017) Influence of thermal treatments on the evolution of conductive paths in carbon nanotube-Al_2O_3 hybrid reinforced epoxy composites. *Langmuir* 33: 9680–9686.
40. Li W, Dichiara A, Zha J, et al. (2014) On improvement of mechanical and thermo-mechanical properties of glass fabric/epoxy composites by incorporating CNT–Al_2O_3 hybrids. *Compos Sci Technol* 103: 36–43.
41. Li W, He D, Dang Z, et al. (2014) In situ damage sensing in the glass fabric reinforced epoxy composites containing CNT–Al_2O_3 hybrids. *Compos Science Technol* 99: 8–14.
42. Haslam MD, Raeymaekers B (2013) A composite index to quantify dispersion of carbon nanotubes in polymer-based composite materials. *Composites Part B-Eng* 55: 16–21.
43. Luo Z, Koo J (2008) Quantitative study of the dispersion degree in carbon nanofiber/polymer and carbon nanotube/polymer nanocomposites. *Mater Lett* 62: 3493–3496.