PROCESSING OF CONDUCTIVE FILLED POLYMERS USING MICROINJECTION

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Abstract

Polystyrene granules were coated by sputtering with an innovative film of stainless steel obtaining this way a composite. To compare results it was necessary to prepare two different composites, mixing polymer granules with steel fibers mechanically in a drum.

Microinjection molding is a processing technique that allowed obtaining a representative sample of each composite. Scanning electron microscope (SEM) allowed the characterization of the coating thickness while the dispersion and distribution of metal particles were analyzed by optical microscopy in polarized light. Results showed a uniform thickness of the coating and good dispersion of the reinforcements in the matrix. Electrical and mechanical properties of the composites were characterized by measuring the electrical resistivity and flexural tests. Considerable values of conductivity were exhibited in composites with carbon nanotubes and a slight increase in the modulus of the polymers due to reinforcement incorporation was noticed.

1 Introduction

Polymers are characterized by being lightweight and inexpensive and present a low electrical conductivity while metals are known to deal very well with electricity although heavy and expensive. Combining these two materials has been of great challenge to integrate electrical and electronics in cars, airplanes, industrial equipment and even in traditional electronics [1].

The materials composed by polymers and conductive loads have attracted enormous interest in industry which is looking to combine the properties of a conductive material with flexibility, lightness and easy processing of polymers [2]. These mixtures of different materials can be classified as composite materials. The application of composites has restricted applications so far mainly due to its cost. However, the miniaturization of technical products has increasing importance in many areas due to the possibility of optimizing technical functions [3].

A conductor composite may be obtained by physical mixing of reinforcements with polymer matrices in solution or by melting the polymer. The combination of melting the polymer matrix is the best method, since it avoids the use of hazardous solvents. Composites preparation process with molten polymers usually requires extrusion and/or injection techniques.

In the microfabrication field, the microinjection molding technique presents great potential considering its high productivity, ability to produce geometric complex parts and the wide available range of materials to process. The key of this is the possibility of dosing and mixing small quantities of molten polymer [4].

Thus, in this research polymer granules were coated with metal particles using an innovative sputtering process and then microinjected for testing. Comparison tests were done with two more processed materials. Processing parameters' effect on the mechanical, morphological and electrical properties of the micro specimens has been studied.

2 Experimental

2.1 Micro specimens

Flexural micro specimens with specific dimensions to best suit the microinjection process were produced as shown in Figure 1.
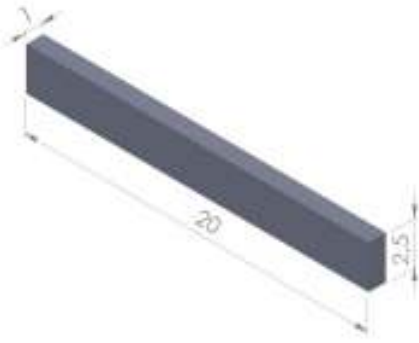
Figure 1 – Flexural micro specimen (dimensions in millimeters).

2.2 Materials

Five different materials were used to produce the micro specimens as described in the following table. Table 2 shows the material data.

Matrix	Reinforcement	Composite (Abbrev.)
Polystyrene	Steel coating (Sputtering) Deposition time: 30min	PS+SS(30 min)
Polystyrene	Steel coating (Sputtering) Deposition time: 5h	PS+SS(5 h)
Polycarbonate	Steel fiber	PC+sf
Polybutylene terephthalate + Carbon nanotubes	Steel fiber	PBT+cnt+sf

Table 1 – Materials used and their abbreviations.

Material	Grade	Manufacturer
PS	PS 145 D	Basf Plastics
PC	Lexan 114R	SABIC Innovative Plastics Europe
PBT + cnt	Polycond 9604	RAPRA
SS Target (Sputtering)	Stainless Steel AISI304	-
Steel fibers (sf)	ECP20E	TBA Electro Conductive Products

Table 2 – Materials' information.

2.3 Sputtering

The developed sputtering equipment was particularly suitable for coating powders, since it ensures a constant vibration of the particles allowing its full surface coating.

The vibration amplitude is defined by the size of the particles to be use. To form these composites it was stipulated as process variables the deposition time as 30minutes and 5hours, percentage of inert gas (argon) as 15% and the maximum power deposition as 500W.

The deposition chamber is able to reach elevated temperatures. Polystyrene is a polymer with a softening temperature of 70 º C and non-conventional dimensions in powders which made necessary to optimize the display system of granules to the type of metal atoms to be deposited. A pulsed power source was used to optimize the process by varying the temperature of the deposition chamber avoiding this way undesirable material fusion.

2.4 Microinjection molding

The micro specimens were produced with microinjection machine Boy 12A equipped with a plasticization screw of 14 mm diameter. The processing conditions were fixed at typical values used in conventional injection which are normally presented in data sheets of each material, and subsequently agreed by trial and error testing. In order to achieve the best processing conditions for these materials, some samples were injected in order to stabilize the process and thus obtain the optimal conditions for producing the specimens, which resulted in the conditions presented in Table 3.

2.5 Characterization techniques and properties

2.5.1 Scanning electron microscopy (SEM)

The technique of scanning electron microscopy was used to better characterize the thickness of metal film-coated polystyrene beads. Sample preparation consisted on fracturing the center of coated polystyrene granules and subsequent fractured section coating with 8nm thickness of gold-palladium to measure the steel coating film. A FEI New NanoSEM200 [5] was used for this analysis.

2.5.2 Determination of mass loss on ignition

The purpose of this test was to determine the percentage of steel present in the injected composites. Following the Portuguese Norm NP2216 methodology allowed obtaining information about the proportion of the present components.

		PS	PS+SS(30min)	PS+SS(5h)	PC	PC+sf	PBT+cnt	PBT+cnt+sf
Profile of temperatures (ºC)	T5	230	230	230	330	300	280	280
	T4	220	220	220	320	290	270	270
	T3	210	210	210	310	280	260	260
	T2	200	200	200	300	270	250	250
	T1	180	180	180	270	260	240	240
Injection pressure (bar)		95	95	95	100	95	100	120
Injection speed (%)		75	75	75	75	75	80	80
Cushion (mm)		10,5	10,5	10	11,2	11,2	10,5	10
Mold Temperature (ºC)		70	70	70	80	80	70	70

Table 3 – Processing conditions (set on the machine).

2.5.3 Optical microscopy of polarized light

The optical microscopy of polarized light analysis was being used to observe the microstructure, also to evaluate the effect of the addition of conductive charges onto polymers and finally to analyze the distribution and dispersion of metal particles.

Once received the samples, an optical analysis was performed by means of an optical microscope Olympus model B using a 3.3x ocular and an objective magnification of 4 and 10x for the observations.

2.5.4 Electrical resistivity measurement Electrical characterization

Electrical resistivity measurement allows characterizing the electrical conductivity of the microinjected composites. These measurements require the use of a Pico-ammeter Keythley 487 with an integrated voltage source, a Faraday cage and Software "Visual I-V".

Table 4 shows the software conditions used for each sample. The test is repeated five consecutive times carrying out an average slope (conductance) of each I-V curve obtained and after the necessary calculations it's reached the values of electrical conductivity for each composite.

Voltage	Min.	Máx.
	-10 V	10 V
Range time	1000 ms	
Step voltage	1 V	

Table 4 – Conditions established in the software "Visual I-V"

2.5.5 Flexural test

The flexural tests were performed in MicroTester equipment, specially designed to characterize the mechanical behavior of micro-components. For each material microinjected, 5 tests were performed, at room temperature,

constant speed of 2 mm / min and with a load cell of 1kN.

3 Results

3.1 Sputtering

The coating of polystyrene beads with a film of stainless steel by sputtering was well succeeded. As the deposition chamber can reach high temperature values, it was consider the hypothesis that the polymer could melt during the deposition process. To avoid this possibility it was used a pulsed source varying the chamber temperature during the process achieving this way a successful coating.

The following figures illustrate images of polymer granules, observed only with loupe.

Figure 2 – a) Polystyrene b) PS coated with stainless steel film.

Figure 2 a) shows that the polystyrene granules used present a non-perfect cylindrical shape and the surface presents some irregularities, not being entirely flat. In

Figure 2 b) is presented the successful results from the coating process showing that the steel film deposited covers completely the PS granules surface as wanted.

3.2 Scanning electron microscopy (SEM)

The following image obtained by means of SEM technology present fractured surfaces of polystyrene granules completely coated with uniform thickness film of steel.
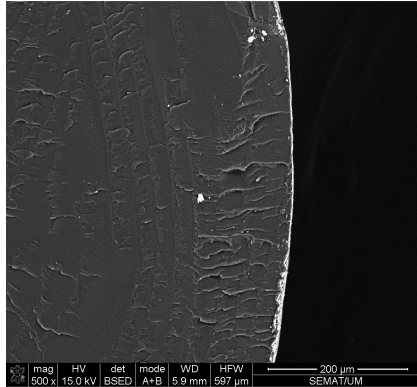

Figure 3 – Fractured granule.

Steel film thickness was measured from coated granules with a deposition time of 30 minutes and 5 hours (Figure 4).
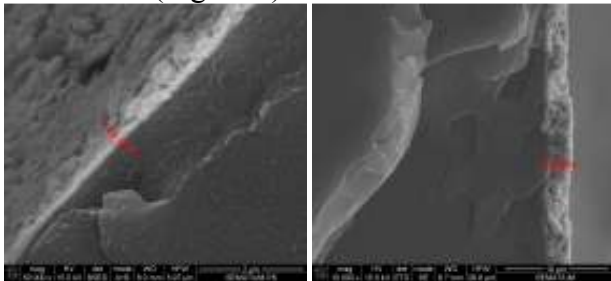

Figure 4 – Samples with deposition time of 30 minutes and 5 hours, respectively

Table 5 shows the average of steel film thickness for the respective deposition time.

Deposition time	30 min.	5 hours
Average thickness (nm)	130	2317

Table 5 - Average film thickness of the steel

It was noticed that a higher deposition time causes a greater thickness of the steel film confirming the expectations. When increasing the deposition time from 30 minutes to 5 hours, the steel film thickness increased approximately 20 times.

3.3 Determination of mass loss on ignition

Results shown in Figure 5 indicate that a high amount of steel film was deposited over the composite mixture of Polycarbonate with steel fibers followed by the mixture PBT+cnt+sf. There isn't much discrepancy between the results obtained for both composite materials due to the similar ratio used when doing the mixture of the granules with the steel fibers. Considering the microinjected specimens using the composite materials developed with the sputtering technique, the following picture shows that the percentage of steel is higher for the composites produced when comparing with other two composites with steel incorporation using a different technique.
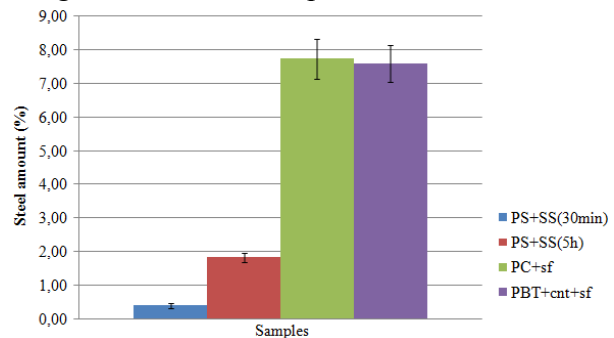

Figure 5 – Steel amount in micro specimens injected

This study allowed verifying by measurements of the electrical resistivity that PC+sf and PBT+cnt+sf composites present higher values of conductivity compared to the other two composites in study which may be explained by the notable difference between the amount of conductive charges present in the composites.

3.4 Optical microscopy of polarized light

The microstructure of PS+SS and PC+sf samples was analyzed using a microscope in bright field option. Attempts were done to evaluate the surface structure of PBT+cnt+sf but, because it had incorporated carbon nanotubes, the obtained images were all dark not allowing the visualization of any detail.

Figure 6 presents a polystyrene sample with a longer time of deposition showing a higher amount of metal particles over its structure. Also visible in the image are the small agglomerations of steel particles appearing over the samples' surface. The particles present different sizes which causes a random size distribution over the structure of the samples but not reaching the nano-scale as wanted.

Because polystyrene is known to be a fragile material the obtained images of the samples appear brittle and they tend to fracture during the cutting process previous to the visualization.

The extremities of the samples presented good adhesion between the composites and the applied resin which was necessary for the cutting stage due to the small size of the specimens. When removed from the samples, nearly none traces of the resin could be observed with the microscope.
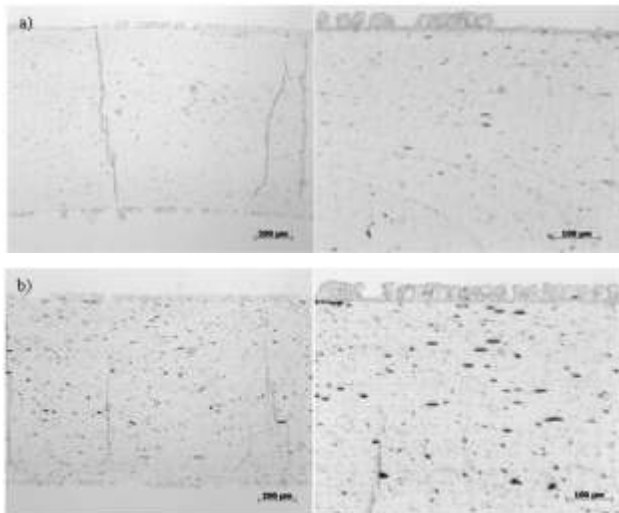

Figure 6 – Longitudinal section in bright field, detail of the bark on the right - a) PS+SS(30min) b) PS+SS(5h).

The following image shows the obtained images in bright field from samples of polycarbonate with steel fibers.
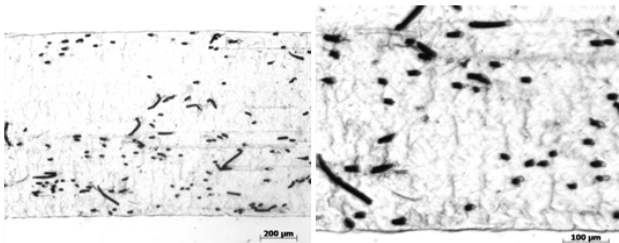

Figure 7 – Longitudinal section in bright field, detail of the bark on the right - PC+sf

A longitudinal section obtained in bright field is shown in Figure 7 presenting both metal fibers dispersed through the matrix and agglomeration points.

To confirm the morphology between the bark and nucleus area of the samples they were also observed with polarized light by microscope technique. With this technique it may be noticed that the bark of the samples presents a higher molecular orientation which is caused by the rapid cooling of the material when in contact with the molding structure that has a lower temperature than the processed composite. Some orientation may also be observed in the nucleus area although in a lower percentage compared to the bark area. This slight orientation of the molecules is due to the flow direction and the cooling rate.

Good adhesion, distribution and dispersion of the reinforcements on the samples' matrix are visible in all the processed samples, a feature of significant value for the increasing of the mechanical properties of the specimens when comparing to a simple polymer.

3.5 Electrical characterization

Once obtained the I-V curves and done the calculations it was achieved the electrical conductivity values for each composite in study which are shown in Figure 8.
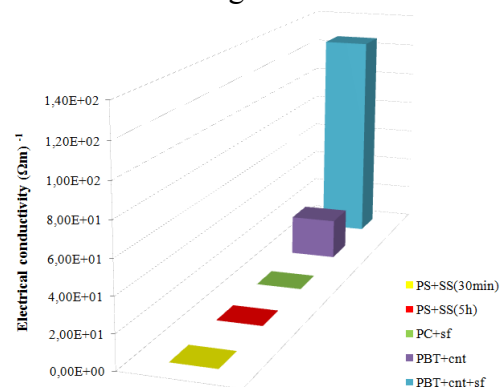

Figure 8 – Electrical conductivity of the studied composites

The reported results in the graphic above show that PS+SS with 30 minutes and 5h treatment and PC+sf composites present none electrical conductivity values change when compared to the known values of the individual polymers used and the steel reinforcements [6][8]. The assigned objectives were not achieved.

Carbon nanotubes are reported in literature as good electrical conductors [8]. To verify this fact it was analyzed the conductivity over the matrix of the PBT+cnt+sf composite in order to check the influence of adding steel fibers. The results showed a great improvement on the electrical properties of the material.

Although PC+sf composite contains the same amount of steel fibers as the PBT+cnt+sf composite it can't conduct electricity due to the low interconnection between the fibers and the polymer matrix and the intrinsic insulating property of the PC.

The composite PBT+cnt is already conductive due to the carbon nanotubes presence which possess good electrical properties [8]. Therefore, when adding steel fibers, even if the interconnection between them and the matrix isn't good, as the composite is already

conductive the final mixture will present good electrical properties due to the intrinsic properties of the PBT+cnt matrix regardless the steel fiber adhesion.

3.6 Flexion test

The mechanical properties of a composite are influenced by the type, amount, distribution, dispersion and filler-matrix interaction of the reinforcements used, increasing with the improvement of these factors.

A comparison between the elasticity modulus (E) of the pure polymer and the composite produced is presented in the figure bellow (Figure 9).
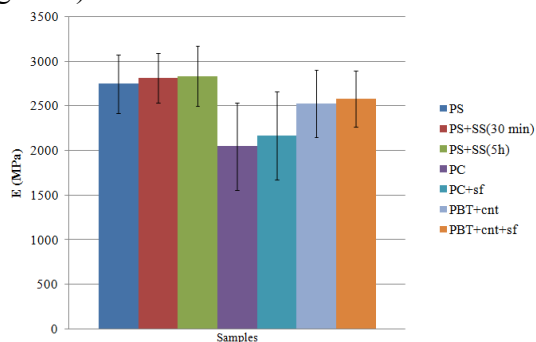
Figure 9 – Modulus of simple polymers and their composites

According to the data shown in the figure above it's possible to verify a similar elastic modulus value for pure PS and composite PS+SS presenting both an identical flexural behavior during the flexion test. However, composites present a higher modulus value of approximately 2% when comparing pure PS with PS coated with steel film for a period of time of 30 minutes and 3% when comparing pure PS with PS coated with steel film for 5h period. Comparing both PS composites the difference of 1% is very low and it could be considered nearly non-significant.

The elastic modulus of the pure PC increases 6% when including steel fibers which may be consider a small value change. PBT+cnt+sf composite exhibit a very low difference between the elastic modulus of the matrix and the final composite increasing only 2%.

As final analysis of the information contained in Figure 9, the value of the modulus of Young of the produced composites increased compared to the respective matrix but not in a notorious matter.

4 Conclusion

The main aim of this project was to innovate the methodology of preparing conductive composites by application of the sputtering technique which proved to be successful.

A coating film covering entirely the polymer granules' surface was obtained without deforming the original shape.

The steel film deposition was analyzed with SEM presenting a uniform thickness without reaching the nanometric size while optical microscopy analysis showed good dispersion of the reinforcements in the matrix.

The bonding between the metal particles depends entirely on the matrix type. When using a conductive matrix as PBT+cnt, steel fibers bonding was promoted and the electrical properties increased. On the other hand, using an insulating matrix decreases the connection between the metal particles so that the composite is less conductive.

In all cases, within the incorporation of reinforcements the elastic modulus increases slightly improving mechanical properties of the polymer increases.

In summary, the electrical conductivity of a material depends not only on the amount of steel used but also in the type of matrix used and the consequent reinforcements' bonding.

5 References

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