Influence of flame retardants on the mechanical properties of glass fiber reinforced compounds in polymeric matrix epoxy and polyester

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Abstract. In the present study, polymeric epoxy and polyester resin reinforced with glass fiber compounds were prepared by adding of flame retardants based on aluminum and magnesium hydroxide in order to evaluate their influence on mechanical properties. An experimental DOE design was developed with two qualitative factors: the resin and retardant type; with two levels each and a quantitative factor: volumetric composition of the retardant with three levels (3%, 6% and 9%). With all possible combinations; tensile, flexural and impact tests were carried out. The results showed that the addition of retardants in different percentages has different influence for each mechanical property. It was evidenced that the 9% HA Aluminum Hydroxide has no significant effect on the tensile strength and its modulus compared to Magnesium Hydroxide HM. Conversely; on the flexural strength, flexural modulus and rupture energy the HM has a slightly lower effect with respect to the HA. For flexural strength and its modulus, the best proportion of retardant was 6%. 3% is the recommendation for rupture energy. The data presented in this document can be used to improve the fire resistance of the existing materials studied.

1. Introduction
The fiberglass has been constituted in an engineering material widely used to improve the mechanical resistance of polymeric materials [1, 2]. The glass fiber reinforced polymer matrix composite has been used in the manufacture of various products due to its excellent physical and mechanical properties. It has been used in the automotive, aeronautical and naval industries as a coating for sports products, in the construction industry in devices such as skylights and decorative elements, as well as in various sports equipment. However, the flammable capacity of polymeric resins induces a potential fire risk for those products. Therefore, in recent years the concern of researchers in materials is the improvement of flame retardancy [3-5].
Industries such as the automotive, aeronautical and nautical industries make great efforts to improve the flame behavior of the composite materials used in the manufacture of their products. Positive results have been found with the use of flame retardants. Flame retardants are chemical substances that are added to polymeric compounds generally in the form of particles (powders) in controlled weight ratios. Several researchers have tested a series of organic and inorganic flame retardants to reduce the flammability of polymeric compounds [6]; In addition, they seek to determine the effect of these on the final mechanical properties [7, 8].
A composite material is a combination of two or more primary materials (metallic, non-metallic, ceramic and plastic). Generally, one of these materials is constituted as a matrix and another as a reinforcement. In glass fiber reinforced polymer composites, the matrix is made up of resin (Epoxy, polyester, etc.) and reinforcing or reinforcing material woven or small cross-linked glass fibers, manufactured by different techniques. Different percentages by weight of the reinforcement material and its shape affect the properties the physical-mechanical properties of the compound [9-12]. Studies have been reported on the positive influence of flame retardants based on aluminum hydroxide and magnesium hydroxide [13-16]; results of these studies showed that the flame resistance of the compounds improved significantly with the addition of said retardants, without considerable adverse effect on the final mechanical properties [8, 13, 17, 18]. One of the advantages over the use of these retardants is that during exposure to the flame, water and non-flammable gases are released, so that the increase in the propagation of the fire is reduced. In addition, they can also absorb heat through reactions that release gas, which produces some cooling. These advantages, among others, have been the reasons for its very common use in many applications [19, 20].

The purpose of this study is to design an experiment to investigate the use of aluminum hydroxide and magnesium hydroxide as filler material to manufacture fiberglass reinforced epoxy and polyester polymeric composite materials; at the same time detect their effects on the mechanical properties.

2. Experimental development

2.1. Design of experiments

An experimental design was established by a factorial design 3^3 (Table 1). Two qualitative variables (type of resin, type of retardant) and a quantitative variable (volumetric composition of the retardant) were used, at two and three levels respectively. Through all possible combinations obtained from the DOE, 5 mechanical properties of the composite material were evaluated: tensile strength (TS), tensile modulus (TM), flexural strength (FS), flexural modulus (FM) and impact resistance (IR). According to specific regulations, 5 replicas were executed for each experimental combination; obtaining 60 experimental runs for each property.

| Factors                          | Low     | medium | High   |
|----------------------------------|---------|--------|--------|
| Type of resin                    | Epoxy   | Polyester | -      |
| Type of retardants               | Aluminum hydroxide | Magnesium hydroxide | -      |
| Volumetric composition of the retardant | 3%      | 6%     | 9%     |

2.2. Preparation of the composite material

For the elaboration of the compound were used: polyester resin series Reichold 33200 Polylite and Repox 6090A and epoxy resin brand QquadCarbon. The reinforcement material was fiberglass type EMC 450 brand Taishan Fiberglass from China. Retardants: Extra pure aluminum hydroxide powder (Fisher Scientific brand) and magnesium hydroxide (grade 95% reagent, Sigma-Aldrich brand). The compound was manufactured by manual stratification, the overall volumetric composition is 70% matrix and 30% reinforcement. The formulations of the compounds are presented in Table 2.

| Material combinations   | Composite (%) |
|-------------------------|---------------|
|                         | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12 |
| Fiberglass              | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
| Epoxy Resin             | 67 | 64 | 61 | 67 | 64 | 61 | -  | -  | -  | -  | -  | -  |
| Polyester resin         | -  | -  | -  | -  | -  | -  | 67 | 64 | 61 | 67 | 64 | 61 |
| Aluminum hydroxide      | 3  | 6  | 9  | -  | -  | -  | 3  | 6  | 9  | -  | -  | -  |
Magnesium hydroxide - - - 3 6 9 - - - 3 6 9
Total 100 100 100 100 100 100 100 100 100 100 100 100

The composition of the retardant is part of the 70% matrix. No reports have been found on minimum ranges established for the addition of flame retardants in composites of resinous matrix, so it was based on compositions smaller than those used by [21].

2.3. Mechanical characterization
The mechanical tensile, flexural and impact tests were followed by the instructions specified in the ASTM D3039-08, ASTM D7264M-07 and ASTM D5628-10 standards respectively; about the preparation of test tubes and testing.

3. Results and discussion

3.1. Experimental analysis
The experimental design was analyzed in Minitab18.1 Statistical Software. Table 3 shows the average of the five replications of the mechanical properties RT, MET, RF, MEF and ER evaluated by destructive tests under previously determined regulations.

Table 3. Average values of Ra and Fd for AGFRP y CGFRP.

| Nº | RESINE | RET | % RET | RT  | MET  | RF  | MEF  | ER  |
|----|--------|-----|-------|-----|------|-----|------|-----|
| 1  | Epoxy  | HA  | 3     | 72,65 | 2037,13 | 196,78 | 5794,06 | 2,53 |
| 2  | Epoxy  | HA  | 6     | 85,32 | 2030,61 | 152,45 | 4495,37 | 2,73 |
| 3  | Epoxy  | HA  | 9     | 79,35 | 2161,81 | 131,85 | 3754,27 | 4,00 |
| 4  | Epoxy  | HM  | 3     | 60,37 | 1819,70 | 134,41 | 3831,63 | 4,42 |
| 5  | Epoxy  | HM  | 6     | 56,56 | 1465,06 | 161,54 | 5082,48 | 2,98 |
| 6  | Epoxy  | HM  | 9     | 57,34 | 1710,30 | 154,34 | 4481,84 | 3,56 |
| 7  | Polyester | HA | 3     | 52,96 | 1980,84 | 163,63 | 4892,47 | 3,35 |
| 8  | Polyester | HA | 6     | 80,09 | 2305,82 | 206,41 | 7518,99 | 3,20 |
| 9  | Polyester | HA | 9     | 92,08 | 2801,39 | 141,12 | 5044,56 | 1,70 |
| 10 | Polyester | HM | 3     | 41,82 | 1715,90 | 150,18 | 4763,11 | 2,57 |
| 11 | Polyester | HM | 6     | 52,67 | 2309,97 | 254,09 | 10705,51 | 2,61 |
| 12 | Polyester | HM | 9     | 90,68 | 2670,32 | 198,07 | 6860,84 | 2,25 |

In Figure 1 we show the main effects of the factors on the output variable (mechanical properties). Regarding RT (Figure 1a); none of the resins offers a maximization, so any of the 2 could be used. the retardant that allows obtaining the highest value of RT is HA. Also, it is indicated that for there to be a maximization of the value of RT it is necessary to use 9% of flame retardant. In the case of FT (figure 1b), the resin that offers a maximization for FT is polyester. On the other hand, the flame retardant that allows to obtain a better behavior to the flexion is the HM, adding itself in volumetric composition of 6%. With respect to ER (Figure 1c), the resin that allows obtaining the highest value of ER is epoxy. The inclusion of the flame-retardant HM allows obtaining the maximum ER by adding a 3% volumetric fraction.
Figure 1. Main effects of factors on mechanical properties. a) Tensile strength, b) Flexural strength, c) Rupture energy.

Figure 2 shows the interactions of the factors and how they affect the mechanical properties RT, FT and ER. In general, the compound with polyester resin shows a better performance of RT and FT using any flame retardant in percentages of 6 and 9%. In contrast, the epoxy matrix compound shows less affectation to its tenacity (ER).

Figure 2. Interactive effects of factors on mechanical properties. a) Tensile strength, b) Flexural strength, c) Rupture energy.
The flame-retardant HA in volumetric composition of 9% shows the least affectation to RT of the compound with polyester matrix (Figure 2a). In the case of FT, the best configuration was: polyester matrix stratified with 6% of HM (Figure 2b). Finally, the tenacity of the compound had less affectation when 3% of the HM retarder was occupied in the epoxy matrix; however, when increasing the percentage of retardant, HA shows less influence than HM (Figure 2c). The global effects are shown in figure 3. For both RT and RF (Figure 3a and 3b respectively), the application of retardant with different addition percentages influences resistance, not so much in ER (figure 3c), where its influence is not significant. This is supported by an ANOVA analysis performed in parallel to the experimental analysis with an adjustment of 61% and with 95% confidence. Although the value of the obtained adjustment was not very high, this gives us an expectation to the experimental continuation with greater replicas and a study in greater depth with each of the fire retardants.

![Figure 3. Effects of experimental factors on mechanical properties. a) Tensile strength, b) Flexural strength, c) Rupture energy.](image)

For the contrast of the results obtained, mechanical tests were carried out on the materials without the addition of retardants, which were shown in Table 4. Compared with the results obtained (Table 3), the properties were affected by the addition of the retarders in the matrix is minimal; and in some cases, improves (combination 11 and 12 for RT and MET, 1,8,11 and 12 for RF and MEF).

| Description of material and different Matrix | Tensile strength, ultimate (MPa) | Tensile modulus (MPa) | Flexural strength (MPa) | Flexural modulus (MPa) | Rupture energy (J) |
|--------------------------------------------|---------------------------------|-----------------------|-------------------------|------------------------|-------------------|
| Composite - Epoxy                          | 83,6                            | 2258                  | 157,4                   | 4331                   | 4,55              |
| Composite - Polyester                      | 85,5                            | 2750                  | 155,2                   | 5410                   | 3,72              |

Table 4. Mechanical properties of the compound without retardant combination
Comparing the results with [13], which indicates that the tensile and flexural strength of glass fiber composite materials with polyester resin with 3% and 6% aluminum hydroxide is lower compared to the pure composite material without retarder, so it establishes that the addition of aluminum hydroxide had a negative impact on tensile and flexural properties; however, in the present study it was determined that the addition of flame retardants does not necessarily have a negative effect on the mechanical properties. For the impact test on the rupture energy a small decrease of this property was evidenced for all the configurations of the material. These results, in turn, contrast those determined by [22], in which it indicates that the effect of the content of flame retardants in the composite materials with Polypropylene was significant. The result of said study obtained an increase in impact resistance for the compounds of 13% compared to those without retarder; therefore, the cause and effect of each type of retardant and its percentage of addition on the different compounds in their original material should be investigated in the future.

Finally, it can be deduced that the application of these HA and HM organic retardants have an acceptable efficiency (the mechanical properties do not vary significantly) and especially because the hydroxides have the reputation of being non-toxic because they are friendly to the environment. In contrast to this, halogen-based flame retardants release toxic smoke, which increases the concentration of poisonous and corrosive gases in the fire, which can easily lead to suffocation.

4. Conclusions
This study shows that the use of flame retardants in polymer matrix composite materials affects the mechanical properties.

The improvement of: RT, MET (obtained in the combination of group 9) and FT, MEF (obtained with group 11) should be investigated in depth in future studies, since they showed higher values than those obtained without adding retardant.

Finally, it is evident that the combinatorial effects of the experimental design factors have different effects on the mechanical properties, so it is recommended to use the best configurations depending on the resistance requirements in specific applications.

5. References
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