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USE OF RECYCLED IN THERMOPLASTIC MATRIX COMPOSITES REINFORCED MATERIALS IN MARINE ENVIRONMENT: CHARACTERIZATION AND PROCESSING.

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Abstract: The use of thermoset matrix composite materials has been common in marine environments. But over time, these usually made from polyester matrices suffer a substantial decline. Thermoplastic matrix does not exhibit this problem, especially when use polyolefin, but nevertheless they are more susceptible to long-term efforts. The use of metal tube based reinforcements can be an interesting alternative for this kind of environment, and in this work has begun studies to determine the industrial feasibility of the process.
The experimental procedure for characterization of the matrices included the following recyclable polymers supplied in the form of pellets: ABS, polypropylene and high impact polystyrene selected for their usual supply potential and low recovery of the waste. The metallic hollow tube reinforcement used is the most common of those used in the automotive industry (E220). In the samples has been made a thermal, mechanical and rheological characterization in order to establish a comparison of effective selection.
To accomplish the process has been used scanning electron microscopy (SEM) for microstructure visualization and analysis of the structures degraded characteristics by sea action and new structures made of FRP.

1. INTRODUCTION.

The composite piles were used for the first time in the late 80s as a replacement of timber piles in the Port of Los Angeles (USA). The first prototype of composite pile was driven in 1987 and consisted in a tube made of recycled plastic coated steel [1,2].
There are several types of compounds piles:
1. Piles with steel core tube (a)
2. Structurally reinforced plastic matrix piles (b)
3. FRP pipe piles filled with concrete (c)
4. Pultruded fiberglass piles
5. Plastic timber piles.

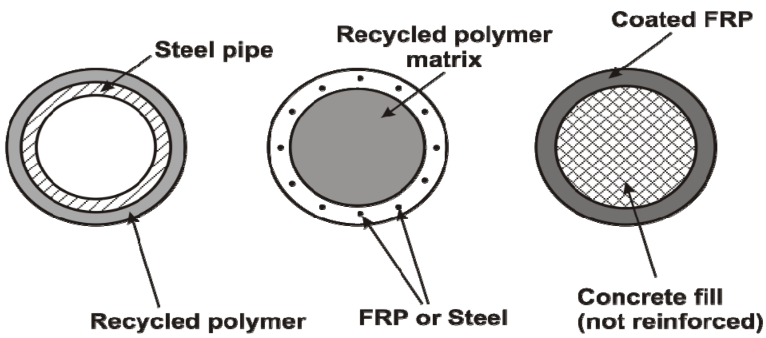

Fig 1. : Schema of Structural Sections

The first three types of piles are considered the best for loading applications and Figure 1 shows a schema of how would be structurally [5].
The use of fiber-reinforced polymers in construction technology has allowed the development of more efficient structures with low weight, high corrosion resistance and the

ability to control their mechanical properties[3]. These materials may have got a performance profile than conventional materials such as steel, wood or concrete.
Some applications of composite piles are:
1. Framework defense in marine environments,
2. Foundation structures for lightweight structures, or in many cases, research subjects in universities laboratories.
3. Currently are analyzing the use of steel tubes with Terocore ® structural foam [4] filling for the construction of bus structures. It enables to use smaller pipe thickness and thus reduce vehicle weight. The foam purpose is to prevent the collapse of the tube walls.
The most important functions of PRF coating are providing a kind of scaffolding during casting. It confines the concrete fill and serves as reinforcement to the pile front tensile stress and degradation concrete.
Therefore, this research studies the possibility of use thermoplastic polymers. Particularly study polymer recycled in order to provide added value. The goal is obtain a composite in which the matrix is a thermoplastic polymer recycled and reinforcing is steel tubes. Don't rule out the use of structural foam inside steel tubes to avoid the collapse of steel tubes in certain applications.

2. EXPERIMENTAL

We study the materials those are object of interest by partner companies:
- Röchling: Samples of recycled in the form of pellets:
ABS computers, ABS alarms, Polypropylene PP1B, Polypropylene PP1T, High Impact Polystyrene (HIPS)
- Flinsa: hollow metal tubes of different diameters and grades according to the company's manufacturing. Only has been used for this study the E220 type.

The number of beams reinforcement per panel varies between 1 and 5 units outside diameter being less than 100 mm.
The goals to be obtained are:
- Design and analysis of a sheet plate of thermoplastic matrix composite material for his introduction into the shipbuilding industry with specific dimensions. They have introduced a series of hollow tubes of steel reinforcement with the ultimate goal of reducing the density of the material used in the matrix.
- The design and analysis has determined the size of the plate, the number of tubes used and the diameter of these. Calculations have been carried out in order to determine what values get a greater decrease in the iron density.
- It used recycled thermoplastic materials to provide added value. We might get a composite in which the matrix is a thermoplastic polymer and reinforcing steel tubes are different qualities of the partner company. It has used structural foam, inside steel tubes, to avoid the collapse of the tubes in some applications.

The polymer characterizations have been carried out on recycled polymers like ABS (computer origin), ABS (alarms origin), HIPS, PP1b, PP1T.

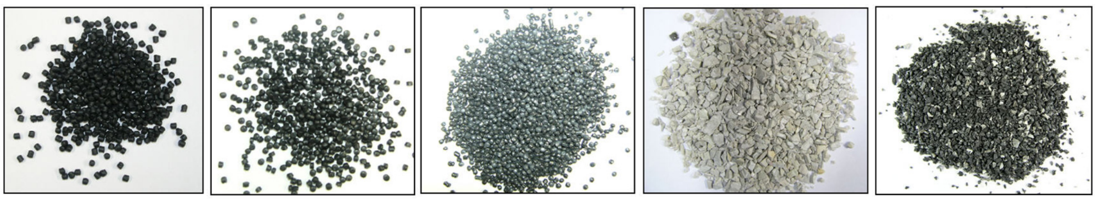

Fig 2. Recycled polymers samples analyzed: PP1B, PP1T, ABS alarms, Computer ABS, HIPS.

Have been used thermal analysis techniques in the characterization of thermoplastic materials corresponding:

1) Differential Scanning Calorimetry (DSC): is a thermoanalytical technique used to study the kinetics of reaction, analysis of purity and polymer curing. The testing unit was a Mettler Toledo DSC system. In a first step, the specimen was heated at a constant rate of 10ºC min-1 from 30 ºC to 200 º C. The second step consisted on a cooling process to eliminate thermal history, and then the temperature was raised again to 200ºC, at a rate of 10ºC min-1, to know the intrinsic crystallinity of the polymer not depending on the process.

2) Thermal gravimetric analysis (TGA): Is used to study the thermal stability and qualitative analysis.

Also we have been achieved a rheological characterization with a capillary rheometer model THERMOHAAKE REOFLIXER, Figure 3. We used the following conditions for each of the 5 samples:

- Nozzle 10 mm for all trials.
- Test temperature: 210 º C, 230 º C and 250 º C.

There were three trials for each of the temperatures and for each sample, except the ABS (computer origin) sample which has performed a test for each temperature. We dried ABS (alarm origin) because is a hygroscopic material. Its performance in production processes can generate gases.

Fig 3. Capillary rheometer used

The mechanical characterization was performed using the tensile test because it provides reliable information on the ultimate strength of materials. These tensile tests were performed using a testing machine model IBERTEST Elib 30 at a speed of 10mm/min under normal laboratory conditions and a load cell of 5 kN according to UNE-EN ISO 527-1.

For samples 1, No 2 and No 3, 10 specimens were obtained through an injection machine (Babyplast™). Only 5 have been tested.

For sample 4, ABS (computer origin), 3 specimens were obtained through a hot-plate press for panel pressing. The work conditions were: 180 º C, 100 kg/cm2 pressure and time: 5 minutes.

Other equipment used is the Scanning Electron Microscopy (SEM). It has been used to study the morphology of the structures degraded by the action of the sea. This equipment has allowed high-resolution imaging of samples with surface topography is quite varied as GRP.

3. RESULTS AND DISCUSSION.

We analyzed several GRP samples of different elements and pieces of fishing vessels scrapped in last years by scanning electron microscopy (SEM).

Figures 4 and 5 shows a 400X magnification image of a GRP's fishing deck for 10 years old. The surface is cracked and there are cracks throughout the surface and in all directions. This implies loss of strength and matrix and reinforcement adhesion.

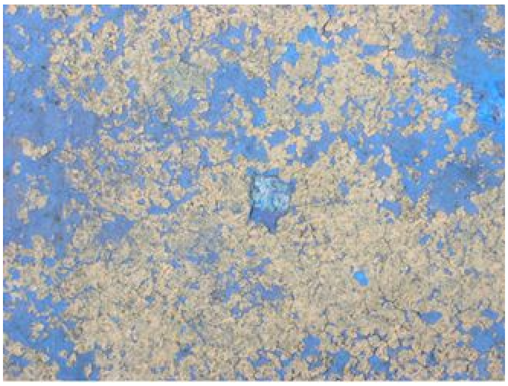

Fig 4. Degraded boat deck *Fig 5. 400x magnification SEM micrograph*

This problem and the big waste of GRP has raised investigate other types of composite materials to replace all these thermosets.

At this point, it was necessary to check that material offers the best features when making a prototype from each of the ranges used:

a) Thermal characterization.

Differential scanning calorimetry: allowed to test the material quality. There have been both in inert gas (nitrogen) and in the air to check the results disparity. Figure 6 can be seen trials on one of the samples.

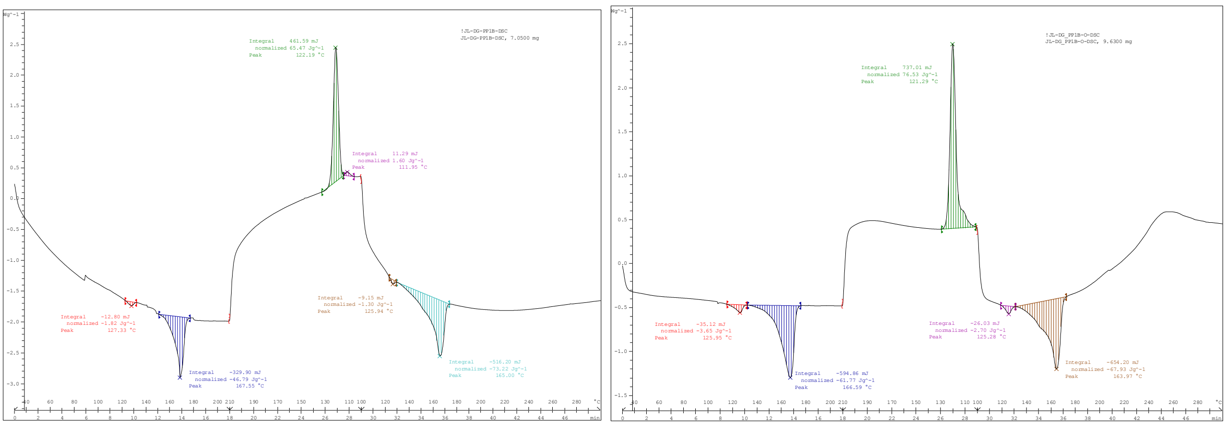

Fig 6. Tests on PP1B samples a) Nitrogen b) air

Thermogravimetric Analysis: It allowed evaluating initial degradation temperature. There have been both in inert gas (nitrogen) and in the air to check for disparity of results. Figure 7 can be seen trials on one of the samples.

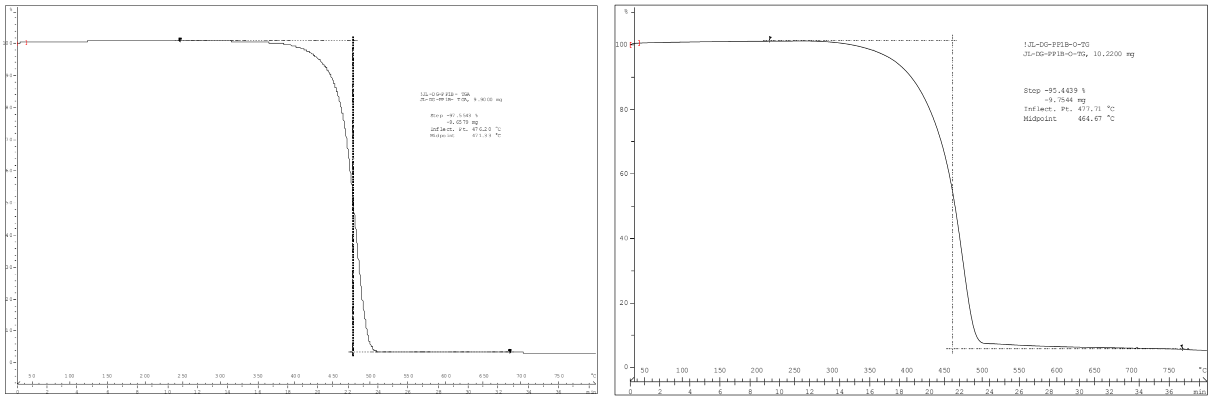

Fig 7. Tests on PP1B samples. a) nitrogen ambient b) oxygen ambient

b) Rheological characterization.
The general procedure for processing plastics is by injection molding. The plastic in a fluid state adapts its shape to a mold and solidify taking the mold form. The material properties: fluidity and viscosity are the most influential in this process of forming.
For this characterization, we used a Thermohaake Rheoflixer capillary nozzle of 10 mm for all trials. Three studies were conducted for each sample at 210 º C, 230 º C and 250 º C. Figure 8 shows the tests performed on a sample.
c) Mechanical characterization.
In order to evaluate the mechanical properties were carried out tensile tests of all materials selected. This has allowed the identification of mechanical properties of resistance as tensile strength, elongation at break and elastic modulus of different materials. Table 1 show the results obtained on a sample.

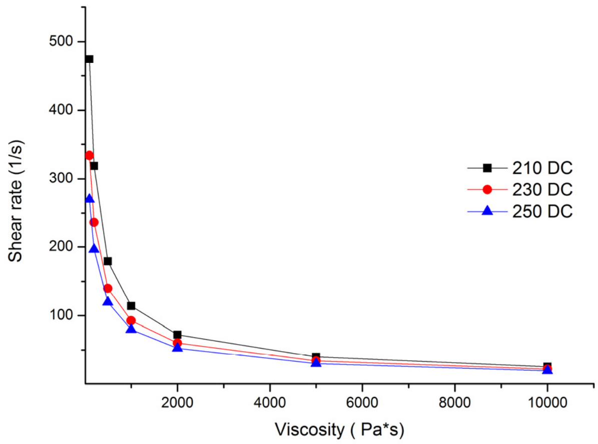

Fig 8. Results of rheological PP1B

PP1B	R(Mpa)	A%	E(Mpa)
1	20,4	25,9	2449,1
2	20,1	29,6	238,1
3	20,7	24,1	229,6
4	21,2	26,9	280,7
5	20,2	24,5	245,4
average	20,5	26,2	248,6
std deviation	0,5	2,2	19,4

Table 1. Results PP1B traction

4. CONCLUSIONS.

The following figures show some comparative graphs of the mechanical properties of the different results on different samples.
Figure 9 shows the compressive stress of all samples and can be seen that the ABS ALARM is the material that has better resistance behavior, as it almost doubles in strength following material is stronger than PP1B.

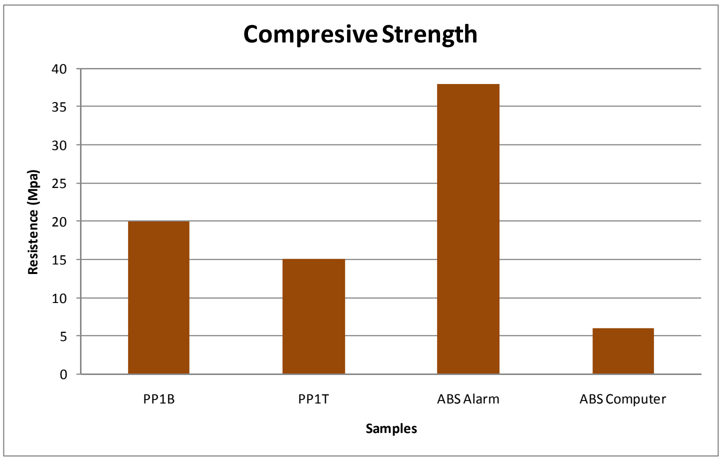

Fig 9. Compressive strength comparison of different materials.

In Figure 10, we can see the percentage of elongation comparison suffered by each material and the best ductile behavior PP1B owns and has lower elongation than the ABS (computers origin).

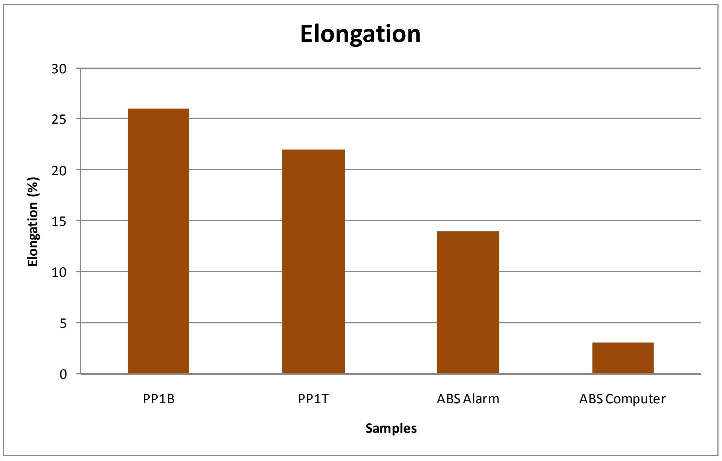

Fig 10. Elongation comparison of different materials.

Results comply with initial expectatives, as it was expected that the ABS had a high resistance due to ABS (alarm origin) material properties meet this criterion but not ABS (computers origin).
The latter can have this behavior because recycling has not been successful or that contain impurities or percentages of other materials.
However, it is one of the materials to be used because of the recycled materials, is the less outlet and therefore could be very attractive economically to use as a matrix.

All recycled thermoplastic materials tested are susceptible to use as a matrix in this new type of composite materials by analyzing the DSC and TGA results. The results of the manufacture of prototypes have been satisfactory for all types of samples, Figure 11.

Fig 11. Example of composite recycling

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