Mechanical Reinforcement of Epoxy Resins using Magnetic Aligned Halloysite

A. Gonzalez-Montiel*, S. Mendoza-Bello*, S. Barrientos-Ramirez*,
L. Flores-Santos*, and G. Montes de Oca-Ramirez*
*CID-KUO, Centro de Investigación y Desarrollo Tecnológico,
52000 Lerma, México. alfonso.gonzalez@desc.com.mx

ABSTRACT

In this work we report the synthesis of magnetite nanoparticles over halloysite (HT) in order to transform this mineral filler into a magnetically alignable material for epoxy nanocomposites. Halloysite nanotubes are treated using a two steps activation method (Sn/Pd) followed by a third step to form the ferrite by means of a coprecipitation method. The ferrite deposits as nanoparticles with a narrow distribution particle size in the range of 3 to 5 nm, as determined by TEM. The crystallinity of the nanoparticles was confirmed by HRTEM and SAED. The use of magnetic Halloysite as "intelligent" polymeric nanofiller in epoxi resins was explored controlling the alignment by means of a magnetic field, obtaining an oriented reinforcement. The magnetic clay-polymer nanocomposites were observed using Optical Microscopy in order to confirm the alignment of the magnetic halloysite nanotubes.

Keywords: Halloysite, magnetic alignment, epoxy nanocomposites, magnetite nanoparticldes and mechanical reinforcement.

1 INTRODUCTION

The orientation of polymer chains subjected to the influence of external electric fields has been an area of extensive study. Controlling the orientation of organic molecules with electric and or magnetical fields has played an important role in commercially interesting devices. The magnetic-field-induced alignment of polymeric materials has been the focus of several research efforts because of the increased reinforcements on mechanical properties due to the anisotropic behavior [1-4]. Polymeric materials can interact with a magnetic field through the diamagnetic anisotropy of the constituent chemical units. The application of a magnetic field during polymer processing produces enhanced mechanical and physical properties with respect to mechanical stretching. In a study, Manko et al.[5] investigated the effect of weak magnetic fields on the properties of Aramid fiber reinforced epoxy plastics and they reported that the ultimate strength and Young's modulus were increased.

Recently, special attentions have been directed to the combination of iron oxide nanoparticles and nanosized materials such as carbon nanotubes (CNTs). Georgakilas et. al. attached magnetite nanoparticles on CNTs by means of an interlinker molecule [6]. Kim et. al. described a method for the decoration of CNTs with monodisperse γ-Fe2O3 magnetic (maghemite) nanoparticles by a modified sol-gel process [7]. Qu et al. published a study that the Fe_2O_3 nanoparticles were introduced into the CNTs via a wet chemical method [8]. Tan et al. published a work that the magnetic iron oxide particle deposition could be controlled selectively on the outer, inner, or both surfaces of CNTs [9]. It is also known that the addition of a nanofiller to a polymeric material enhance the mechanical properties of the composite and if the nanofiller is preferentially oriented an additional increment in the mechanical properties is observed[10].

In the present study, we report the synthesis of an epoxy-compatible nanoclay based on a purified Halloysite, . Halloysite (HT) is a aluminosilicate clay, possessing hollow tubular structure in the submicrometer range. The halloysite tubes were covered with magnetite nanoparticles (here referred to as clay-magnetite) and were used to reinforce the mechanical properties of the epoxy resin due to a magnetic orientation of the clay-magnetite particles.

2 EXPERIMENTAL

Polymer composites of clay-magnetite and epoxy resin were prepared by metalizing a commercial grade of halloysite nanoclay (the clay was supplied Macro-M) that was surface modified with a block copolymer compatible with PMMA. The metalized clay will hereafter be identified as FHTFe.

In order to obtain the clay-magnetite composite a synthesis of magnetite nanoparticles over the purified halloysite was carried out first sensitizing the surface using a two steps activation method (Sn/Pd) followed by third step to obtain the ferrite by a common chemical coprecipitation technique [Figure 1]. A narrow distribution of particle size from 3-5nm was found by TEM. The crystallinity of the nanoparticles was confirmed by HRTEM and SAED. To confirm the magnetic properties of the clay-magnetite composite VSM was performed.

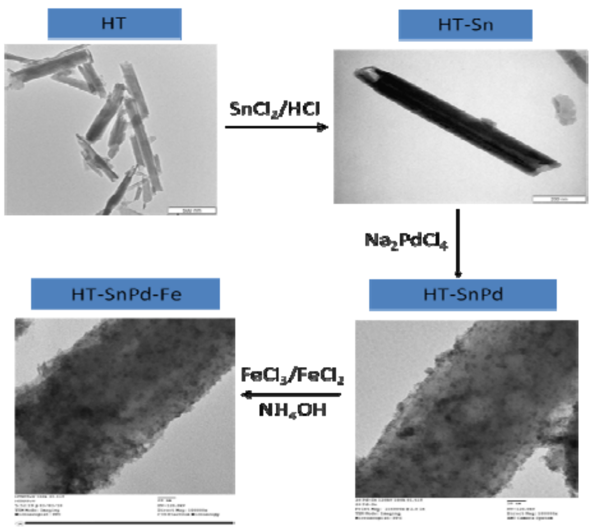
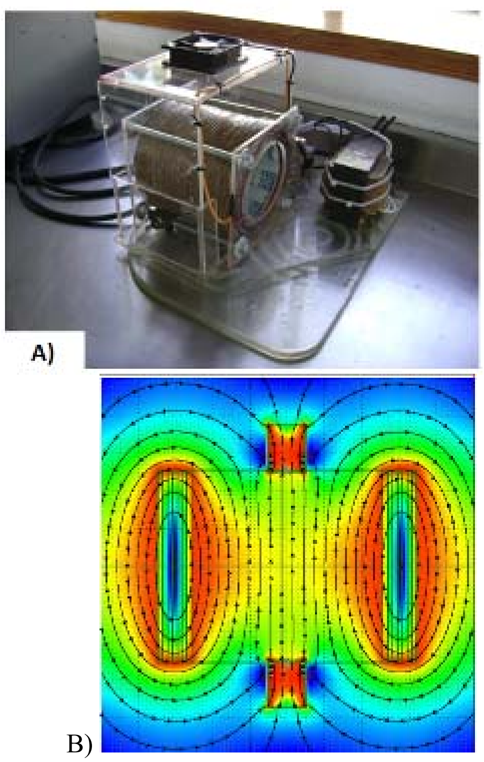


Figure 1. Steps of the metallization process of Halloysite

The final composites were prepared by dispersing the magnetic halloysite into epoxy resin (Epon 828) and then proceeding to cure with triethylenetetramine (TETA) inside an electromagnet [Figure 2A].



B)

Figure 2. A) The electromagnet used to generate the magnetic alignment of Halloysite and B) lateral view of the electromagnet representing the final alignment expected on the epoxy samples.

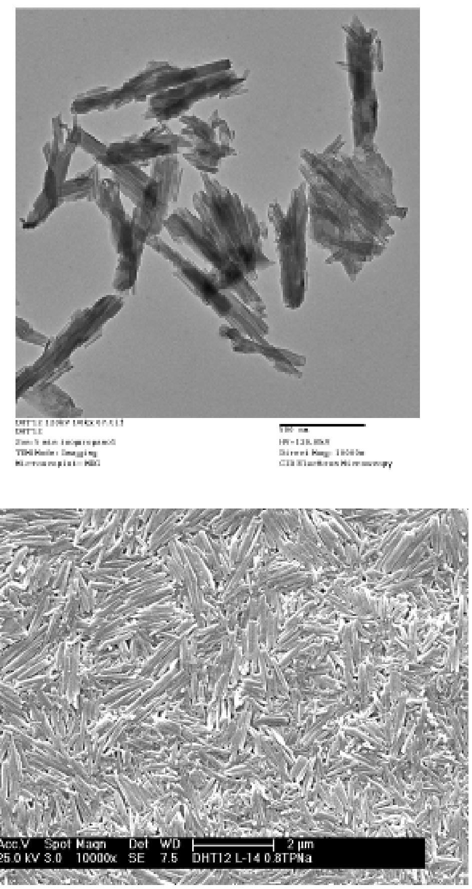
The use of the magnetic Halloysite as "intelligent" polymeric nanofiller in epoxy resin was explored at three different levels 0.5, 1 and 2 weight percent. The controlled alignment was achieved by means of a directional magnetic field, obtaining the oriented reinforcement [Figure 2B]. The microstructure evolution and alignment due to the magnetic processing of the clay-magnetite/epoxy system was evaluated by optical microscopy. The mechanical behavior of the magnetically processed epoxy composites was determined in a uniaxial tensile testaccording to ASTM D638.

3 RESULTS AND DISCUSSION

3.1 Halloysite Characterization.

SEM (FEI-Phillips XL30) and TEM (JEOL 1200EX) were performed on the samples of halloysite [Figure 3], from them it can be seen that the material is highly pure and shows an homogeneous tubular morphology with an external diameter between 100-200nm, an internal diameter of 20-50nm and a length of 0.5-1.5microns.

A)

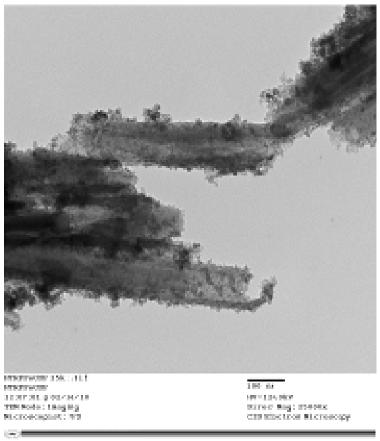


B)

Figure 3. A) TEM and B) SEM images of the pure HT obtained from MacroM.

3.2 Clay-magnetite characterization.

Figure 4 depict TEM photomicrographs of the halloysite clay after the metallization process. Deposits of iron on the nanotubes are readily apparent, their morphology and size are also well determined in these pictures.



A)

B)

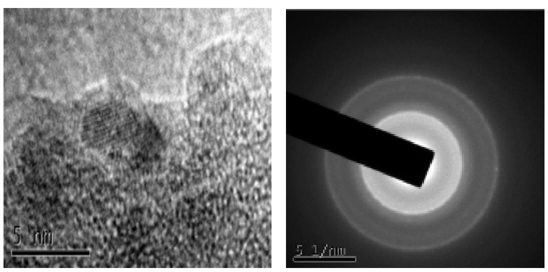


Figure 4. TEM images of A) the magnetite metalized HT, B) High Resolution image and SAED respectively of the magnetite metalized HT.

The magnetite nanoparticles deposit on the surface of the halloysite with high dispersion and homogeneity in sizes ranging from the 3-5nm. A potential superparamagnetic effect can be expected due to the small size of the magnetite which will help on the alignment of the material once dispersed into the epoxy resin.

.

3.3 Optical Microscopy characterization of Clay-magnetite/Epoxy composites

Once the nanocomposites were cured inside the electromagnet their morphology was assessed by optical microcopy [Figure 5] to confirm the degree of alignment of the magnetic material.

A)

B)

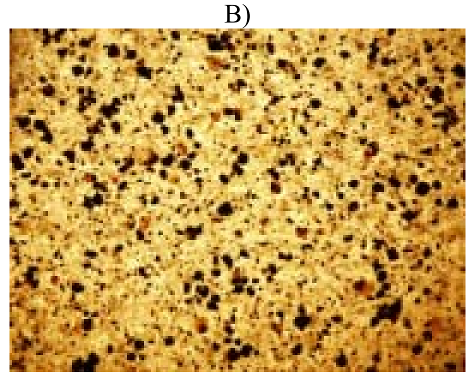


Figure 5. Optical Microscope images of the aligned clay-magnetite/epoxy composites with 1% load of magnetic HT . Up to down 4X amplification (A) with magnetic field (B) without magnetic field.

Figure 5 shows that the clay-magnetite material is highly aligned inside the epoxy matrix on a preferred direction according to the flux lines inside the electromagnet. Clusters/agglomerates of magnetic material are already apparent at the 1.0 weight percent loading of the magnetite clay. From a second set of micrographs is possible to conclude that. compositions with 2 weight percent of the magnetic halloysite show increased clustering of the filler and this should also influence negatively the mechanical properties due to the lack of dispersion of the filler.

3.4 Mechanical characterization of Clay-magnetite/Epoxy composites

A uniaxial tensile test (according to ASTM D638-) was performed on the cured samples of clay magnetite and epoxy. Data onmodulus, strain at break and stress at break rare summarized on Figures 6 to 8.

Note: the nomenclature SC and CC correspond to the samples without magnetic alignment and with magnetic alignment respectively.

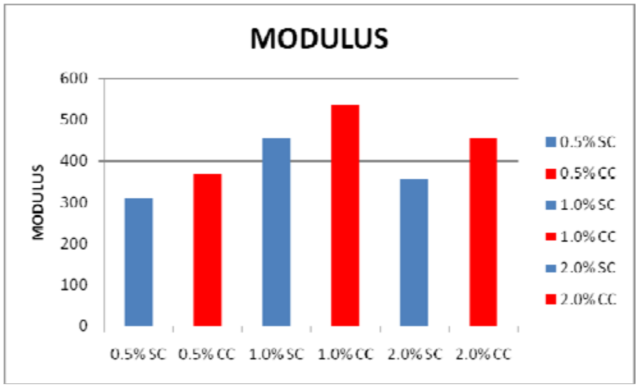


Figure 6. Tensile modulus results.

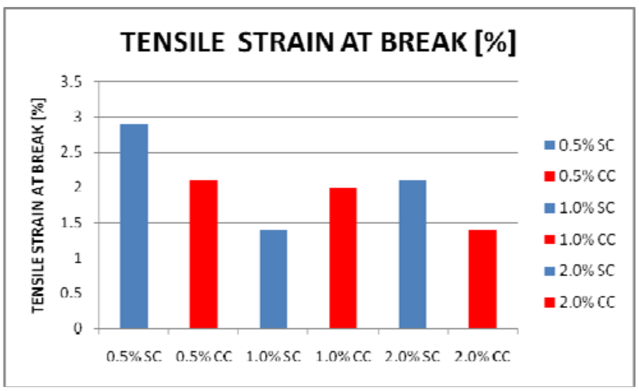


Figure 7. Strain at break results

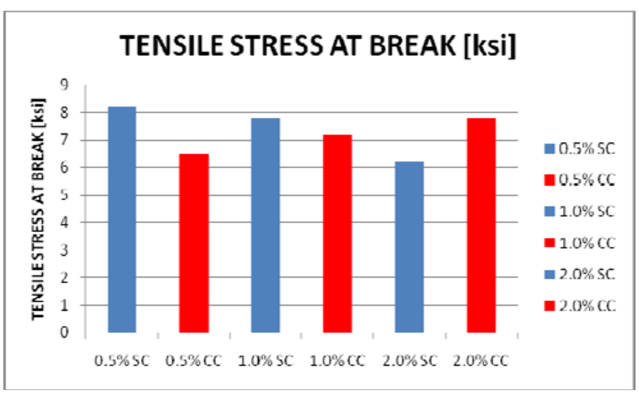


Figure 8. Stress at break results

Tensile measurements correlate well with the results of optical microscopy, the best reinforcement is obtained when the composites have a 1 weight % of the clay-magnetite. It is also important to note that this composition also shows the best reinforcement of the samples prepared without magnetic alignment. More studies on this effect have to be carried out tofully explain this phenomena.

4 CONCLUSIONS

Composites of magnetic metalized halloysite and epoxy were obtained. Magnetic alignment was effectively induced in these composites using the parallel magnetic field generated by an electromagnet. Clustering or aggregation of the magnetic material was observed to be a function of the effective weight loading of the composites. Composites with one percent weight loading of the clay-magnetite render the best increment in mechanical and thermal properties as compared to 0.5 and 2 weight percent compositions.

.

REFERENCES

[1] Benicewicz, B. C.; Smith, M. E.; Earls, J. D.; Priester, R. D.; Setz, S. M.; Duran R. S.; Douglas, E. P. Macromolecules, 31, 4730 (1998).
[2] Ezure, H.; Kimura, T.; Ogawa, S.; Ito, E. Macromolecules, 30, 3600 (1997).
[3] Anwer, A.; Windle, A. H. Polymer, 34, 3347 (1993).
[4] Al-haik, M. S.; Garmestani, H.; Li, D. S.; Hussaini, M. Y.; Sablin, S. S.; Tannenbaum, R.; Dahmen, K. J. Polym. Sci.: Part B: Polym. Phys., 42, 1586–1600 (2004).
[5] Manko, T. A.; Dzhur, E. A.; Sanin, F. P.; Ermolaev, I. M. Mech Compos Mater, 37, 174 (2001).
[6] Georgakilas, V.; Tzitzios, V.; Gournis, D.; Petridis, D. Chem. Mater., 17, 1613 (2005).
[7] Kim, I. T.; Nunnery, G. A.; Jacob, K.; Schwartz, J.; Liu, X. T.; Tannenbaum, R. J. Phys. Chem. C, 114, 6944 (2010).
[8] Qu, S.; Huang, F.; Yu, S. N.; Chen, G.; Kong, J. L. J. Hazard. Mater., 160, 643 (2008).
[9] Tan, F. Y.; Fan, X. B.; Zhang, G. L.; Zhang, F. B. Mater. Lett., 61, 1805 (2007).
[10] Pan, J.; Yao, J.; Xu, L.; Ou, H.; Huo, P.; Li, X. and Yan, Y. J. Phys. Chem C. 115, 5440-5449 (2011).