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## BIONANOCOMPOSITES FOR INDUSTRIAL APPLICATIONS: STRUCTURE-PROPERTY RELATIONSHIPS

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#### Introduction

Bionanocomposites are an emerging class of nanostructured biomaterials, involving a bioderived polymer combined with organic or inorganic fillers, showing at least one dimension at the nanometer scale [1]. These promising materials have potential industrial applications as an alternative to nanocomposites based on petrochemical thermoplastics, in attempting to solve the environmental concerns related to the intensive utilization of non-renewable resources [2]. Similarly to the nanocomposites based on traditional polymers, the introduction of very low nanofiller loadings allows enhancing some inherent properties of biopolymers, such as brittleness, low melt viscosity and low heat distortion temperature, which remarkably limit the utilization of these materials for a wide range of industrial applications [3]. In this work, bionanocomposites based on five different commercial biopolymers, namely four materials belonging to MaterBi® family having proprietary composition (MB1, MB2, MB3, MB4) and a Bioflex sample (BF), and containing 5 wt.% of organo-modified clays (CL20A or BYK) or nanosized calcium carbonate (Socal), were prepared through melt compounding and then subjected to a further processing step, aiming at evaluating their suitability for film blowing or pipe extrusion processes. A systematic rheological characterization of the materials, both in shear and in non-isothermal elongational flow was performed, aiming at obtaining a detailed assessment of the bionanocomposite processing behavior; furthermore, the mechanical behavior of the resulting materials was assessed. This way, it was possible to identify the most promising systems suitable for upscaled film blowing and pipe extrusion operations.

#### **Results and discussion**

Figure 1 reports some representative complex viscosity curves as a function of frequency for both unfilled matrices and bionanocomposites. Regardless of the biopolymeric matrix, the introduction of both types of organo-modified clays caused a significant modification of the material low-frequency rheological response, involving a slowdown of the relaxation processes of the biopolymer macromolecular chains due to the achievement of an intercalated morphology [4]. By contrast, bionanocomposites containing Socal exhibited a rheological behavior quite similar to that of the unfilled matrices, notwithstanding higher viscosity values.

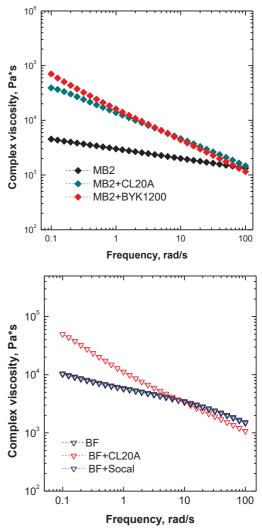


Figure 1: Complex viscosity curves for MB2- and BF-based bionanocomposites (the curves of unfilled matrices are also included).

The analysis of the high-shear rheological response, performed through characterization in a capillary rheometer, suggested a marginal effect of the incorporated nanofiller on the trends of the shear viscosity curves; similar results were obtained from the characterization of the material behavior under non-isothermal elongational flow, as the presence of all type of embedded filler does not remarkably affect the deformability of the biopolymer melts. The mechanical characterization of the bionanocomposites pointed out a beneficial effect of the embedded nanofillers on the elastic modulus of the biopolymers, owing to the homogeneous dispersion of the nanofillers within the host matrices and the good extent of interfacial adhesion (as confirmed by SEM analyses), notwithstanding a slight reduction of the material ductility.

Aiming at evaluating the suitability of the formulated bionanocomposites for the production of blown films or irrigation pipes, their processing behavior was assessed and compared to that of LDPE and HDPE samples, which represent the standard materials usually employed at industrial level for film blowing and pipe extrusion processes, respectively [5]. The flow curves of the studied materials are reported in Figure 2.

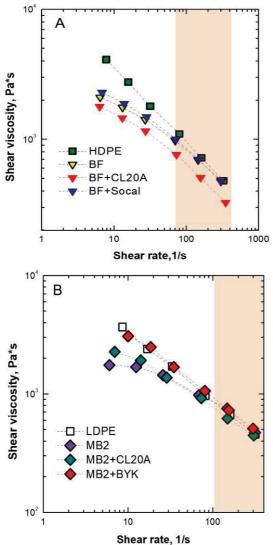


Figure 2: Flow curves for materials suitable for (A) pipe extrusion and (B) film blowing operations.

As far as the behavior of the materials for pipe extrusion applications is concerned (Figure 2A), the analysis of the rheological behavior in the typical shear rate range involved in the extrusion processing allowed for identifying unfilled BF and BFbased nanocomposites as suitable systems, since they exhibited a similar processability compared to HDPE. Besides, looking at Figure 2B that reports the flow curves of materials suitable for film blowing, it is evident that MB2 exhibits a rheological behavior very similar to that of LDPE, indicating that the processability of this biopolymer matches that of the standard material. Furthermore, the rheological characterization performed on MB2-based nanocomposites suggests that the introduction of either CL20A or BYK nanofillers did not significantly modify the rheological behavior of the unfilled matrix. In fact, the shear viscosity values of the MB2-based bionanocomposites are almost unchanged as compared to those of the unfilled biopolymer, highlighting that the processability of MB2 biopolymers is not negatively affected by the presence of embedded nanoclays.

Based on the previous considerations about the rheological behavior of the studied bionanocomposites, the materials showing best processability were then selected for the production of blown films or irrigation pipes and the mechanical properties of the so-processed materials were characterized through tensile tests: the obtained results indicated that the selected bionanocomposites show adequate performances, thus confirming their suitability for these specific industrial applications as an alternative to traditional thermoplastics.

#### Conclusions

In this work, bionanocomposites based on several commercially available biopolymers and containing nanofillers differing for chemical nature and aspect ratio were successfully produced through melt extrusion, and their rheological and mechanical properties were thoroughly assessed. In particular, the characterization of the processing behavior of the formulated materials allowed selecting bionanocomposites suitable for the production of blown films or irrigation pipes. Additionally, the mechanical characterization of the materials subjected to film blowing or pipe extrusion indicated that the selected bionanocomposites show adequate performances, thus confirming their possible industrial exploitation as an alternative to traditional thermoplastic materials.

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