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Graphical abstract
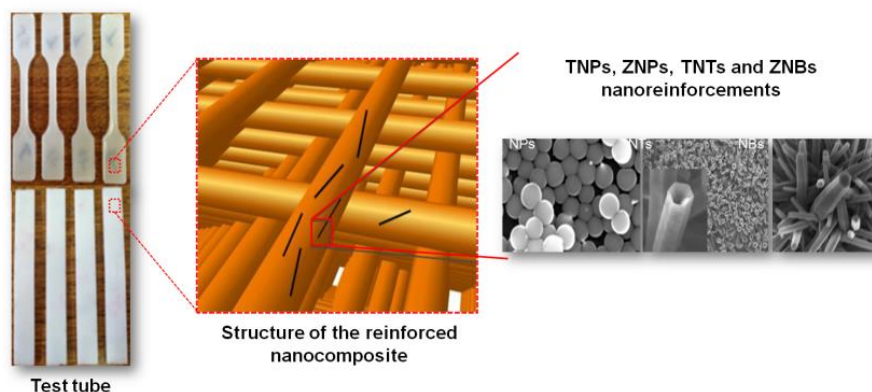
Development of nanocomposite materials with thermostable matrix from nanoreinforcement of titanium dioxide (TNPs and TNTs) and zinc oxide (ZNPs and ZNBs) on epoxy resin matrix

Abstract

In the present investigation, nanocomposite materials were developed with a thermostable resin matrix reinforced with three types of 1D metal oxide nanostructures, also known as polymer matrix nanocomposite materials. These reinforcements were based on commercial zinc oxide nanoparticles (ZNPs) and titanium dioxide nanoparticles (TNPs) and nanostructures synthesized by the authors specifically titanium dioxide nanotubes (TNTs) and zinc oxide nanobars (ZNBs) which were placed in solution with ethyleneglycol (1.5 g) outside and inside the epoxy resin. The nanocomposites were manufactured by curing reactions with different loads (0.5 %, 1.0 % and 1.5 %), in two

types of molds specially designed for this study. In this way the mechanical properties were characterized by tensile tests (by the ASTM D638 standard) and bending (under the ASTM D790 standard). The tests revealed changes in the behavior of the epoxy resin, however, it was possible to maintain the mechanical properties in some cases where the nanoreinforcement was TNPs, while a decrease in the flexural modulus of the epoxy resin was achieved thanks to the nanostructures, where ethyleneglycol also acted as a plasticizer. For all cases, especially those that did not decrease the mechanical properties, the resin potentially acquired new properties. The guidelines that marked the results were: the greater the homogeneity in the morphology of the nanostructure, the smaller sizes and the narrow size distribution of the nanostructures, adding a good dispersion in the exterior and inside of the epoxy resin. Additionally, the measured mechanical properties are improved. On the contrary, with bad distribution, heterogeneity, larger size and poor dispersion, the properties are evidently diminished.

Desarrollo de materiales nanocompuestos con matriz termoestable a partir de nanorefuerzos de dióxido de titanio (TNPs y TNTs) y óxido de zinc (ZNPs y ZNBs) en matriz de resina epóxica

Resumen

En la presente investigación, los materiales nanocompuestos se desarrollaron con una matriz de resina termoestable reforzada con tres tipos de nanoestructuras de óxido metálico 1D, también conocidas como materiales de nanocompuestos de matriz polimérica. Estos refuerzos se basaron en nanopartículas de óxido de zinc (ZNPs) y dióxido de titanio (TNPs) y nanoestructuras sintetizadas por los autores específicamente nanotubos de dióxido de titanio (TNTs) y nanobarras de óxido de zinc (ZNBs) que se colocaron en solución con etilenglicol (1.5 g) por fuera y por dentro de la resina epoxi. Los nanocompuestos se fabricaron mediante reacciones de curado con diferentes cargas (0.5 %, 1.0 % y 1.5 %), en dos tipos de moldes diseñados especialmente para este estudio. De esta manera, las propiedades mecánicas se caracterizaron por pruebas de tracción (regidas por ASTM D638) y flexión (según ASTM D790). Las pruebas revelaron cambios en el comportamiento de la resina epoxi, sin embargo, fue posible mantener las propiedades mecánicas en algunos casos donde el nano refuerzo era TNPs, mientras que se logró una disminución en el módulo de flexión de la resina epoxi gracias a las nanoestructuras donde el etilenglicol también actuó como plastificante. Para todos los casos, especialmente aquellos que no disminuyeron las propiedades mecánicas, la resina potencialmente adquirió nuevas propiedades. Las pautas que marcaron los resultados fueron: cuanto mayor es la homogeneidad en la morfología de la nanoestructura, los tamaños más pequeños y la distribución estrecha de tamaño de las nanoestructuras, agregando una buena dispersión en el exterior y el interior de la resina epoxi. Adicionalmente, se mejoran las propiedades mecánicas medidas. Por el contrario, con una mala distribución, heterogeneidad, mayor tamaño y escasa dispersión, las propiedades evidentemente disminuyen.

Development of nanocomposite materials with thermostable matrix from nanoreinforcement of titanium dioxide (TNPs and TNTs) and zinc oxide (ZNPs and ZNBs) on epoxy resin matrix

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Abstract

In the present investigation, nanocomposite materials were developed with a thermostable resin matrix reinforced with three types of 1D metal oxide nanostructures, also known as polymer matrix nanocomposite materials. These reinforcements were based on commercial zinc oxide nanoparticles (ZNPs) and titanium dioxide nanoparticles (TNPs) and nanostructures synthesized by the authors specifically titanium dioxide nanotubes (TNTs) and zinc oxide nanobars (ZNBs) which were placed in solution with ethyleneglycol (1.5 g) outside and inside the epoxy resin. The nanocomposites were manufactured by curing reactions with different loads (0.5 %, 1.0 % and 1.5 %), in two types of molds specially designed for this study. In this way the mechanical properties were characterized by tensile tests (by the ASTM D638 standard) and bending (under the ASTM D790 standard). The tests revealed changes in the behavior of the epoxy resin, however, it was possible to maintain the mechanical properties in some cases where the nanoreinforcement was TNPs, while a decrease in the flexural modulus of the epoxy resin was achieved thanks to the nanostructures, where ethyleneglycol also acted as a plasticizer. For all cases, especially those that did not decrease the mechanical properties, the resin potentially acquired new properties. The guidelines that marked the results were: the greater the homogeneity in the morphology of the nanostructure, the smaller sizes and the narrow size distribution of the nanostructures, adding a good dispersion in the exterior and inside of the epoxy resin. Additionally, the measured mechanical properties are improved. On the contrary, with bad distribution, heterogeneity, larger size and poor dispersion, the properties are evidently diminished.

1. Introduction

Natural polymers such as cellulose, rubber, wool, silk, among others, have been used since the beginning of history, but it was not until the twentieth century that there was a breakthrough in the development of this type of material, since they enter the scene the synthetic polymers derived mainly from petroleum [1,2], which managed to expand the field of action of this type of material

and replace in many applications, due to their intrinsic properties, to the metallic and ceramic materials. In particular, polymers can be classified according to the displacement of their chains; thermostable (unlike thermoplastics) change irreversibly under the influence of heat and can not melt so only get degraded. This behavior is due to the fact that in the formation of this type of polymers, between the chains, new cross-links or covalent three-dimensional lattices are created (Figure 1) that impede the displacements between the polymer chains. The formation of said crosslinks is also known as a curing reaction, which is crucial in obtaining the thermosetting material. The curing of thermosets is complex and includes several stages, beginning with the formation and linear growth of the chains that soon begin to branch out and subsequently to crosslink. As the reaction progresses the molecular weight increases rapidly and several chains join in a high molecular weight lattice [3]. The chains of macromolecules to form crosslinks and lattices, have numerous covalent bonds that give the material very high mechanical, thermal and chemical resistance properties that make them suitable for multiple applications [4].

1.1 Thermostable matrices (epoxy resin)

The thermostable synthetic resins called epoxy resins are distinguished by their good properties, among which we can distinguish their high resistance to compression, traction, shear, impact and abrasion (when compared with other polymers) [5,6]. However, this type of thermoset polymers are not used by themselves in practically any application, but thanks of their good adhesion, they form mixtures with other materials, therefore it is thought in the use of this material as a matrix in the manufacture of composite materials [7,8].
The simplest epoxy formulation is formed by a resin and a hardener or curing agent with which the resin reacts to form a solid. When the formulation is perfect, the resin will harden forming the three-dimensional network [9]. Specifically, the resin used to develop this work is composed of epichlorohydrin (Figure 2a) and bisphenol A (Figure 2b), which together with a hardener forms the thermostable polymer.
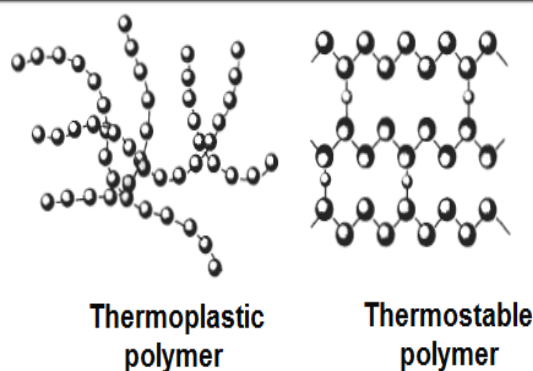Epoxy resins have the particularity of being present in many industrial applications, including

Figure 1. Characteristic structures thermoplastic polymers and thermoset polymer [5].
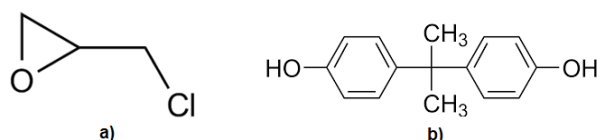

Figure 2. Epoxy resin components. a) Epichlorohydrin, b) bisphenol A [10].

coatings, adhesives, insulating materials in electrical and electronic applications, and advanced composite materials [10,11]. However, in all these applications, the epoxy resins are fragile and rigid due to their nature and have poor resistance to the propagation of cracks, adding a low resistance to impact compared to other thermoplastics and even worse than metals, therefore its final applications are limited to other factors [12], which in order to reduce costs and/or improve the properties of these resins, flexibilizers, fillers, pigments, thixotropic agents, other resins and reinforcing materials are added, to form in the latter case, composite materials. Especially when one of these phases has at least one dimension in the nanometer scale (1D) these are called *nanocomposites*. In this way, a final product is obtained with greater resistance to traction, compression, bending and impact, better resistance to heat and less shrinkage and coefficient of thermal expansion [13], and properties that only on a nano scale is possible to achieve.

1.2 Nanocomposites with epoxy resin matrix

A nanocomposite of epoxy resin matrix is characterized by the homogeneous dispersion of filler nanomaterials that have at least one

dimension in the nanometer scale, these can be nanoparticles (NPs), nanowires (NWs), nanobars (NBs), nanotubes (NTs), nanofibers (NFs) among others [14,15]. All the properties and applications of the mentioned nanostructures generate high expectations in the manufacture of this new type of material and thus achieve to implant said properties to polymer matrices. The resulting properties become unique thanks to the large fraction of filler atoms that reside on the surface of the nanostructures and that produce strong interfacial interactions with the polymer that surrounds them. In the case that NPs and / or nanostructures do not agglomerate after the formation of the polymer, such materials provide a significant improvement both in stiffness and toughness, with a much lower load content than what is achieved with other types of reinforcements; they are microparticles or microstructures [16].

However, a homogeneous dispersion of the nanoparticles in a polymer matrix is a very difficult task due to the strong tendency of the nanoparticles to agglomerate [17]. Consequently, the so-called nanoparticle-filled polymers sometimes contain a series of loose groups of particles and the properties are even worse than conventional fillers, so we will work on a dispersion method which is based on dissolving the agglomerates of NPs and nanostructures in a liquid that has an affinity with the polymer matrix.

The fundamental change in the properties of the material becomes evident, if one takes into account, for example, a small crack that propagates through the material. This is interacting with many nanoparticles instead of crossing only a few microparticles, therefore, it is expected that there is greater energy consumption. Specifically, the nanometric reinforcement improves the flexural modulus, without losing the flexural strength. This effect is also accompanied by improvements in fracture strength and impact energy which, however, largely depend on the filling content [16].

Other properties besides the mechanical as mentioned above undergo changes; Amir Mostafaei et al. [18] reports the use of ZNBs to improve the corrosion resistance of epoxy paints. Changes in tribological properties were reported by L. Chang at el. [19], thanks to the contribution of

TiO$_2$ nanostructures. According to Siu-Ming Yuen et al. [20] compounds with epoxy matrix and TiO$_2$ reinforcements have exhibited excellent mechanical and magnetic properties. This demonstrates the large number of effects that the production of nanocomposites of polymer matrix reinforced with these two types of metal oxides can produce. Its effect is not only limited to the improvement of mechanical properties.

Table 1 shows nanocomposites of polymer matrix and nanostructures, their dispersion and some effects. Thus, the materials developed in this work are composed of a matrix of thermosetting polymer and 1D reinforcements of titanium dioxide (TNPs and TNTs) and zinc oxide (ZNPs and ZNBs), also known as polymer matrix nanocomposite materials. These compounds have essentially optical, electrical, biological and chemical properties [21-25], which are intended to be transferred to the resin that lacks these qualities.

It is also expected that these nanometric oxides, due to their very small size and, in addition to their high aspect ratio (specific surface area), substantially improve the mechanical properties [16]. Added all these characteristics and a homogeneous distribution in the matrix, it is known that the development of hybrid materials substantially increases the field of action of this type of polymers, thinking that currently non-metallic materials acquire greater industrial diffusion, it is a necessity to replace metal alloys in many applications.

2. Experimental section

For the development of nanocomposite materials with a thermoset matrix, a commercial epoxy resin and three types of metal oxide nanostructures were used as reinforcement as a polymer matrix. These reinforcements were based on commercial zinc oxide nanoparticles (ZNPs) and titanium dioxide nanoparticles (TNPs) and nanostructures synthesized in previous studies [1]; titanium dioxide nanotubes (TNTs) and zinc oxide nanobars (ZNBs), which were dispersed homogeneously in ethylene glycol solution, with the aim of avoiding agglomerations. It was carried out curing reactions with different loads (0.5 %, 1.0 % and 1.5 %), in two types of molds specially designed for this study.

Table 1. Polymeric matrix nanocomposites and their reported effects.

| Reinforcement	Dispersion	Effect
TNPs (17 nm, 50nm y 220 nm)	Ultrasound	The smaller NPs produce better mechanical properties.
Nanoclays (sheets)	Mechanical	5 % wt, obtains the best mechanical properties.
TiO$_2$ microparticles	Mechanical	4% by weight improves tenacity. For greater quantities, deterioration of the mechanical properties occurs.
SiO$_2$ microparticles	Ultrasound	Increase in mechanical properties for large volumes (30 %).
TNPs (5 nm)	Ultrasound	Increase in bending properties for 1 % and decay for 2 % load.
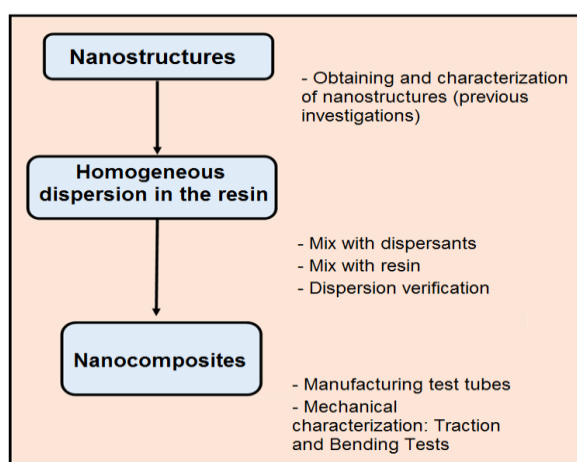
Figure 3. Outline summary of the stages of the experimental methodology.

The characterization of the materials obtained was carried out by means of the manufacture of mold-shaped specimens in the form of halteres for tensile tests (by the ASTM D638 standard) and specimens obtained by machining for the bending tests (under the ASTM D790 standard). The experimental method by stages is summarized in Figure 3.

2.1 Homogeneous dispersion methods of nano-structures in the epoxy resin

The nanostructures used as reinforcement are generally not completely dispersed in the matrix, due to their low affinity and tendency of the nanostructures to agglomerate, which is why they decant before the curing process complements. This is very counterproductive to the mechanical properties of the product. Therefore, it is important to obtain a good dispersion method of the nanostructures so that the properties of the nano-composite are homogeneous, making reference to the entire material. To test the partial dispersion of the nanostructures in the resin, a rectangular test piece 100 mm long, 40 mm wide and 3 mm thick was made. The mixture was 10 g of epoxy resin L20 and 2.5 g of hardener EPH 573, both purchased from the company R&G Faserverbundwerkstoffe® Composite Technology. Nanoreinforce was added in two ways (Table 2). The percentage was 1.5 % w/w because it is the highest load percentage. Thus, the homogeneity was verified in a magnifying glass (2x).

In the present investigation, two types of dispersion were used; the first was mechanical agitation of the nanostructures and the second was mechanical agitation of the nanostructures in ethyleneglycol. It should be noted that a crosslinker was used that solidified together with the epoxy resin at 15 minutes, because the shorter the time less decantation occurs due to gravity. Ethyleneglycol, which is used in the industry as a plasticizer, was used to disperse as it is able to dissolve the oxides and destroy the agglomerates, and in turn is a miscible liquid in the resin.

2.2 Nanocomposites production based on the epoxy resin and the nanostructures of the metallic oxides

The crosslinking reaction of the resin with the nanostructures homogeneously dispersed in ethyleneglycol was carried out by varying the reinforcing filler; the reaction times were varied to find a better cure before decanting the nanostructures. Once the nanocomposite was prepared, the test pieces were manufactured according to the standards established in ASTM

D638 and ASTM D790 standards. It should be taken into account that NPs of TiO_2 (size smaller than 20 nm) and ZnO (size greater than 80 nm) and TNTs and ZNBs obtained in previous investigations [1] were added. These NPs were acquired in Sigma Aldrich, both with analytical quality. The composition of the epoxy resin used is epichlorohydrin plus bisphenol A, while the crosslinking agent was a diamine, both components has in common a low viscosity for a better behavior in the mixture. The mixing ratio between the epoxy resin and the crosslinking agent was 4:1 with a curing process at 18 °C for 24 hours. It should be noted that the resin solidified at about 15 minutes.

Nanocomposites of thermostable matrix with different charges in percentage by weight were prepared (see Table 3). Each nanostructure was used separately in the synthesis of the nanocomposite. For the bending and tensile tests, samples were prepared, obtaining them from a 10 x 10 cm plate of prepared nanocomposite, for the other standards the special crosslinking reaction was carried out.

For each quantity and form of nanorefuerzos, two molds were used, one in the form of "halters" for tensile testing and one square that was used to obtain the specimens for bending as shown in Figure 4.

Each charge was dried at 100 °C and poured into 1.5 g of ethylene glycol and mixed by means of a magnetic stirrer for 10 minutes, after which 66.8 g of epoxy resin and 16.7 g of cross-linking agent were added to this mixture. The resulting mixture was stirred again for 5 minutes until it was completely homogeneous.

Following this, the content was deposited in the two aluminum molds. To finish the process the molds were introduced to the Binder incubator model Gmbh-ED 53 with controlled temperature of 18 °C for 24 hours.

2.2.1 Characterization and determination of properties of the nanocomposite

The mechanical properties of the nanocomposites with epoxy resin matrix were measured by means of tensile and bending tests, which are described below.

• **Traction test:** ASTM D-638 [26] is used for the determination of tensile properties of pure or reinforced plastics (thermostats and thermo-plastics). The specimens were obtained directly from a mold in the shape of "halters" (Figure 5a) with the following dimensions: W_1: 6 mm, W_2: 19 mm, T: less than 2 mm, L_1: 100 mm, L_2: 36 mm (Figure 5b). The test was carried out in the same equipment of the previous section, using an additional accessory as shown in Figure 5c).

For isotropic materials, such as epoxy resin L20, the test was repeated 5 times for each mixture. The test speed is relative, depending on the head of the machine; in this case a speed of 50 mm/min was used.

Table 2. Dispersion methods used.

Reinforcement	Preparation
TiO₂ and ZnO nanostructures	Added to the mixture after drying at 100 °C for 2 hours.
	Added to the mixture after drying at 100 °C for 2 hours and then mixed with 1.8 % by weight of the ethyleneglycol mixture.

Table 3. Mixing ratio: nanoreinforcements – resin – ethyleneglycol.

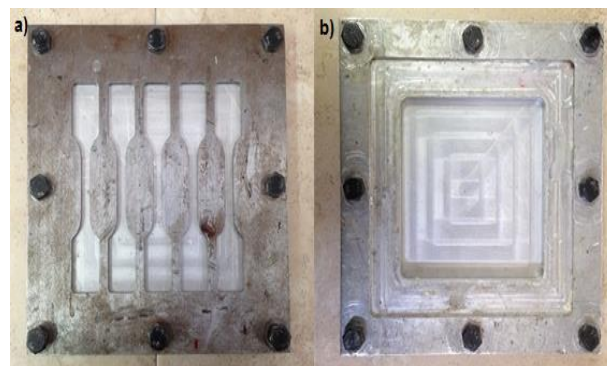| Weight (g)	Mixing ratio (w/w, %)				
	0.0	0.0	0.5	1.0	1.5
Nanoreinforcement	0.0	0.0	0.4	0.8	1.2
Dispersing agent; ethyleneglycol	0.0	1.5	1.5	1.5	1.5
Resin + cross-linking agent	83.5	83.5	83.5	83.5	83.5

Figure 4. Sample molds. a) Tensile strength test and b) Bending resistance test.

• **Bending test:** The flexure test was carried out on the KARG industrietechnik model smar Tens 005 (Figure 6), property of the Technological Development Unit (UDT) of the Universidad de Concepción. This test was performed under the ASTM D790 standard [27].

This method is used to determine the flexural properties of pure plastics, reinforced and electrical insulators, is applicable in rigid and semi-rigid materials. The configuration corresponds to a three-point test.

The development of the test under the standard also consists of a rectangular section bar that rests on two breaks and is loaded by a punch that acts in the average distance between the breaks as shown in Figure 7a. For this test, rectangular specimens that were machined from a 10 x 10 cm square of the epoxy matrix nanocomposite were manufactured, their dimensions were 10 cm long (L), 1.27 cm wide (w).

The thickness of the specimens (h) was variable and remained below 0.2 cm. The above is shown in Figure 7a, 7b and 7c. To carry out this test, the following considerations were followed:

- The relationship between the support distance and the thickness of the sample was 16:1, and
- The specimen was deflected until the rupture on the outer surface of the specimen or until the maximum deformation (5 %). In order to comply with the last requirement, the measurements were made with a deformation speed of 0.01 mm/min.

3. Results and discussion

3.1 Homogeneous dispersion of nanostructures in epoxy resin

The two types of dispersion performed are shown in Figure 8a (mechanical agitation of the nanostructures) and Figure 8b (mechanical agitation of the nanostructures in ethyleneglycol).

Furthermore, in Figure 8b) and 8b1) a decantation of nanoparticles agglomerates is observed, this occurred in all cases in which they were added without dispersant. In 8a) and 8a1) it is evident that it was apparently dispersed, since no agglomerated particles similar to the previous case were found, a

2x magnifying glass was used to verify the problem, not being agglomerated.
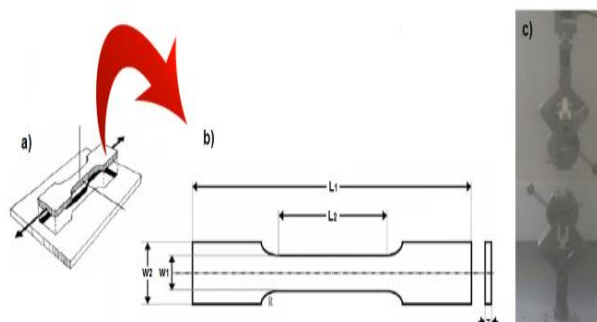

Figure 5. Details of tensile strength test: a) Mold in the shape of "halters" used, b) Scheme of tensile test tube and c) Accessory used for tensile test.

Figure 6. Team KARG industrietechnik model smar Tens 005, equipment used for tensile strength and bending tests.
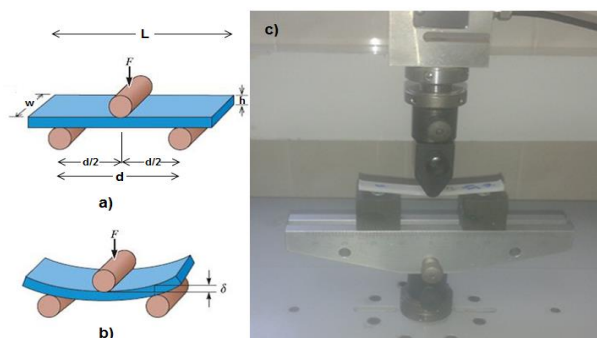

Figure 7. Bending test details: a) Dimensions of: supports, L: length, h: thickness, d: distances between supports, w: width of specimen, b) Deformation produced and c) Actual bending test, the accessories used are observed.
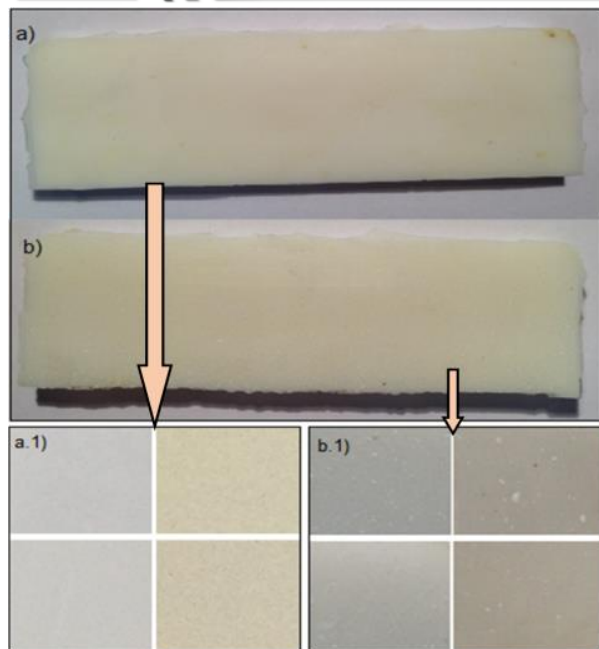
Figure 8. Partially homogeneous dispersion display: a) Test tube with visible homogeneity, b) test tube with evident agglomeration of the reinforcements. a.1) it can be seen that the 4 charges see an apparent dispersion. b.1) there is evidence of agglomeration in the 4 types of reinforcements.

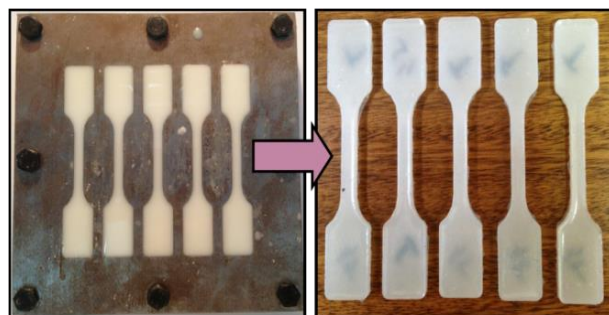**Figure 9.** Material obtained from a) without lid and) with lid.

Figure 10. Tensile test tubes. a) In mold, b) outside the mold.

3.2 Production and evaluation of samples of epoxy matrix and nanostructures of metal oxides

The preparation of epoxy resin matrix nano-composites L20 was carried out with four types of reinforcements: TNPs, TNTs, ZNPs and ZNBs in 0.5 %, 1.0 % and 1.5 % fillers mixed with ethyleneglycol (1.5 g). The resin was prepared together with the aforementioned mixtures and cured with the respective cross-linking agent at 18 °C for 24 hours in molds specially prepared for this investigation. For this process it was ruled out to use the molds with a lid since air confinement was produced which formed bubbles, consequently the formation of pores and cracks, leaving the material unusable (Figure 9). The mechanical properties of the nanocomposites prepared by tensile test and bending test were evaluated.

3.2.1 Mechanical properties by tensile test

Test pieces were obtained in the form of halteres extracted directly from the mold (see Figure 10), from which the maximum tensile stress was measured. The results obtained from the test are shown in Table 4 and Figure 11.

It is observed that the amount of ethyleneglycol supplied to the resin does not affect the maximum tensile stress. So, it is found that ethyleneglycol is a good dispersant of the nanomaterials outside and inside the epoxy resin and by itself has no effect on the mechanical properties of traction. The standard deviation of the samples shows a very similar dispersion in the data obtained for all loads.

Regarding the elaborated nanocomposites, it was determined that with reinforcements of TNPs maximum tensile stress for 1.0 % increases slightly, which reached 11 % with respect to the same property in the resin with ethylene glycol. The increase in maximum tensile strength of the TNPs is explained because they are smaller than 20 nm on average and thanks to this they act as a brake or obstacle to the propagation of cracks [16], which required an effort greater to achieve the break. Added the effect due to its large specific volume, which is achieved a transfer of tensions from the matrix to the reinforcement. Some studies report an increase in mechanical properties in traction, although well above the 11 % obtained in this study [16, 28-31].

Table 4. Tensile test results for nanocomposites.

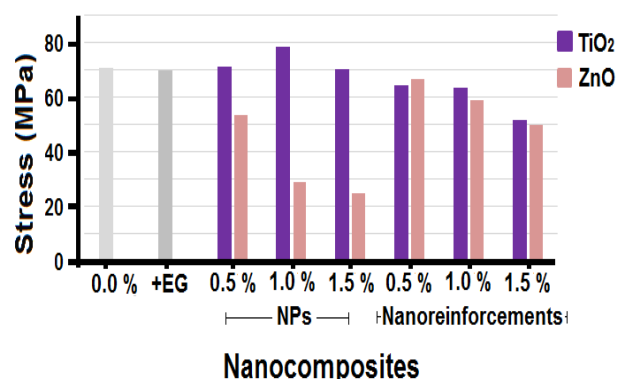| Mixing ratio (%)	Maximum tensile stress, σ (MPa)					
	TNPs	TNTs	ZNPs	ZNBs	Cured resin	+EG
0.5	71.1 ± 9.3	64.3 ± 7.4	53.5 ± 7.6	66,7 ± 6.1	70.8 ± 10.5	70.1 ± 9.7
1.0	78.7 ± 7.1	63,5 ± 10.2	29.0 ± 8.7	58,8 ± 6.4	-	-
1.5	70.6 ± 7.9	51.7 ± 8.3	25.0 ± 9.3	50.0 ± 8.3	-	-

+EG: Ethyleneglycol added to resin.

Figure 11. Maximum tensile stress obtained for each set of test tubes.

The 0.5 % and 1.5 % contributions maintained the mechanical properties, but like the 1.0 % load they potentially delivered new properties to the resin. Similar effects were obtained by Yuanxin Zhou et al. [32], which reports that for 1.0 % of TNPs of size between 5 and 40 nm an increase was achieved, this being lower for 0.5 % and 1.5 %. It can be concluded that the mechanical properties did not vary substantially and in the case of 1.0 % it is feasible to think that the maximum tensile strength was improved, which should be checked by repeating the test.

In the case of TNTs, there was a slight decrease for 0.5 %, following a downward trend for larger quantities, reaching a decrease of 26 % to 1.5 %. The decrease was possibly due to the synthesis, since NaOH was used in a very high concentration which caused the contamination of the mixture. In the case of 1.5 % more noticeably the cause of decrease was due to the fact that the TNTs significantly increased the volume compared to the NPs, Behzad Shirkavand Hadavand et al. [33] reported similar effects, decreases in maximum tensile stress for loads of 1.5 % of NTs due to the formation of agglomerates and the greater volume they possess. These agglomerates cause a propagation of cracks and induce the final failure.

As regards the ZNPs, it is observed that the property of tensile strength was considerably reduced, and the higher the percentage of reinforcement added, the less effort was required to achieve the rupture. Therefore, a decrease was obtained from 23 % with 0.5 % load to 70 % with 1.5 % load compared to the maximum tensile stress of the pure resin. The large particle size, greater than 90 nm, and the irregular size distribution caused abrupt deterioration of the material in response to traction. It is possible that this large size and weight of the nanoparticles produced a decantation, leaving areas with higher percentages and others with lower percentages of charges. Furthermore, these large particles decreased the crosslinking density of the resin, since they occupied a volume that caused the inhibition of the covalent interactions between the epoxy resin and the hardener.

Yu Dong et al. [34] and Leandro José da Silva et al. [35] report that as the particle size grows, the amounts used to achieve a good effect are greater, according to Yu Dong et al. As the aggregate of microparticles increases from 1.0 % to 8.0 %, the tensile stress gradually improves.

For the ZNBs due to the size, the maximum tensile stress for all the loads decreased, with a downward tendency when the percentage of contribution increased. The cause was the large size of the bars and therefore their weight, the size affected the cross-linking and the weight helped the heterogeneity of the mixture. As mentioned above when increasing the size of fill and considering the large size of the ZNBs (practically they are microbars) they decanted and agglomerated, which is harmful and causes disastrous consequences in the material, since they produce a lower maximum tensile stress [36].

The size and the percentage were decisive in the maximum tensile stress, for 1.0 % of TNPs of size of 20 nm an inconclusive improvement was observed, not so for other loads of reinforcements. The best results were obtained for the TiO$_2$

nanostructures because they had a smaller size and a narrow size distribution. On the contrary, the large size and large distribution of these caused the ZnO nanostructures to produce a defective material. The dispersion technique probably influenced, since the larger they have to decant with greater speed, an agglomeration of reinforcements occurs in the lower part of the specimens.

3.2.2 Measurement of mechanical properties by bending test

Standard and rectangular specimens were obtained from a square piece of 100 mm on each side by machining. Five specimens were also used for the bending test (according to ASTM D790). What can be observed in Figure 12.

From the results presented in Table 5 and Figure 13, it is first observed that ethyleneglycol significantly affected the maximum resistance to bending and the maximum deformation by bending (%), increasing the first by 14 % and the second probably exceeding the 5 % deformation limit. The deformation was greater because it acted as a plasticizer, which decreased the intensity of the bonds between polymer molecules, causing a greater free volume between chains [37].

The increase of the modulus and the maximum resistance to bending is not concordant with the theory and it is necessary to carry out a separate study to determine the real effects of ethylene glycol and parameters that may change its behavior.
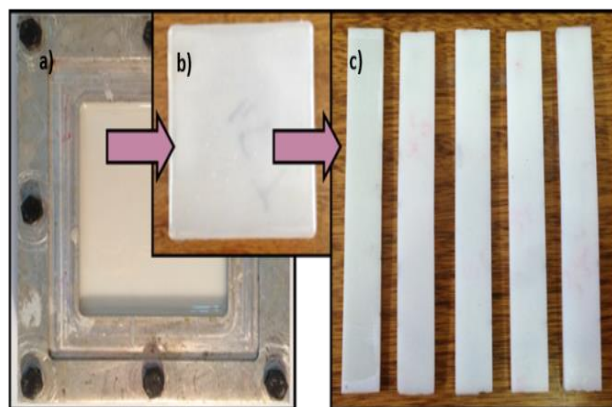

Figure 12. Bending test tubes: a) Obtaining mold, b) Sample for manufacturing test pieces and c) Test tubes machined and ready for the bending test.

For the nanocomposites reinforced with TNPs it was evidenced that the behavior was very similar to the pure resin with respect to the maximum resistance to bending. Figure 13a shows an important change, since a greater deformation and a lower flexural modulus are obtained for all the loads, a result consistent with what was previously explained in traction. NPs both in flexion and traction maintained their properties, adding the greater deformation and less modulus in this last test.

The TNTs contributed a greater elastic deformation, but decreased the maximum resistance to bending. Studies of this group have shown the same result. This is due to the fact that the greater the volumes of the aggregates, the more effective cross-links are avoided. This means that the covalent interactions between the prepolymer (epoxy resin) and the diamine crosslinker are decreased.

The greater deformation is due to the increase of the free volume of the resin, producing movements of the molecular chains. Therefore, at lower efforts greater deformations occur. It should be noted that using 1.0 % of TNTs showed an atypical behavior, which does not agree with the trend shown in Table 5, behavior also exposed in the sample with ethyleneglycol.

On the other hands, by reinforcing the nanocomposites with ZNPs and ZNBs, a much higher decay was obtained due to the large size they possessed. Unlike the TNPs which acted as a brake to the advance of the defects (in stress), the ZNPs and ZNBs have a lot of volume acting as concentrators of stress, causing the failure of the material. In addition, there was a decrease in the formation of bonds in the resin due to this volume which produced a material with greater deformation at equal stresses, but with fracture at low stresses. The effects in the ZNBs were greater than in the ZNPs since they have a larger size and volume.

The guideline that marked the results of this test was a gradual decrease of the maximum resistance to bending, adding a lower flexural modulus for all loads. A material with a lower flexural modulus was achieved. In both tests, the same tendency can be observed in the majority of the elaborated nanocomposites. As mentioned above, size, volume and dispersion marked the performance of nanocomposites.

Table 5. Results obtained by bending tests for nanocomposites.

Mixing ratio (%)	Maximum resistance to bending, (MPa)					
	TNPs	TNTs	ZNPs	ZNBs	Cured resin	+EG
0.5	115.9 ± 0.4	100.6 ± 2.5	82.3 ± 2.8	87.0 ± 4.6		
1.0	107.2 ± 3.2	115.5 ± 1.0	96.7 ± 4.9	80.6 ± 3.5	116,8 ± 4.6	135,7 ± 4.6
1.5	113.1 ± 3.1	98.4 ± 13.6	100.0 ± 6.5	79.7 ± 5.2		

Mixing ratio (%)	Bending module, (MPa)					
	TNPs	TNTs	ZNPs	ZNBs	Cured resin	+EG
0.5	3473.9	3283.5	2752.5	2929.1		
1.0	3416.6	4875.8	3131.6	2874.4	3814.7	5590.1
1.5	3395.2	3340.5	3149.6	2854.1		

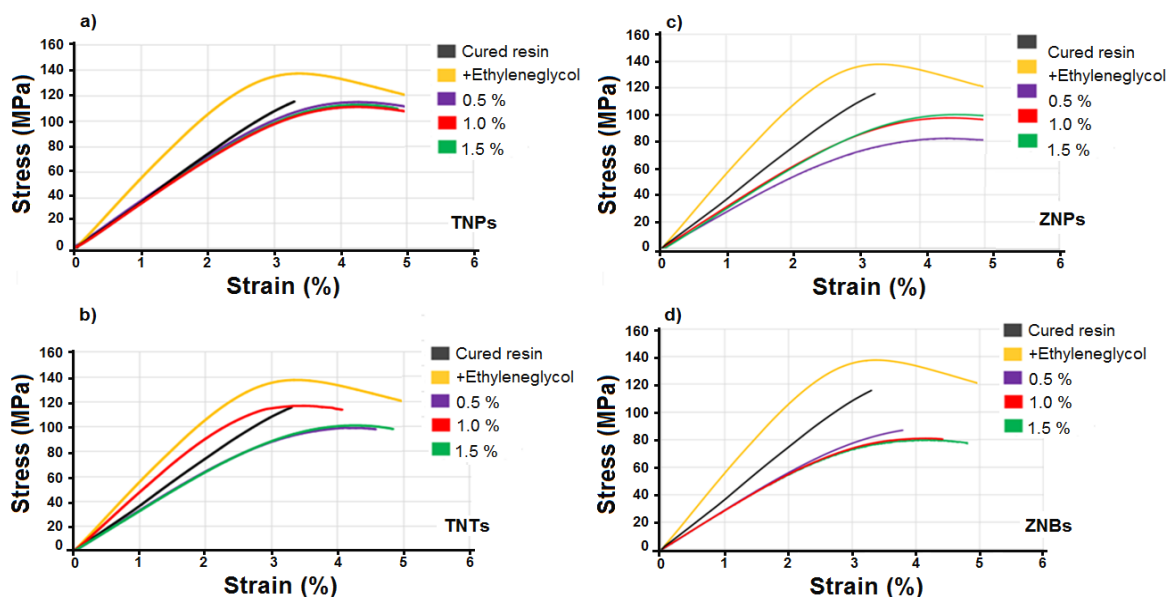+EG: Ethyleneglycol added to resin.

Figure 13. Bending stress curves (MPa) vs Strain in response to bending (%) for epoxy resin, epoxy resin with ethylene glycol and epoxy resin with 0.5 %, 1.0 % and 1.5 % titanium dioxide nanostructures : a) TNPs, b) TNTs and zinc oxide nanostructures: c) ZNPs, d) ZNBs.

Better results were obtained for NPs with sizes of 20 nm and a narrow distribution of these and on the contrary, worse results were obtained for ZNBs and ZNPs which have in common large sizes and wide distribution of these. Probably the mechanical dispersion was affected by the curing time and/or the type of dispersion used, creating gradients of concentrations due to decantation by gravity.

4. Conclusions

From the research carried out, it is concluded that:

• By adding ethylene glycol to the nanostructures, a greater dispersion was achieved in the exterior and a greater affinity of these with the resin, resulting also in a better dispersion in it compared to the nanostructures alone.

• The mechanical properties of the elaborated nanocomposites were studied: maximum tensile stress, maximum flexural strength, flexural modulus and elongation. The NPTs contributed to the material a greater elasticity for the same efforts, in addition to maintaining the other properties studied. The TNTs gradually decreased and slightly the properties measured in tensile and flexion, also achieved a material with lower flexural modulus. For the ZNPs and ZNBs, the maximum tensile stress, maximum flexural

strength and flexural modulus were substantially reduced.

• Properties such as: homogeneity, size, size distribution, and dispersion in the matrix are the 4 characteristics that determined the quality of the nanocomposite.

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Conflicts of interest

The authors declare that they have no conflicts of interest of aby kind in relation to the publication.

Acronyms and symbols

NPs	Nanoparticles
NFs	Nanofibers
NWs	Nanowires
NTs	Nanotubes
TNTs	Titanium dioxide nanotubes
ZNBs	Zinc oxide nanobars
ZNPs	Zinc oxide nanoparticles
σ	Maximum tensile stress
h	Thickness
w	Wide
L	Long

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