RELEVANCE OF PROCESSING PARAMETERS AND STRUCTURE OF LAYERED SILICATE BIONANOCOMPOSITES ON THEIR FINAL APPLICATION PROPERTIES

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Abstract
Polymer layered silicate nanocomposites' final properties are highly dependent on their reinforcement composition, morphology, dispersion, orientation and distribution through the polymeric matrix. Poly(lactic acid) (PLA) based nanocomposites were prepared using different silicate systems (Cloisite 20A and 30B) and varying extrusion (screw rotation rate) and injection molding (injection rate) parameters. Mechanical properties, specially elastic modulus and resilience, increased when Cloisite 30B was used. These results were verified by measuring micro-structural parameters (agglomeration factor and distances) from TEM images. The nanocomposites showing higher elastic modulus and resilience were the ones containing Cloisite 30B, which also shoed smaller agglomeration factor and lower and narrower distribution of the distances to the closest neighbours.

1 Introduction
Poly (lactic acid) or PLA is one the most important biodegradable and biocompatible polymers. It can be derived from renewable sources; it is friendly with the environment and exhibits interesting physical properties. All these features make PLA an attractive alternative for other plastic materials which degrade too slowly and have their origin in non renewable petrochemical resources. However, the thermal and mechanical properties of PLA need to be improved in order to make it extensively interesting for industrial applications [1].

The properties of polymer-layered nanocomposites are highly dependent on the morphology of the reinforcement, its size, volume fraction, dispersion and exfoliation degree, among others. Therefore, in order to obtain the best possible properties, the composition and the processing conditions need to be optimized, since these control the microstructure of the material. [2, 3].

In this work we present some of the preliminary results of our ongoing research. First we point out the importance of a good design of experiments to obtain coherent results. Then we show the relevance of the study of the resulting micro-structure of the composites in order to be able to interpret, understand and link both, processing parameters and final properties.

2 Materials and testing methods

Poly(lactic acid) grade 3051D, Natureworks® LLC was used as provided by Cargill-Dow. It was received in pellet form, having a melt flow index of 9 g 10 min^{-1} (190 ºC and 2.16 kg). The mechanical properties of the injection molded neat PLA are: Young's modulus 2431 MPa, tensile strength 64 MPa, and resilience 16,2 KJ/m^2. Organically treated montmorillonite Cloisite® 30B and 20A from Southern Clay Products (Gonzales, TX) were used as reinforcements.

2.1 Sample preparation

PLA/clay samples were prepared in a Brabender Plasticorder DSE 20/40D co-rotating twin-screw extruder, the total production of which was 1.5 Kg h^{-1}. The configuration of the screws was specially designed for an optimal mixture between matrix and nanoaditives and the relation L/D for the screws was 40. Before processing, PLA was dried for 4 h at 80ºC and the clays for 12 h at 80ºC. With the compounded composite materials A-type specimens (ISO 527) for mechanical testing were injection moulded in a Sandretto OTTO machine, 150 Tn. The composites were dried again for four hours at 80 ºC prior to the injection moulding of the specimens.

In order to analyze the influence of the processing parameters and the composition of the nanocomposites on the final mechanical properties of the injected specimens, a design of experiments (DOE) was carried out. The most important process variables were selected to optimize the compounding, such as screw speed (120, 300 and 650 rpm), parameter that favours delamination of the clays, and injection moulding rate (120 mm/s and 240 mm/s) which may vary the orientation of clays through the polymeric matrix. The composition was also varied by using different clays (Cloisite 20A and 30B), although the weight fraction was constant (5 wt%). The difference between the two grades of clay used is mainly the type of surface treatment they have. The analysis of the resuslts was carried out using MiniTab 16 program. This software performs a multifactorial analysis and allowed us to relate the final material properties to the applied process parameters using statistical techniques. With a confidence level of 99%, by means of standard errors, the statistically significant (process) parameters have been identified and their effect analyzed.

2.2 Mechanical properties

Tensile strength and elastic modulus were measured in a conventional mechanical testing machine, Hounsfield H25K5, at a strain rate of 10 mm min^{-1}. Halterio specimens type A, of 150x10x4 mm were tested. Impact resistance was measured using a Charpy pendule on 80x10x4 mm moulded samples in an ATS-Faar Impact-15 machine. Mechanical characterization was done according to ISO 527 norm for tensile tests and to ISO 357 for the impact test.

2.3 Micro-structural characterization

Transmission Electron Microscopy (TEM) images were recorded on a Philips CM120 Biofilter microscope, using an accelerating voltage of 120 kV. The samples were previously ultramicrotomed into 100nm-thick nanocomposite slices using a Leica Ultracut UCT crioultramicrotome. ImageJ software was used to analyze the TEM images and to obtain information related with the micro-structure of the nanocomposites. An agglomeration parameter (relation between the area and the perimeter of the clay stacks) has been measured as well as the distances to the closest neighbours of each clay stack [4, 5].

3 Results

3.1 Composition and processing parameters vs mechanical properties

Following DOE, samples were extruded and injection moulded using different processing parameters, and then they were mechanically tested. The results of the measurements are shown in Table 1. It is clearly evident that clay 30B gives better results for all the measured properties, probably due to the organic-modification which is more likely to be compatible with PLA matrix than the one 20A has. Concerning the effect of the rotation speed of the extruder screws, it seems not to affect the tensile strength nor the impact resistance when 30B clay is used. When 20A has been used, however, an increase in screw rotation speed implies a decrease for the impact resistance. Regarding Young's modulus, a maximum has been found for intermediate screw rotation speeds regardless of the type of clay used. Finally, the injection moulding rate does not seem to significantly affect any of the measured properties. The effect of the considered processing parameters on the final tensile strength is insignificant, even the effect caused by the type of clay.

Clay	Extrusion speed (rpm)	Injection rate (mm/s)	σ (Mpa)	E (Mpa)	Resilience (KJ/m2)
30B	**120**	**120 mm/s**	68,1±1,2	3663±43	17±0,7
30B	**120**	**240mm/s**	68,2±1,1	3681±48	16,1±1
30B	**300**	**120 mm/s**	68,9±2,4	4071±7	15,6±1,6
30B	**300**	**240mm/s**	62,0±2,2	3992±23	15,4±0,8
30B	**650**	**120 mm/s**	68,4±1,2	3638±55	16,1±1
30B	**650**	**240mm/s**	69,1±0,8	3665±32	15,8±0,8
20A	**120**	**120 mm/s**	65,6±1,6	2921±62	14,3±0,8
20A	**120**	**240mm/s**	66,3±0,9	2903±15	13,9±1
20A	**300**	**120 mm/s**	64,6±1,6	2622±133	14,1±0,4
20A	**300**	**240mm/s**	63,9±0,1	2546±69	13,9±0,7
20A	**650**	**120 mm/s**	66,7±0,7	3478±20	12,9±0,7
20A	**650**	**240mm/s**	63,6±2,1	3471±50	12,5±0,5

Table 1. Mechanical testing results for all PLA/clay samples.

As can be concluded from the data presented in Table 1, even for a very reduced number of varying parameters (just in this case), it is not trivial to deduce how the processing parameters should be tuned for optimizing the final properties.

Therefore, in order to identify the processing and compositional parameters (or combinations thereof) that are significant, a multi-factorial analysis has been carried out (figure 1) using Minitab 16 program. The statistically significant parameters have been determined according to a confidence level of 99%.

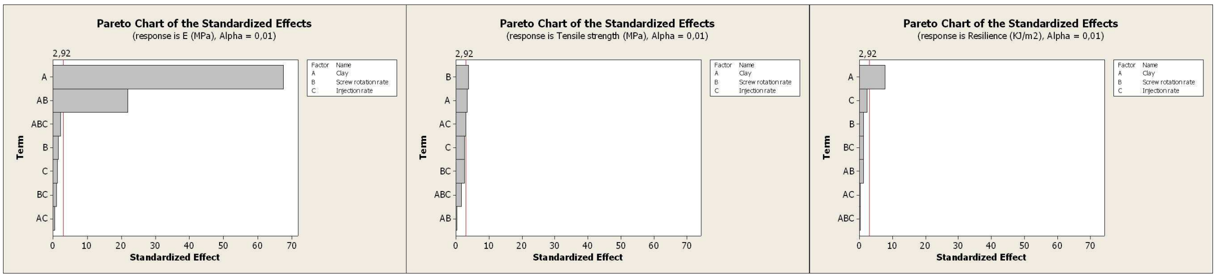

Figure 1. Pareto charts showing statistically significant parameters for each response in mechanical testing. Parameter A corresponds to the type of clay, B to the extruder-screw rotation speed, and C to the injection rate of the injection moulding machine.

As shown in figure 1 (where A represents clay type, B extruder-screw rotation speed and C injection rate), the effect of each of the considered processing parameters (and their combinations) on the measured mechanical properties was estimated. Those parameters (or combinations of parameters) reaching beyond the red line are considered statistically relevant. In a general view, it is evident how the clay type has a relevant effect (which is over 60 for elastic modulus and almost 10 for the resislience) on the material's final properties. For the elastic modulus, a combination of both clay type and screw speed seems to be also relevant. Despite the fact that, according to the performed statistical analysis, the type of clay and the extruder-screw rotation speed would seem to be parameters significantly affecting the measured tensile strength, their normalized effect are so small (lower than 3) that in practice they can be considered irrelevant. This point is confirmed by the very small changes observed for the tensile strength in Table 1.

3.2 Relevance of the micro-structure

The micro-structure of the composites is directly related with the composition and processing parameters, as well as with the materials final physico-chemical properties. It is, therefore, the link between processing and final properties. Hence, by studying the micro-structure a better understanding of the final behaviour of the material can be obtained, as well as an understanding of the effect of processing on that behaviour. This would ultimately allow to predict the properties of the transformed materials as a function of the processing parameters. In order to establish this relationship, the micro-structure of the samples has been studied by transmission electron microscopy, followed by image analysis.

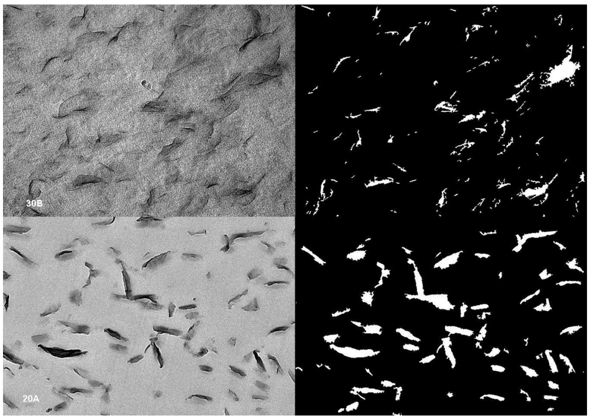

Figure 2. Original TEM images for samples processed at 120 rpm screw speed and 12 mm/s injection moulding rate and their binarized images.

The image analysis process begins with the binarization of the TEM micrographs (Figure 2), followed by the calculation of relevant morphological parameters, such as the shape, area or perimeter of all clay stacks and also the distances to the closest neighbours through the polymeric matrix (Figure 3).

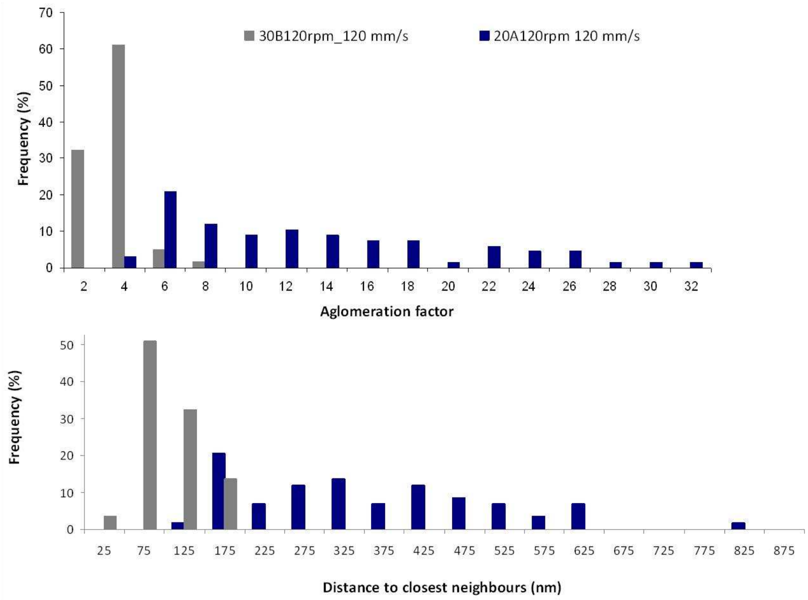

Figure 3. Micro-structural parameters for samples containing different clay types.

The agglomeration factor (relationship between area and perimeter of each stack) and distances to closest neighbours from each stack to the others have been measured for two samples prepared using same processing conditions but with different reinforcement. Both samples contain the same amount of reinforcement, so the one having a smaller agglomeration factor and lower and narrower distribution of distances between neighbours should also have a better degree of exfoliation of the reinforcement, which in turn should yield improved mechanical properties. Comparing the structural data obtained for these two samples (Figure 3), it is observed that, as expected from the mechanical measurements, the sample prepared using Cloisite 30B shows a higher degree of distribution and exfoliation.

The same type of analysis was followed for samples containing 30B clay but processed in different conditions. As seen in the mechanical results, the effects of these variations are smaller and more difficult to detect. The micro-structural parameters were calculated using a reduced number of TEM images and as expected no significant difference was found (Figures 4 and 5). Again, the results obtained in the mechanical experiments are matched by the results of the image analysis: there is only a minor effect of the processing parameters on the final micro-structure and, therefore, the obtained mechanical properties are practically not affected by the processing conditions.

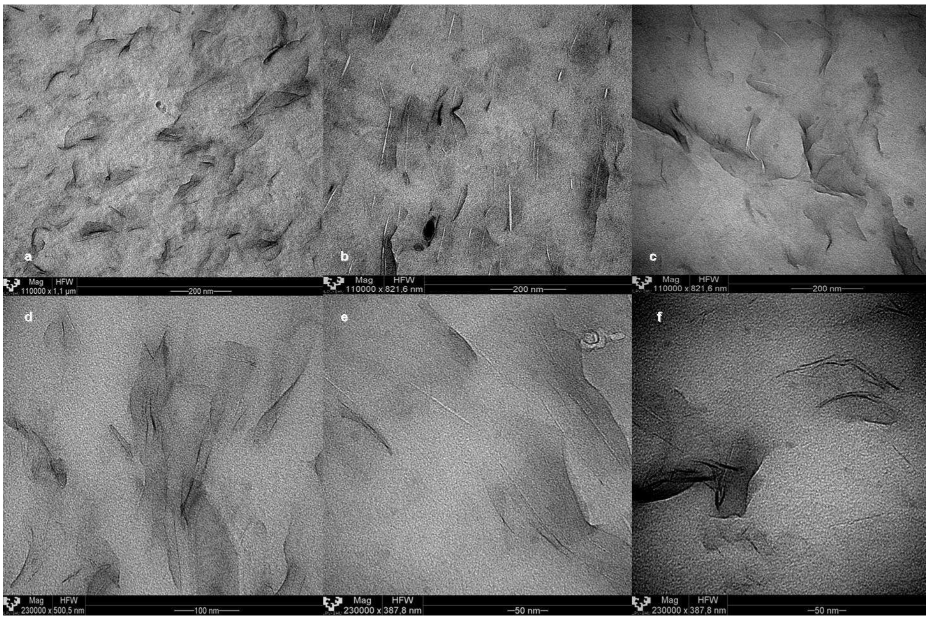

Figure 4. TEM images for nanocomposites containing Cloisite 30B clay processed at 120 rpm (a, d), 300 rpm (b, e) and at 650 rpm (c, f).

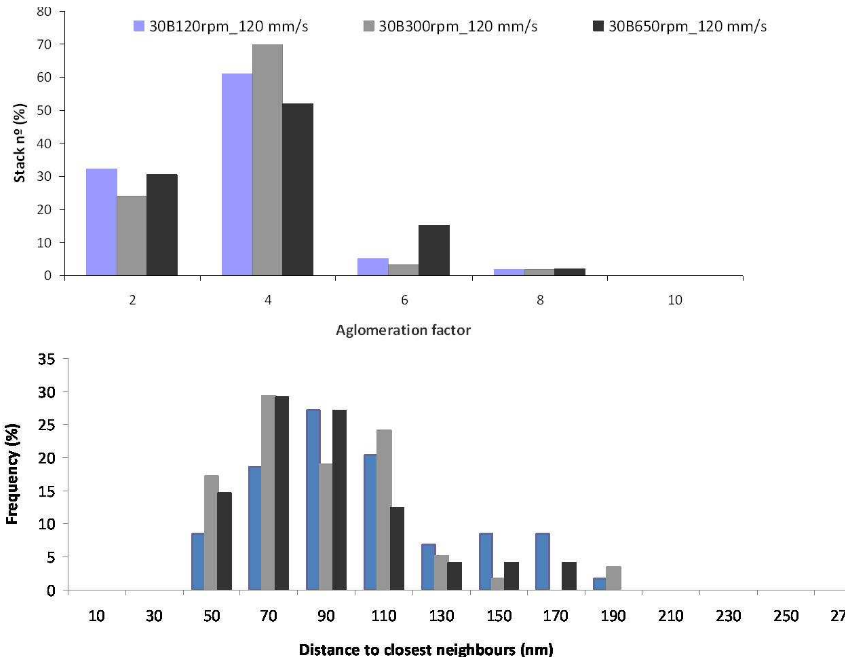

Figure 5. Micro-structural parameters for samples containing Cloisite 30B processed at different conditions.

To obtain more reliable conclusions more images should be analyzed; an amount of images that will provide representative information of the entire micro-structure. This requires new techniques based on automated image analysis or three dimensional characterization techniques [6, 7].

4 Conclusions

In order to analyze, understand and predict composites' final properties, the micro-structure and its related parameters seem to be the key. For the calculation of these parameters transmission electron microscopy followed by the analysis of the images acquired is a suitable technique. However, if reliable information is required, automated image analysis is necessary for the calculation of representative micro- structural parameters.

Regarding the relationship between composition and processing parameters with the final properties, multi-factorial analysis and Pareto charts help to understand how some parameters (or combinations) affect or not the final properties.

In this report we have shown some preliminary results of our ongoing research. For future work, the analysis of the micro-structural parameters with the composition, the processing and materials final properties is proposed.

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