



An insight into the interaction between functionalized thermoplastic elastomer and layered double hydroxides through rheological investigations

Rossella Arrigo^a, Nadka Tzankova Dintcheva^{a,*}, Giuseppe Tarantino^a, Elisa Passaglia^b,
Serena Coiai^b, Francesca Cicogna^b, Sara Filippi^c, Giorgio Nasillo^d, Delia Chillura Martino^d

^a Dipartimento di Ingegneria Civile, Ambientale, Aerospaziale, dei Materiali, Università di Palermo, Viale delle Scienze, Ed. 6, 90128 Palermo, Italy

^b Istituto di Chimica dei Composti Organometallici (ICCOM-CNR), UOS Pisa - Via Moruzzi 1, 56124 Pisa, Italy

^c Dipartimento di Ingegneria Chimica, Università di Pisa, via Diotisalvi 2, 56126 Pisa, Italy

^d Centro Grandi Apparecchiature-ATeN Center, Università di Palermo, Via Filippo Marini, 14, 90128 Palermo, Italy

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ABSTRACT

Nanocomposites based on maleated poly(styrene-ethylene-co-butylene)-styrene copolymer (SEBSgMA) and organo-modified layered double hydroxide (OLDH) have been formulated with the aim to investigate the effects of interfacial interactions between the grafted maleic anhydride groups of the copolymer and the OLDH nanolayers on the rheological properties of nanocomposites. The spectroscopic analysis indicates the establishment of specific polymer/nanofiller interactions, whose extent has been highlighted through morphological and rheological investigations. Specifically, oscillatory melt rheology and shear relaxation tests have been considered in order to deeply investigate the interfacial bridging interactions. Obtained results highlight that SEBSgMA-based nanocomposites containing a high amount of OLDH show solid-like rheological behavior, quite similar to that of crosslinked polymers, attributable to the formation of a gel-like structure.

1. Introduction

In polymer-based nanocomposites, the interactions established at the interface between dispersed inorganic nanoparticles and macromolecular chains represent a key factor to obtain hybrid materials with superior properties [1–3]. Indeed, the enhancement of the nanocomposite final properties depends largely on the distribution and dispersion of the nanoparticles within polymer matrix and on the morphology of resulting nanocomposite, as well as on the state of the interfacial region [4–6]. In this view, in an ideal nanocomposite containing layered nanoparticles, the inorganic nanofillers are completely separated into individual layers, resulting in the formation of a fully exfoliated morphology, and a large contact surface area between the two phases is obtained [7,8]. So far, several approaches have been pursued to enhance the dispersion of inorganic nanoparticles within polymers and to improve the state of interfacial region, including the functionalization and/or organo-modification of the nanofillers [9–12] as well as the addition of a compatibilizer to system [13,14]. In the case of layered double hydroxides (LDHs)-containing nanocomposites, the modification of the nanoparticles can be achieved through the exchange of the interlayer anions with anionic organo-modifiers that increase the distance between the inorganic layers, facilitating the intercalation of

polymer chains into the inter-layer galleries and, at the same time, enhance the compatibility of LDHs with the matrix [15–18]. A further method to improve the interfacial interactions and, hence, the morphology of polymer-based nanocomposites is the functionalization of the polymer backbone with polar groups, such as maleic anhydride [19,20], acrylic acid [21] or epoxy [22], which are able to interact with the added nanoparticles. For instance, Chen et al. [23] formulated nanocomposites based on maleated polypropylene and organo-modified LDHs obtaining fully exfoliated morphology, which is invoked as responsible for their enhanced flame-retardant properties and thermal stability. Lonkar et al. [24] prepared maleated polypropylene/LDHs nanocomposites by direct melt intercalation method, verifying the occurrence of interactions between maleic anhydride polar groups and nanoparticles that cause the formation of exfoliated structures with consequent obtainment of a homogeneous dispersion of LDHs layers. Recently, it has been demonstrated that in polyolefin/organo-LDH nanocomposites increasing the amount of the organo-LDH, the functionalization of polyolefins with maleic anhydride functionalities brings about to the obtainment of strong ionic interactions between macromolecules and inorganic nanoparticles, which are likely established between the carboxyl groups on the polymer and the inorganic layers with the assistance of the organo-LDH surfactant [25]. The occurrence

* Corresponding author.

E-mail address: nadka.dintcheva@unipa.it (N.T. Dintcheva).

of strong polymer-nanoparticles interactions, thus, favors the obtainment of intercalated and exfoliated morphologies but also causes the formation of interconnected structures of nanofillers, such as percolative networks [26], modifying the dynamics of macromolecular chains and the melt-state behavior of the nanocomposite [27,28]. For this reason, the study of the rheological behavior of polymer/layered nanoparticles nanocomposites allows to gain a fundamental understanding of the possible interactions between dispersed nanoparticles and matrix, as well as between nanoparticles themselves. Indeed, it is known that oscillatory melt rheology is a very sensitive method to characterize the microstructure of polymer melts; particularly, when the formation of complex architectures of nanofillers occurs, significant changes in the dynamic moduli and complex viscosity spectra can be observed [29–31]. By considering the interest in preparation of nanocomposites based on thermoplastic elastomers, exhibiting rubber-like property and melt processability comparable to conventional thermoplastics, in this work poly(styrene-(ethylene-co-butylene)-styrene) triblock copolymer (SEBS) and maleic anhydride functionalized SEBS (SEBSgMA) were selected as matrices and used for the preparation of nanocomposites with an organo-LDH (OLDH). The nanocomposites have been formulated through melt mixing and attention was given to verify the occurrence of interfacial interactions between the polymer functional groups and the nanoparticles layers. For this purpose, accurate spectroscopic, morphological and, in particular, rheological measurements have been performed and the obtained results allowed to relate the microstructure of nanocomposites with the establishment of specific polymer/nanofillers interactions.

2. Experimental part

2.1. Materials

A maleated poly(styrene-(ethylene-co-butylene)-styrene) triblock copolymer (SEBSgMA) is a commercial sample *Kraton*[®] (Houston, TX, USA) *FG1901X Polymer*, having polystyrene content of about 30 wt% and maleic anhydride content about 1.4–2.0 wt%.

A poly(styrene-(ethylene-co-butylene)-styrene) triblock copolymer (SEBS) is a commercial sample *Kraton*[®] (Houston, TX, USA) *G1633E Polymer*, having polystyrene content of about 29.5 wt%.

A Magnesium Aluminum Layered Double hydroxides modified with hydrogenated fatty acids Perkalite F100S (OLDH) (the amount of hydrogenated fatty acids, stearate and palmitate, is 55 wt% and a low content of free carboxylic salts is present) was kindly supplied by Akzo Nobel (Amsterdam, The Netherlands).

2.2. Nanocomposites processing

The preparation of SEBSgMA/OLDH and SEBS/OLDH nanocomposites was carried out using a Brabender (Duisburg, Germany) mixer at 170 °C, 50 rpm for 5 min. The OLDH was added at three different content 1, 2.5 and 5 wt%. The pristine SEBSgMA and SEBS copolymers were subjected to the same processing. During the processing the torque values were recorded. All specimens used for the different characterizations were prepared by a compression molding step, using a Carver Press (Wabash, IN, USA) at the same processing temperature, for 5 min, under a pressure of about 30 MPa. Small pieces of pristine copolymer SEBSgMA as well as of SEBSgMA/OLDH 5 wt% composite (around 1.5 g) were placed into a cellulose extraction thimble and extracted with boiling chloroform for 8 h. The non-extractable fraction was vacuum dried to constant weight.

2.3. Characterizations

FT-IR analysis was carried out by using a Perkin Elmer (Waltham, MA, USA) FT-IR spectrometer (mod. Spectrum Two). The spectra were collected by performing 32 scans between 4000 and 450 cm⁻¹.

WAXD patterns were obtained by a Siemens (Aubrey, Texas, USA) D-500 diffractometer in the reflection mode with an incident X-ray wavelength of 0.1542 nm, on specimens thick about 2 mm.

Scanning Electron Microscopy (SEM) investigation was performed on nitrogen-fractured radial surfaces of all specimens by a Philips (Amsterdam, The Netherlands) ESEM XL30 equipment.

Transmission Electron Microscopy (TEM) observations were performed by JEOL (Akishima, Japan) JEM-2100 microscope with an acceleration voltage of 200 kV.

Rheological tests were performed using a strain-controlled rheometer (mod. ARES G2 by TA Instrument, New Castle, DE, USA) in parallel plate geometry (plate diameter 25 mm). The complex viscosity and storage and loss moduli were measured performing frequency scans from 10⁻²–10² rad/s at 170 °C. The strain amplitude was $\gamma = 2\%$, which preliminary strain sweep experiments proved to be low enough to be in the linear viscoelastic regime. Linear stress relaxation measurements were carried out submitting the samples to a single step strain $\gamma_0 = 1\%$, and the shear stress evolution during time $\sigma(t)$ was measured to obtain the relaxation modulus $G(t) = \sigma(t)/\gamma_0$. Time sweep tests were carried out at 170 °C, $\omega = 0.1$ rad/sec, $\gamma = 2\%$ and for a time of 10⁴ s.

As regards the reproducibility of the obtained results, it was satisfactory ($\pm 5\%$).

3. Results and discussion

Nanocomposites based on SEBSgMA and containing different amount of OLDH have been formulated through melt mixing and the torque values recorded during the processing are reported in Fig. 1 (a). The values of the torque of neat matrix remain almost unchanged during the processing time, indicating that the chosen processing time is enough to obtain a homogeneous system and that no significant structural changes occur. The addition of 1 wt% of OLDH does not modify the trend of the torque with respect to the neat matrix, while the samples containing higher amounts of nanoparticles show a different behavior. Particularly, the torque values for SEBSgMA/OLDH nanocomposites containing 2.5 and 5 wt% of OLDH significantly increase at short processing times and remain higher than those of the neat matrix during the whole processing time. On the contrary, the trend of the torque as a function of the processing time for the samples based on unmodified SEBS and OLDH (Fig. 1 (b)) did not show difference between the neat matrix and composites; although for the system containing 5 wt% of OLDH higher values are obtained with respect to the neat matrix, the torque remains quite constant for the whole processing time. This different trend might be due to a different morphology of the two series of composites (SEBSgMA/OLDH vs SEBS/OLDH). Indeed, the increase of the torque for polymer nanocomposites based on layered fillers is due to fracturing of nanoparticles into smaller aggregates as well as to delamination and favorable interactions between layers and polymer chains. However, on the basis of our previous work on composites prepared by mixing polyethylene functionalized with MAH and OLDH [32], it is also possible that SEBSgMA is converted in an ionomer in the presence of OLDH thus behaving like ionic coupling agent and determining the formation of a gel-like structure by the direct chemical interaction between the carboxylic groups of the polymer and metal ions present in LDH [15]. The overall effect of this phenomenon may also cause the torque increase. Accordingly, to investigate in depth the interactions between functionalities of SEBSgMA and OLDH, FTIR analysis was carried out and in Fig. 2 the spectra in the range 2000–1550 cm⁻¹ of neat SEBSgMA and OLDH-containing nanocomposites are shown. In the spectrum of SEBSgMA, two peaks at 1788 and 1870 cm⁻¹ can be noticed, which can be attributable to the asymmetric and symmetric stretching vibrations of the grafted succinic anhydride functionalities, respectively [25], even if they partially overlap with two typical absorption bands of aromatic overtones of styrene-blocks at about 1870 and 1800 cm⁻¹. Furthermore, a peak at

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