



## Macromolecular Nanotechnology

# Linear and non-linear rheological behavior of polypropylene/polyamide blends modified with a compatibilizer agent and nanosilica and its relationship with the morphology



Leire Sangroniz<sup>a</sup>, Jordana K. Palacios<sup>a</sup>, Mercedes Fernández<sup>a</sup>, José Ignacio Eguiazabal<sup>a</sup>, Antxon Santamaria<sup>a,\*</sup>, Alejandro J. Müller<sup>a,b,\*</sup>

<sup>a</sup> POLYMAT and Polymer Science and Technology Department, Faculty of Chemistry, University of the Basque Country UPV/EHU, Paseo Manuel de Lardizabal 3, 20018 Donostia-San Sebastián, Spain

<sup>b</sup> IKERBASQUE, Basque Foundation for Science, Bilbao, Spain

## ARTICLE INFO

## Article history:

Received 17 May 2016

Received in revised form 22 July 2016

Accepted 30 July 2016

Available online 1 August 2016

## Keywords:

Polymer blends  
Nanocomposites  
Morphology  
Rheology  
Coalescence  
LAOS

## ABSTRACT

The morphology of immiscible 80/20 polypropylene/polyamide 6 (PP/PA) blends that contain different types of nanosilica and a compatibilizer agent was correlated with their linear and non-linear rheological behavior. Polypropylene grafted with maleic anhydride (PPgMA) was used as compatibilizer agent. Two types of modified silica nanoparticles were added to the blends, one hydrophilic (NSE) and the other hydrophobic (NSH). SEM and TEM microscopy were employed to observe the sea-island morphology of the 80/20 blends. The size of the PA droplets was reduced 12 times when the compatibilizer agent was added; and 25 times when hydrophobic nanosilica (NSH) was additionally included in the formulation. TEM results revealed that NSH particles are preferentially located at the PP-PA interface, whereas NSE particles remain inside the PA droplets. A good agreement between morphology and Small Amplitude Oscillatory Shear tests (SAOS) was observed. At low frequencies a suspension-like rheological behavior was identified for the blends containing nanosilica. The results at intermediate frequencies allowed the evaluation of the shape relaxation time of the droplets. Large Amplitude Oscillatory Shear tests (LAOS) results correlate well with droplets size. The coalescence promoted by flow was investigated, and in the case of the neat binary blend, coalesced blends were obtained. Employing LAOS results determined by measuring blends with a wide range of droplet sizes, an inversely proportional function of a characteristic LAOS parameter with the diameter of the droplets was obtained.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Immiscible polymer blends exhibit a variety of morphologies [1–3] that determine the final properties of the material [2–4]. However, these immiscible blends are characterized by a high interfacial tension and poor adhesion between the phases, which lead to poor mechanical properties [1,5]. Therefore, compatibilization is needed to obtain a finer dispersion of the minor phase, reduce the interfacial tension and enhance adhesion between phases [1,2,5]. Polymer blends have been

\* Corresponding authors at: POLYMAT and Polymer Science and Technology Department, Faculty of Chemistry, University of the Basque Country UPV/EHU, Paseo Manuel de Lardizabal 3, 20018 Donostia-San Sebastián, Spain (A.J. Müller and A. Santamaria).

E-mail addresses: [antxon.santamaria@ehu.es](mailto:antxon.santamaria@ehu.es) (A. Santamaria), [alejandrojesus.muller@ehu.es](mailto:alejandrojesus.muller@ehu.es) (A.J. Müller).

compatibilized adding block or grafted copolymers or by reactive compatibilization [5]. However, another compatibilization strategy, based on the addition of organic or inorganic fillers has been developed recently [6–12]. Addition of fillers can change mechanical, thermal and electrical properties of the blends by modifying the morphology. The level of dispersion and the location of the fillers are both crucial for the final behavior.

The use of nanoparticles to stabilize immiscible polymer blends is a more versatile strategy as compared to copolymers, since a specific copolymer is needed for each polymer blend [12,13].

Nanofillers can be situated in one of the phases, at the interface between the matrix and the dispersed phase, or both. In case of location at the interface, size reduction of the dispersed phase is favored by the hindrance of coalescence, since the nanofillers form a physical barrier around the droplets. In addition, interfacial adhesion can be improved depending on the affinity between polymer phase and nanofiller [10,11].

The morphology of immiscible blends can be significantly affected by flow [2,3]. The final morphology of an immiscible blend submitted to flow results from a balance between coalescence, which leads to minimize the energy of the system, and droplet break up, which arises from the forces induced by the matrix. Flow induced coalescence in polymer blends and nanocomposite blends has been reported in the literature [6,14–18], including the reduction of the coalescence due to the addition of compatibilizers [15] and fillers [6,16].

The rheological features of immiscible polymer blends are influenced by the concentration of each phase, flow geometry, type of flow field and interactions between phases, among others. Nevertheless, the most influencing factor on the linear and non-linear rheological behavior is the morphology and the interfacial tension between the phases [3,19].

Immiscible blends containing nanofillers have been analyzed in the linear viscoelastic regime, and properties, such as the interfacial tension, have been estimated by the application of viscoelastic models, like the Palierne model [7,15]. Since this model was proposed initially for polymeric emulsions [20], it has been modified to take into account the presence of fillers [21].

The rheological behavior under non-linear conditions is also interesting because during regular processing operations the large strains applied lead to a non-linear response. This issue has been reported in several works [22,23] in which Large Amplitude Oscillatory Shear (LAOS) flow tests have been used to study topology and morphology of the blends. For instance, Reinheimer et al. [24] found a relationship between LAOS measurements and the size and size distribution of the droplets in emulsions. More recently, Hyun et al. [25–28] used a parameter that quantifies the non-linear viscoelasticity and its relation with the size of the droplets in immiscible blends that contain different types of fillers.

In a previous work [29], the rheological behavior of immiscible polypropylene/polyamide 6 (PP/PA) 80/20 blends containing hydrophobic nanosilica was reported. The nanosilica caused a dramatic refinement of the PA dispersion within the PP matrix. However, rheological measurements showed that NS did not act as a compatibilizer. In fact, lack of adhesion between the phases and relatively poor mechanical properties of the nanocomposite blends was observed.

In this paper, 80/20 PP/PA blends containing PPgMA (polypropylene grafted with maleic anhydride) as compatibilizer and two types of nanosilica are investigated. The morphology of the blends and the nanocomposite blends was observed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The linear and non-linear viscoelastic properties of the blends are studied by small amplitude (SAOS) and large amplitude (LAOS) oscillatory shear measurements, to demonstrate that both rheological techniques offer complementary results. Finally, coalescence triggered by continuous shear flow is analyzed. A wide range of droplets sizes provides us the possibility of establishing a correlation between the size of the droplets and a characteristic LAOS derived parameter.

## 2. Experimental

### 2.1. Materials

The polymers used in this study were isotactic polypropylene (PP) supplied by Repsol (ISPLEN PP070G2M) (MFR = 12 g/10 min (230 °C/2.16 kg)) and polyamide 6 (PA) from LANXESS (Durethan B 30 S) (MFI = 102 g/10 min (260 °C/5 kg)). Polypropylene grafted with maleic anhydride (PPgMA), supplied by DuPont (Fusabond P353) (MFR = 22.4 g/10 min (160 °C/325 g)), was used as compatibilizer agent. Two modified nanosilica (NS) were employed: a hydrophobic nanosilica (NSH), supplied by CABOT (CAB-O-SIL TS 530, surface area of 225 m<sup>2</sup>g<sup>-1</sup>, average particle (aggregate) length of ca. 200–300 nm) treated with hexamethyldisilazane, and a hydrophilic nanosilica (NSE) supplied by Skyspring Nanomaterials, Inc. (6852HN, surface area of 90–130 m<sup>2</sup>g<sup>-1</sup>, dimensions of 10–20 nm), which contains epoxy groups.

### 2.2. Blend preparation

The materials were dried overnight under vacuum at 80 °C prior to extrusion. The blends and blend nanocomposites were prepared in a Collins co-rotating twin screw extruder at 40 rpm, with a profile temperature range from 200 to 240 °C. The PP/PA ratio was 80/20 weight/weight. PPgMA was added as 10% with respect to the PA phase; and nanosilica (NSE or NSH) as 5% with respect to the total amount of the blend. The blends were compression molded using a hydraulic press at 235 °C. The compositions of the prepared samples are indicated in Table 1.

Download English Version:

<https://daneshyari.com/en/article/1401184>

Download Persian Version:

<https://daneshyari.com/article/1401184>

[Daneshyari.com](https://daneshyari.com)