Comparison Between the Mechanical and Tribological Properties of Parts Manufactured by Injection Out of Polyamide Reinforced with Glass Fibres and Glass Microspheres

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The use of polymeric materials to replace metal or wood has become increasingly popular lately in most fields of activity. Specific amounts of reinforcement materials have been included in the structure of these polymeric materials in order to improve their mechanical properties. The increasing popularity of these types of materials was accompanied by the development of different machinery and technologies designed to process them, so as to make them as productive as possible and to achieve inexpensive high performance parts. Natural polyamide 6.6 is a polymeric material noted for its high rigidity, hardness, impact resistance, etc. The reinforcement materials added improve the mechanical properties of this type of material. Our research consisted of a comparative study of the behavior of polyamide reinforced with glass fibers and glass microspheres when subject to different mechanical stresses. The test specimens were processed by injection and relied on an experimental Taguchi plan with six input parameters each of them with two levels. The materials employed to carry out the comparisons designed to determine the mechanical and tribological properties were natural polyamide 6.6 reinforced with 30% glass fibers and 1% furnace black, and natural polyamide 6.6 reinforced with 30% glass microspheres and 1% furnace black used to prevent microsphere agglomerations. Considering all these issues, the actual research was focused on tensile stress vs. tensile strain comparisons at 23°C and 60°C, and on determining the friction coefficient using disc rotation and oscillation, XRD analysis, Scanning Electron Microscopy (SEM) and EDAX analysis. As concerns tensile stresses, high values were recorded both on the 23°C and 60°C tests when polyamide was reinforced with glass fiber. This is also supported by the SEM structure for the two composite materials under survey. The mean value of the disc rotation friction coefficient was lower when glass fiber was used as reinforcement material. This was also the case with the disc oscillation friction coefficient. The diffraction study conducted on the two materials revealed that polyamide 6.6 reinforced with 30% glass fiber did not have an amorphous structure, given the high number of peaks resulted further to diffraction, whereas polyamide 6.6 reinforced with glass microspheres exhibited an amorphous structure and a structure-specific diffraction. The chemical elements spectrum (EDAX analysis) reveals high mass and atomic percentages of C, O, Ca for both composite materials under survey.

Keywords: fibers, microspheres, glass, mechanical properties, tribology, spectrum

Polymeric composites have been increasingly common in any field of activity due to the remarkable improvement of their mechanical, thermal, electrical, magnetic and tribological properties as compared to the same properties of the "classical" materials (metallic alloys, earthenware, polymers) [1, 2].

The matrix of a composite is the material that provides the mostly mechanical and sometimes chemical links established with the material added as threads, fibers or particles, or even mixtures of these, by preserving their spatial dispersion, by conveying the mechanical or other stresses applied to the whole composite and often by protecting them from operational or environmental aggression. The materials added determine and/or enhance the properties of the polymeric composite (for instance, mechanical strength, wear resistance) [3- 9].

In addition to improving their mechanical properties, polymer reinforcement lowers their price and solves certain processing problems. Generally speaking, the factors influencing the choice of the reinforcement materials are: the properties of the reinforcement materials, the level of mechanical strength aimed at and their manufacture costs. The reinforcement materials may be fibers, microspheres and flakes.

The reinforcement fibers may be: glass fibers (filaments, hollow fibers); carbon fibers; aramid high performance fibers; synthetic high performance fibers (polyamide-imide fibers, phenolic fibers, inorganic fibers: aluminum, beryllium, boron nitride, titanium oxide).

The percentage of fibers mixed to the polymer depends on the final use of the injected parts and may be up to 60%. The carbon, glass or aramid fibers may be short or cut. The fibers follow the injection direction during processing, which influences both the processing conditions and the properties of the injection moulded part.

The reinforcement microspheres have diameters ranging from 5μm to 800μm, and are made of glass or polymers. Microspheres have the following advantages: they enhance polymer flow quality and they contribute to the even distribution of internal stresses. The use of glass microspheres considerably enhances the mechanical characteristics of polyamide 6.6, especially as concerns its elasticity, while at the same time improving the thermal performance of the product.

The most common material employed to reinforce thermoplastic materials is glass fiber, due to its high mechanical strength, rigidity, crack strength and size stability. Its wear resistance is also very high. It is used

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especially for processed parts operating at high temperatures such as bearings, levers, brackets, heat insulators and spacers.

The materials added to polyamide are glass fibers, glass spheres and furnace black. Here are some of the advantages of these added materials: higher rigidity, size stability improvement and contraction reduction.

Furnace black is used to prevent microsphere agglomerations [10]. The enrichment of a polymeric matrix with furnace black improves its thermal and electrical conductibility. The furnace black used must be chosen very carefully, bearing in mind the later use of the composite.

Important aspects related to composite structure refer to polyamide adhering to the glass microspheres (fig. 1) and to the friction occurring in the interface of the polymeric material, [12, 13]. Thus, figure 2 shows a friction and energy dissipation contact model [12]. The cohesive wear processes are the result of the "micro-chipping" process caused by the harder metallic interface asperities on the polymer surface, whereas the energy spent for this process depends on the polymer tensile stress and tensile strain, on its hardness, on the geometric parameters of the hard surface asperities and on the latter height and "cutting" angle [13].

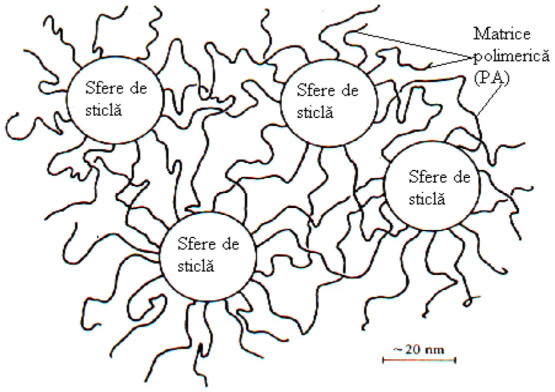


Fig. 1. A model of polyamide adhesion to glass spheres, [11]

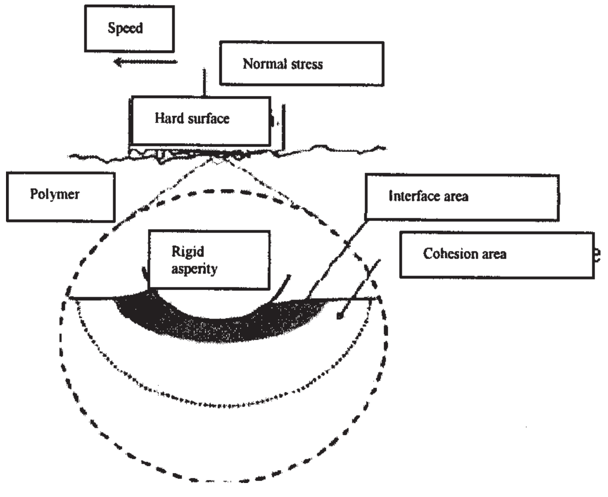


Fig. 2. Example of friction and wear process model, [12]

Experimental part

The experiment was planned according to an experimental Taguchi plan [14, 15].

The model proposed by Viger and Sisson is also easy to study; this is the matrix model of the system comprising "I" factors: F_1, F_2 ... F_i each factor having n_i levels. Each experiment was conducted three times. The proposed matrix model takes into consideration six technological parameters with two levels (table 1). The coefficients of a type (1) model were determined:

$$Z_t = M + T_{top} + t_{inj} + t_r + S_s + P_{inj} + T_{mat} + P_{inj} T_{top} + P_{inj} t_{inj} + P_{inj} t_r + P_{inj} S_s + P_{inj} T_{mat} \qquad (1)$$

where:

M-overall average,

T_{top}-melting temperature, [°C];

t_{inj}-injection time, [s], t_r-cooling time, [s],

S_s-screwing speed, [mm],

P_{inj}-injection pressure, [MPa],

T_{mat}-matrix temperature, [°C].

16 experimental tests were to be made after the orthogonality and number of degrees of freedom conditions have been analyzed. We proceeded with the analysis of the model graph (fig. 3a) which was compared with the standard graph (fig. 3b), thus obtaining the layout of the columns of independent factors used for the whole experimental research plan. The most significant influence on the process is exercised by the injection pressure followed by the smeltery temperature, the matrix temperature. Then comes, with less significant influences, screw speed, the injection time and the cooling time.

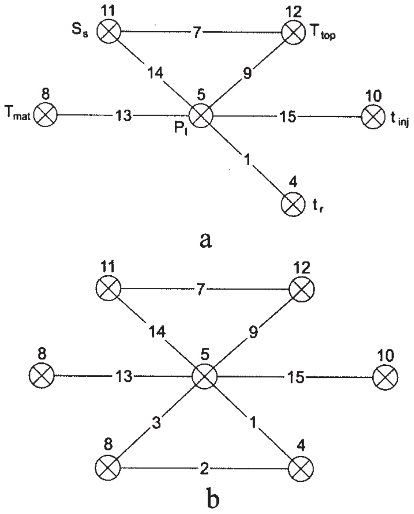


Fig. 3. Analysis of the model: a-model graph; b-standard graph

Results and discussions

A set of experiments were conducted in order to point out the outcome of the comparisons between the two types of polyamide. Polymeric composites have been increasingly common in any field of activity due to the remarkable improvement of their mechanical, thermal, electrical, magnetic and tribological properties as compared to the same properties of the "classical" materials (metallic alloys, earthenware, polymers) [16, 17]. The tribological characteristics of polyamide are: low friction coefficient and wear rate, fast wear in water, relatively low operation temperature limit, good endurance strength, better mechanical damping and better dry sliding wear behavior.

A Universal UMT-2 pin-on-disc Tribometer (CETR-Center of Tribology, INC. USA) was used to determine the tribological behavior of natural polyamide 6.6 reinforced with 30% glass fiber and 1% furnace black, and of natural polyamide 6.6 reinforced with 30% glass microspheres and 1% furnace black. This equipment is the most suitable due to the simplicity of its triboelements. The choice of the tribosystem, of the torque of the materials used to manufacture the components, of the friction conditions, of the environment temperature and humidity play an important role in the performance of the tests. The friction coefficient was determined in dry sliding conditions by OL60 disc rotation and oscillation at an 180° angle. Here were the testing conditions: thrust force Fz=15N, disc rotation n=60rot/min, distance between the disc rotation axis and the pin-disc contact area r=15mm, friction time t=300s and size of the 6mm diameter specimen. The initial disc roughness was Ra=0.6μm.

We used the following mathematical relations to calculate the specific pressure, sliding speed and friction length:

$$Fz=pA \qquad (2)$$

$$T=L/v \qquad (3)$$

$$n=30v/r\pi \qquad (4)$$

where:

p is the specific pressure, [MPa];

A - the pin-on-disc contact area with a 6mm diameter, [mm^2];

v - the sliding speed, [m/min] and r is the testing radius, [mm].

We determined a sliding speed of 94.2m/min and a friction length of 471m.

The disc rotation friction coefficient for the two materials (fig. 4) decreases rapidly during the first 30s, after which it increases slightly throughout the testing period for polyamide reinforced with 30% glass microspheres and it decreases lightly for polyamide 6.6 reinforced with 30% glass fiber. The mean values of the rotation friction coefficient is 0.1516 for polyamide 6.6 reinforced with 30% glass fiber and 0.1897 for polyamide 6.6 reinforced with 30% glass microspheres. The longer the testing time, the more stable the value of the friction coefficient.

The oscillation friction coefficient variation for the two materials (fig. 5) is approximately constant for polyamide reinforced with 30% glass microspheres, whereas for 30% glass fiber polyamide the friction coefficient exhibits a continuous increase. The mean value of the oscillation friction coefficient is 0.1688 for polyamide 6.6 reinforced with 30% glass fiber and 0.2167 for polyamide 6.6 reinforced with 30% glass microspheres. Given the continuous increase tendency of the friction coefficient in 30% glass microsphere polyamide 6.6, the experiment was repeated for a longer testing time (fig. 6), which brought about the stabilization of the friction coefficient variation to a mean value of 0.2748. The friction coefficient variations shown hereunder do not include the noise factors.

The reported results and their accurate interpretation contribute to composite optimization or to a tribological hierarchy of the tested materials. The choice of the tribosystem, of the torque of the materials used to manufacture the components, of the (dry or lubricated) friction conditions, of the environment temperature and humidity plays an important role in the performance of the laboratory tests.

The tensile tests were conducted at room temperature and 60°C, respectively, using a computer-controlled testing machine (Instron 3382) with a constant crosshead speed of 5mm/min according to ISO 527-3: 2003 recommendations. For each testing temperature, many specimens were tensile tested to determine the tensile strength and tensile strain at tensile strength (engineering). All of the specimens were prepared according ISO 527-3: 2003 recommendations to achieve type 1B test samples (recommended for fiber-reinforced (thermo) plastics).

Figures 7a and 7b show the tensile stress results reported for natural polyamide 6.6 with 30% glass fiber. Representative tensile stress vs. tensile strain curves were plotted to reveal the homogeneity (uniformity) of mechanical properties. Experimental data show that tensile stress reached 66.92 ± 0.91 MPa at 23°C and 38.58 ± 0.80 MPa at 60°C, respectively. Tensile strain at fracture increased from 7.06 ± 0.24% at 23°C to 33.60 ± 0.47% at 60°C, respectively.

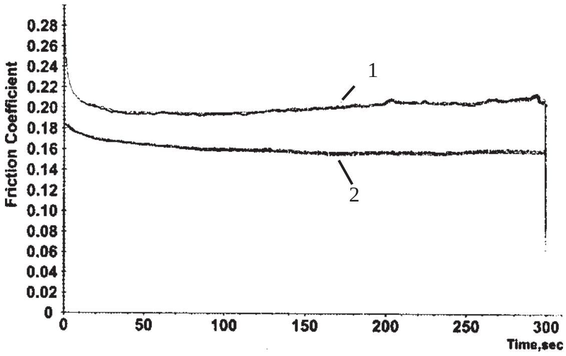


Fig. 4. Variation of the rotation friction coefficient: 1-polyamide 6.6+30% microspheres; 2-polyamide 6.6+ 30%fiber

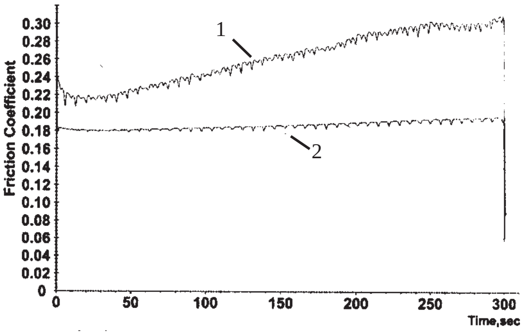


Fig. 5. Variation of the oscillation friction coefficient: 1-polyamide 6.6+30% microspheres; 2-polyamide 6.6+ 30%fiber

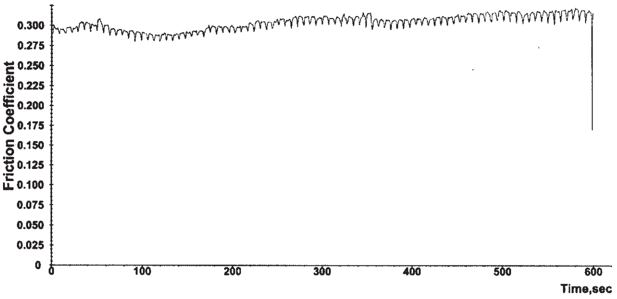


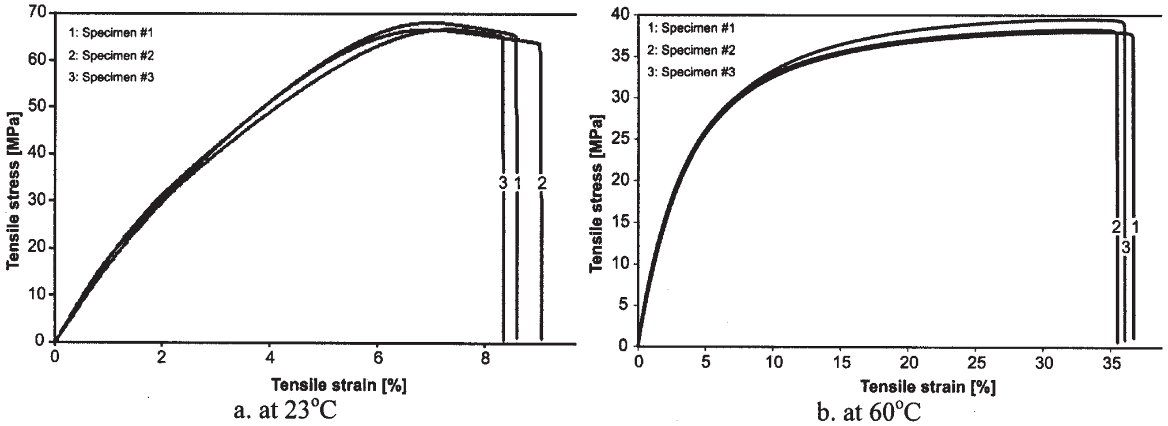
Fig. 6. Variation of the oscillation friction coefficient for polyamide 6.6 with 30% glass microspheres, for t=600s

The tensile stress results reported for natural polyamide 6.6 with 30% glass microspheres are shown in figures 8a and 8b. Experimental data show that tensile stress reached 40.64 ± 1.79 MPa at 23°C and 24.33 ± 0.53 MPa at 60°C, respectively. Tensile strain at fracture increased from 6.07 ± 0.14% at 23°C to 46.63 ± 0.47% at 60°C, respectively.

Please note that the results recorded for glass fiber reinforced polyamide were better at both 23°C and 60°C.

An X'Pert Pro MRD diffractometer manufactured by Panalytical was used for XRD analysis. Figures 9a and 9b show the snapshots taken further to this analysis. The scanning was conducted on a 5mm area at a 2theta interval and between (95.0036-59.9932) degrees.

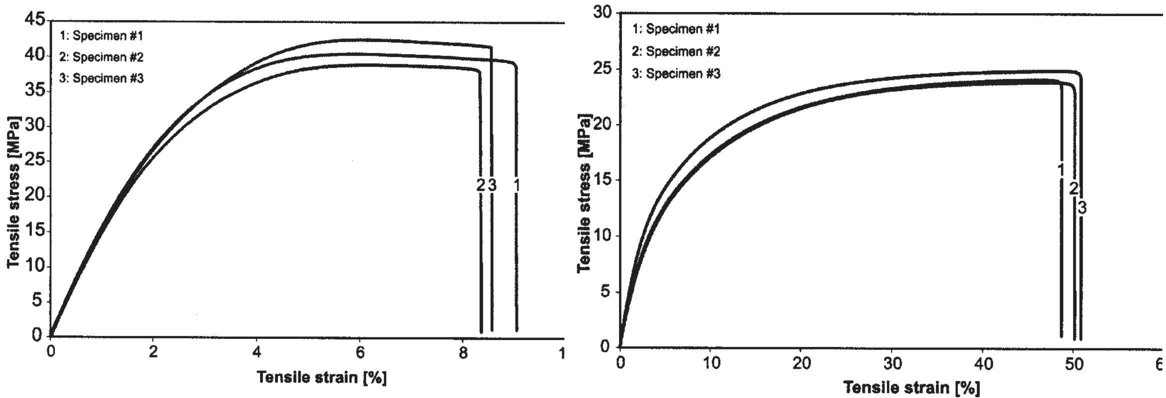
No diffraction peaks were reported for polyamide 6.6 with 30% glass fiber (fig. 9a) within the 5-20 range, whereas within the 20-60 range there were such peaks characteristic of specific phases. The high number of peaks resulting further to diffraction confirms that it is not an



a. at 23°C

b. at 60°C

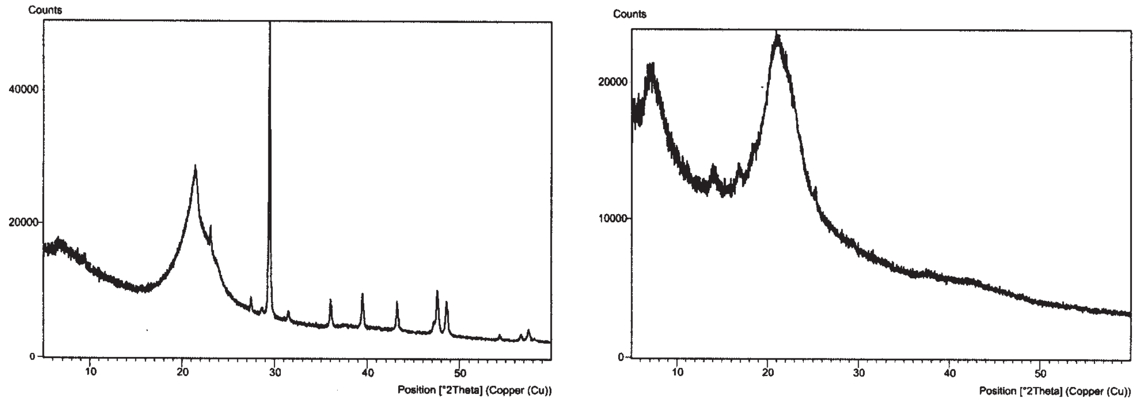
Fig. 7. Tensile stress vs. tensile strain for 30% fiberglass polyamide 6.6



a. at 23°C

b. at 60°C

Fig. 8. Tensile stress vs. tensile strain for 30% glass microsphere polyamide 6.6



a. Glass fiber

b. Glass microspheres

Fig. 9.
XRD Analysis

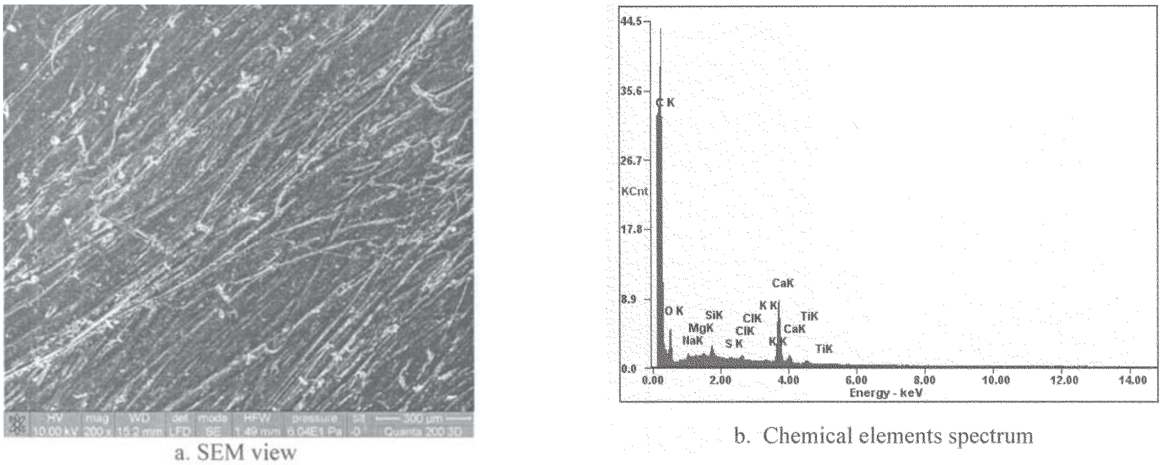
amorphous structure. We were able to determine the network parameters: a=5.05; b=6.11; c=12.07; alpha=78.64; beta=74.02; gamma=136.15. The software employed enabled us to detect a significantly high percent of CCaO$_3$ phase with different amplitudes and 2 n-Paraffin peaks. CCaO$_3$ - rhombohedral crystalline system; CH2 - orthorhombic crystalline system. The bigger the peak amplitude, the higher the amount of phase present.

30% glass microsphere polyamide 6.6 (fig. 9b) exhibits an amorphous structure and an amorphous structure specific diffraction. It is also called “camel hump” in literature. The software detected the following phases: C29H60 - unknown crystalline structure; C16H16N10NiO10 – unknown crystalline structure; C20H20Cl2CoN4 – monoclinic structure.

An Electronic double electron and ion beam QUANTA 200 3D Microscope was used to conduct SEM (Scanning Electron Microscopy) analysis. The snapshot was taken considering the following parameters: secondary electron acceleration stress - 15Kv; magnification factor - 200X; working distance - 15.2mm; LFD (Large Field Detector) used to analyze non-conducting specimens (polymers, textile fibers, powders, etc.); tilt - 0°; pressure in the microscope chamber - 60Pa.

In 30% glass fiber polyamide 6.6, SEM analysis (figure 10a) reveals an even structure with uninterrupted unidirectional dendrite branches with small random bends.

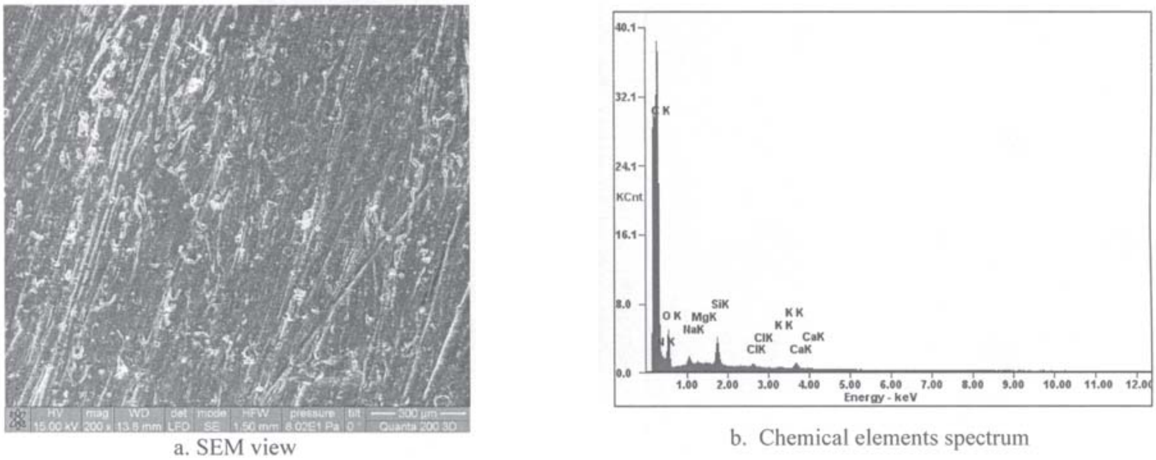
Energy dispersive X-ray spectroscopy (EDAX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. Thus, figure 10b shows the chemical element spectrum at a spectrum gathering time of 243s. The main chemical elements are revealed depending on the peaks of their corresponding energies. Therefore, the representative mass percentages are 59.29 for C, 22.76 for O and 13.59 for Ca, whereas the



a. SEM view

b. Chemical elements spectrum

Fig. 10. SEM analysis – polyamide 6.6 with 30% glass fiber



a. SEM view

b. Chemical elements spectrum

Fig. 11. SEM analysis - polyamide 6.6 with 30% glass microspheres

Table 1
INPUT PARAMETERS
VARIATION LEVELS

Input parameter *Levels*	T_{top} [°C]	t_{inj} [s]	t_r [s]	S_s [mm]	P_{inj} Kgf	T_{mat} [°C]
Level 1	265	10	15	20	60	40
Level 2	285	15	20	28	75	70

atomic percentages are 72.16 for C, 20.80 for O and 4.96 for Ca.

As for polyamide reinforced with glass microspheres, the snapshot was taken considering the following parameters: secondary electron acceleration stress - 15Kv; magnification factor - 200X; working distance – 13.8mm; LFD (Large Field Detector) used to analyze non-conducting specimens (polymers, textile fibers, powders, etc.); tilt - 0°; pressure in the microscope chamber - 80Pa. SEM analysis (fig. 11a) generally reveals an even structure with microspheres following the injection direction.

When glass microspheres are used, figure 11b shows the chemical elements spectrum at a spectrum gathering time of 282s. The main chemical elements are revealed depending on the peaks of their corresponding energies. Therefore, the representative mass percentages are 61.33 for C, 8.34 for O and 2.06 for Ca, whereas the atomic percentages are 69.86 for C, 8.14 for O and 0.70 for Ca.

Conclusions

The use of polymeric materials to replace metal or wood has become increasingly popular lately in most fields of activity. Specific amounts of reinforcement materials have been included in the structure of these polymeric materials in order to improve their mechanical properties. The increasing popularity of these types of materials was accompanied by the development of different machinery and technologies designed to process them, so that to make them as productive as possible and to achieve inexpensive high performance parts. The experimental research has followed a Taguchi plan with six input parameters each of them with two levels. The materials employed to carry out the comparisons designed to determine the mechanical and tribological properties were natural polyamide 6.6 reinforced with 30% glass fibers and 1% furnace black, and natural polyamide 6.6 reinforced with 30% glass microspheres and 1% furnace black (used to prevent microsphere agglomerations). Considering all these issues, the actual research was focused on tensile stress vs. tensile strain comparisons at 23°C and 60°C, and on determining the friction coefficient using disc rotation and oscillation, XRD analysis, Scanning Electron Microscopy (SEM) and EDAX analysis. As concerns tensile stresses, high values were recorded both on the 23 and 60°C tests when polyamide was reinforced with glass fiber. This is also supported by the SEM structure for the two composite materials under survey. The mean value of the disc rotation friction coefficient was lower when glass fiber was used as reinforcement material. This was also the case with the disc oscillation friction coefficient. The diffraction study conducted on the two materials revealed that polyamide 6.6 reinforced with 30% glass fiber did not have an amorphous structure, given the high number of peaks resulted further to diffraction, whereas polyamide 6.6 reinforced with glass microspheres exhibited an amorphous structure and a structure-specific diffraction. The chemical elements spectrum (EDAX analysis) reveals high mass and atomic percentages of C, O, Ca for both composite materials under survey.

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