Materials & Design 131 (2017) 232–241

Contents lists available at ScienceDirect

Materials & Design

journal homepage: www.elsevier.com/locate/matdes

Unrevealing the effect of different dispersion agents on the properties of ethylene–propylene copolymer/halloysite nanocomposites

E. Bischoff[a,b], G.P.O. Gonçalves[a], D.A. Simon[a,b], H.S. Schrekker[a], M. Lavorgna[c], L. Ambrosio[c], S.A. Liberman[a], R.S. Mauler[a,*]

[a] Institute of Chemistry, Universidade Federal do Rio Grande do Sul – UFRGS, Av. Bento Gonçalves 9500, Porto Alegre, RS 91501-970, Brazil
[b] Federal Institute of Rio Grande do Sul – IFRS, Campus Farroupilha, Av. São Vicente 785, Farroupilha, RS 95180-000, Brazil
[c] National Research Council, Institute for Composite and Biomedical Materials, P.le E. Fermi, 1, 80155 Portici (Naples), Italy

A R T I C L E I N F O

Keywords:
Compatibilizing agents
Hydrocarbon resin
Halloysite nanotubes
Heterophasic ethylene-propylene
AFM analysis

A B S T R A C T

The properties of polyolefin nanocomposites strongly depend on the dispersion level of the nanoparticles and the addition of dispersion agents contributes to improving their performance. In this study, the morphology and the mechanical properties of heterophasic ethylene-propylene copolymer/halloysite nanocomposites were tailored by using two hydrogenated hydrocarbon resins: 90% and 100% hydrogenated and two compatibilizing agents: poly(propylene-g-maleic anhydride) and poly(ethylene-octene-g-maleic anhydride). The transmission electron microscopy indicated that the best dispersion of the halloysite nanotubes was achieved when hydrogenated hydrocarbon resins and poly(propylene-g-maleic anhydride) were used simultaneously. All nanocomposites showed an increase in mechanical stiffness and the most pronounced increase of 46% in the Young modulus was achieved with the system containing halloysite, poly(propylene-g-maleic anhydride) and the hydrocarbon resin with the higher degree of hydrogenation. Poly(ethylene-octene-g-maleic anhydride) caused the halloysite nanoparticles to concentrate preferentially in the rubber domains, wherein these hindered the crystallization of polypropylene and polyethylene chains, as showed by atomic force microscopy. In this case, the composite exhibited both high stiffness and improved toughness. These results highlight the key role of dispersion agents in promoting a good balance in the mechanical properties of resulting nanocomposites based on halloysite particles and heterophasic ethylene-propylene copolymers.

1. Introduction

Currently, heterophasic ethylene-propylene copolymers (EPP) are produced by sequential multistage polymerization processes with Ziegler-Natta catalysts [1] and consist of ethylene units randomly inserted into the predominantly polypropylene sequence [2]. Due to this chemical structure, in the solid state, EPP presents a dispersed rubbery phase (EPR) embedded in the polypropylene matrix, which promotes high toughness and impact resistance at low-temperature [3]. Nevertheless, the presence of the elastomeric component inevitably has a detrimental effect on the material's stiffness [4]. Thus, the incorporation of rigid nanoparticles represents a promising approach to tailor both stiffness and toughness, which is required for many applications.

The effect of halloysite nanotubes (HNT) on the mechanical and thermal properties of polymer nanocomposites has been the subject of various studies [5–7]. HNT having the molecular formula $Al_2Si_2O_5(OH)_4{\cdot}nH_2O$ is an abundant natural nanomaterial that consists of hollow cylinders formed by multiple rolled layers, composed of a SiO_2 outer layer and an Al_2O_3 inner layer of the tubes [8]. Due to this chemical composition, HNT is a polar hydrophilic material, which makes its dispersion within a non-polar polymeric matrix difficult to be achieved.

An optimized dispersion and distribution of nanofillers is an important prerequisite to reach advanced performances in polymer nanocomposites. Therefore, efforts have been addressed to improve the dispersion of HNT in a polymer matrix by modifying its surface with organic moieties such as organosilanes [9], ionic liquids [10] and surfactants [11]. Although, this is an effective method, the process is relatively complex, expensive and time-consuming [12], especially if applied on an industrial scale.

Thus, the addition of a polar compatibilizer such as poly(propylene-g-maleic anhydride) (PP-g-MA) or poly(ethylene-octene-g-maleic anhydride) (EO-g-MA), easy to be processed with the polymer, represents a valid approach to improve the HNT dispersion [13]. As already

* Corresponding author.
E-mail address: raquel.mauler@ufrgs.br (R.S. Mauler).

http://dx.doi.org/10.1016/j.matdes.2017.06.033
Received 28 March 2017; Received in revised form 23 May 2017; Accepted 13 June 2017
Available online 14 June 2017

Table 1
Samples codes and compositions (%).

Code	Composition					
	EPP	PP-g-MA	EO-g-MA	HHR	PHR	HNT
EPP	100	–	–	–	–	–
EPP/PP-g-MA	98	2	–	–	–	–
EPP/EO-g-MA	98	–	2	–	–	–
EPP/HHR	95	–	–	5	–	–
EPP/PHR	95	–	–	–	5	–
EPP/HNT	98	–	–	–	–	2
HR nanocomposites						
EPP/HNT/HHR	93	–	–	5	–	2
EPP/HNT/PHR	93	–	–	–	5	2
PP-g-MA nanocomposites						
EPP/HNT/PP-g-MA	96	2	–	–	–	2
EPP/HNT/PP-g-MA/HHR	91	2	–	5	–	2
EPP/HNT/PP-g-MA/PHR	91	2	–	–	5	2
EO-g-MA nanocomposites						
EPP/HNT/EO-g-MA	96	–	2	–	–	2
EPP/HNT/EO-g-MA/HHR	91	–	2	5	–	2
EPP/HNT/EO-g-MA/PHR	91	–	2	–	5	2

reported by other authors who used montmorilonite (MMT) as filler in PP [14,15], the dispersion may significantly improve by using selected compatibilizing agents such as Hydrogenated hydrocarbon (HR). These HR are amorphous polymers that are miscible with the amorphous fraction of PP [16] and, due to their low molecular weight and viscosity [17], may act as a processing aid to facilitate the clay dispersion. Cimmino et al. [16] showed that cycloaliphatic monomer based HR enhanced the dispersion of unmodified and modified MMT in PP, leading to a significative improvement in the mechanical properties and water vapor permeability. Another study that used the same approach afforded PP nanocomposites with higher thermal stability [17].

To date, no studies have addressed the understanding of a possible synergism between compatibilizing agents and HR in the improvement of mechanical and functional properties of EPP/HNT nanocomposites. So, the main objective of this study is to understand the effect of these dispersing agents on the HNT dispersion and distribution as well as the morphology of the dispersed rubber phase and their interfacial interactions with the polypropylene matrix.

2. Experimental

2.1. Materials

Braskem S.A. (Brazil) provided EPP with a melt flow index (MFI) of 27.7 g/10 min (230 °C/2.16 kg) and total ethylene content of approximately 14 wt%. HNT was acquired from Sigma-Aldrich. The HNT has specific gravity of 2.53 g·cm^{-3}, surface area of 64m^{2}·g^{-1}, pore volume of 1.26–1.34 mL·g^{-1}, cation exchange capacity of 8.0 mEq·g^{-1} and Zeta potential of 222.543 mV. The hydrocarbon resins Regalite R1125 (HHR), 100% hydrogenated, and R1090 (PHR), 90% hydrogenated were obtained from Eastman Chemical Co. The compatibilizing agents Polybond 3150, poly(propylene-g-maleic anhydride) (PP-g-MA) with a MA content of 0.5 wt% and MFI of 50 g/10 min (230 °C/2.16 kg), and SCONA TSPOE 1002 GBLL, poly(ethylene-octene-g-maleic anhydride) (EO-g-MA) with a MA content in the range of 1.45–1.65% and MFI of 6–23 g/10 min (190 °C/21.6 kg), were purchased from Chemtura and *BYK* Additives & Instruments, respectively.

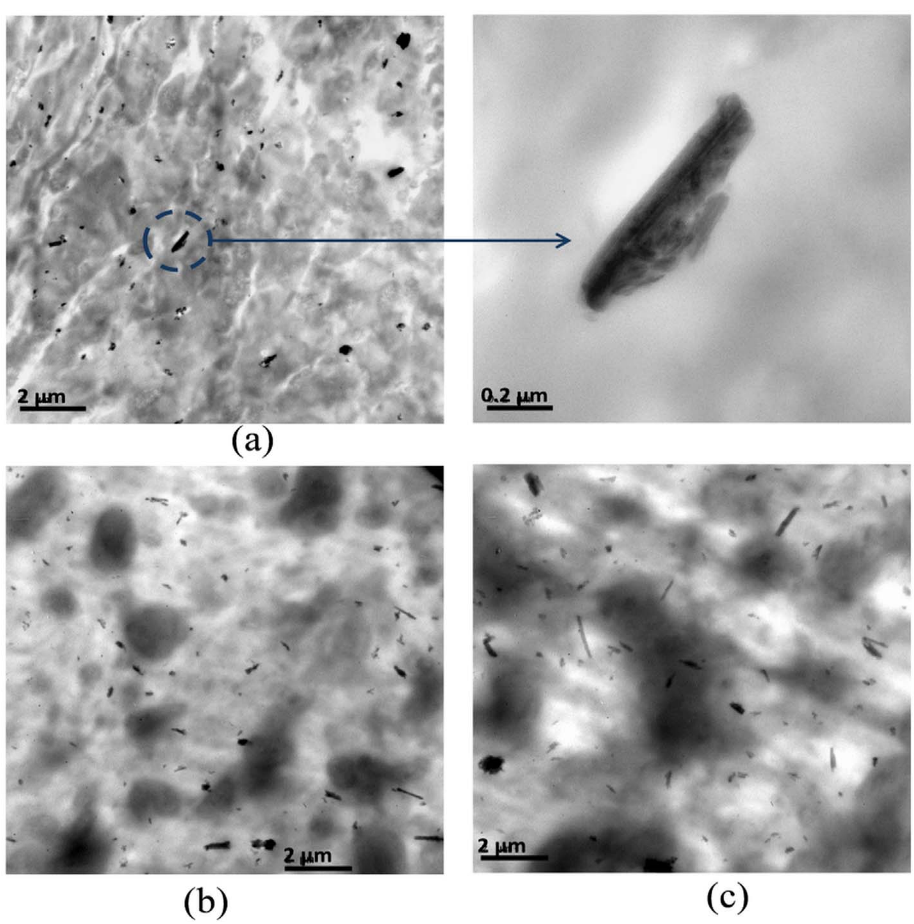

Fig. 1. TEM images of (a) EPP/HNT, (b) EPP/HNT/HHR and (c) EPP/HNT/PHR nanocomposites.