Applications of TEM Automated Image Analysis in polymer nanocomposites

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Introduction

Composite materials are widely used because the beneficial effect of adding a dispersed phase (most often acting as reinforcement) on the final properties largely overcomes the extra processing complexity. The extent of the reinforcing effect depends on the properties of the matrix and the reinforcement, their mutual (chemical) compatibility, and the size, shape, dispersion, orientation, etc. of the reinforcement within the composite material, i.e. the microstructure of the reinforcement. Understanding the relationships between the microstructure and the final properties would allow the design of more efficient composite materials, with optimal final properties.

Ideally 3D techniques should be used for the characterization of the microstructure to account for possible anisotropies, but the generally available 3D/bulk, nanoscale characterization techniques (i.e. x-ray diffraction, Focused Ion Beam SEM, and TEM tomography) are limited or have severe shortcomings. An alternative to these techniques is the analysis of a large number of standard (2D) TEM images, from which the characterization of the microstructure can be performed. In order to perform such analysis objectively Automated Image Analysis (AIA) can be used, rather than carrying it out by hand.

Here we report on the use of AIA in two different applications. First, we will show how it has been used to find the relationship between the processing conditions, microstructure and final (mechanical) properties of poly(lactic acid)/nanoclay (PLA/nanoclay) composites. Up to date the use of of AIA in the field of polymer/nanoclay composites in nonexistent, and the image analysis results found in literature have been obtained by analyzing the images in a one by one basis (e.g. Williams 2009). In the second application, AIA is used to help with the classification carbon black particles into four shape categories. Carbon black is used as reinforcing agent in rubbers. The reinforcing effect depends, among other factors, on the size and shape distributions of the carbon black particles (Herd 1993). The shape of the individual carbon black particles can be classified into four categories (i.e. spheroidal, ellipsoidal, linear and branched), the relative occurrence of which defines the reinforcing potential of the analyzed carbon black.

Materials and Methods

All the Transmission Electron Microscopy (TEM) images were acquired in a Philips CM120 Biofilter microscope, using an accelerating voltage of 120 kV. For each material, the micrographs were acquired in similar illumination conditions in order to facilitate the subsequent automated image processing and analysis.

The six used PLA/nanoclay composite samples (Natureworks LLC grade 3051D PLA containing 5 wt. % Cloisite 30B montmorillonite clay) were prepared by extrusion at three different screw speeds and injection moulding at two injection speeds (see Iturrondobeitia 2014 for a full explanation).

The samples were ultramicrotomed using a Leica Ultracut UCT ultramicrotome to 130 nm thickness slices. 10 micrographs for each sample at a magnification of 66 kX (1.1 nm·pixel-1) were analyzed.

For the second application, carbon black of grade Vulcan XC605, which was supplied by Cabot Corporation, was used. The samples were prepared according to the instructions for dry powder in Ref. [6]. The selected pixel size was 2.34 nm for this application.

The image analysis was performed similarly in both cases. First the optimal binarization parameters were found for one of the images to be analyzed, and then the same binarization procedure was automatically applied to the rest of the images. The binarization optimization step is not automated, and the best combination of parameters (type of initial filter, type of threshold, morphological transformations to smooth the binarized objects, etc.) were selected by visual inspection of the corresponding results.

The aim of the image analysis in the case of the PLA/nanoclay samples was to obtain a statistically representative, quantitative characterization of the clay microstructure within the polymer matrix. Several parameters (such as the number of clays per unit area, the length and thickness if the clays, the distance to the four nearest neighbours, the orientation, etc.) were calculated from the binarized images.

In the case of the carbon black, the aim was to compute a set of shape descriptors for each of the carbon black aggregates present in the images. These descriptors would subsequently be used to train certain machine learning algorithms in order to generate models that would predict the shape class of any unclassified carbon black aggregate.

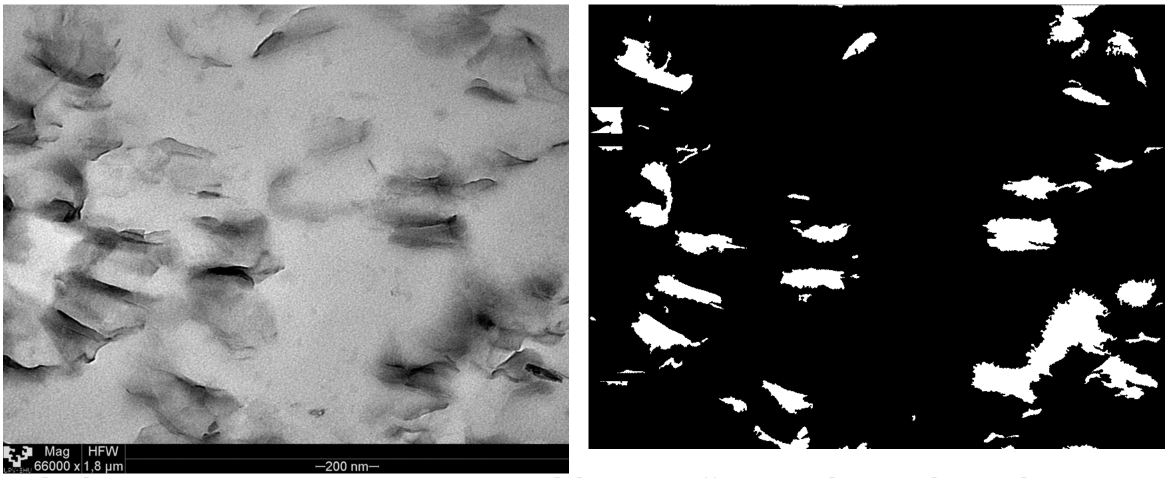
Since the goal of the study is different in the two cases, and the nature of the study objects and as a result of the analyzed images is different, the optimal binarization procedure differed for the two applications.

Results

As shown in Figure 1, optimizing the binarization of the PLA/nanoclay TEM images is not a trivial task. The grey values of the objects of interest cover a very wide range, even overlapping with those of the background. As a result, the binarization considered optimal is far from being perfect. Nevertheless, as shown in table 1, there is a clear correlation between the some of the measured microstructure parameters and the processing conditions, and also between the microstructure and the final properties. These results allow obtaining a better understanding of the processing — final properties relationships.

Figure 1.(Right) Result of the segmentation of (left) a TEM micrograph of PLA/nanoclay.

Two main processing parameters were adjusted to produce the six PLA/nanoclay samples included here: the screw rotation speed during extrusion, and the injection moulding speed. By matching the mechanical properties (just the elastic modulus is shown here) to the injection moulding speed, it can clearly been said that the injection moulding speed has no significant effect in the final mechanical properties. On the other



hand, the extrusion screw rotation speed has an effect on the mechanical properties. Anyway, if the microstructural characterization of the samples were not known it would be difficult to explain why the measured elastic modulus increases by varying the extrusion speed up to a certain point, but not anymore beyond that screw speed. Although it could be expected that by applying more severe processing conditions the dispersion of the clay would be enhanced resulting in higher elastic moduli, the experimental results show otherwise.

Table 1. Selected processing conditions, microstructural parameters and mechanical properties for the PLA/nanoclay composites.

Processing		*Microstructure*		*Mechanical*
Injection speed (mm/s)	**Extrusion speed (rpm)**	**Distance to neighbours**	**Aspect ratio**	**E (Mpa)**
120	120	519	12	3355
240	120	520	12	3587
120	300	409	14	3780
240	300	485	16	3604
120	650	305	6	3370
240	650	331	6	3303

By considering also the data obtained from the microstructural analysis it is observed that as expected increasing the extrusion screw speed leads to a better dispersion of the clays (evidenced by a smaller distance between neighbouring clays). However, the enhanced dispersion is not corresponded by an increase in the elastic modulus. By considering the aspect ratio of the clays (calculated combining the average particle length obtained for the image analysis and the average particle thickness obtained from x-ray diffraction data) a correlation between this parameter and the elastic modulus is observed. Thus, it can be concluded that whereas the more severe processing conditions achieve a better dispersion of the clays, they also seem to break these laminar reinforcing elements reducing the aspect rat[illegible] negative impact on the measured mechanical property.

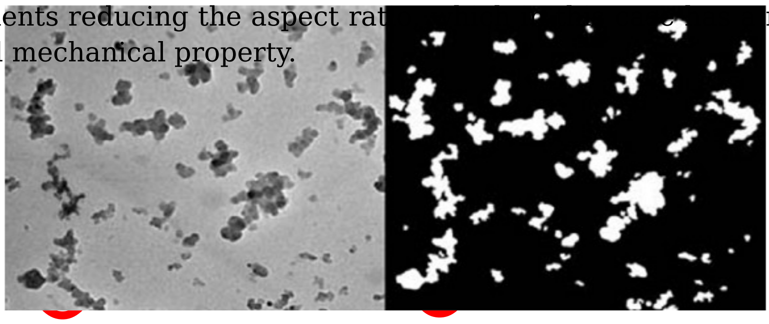
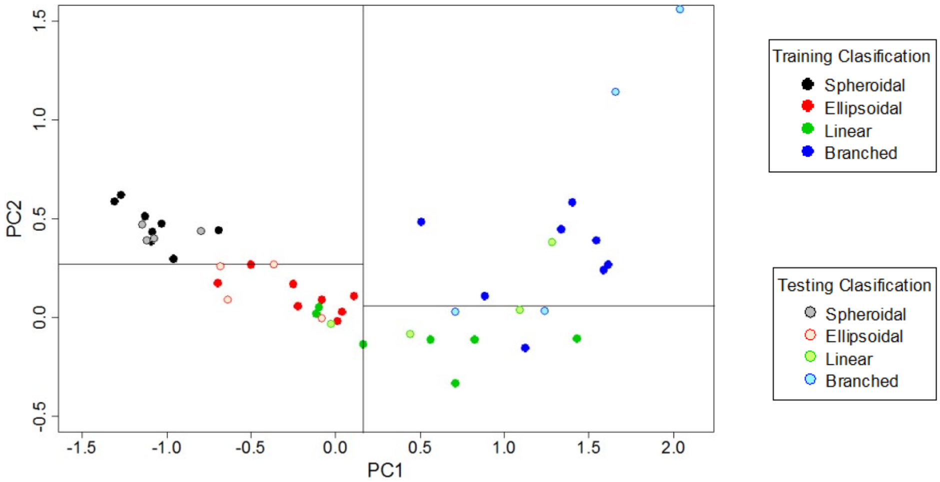


Figure 2. (Top left) TEM image of carbon black particles (aggregates), (top right) corresponding binarized image, and (bottom) example of extracted individual carbon black aggregate.

In the case of the image analysis performed for the carbon black, the binarisation process was less demanding because there is a better contrast between the objects of interest and the background of the images. As shown in Figure 2, the aggregates were detected and binarised, and then separated into individual images. For this study 48 individual objects were analysed, 12 per shape class, and for each of the objects a set of 21 shape descriptors (geometrical and morphological) were computed (Fernandez



Martinez 2014).

Figure 3. Results obtained by the classification tree, shown in terms of the first two principal components. The model splits the space in four areas, corresponding to the four shape classes.

Then, by means of a principal components analysis the high dimensionality of the data set was reduced to just three variables (and still keeping the 90 % of the overall variance of the data). Finally, the classification was performed using decision trees based on evolutionary algorithms. The overall accuracy of the obtained classification model (graphically shown in Figure 3) was 75 %. Although this preliminary study was performed only with a set of 48 objects, the goal of this work is to apply the obtained classification models (the one shown in Figure 3 or others) to classify thousands of carbon black aggregates for each carbon black grade under study, and therefore automating the entire process is important.

Conclusion

Here we present two examples of the used of Automated (TEM) Image Analysis in the field of polymer nanocomposites. In the first study system the AIA is a very effective technique to obtain statistically representative data of the microstructure of the composite, which can be used to get a better understanding of the mechanical properties of the materials. In the second study system the analysis is used to perform, object by object, a quantification of the shape of the carbon black aggregates by computing a set of descriptors. These data are then used to generate models that will predict the shape class of unclassified aggregates. Again, the use of AIA is very important due to the high number of carbon black aggregates required for a correct quantification of relative occurrence of each shape class within a carbon black sample.

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