Study of the mechanical properties of magnetic composites supported on a PU matrix

Estudio de las propiedades mecánicas de compositos magnéticos soportados en una matriz de PU

MARTINEZ-MORENO, Miguel†, FUENTES-RAMÍREZ, Rosalba*, CONTRERAS-LOPEZ, David and GALINDO-GONZALEZ, Rosario

Universidad de Guanajuato, Natural and Exact Sciences division, Department of Chemical Engineering, Noria Alta S/N, Noria Alta, 36050, Guanajuato, Guanajuato, México.

ID 1st Author: *Miguel, Martinez-Moreno* / **ORC ID**: 0000-0002-0992-8505, **CVU CONACYT ID**: 958747

ID 1st Coauthor: *Rosalba, Fuentes-Ramírez* / **ORC ID**: 0000-0003-0520-3387, **CVU CONACYT ID**: 202669

ID 2nd Coauthor: *David, Contreras-Lopez* / **ORC ID**: 0000-0003-1384-4766, **CVU CONACYT ID**: 38297

ID 3rd Coauthor: *Rosario, Galindo-Gonzalez* / **ORC ID**: 0000-0002-3612-1555, **CVU CONACYT ID**: 223987

DOI: 10.35429/EJT.2021.5.9.8.13 Received March 12, 2021; Accepted June 30, 2021

Abstract

Magnetic nanoparticles have been used to confer better properties to materials, particularly to polymers. Due the properties of the polymer, such as flexibility and lightness, combined, white nanoparticles provide other properties such as microhardness, corrosion resistance, among others. In this study, three types of nanoparticles were elaborated: magnetite, cobalt ferrite and nickel ferrite, through the coprecipitation method used in the elaboration of skin-like polyurethane (PU) -based composites. Specimens were made at different nanoparticle weights (0.1%, 0.3%, 0.5% and 1.0%). Likewise, the hardness was measured by means of a phase II Model PHT-2500 portable digital hardness tester and the tension tests were carried out on an Autograph Shimadzu universal machine. The stress results were plotted using the Jupyter Notebook for interpretation. Finding some improvements in the materials manufactured using the different ferrites already mentioned.

Magnetic nanoparticles, Magnetic polymers, Mechanical properties

Resumen

Se han utilizado nanopartículas magnéticas para conferir mejores propiedades a los materiales, especialmente a los de tipo polimérico. Esto es de gran interés debido a que se combinan las propiedades del polímero, como la flexibilidad y ligereza, mientras que las nanopartículas aportan otras propiedades como lo son la microdureza, resistencia a la corrosión, entre otras. En el presente trabajo se elaboraron tres tipos de nanopartículas: magnetita, ferrita de cobalto y ferrita de níquel, mediante el método de coprecipitación utilizándose en la elaboración de compositos a base de poliuretano (PU) tipo piel. Se elaboraron probetas a diferentes pesos en nanopartículas (0.1%, 0.3%, 0.5% y 1.0%). Asimismo, se midió la dureza por medio de un probador de dureza digital portátil marca phase II Model PHT-2500 y los ensayos de tensión se realizaron en una máquina universal Autograph Shimadzu. Los resultados de tensión se graficaron utilizando Jupyter Notebook para su interpretación. Encontrando algunas mejoras en los materiales fabricados utilizando las distintas ferritas ya mencionadas.

Nanopartículas magnéticas, Polímeros magnéticos, Propiedades mecánicas

Citation: MARTINEZ-MORENO, Miguel, FUENTES-RAMÍREZ, Rosalba, CONTRERAS-LOPEZ, David and GALINDO-GONZALEZ, Rosario. Study of the mechanical properties of magnetic composites supported on a PU matrix. ECORFAN Journal-Taiwan. 2021. 5-9: 8-13

* Correspondence to Author (e-mail: rosalba@ugto.mx)
† Researcher contributing as first author.

June, 2021 Vol.5 No.9 8-13

Introduction

In composites, polymers are among the most used materials as matrix, and polyurethane (PU) has been of great interest due to its wide field of applications. As reinforcement, ferrites have been used for the elaboration of magnetic composites, due to the magnetic properties they present, together with the excellent chemical stability, thermal stability and mechanical hardness, the characteristics of lightness, easy processing, etc., are combined [IV, VI, VIII-X].

Another advantage that exists in the use of ferrites are their low manufacturing cost, and therefore various studies have been carried out on their synthesis and characterization, as well as the resulting properties [III]. On the other hand, polyurethane has been widely used for being a strong and versatile material, besides having properties of a good thermal insulator, low weight, versatility, durability, low cost, and comfort [VII].

That is why the interest in the use of ferrite nanoparticles in polymeric matrices, because together with the improvement of mechanical and chemical properties, it also occurs in electrical conduction and resistance to corrosion of materials [V]. Therefore, magnetic composites are candidates for use as coatings. Finally, it is important to mention that these materials have the property of absorbing microwave frequencies, being applied in the use of coatings and paints [I, II]

Methodology

By the coprecipitation method, three types of ferrites were synthesized, magnetite, cobalt ferrite and nickel ferrite. For them, 0.5 M $FeCl_2$, $CoCl_2$ and $NiCl_2$ solutions, 1 M $FeCl_3$ and 2 M NaOH as precipitating agent were used. The $FeCl_2$, $CoCl_2$ and $NiCl_2$ solutions were mixed with the $FeCl_3$ solution for the elaboration of each ferrite and heated to 80 ° C. Subsequently, 1.2 mL of polyethylene glycol (PEG) were added. The NaOH solution was heated with magnetic stirring to 80 ° C, to destabilize the solution, then the mixture of chloride salts was added dropwise to the NaOH solution. The addition was completed, stirring was maintained for 30 minutes, it was precipitated, and the nanoparticles were washed with distilled water and ethanol. They were left to dry for 24 hours at 70 °C.

For the elaboration of the composites, skin-like polyurethane was used, considering the stoichiometric amounts of polyol and isocyanate. The nanoparticles were added to the polyol with a weight a ratio of 0.1, 0.3, 0.5 and 1.0 % with respect to the mass of the polyurethane. They were mechanically stirred for 5 minutes, the isocyanate was added and stirring was continued for 15 seconds to initiate the reaction. The polyurethane was poured into silicone rubber molds according to the ASTM E 8-79 standard to obtain the composites. All samples were obtained in triplicate.

With the help of an Autograph Shimadzu universal machine, the tension tests were carried out, obtaining the data in Trapezium software and with the help of Jupyter Notebook, the corresponding graphs were generated for their interpretation. A portable digital hardness tester, brand phase II Model PHT-2500 was used for hardness determination.

The interior of the composites was analyzed with the help of an Amszoom microscope, to qualitatively observe how homogeneously the nanoparticles were dispersed within the polymeric matrix.

Results

In Figures 1, 2 and 3 we can see the micrographs of the magnetite, cobalt ferrite and nickel ferrite respectively, observing that the magnetite has a particle average size of 30 nm and present spherical shapes, the cobalt ferrite has average size of 20 nm and with hemispherical particles, in addition to presenting an agglomeration and, finally, the nickel ferrite has average size between 40 nm, with a spherical shape and agglomerations.

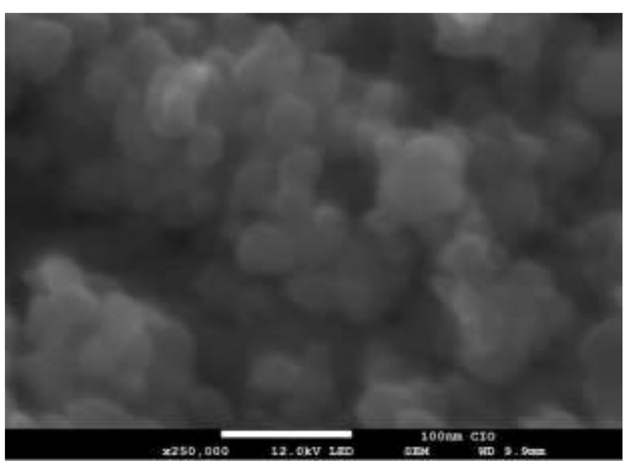

Figure 1 Magnetite micrograph
Source: Own Work [JEOL SU 3500 SEM Hitachi]

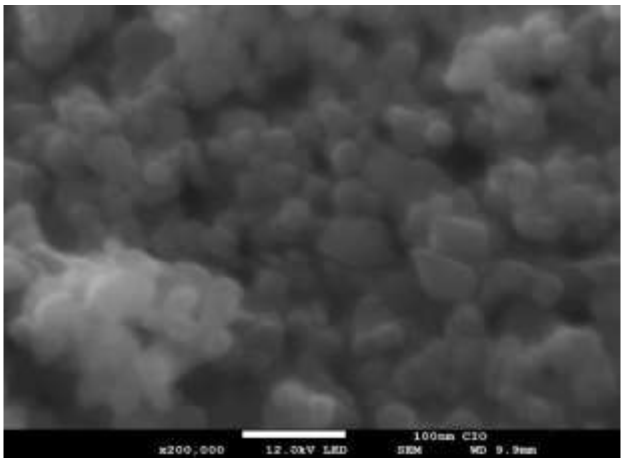

Figure 2 Cobalt ferrite micrograph
Source: Own Work [JEOL SU 3500 SEM Hitachi]

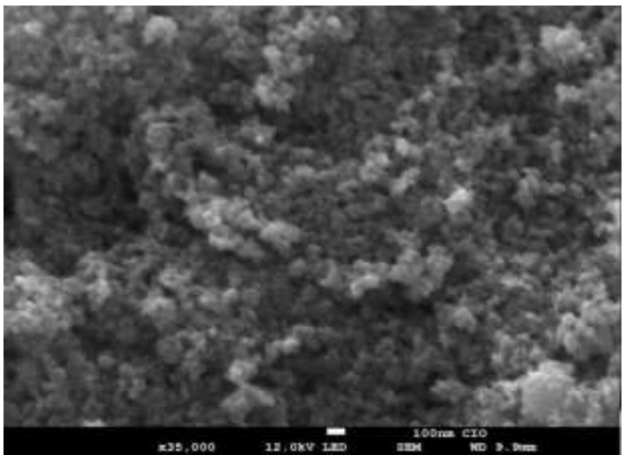

Figure 3 Nickel ferrite micrograph.
Source: Own Work [JEOL SU 3500 SEM Hitachi]

Figure 4 shows the polyurethane specimen obtained without the addition of nanoparticles, while Figure 5, 6 and 7 show the polyurethane composites with different percentages of magnetite, cobalt ferrite, and nickel ferrite respectively.

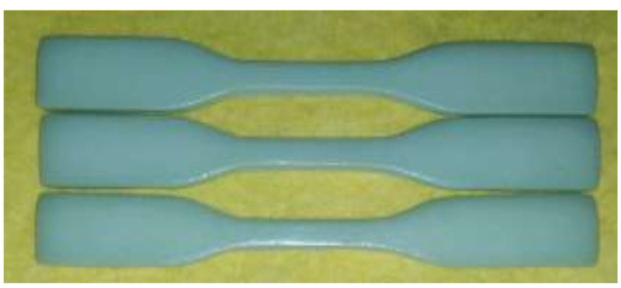

Figure 4 Polyurethane with 0% NPS
Source: own work.

Figure 5 Magnetite composites. Top left (0.1%), top right (0.3%), bottom left (0.5%) and bottom right (1.0%).
Source: Own Work.

Figure 6 Cobalt ferrite composites Top left (0.1%), top right (0.3%), bottom left (0.5%) and bottom right (1.0%).
Source: Own Work

Figure 7 Nickel ferrite composites. Top left (0.5%), top right (0.1%), bottom left (1.0%) and bottom right (0.3%)
Source: Own Work

The color change that the composites acquire when adding the nanoparticles (NPS) in their different concentrations to the polymer matrix is appreciated. It should be noted that, by increasing the concentration of nanoparticles in the composite, they begin to agglomerate as can be seen in the Figures 8, 9 y 10

Also, it is important to note that depending on the composite, there is a different behavior, such is the case of magnetite composites, where there was a good distribution below 0.5% w/w, while at 1.0% w/w, the nanoparticles began to agglomerate. With cobalt ferrite, agglomeration occurred from 0.1% w / w, which increased when adding more nanoparticles.

Finally, in nickel ferrite composites at low percentages there is no agglomeration, but from 0.5% w / w agglomeration of the nanoparticles start. These agglomerations can be observed with the naked eye on the surface of the composites, but it is more visible when the interior is analyzed under the microscope as can be seen in the (see Figures 8, 9 y 10).

Figure 8 PU-magnetite interior (0.3% w / w)
Source: own work [Amszoom Microscope]

Figure 9 PU-Cobalt Ferrite interior (0.3% w / w)
Source: own work [Amszoom Microscope]

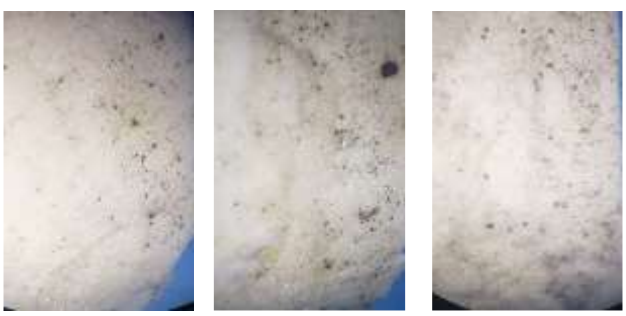

Figure 10 PU-cobalt ferrite exterior (0.3%, 0.5% and 1.0% w / w)
Source: own work [Amszoom Microscope]

The data obtained from the stress tests were obtained from the Trapezium software, load data (kN) and elongation length, with these data the stress (MPa) and deformation (%) were obtained, the corresponding graphs are presented in the Figures 11, 12 y 13.

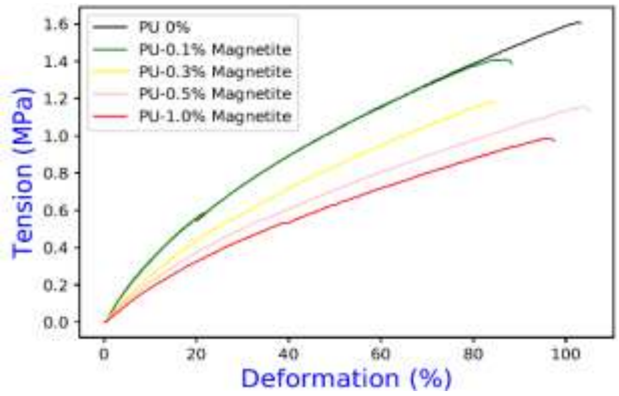

Figure 11 PU-Magnetite tension test
Source: own work [Jupyter Notebook].

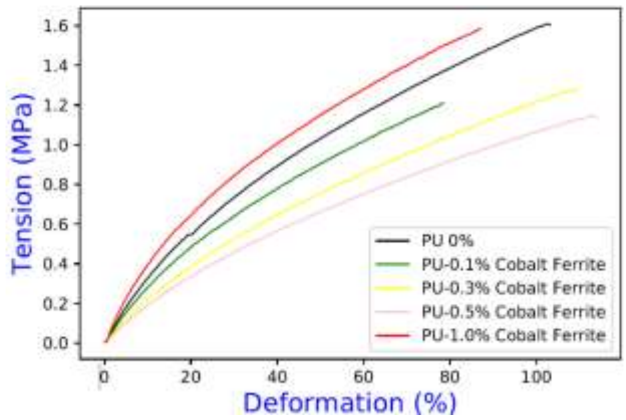

Figure 12 PU-Cobalt Ferrite tension test.
Source: own work [Jupyter Notebook]

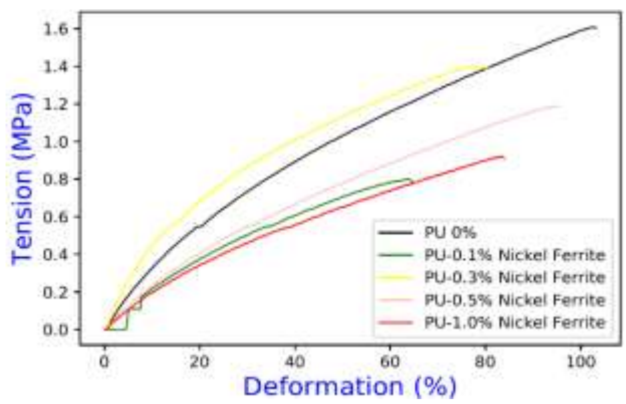

Figure 13 PU-Nickel Ferrite tension test
Source: own work [Jupyter Notebook]

We can see that when comparing the tensile strength of composites with magnetite, the material without nanoparticles is the one with the highest resistance, although the composite at 0.1% w/w presents a similar behavior, as nanoparticles are added, the resistance to tension, this is due to the fact that when adding nanoparticles, there are less crosslinks between the polymer chains, resulting in lighter materials with greater porosity, causing a decrease in the number of links between PU main chains and, therefore, decreases the tension.

When cobalt ferrite is added to matrix, the results are not improved to 0.1, 0.3 and 0.5% w/w since the resistance is decreased, although the ductility increases, since these materials reach greater deformations before fracture. It is interesting that at 1.0% w/w the tensile strength grows even above the composite without nanoparticles. The tension decreases due to what has already been explained about the crossovers, logically adding 1.0% w/w of cobalt ferrite should further decrease the tensile strength. This may be since at a certain moment said property no longer depends on the polymeric material and its chains, but rather on the reinforcement and its intrinsic properties, occupying the gaps that are available in the matrix.

On the other hand, when analyzing the composites with nickel ferrite, it is observed that at 0.1% w/w the resistance is very low and when adding 0.3% w/w the effort increases considerably since it presents a zone of notorious stiffness, the composites with 0.5 and 1.0% w/w show a decrease in effort for what has already been explained. The composition at 0.3% presented a good distribution of nanoparticles, hence it has presented better results.

It must be considered that these results depend on the homogenization of the nanoparticles in the matrix. We determined that the material with the best tensile strength is the 1.0% cobalt ferrite composite, which could be due to the nanoparticle size and distribution in the sample. To obtain better results, composites could be made using some method to better homogenize the nanoparticles, since mechanical agitation is not the best option. The presence of nanoparticles as reinforcement provides the composite with an increase in hardness with respect to the polymer, since the lower hardness occurs when the material does not have nanoparticles and as they increase, the hardness increases. Tables 1, 2 and 3 show the results obtained from the hardness tests for the polyurethane composites with magnetite, cobalt ferrite, and nickel ferrite, respectively.

Ferrite percentage (%)	Average hardness (HB)
0.0	182
0.1	200
0.3	197
0.5	207
1.0	217

Table 1 Hardness measured for the PU-Magnetite composite
Source: Own Work [Word]

In the PU-Magnetite composites it is observed that when adding nanoparticles, the hardness increases, when it reaches 1.0% w/w the highest hardness is reached, and we could observe that at 0.3% w/w the hardness decreases with respect to 0.1% w/w, which could be due to the presence of the NPS in the polymeric matrix but also to the intermolecular forces that are generated such as those of Van Der Waals or dipole moments.

Ferrite percentage (%)	Average hardness (HB)
0.0	182
0.1	202
0.3	210
0.5	210
1.0	193

Table 2 Hardness measured for the PU-Cobalt Ferrite composite
Source: own work [Word]

The PU-Cobalt Ferrite composites show that there is also a considerable increase in hardness when increasing the number of nanoparticles, although from 0.5% w/w no improvement, since the same results are obtained as at 0.3% w/w even at 1.0% w/w there is a decrease in hardness.

The explanation as already mentioned, of intermolecular forces that occur inside the matrix together with the lower presence of nanoparticles at that point could explain the decrease in hardness.

Ferrite percentage (%)	Average hardness (HB)
0.0	182
0.1	199
0.3	210
0.5	215
1.0	195

Table 3 Hardness measured for the PU-Nickel Ferrite composite
Source: own work [Word]

Finally, composites with Nickel Ferrite also show an increase as the number of nanoparticles increases. Similarly, the hardness increases up to 0.5% and when the number of nanoparticles is doubled, the hardness decreases considerably.

Acknowledgment

The authors are grateful to the University of Guanajuato (UG) for its financial support of this work (2021). Miguel Angel Martinez acknowledges to Mexican Council for Science and Technology (CONACyT) for her master's scholarship and CIIC UG 135/2021 "Generation of polymeric nanocomposites for the development of surface protection and analysis of the resulting mechanical properties"

Conclusions

It is possible to obtain a synergy between the properties of the polyurethane and the ferrite nanoparticles, obtaining improvements in the mechanical properties, being more evident in the hardness of the materials than in the resistance to tension, where due to the porosity and agglomerations of the nanoparticles the best results were not obtained.

References

[I] Acikalin, E., Atici, O., Sayinti, A. & Coban, K., Erkalfa, H. (2013). Preparation of dendritic waterborne polyurethane-urea/Ni–Zn ferrite composite coatings and investigation of their microwave absorption properties. Progress in Organic Coatings, 76, 972-978.

[II] Asadinia, E., Pakshir, M & Hosseini, S. (2020). Synthesis of (Ba4Zn2-xMnxFe36O60) U-type hexaferrite pigments and studying their influence on the protective performance, mechanical behavior and microwave absorption properties of polyurethane paint coatings. Progress in Organic Coatings, 139, 1-17

[III] Facundo I. & Trejo M. (2017). Magnetita nanoparticulada y los métodos más utilizados de obtención. Coordinación General de Estudios de Posgrado e Investigación, 52, 1-12.

[IV] García C., Escareño, C. (2006). Preparación de compósitos magnéticos mediante la síntesis in situ de nanopartículas magnéticas de una matriz polimérica. Sociedad Mexicana de Ciencia y Tecnología de Superficies y Materiales , 19, 20-24.

[V] Martínez M., Gamez, C., Fuentes, R. & Contreras D. (2020). Study of the anticorrosive properties of magnetic composites. Journal of Technology and Innovation, 7, 13-18.

[VI] Muntean, E., Stoia, M. & Pacurariu, C. (2018). Facile synthesis, characterization and magnetic properties of manganese ferrite/carbon composites. Thermochimica Acta, 667, 122-131.

[VII] Vasco N., Ferreira A. & Barros T. (2018). Polyurethane Foams: Past, Present, and Future. Materials, 11, 1-35.

[VIII] Lara P. (2005). Síntesis y caracterización de nanocompositos magnéticos. Ingenierías, 8, 47-51.

[IX] Prokopenko, S., Mazurenko, R., Gunja, G., Abramov, N., Makhno, S. & Gorbyk, P. (2020). Electrophysical properties of polymeric nanocomposites based on cobalt and nickel ferrites modified with copper iodide. Journal of Magnetism and Magnetic Materials, 494, 165.

[X] Soto, G., Meiorin, C., Actis, D., Mendoza Z., Moscoso L., Muraca, D., Mosiewicki, M & Marcovich N. (2018). Magnetic nanocomposites based on shape memory polyurethanes. European Polymer Journal, 109, 8-15

.