Journal of Alloys and Compounds 616 (2014) 569–576

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

# The effect of polystyrene blocks content and of type of elastomer blocks on the properties of block copolymer/layered silicate nanocomposites

Zina Vuluga [a,*,1], Denis Mihaela Panaitescu [a,*,1], Catalina Gabriela Sanporean [b,2], Constantin Radovici [a], Raluca Gabor [a], Cristian Andi Nicolae [a], Mihai Cosmin Corobea [a], Michaela Iorga [a], Dorel Florea [a]

[a] National Research and Development Institute for Chemistry and Petrochemistry-ICECHIM Bucharest, 202 Spl. Independentei, 060021, Romania
[b] Department of Mechanical and Manufacturing Engineering, Aalborg University, Aalborg, Denmark

ARTICLE INFO

*Article history:*
Received 28 March 2014
Accepted 20 July 2014
Available online 30 July 2014

*Keywords:*
Elastomers
Inorganic materials
Nanostructured materials
X-ray diffraction
AFM
DMA properties

ABSTRACT

The aim of the present work was to understand the block copolymer/layered silicate interactions as function of polystyrene blocks content and of the type of elastomer blocks in the block copolymer. Using dynamical melt intercalation method, styrene triblock copolymer/Dellite 67G nanocomposites were obtained. The properties of nanocomposites were evaluated by morphological (XRD and AFM), thermal (DSC), mechanical and dynamic mechanical (DMA) analysis. The polystyrene chains of block copolymer preferentially intercalated into the galleries of Dellite 67G and probably interacted with the surface of the silicate increasing the uniform dispersion of the silicate in the polymer matrix. Homogenous nanocomposites having ordered lamellar structure were obtained. The silicate agglomerates were split into stacks of 3–4 layers which were evenly dispersed in the polymer matrix. The block copolymer/Dellite 67G interaction was reflected in the increasing of stiffness (modulus and hardness) with maintaining of toughness, up to 30 wt.% Dellite 67G. Over 30 wt.% silicate the mechanical properties decreased, probably as result of the agglomeration of silicate particles. AFM investigation brought complementary information to XRD patterns of the nanocomposites revealing a second type of intercalated structures with interlamellar distance higher with one order of magnitude.

## 1. Introduction

Thermoplastic elastomers have gained a great importance in the last years due to their unique combination of the rubber properties and thermoplastic processability and recyclability [1]. These properties made the thermoplastic elastomers commercially important materials widely used in various applications, ranging from adhesives, sealants, coatings, footwear up to automotive parts, impact modifiers in engineering plastics and wire insulation. However, further improvement of properties is required to fulfil the demands of engineering applications. So far, many researchers have tried to improve the performance of thermoplastic elastomers and the incorporation of a layered silicate (montmorillonite) has been reported as an efficient method [2–7]. Thermoplastic elastomer/layered silicate nanocomposites with better mechanical and thermal properties as compared to those of neat block copolymer, were prepared using melt intercalation [5,7–12], solution casting [8,12–14], masterbatch [8] or sol–gel process [15–18].

Among the thermoplastic elastomers, the triblock copolymers with typical example the polystyrene–*block*-polybutadiene–*block*-polystyrene triblock copolymer (SBS) are a special category characterized by high service temperature and good solvent resistance. The non-polar nature of block copolymers makes very difficult the uniform dispersion of layered silicates. To improve the dispersion and further expanding the interlayer spacing of the montmorillonite, block copolymers with grafted functional groups (such as maleic anhydride and acrylic acid) have been used [9,11,19]. Few reports describe the interactions in block copolymer/layered silicate nanocomposites [13,20]. Vaia and Giannelis showed that styrene blocks intercalate into the interlayer of silicate via Lewis acid–base interaction and the elastomer blocks do not interact with silicate [21]. A model was also proposed for block copolymer/layered silicate nanocomposites and it consists of polystyrene segments located close to the layered silicate surface and elastomeric blocks in the center of the gallery [13].

The present work is a systematic study of the influence of layered silicate on the properties of block copolymers with the

---

* Corresponding authors.
*E-mail addresses:* zvuluga@yahoo.com (Z. Vuluga), panaitescu@icf.ro (D.M. Panaitescu).
[1] Zina Vuluga and Denis Mihaela Panaitescu contributed equally to this work.
[2] Previously Potarniche.

http://dx.doi.org/10.1016/j.jallcom.2014.07.144
0925-8388/

aim to understand the block copolymer/layered silicate interactions as function of polystyrene blocks content and of type of elastomer blocks in the block copolymer. This is very important for tailoring the stiffness–toughness properties of these materials for automotive and other applications. The amount of layered silicate in the composites was varied over a wide range, from 0 to 50 wt.% to determine the maximum concentration of silicate which can be uniformly dispersed in the block copolymer matrix by melt intercalation. Styrene block copolymers with linear or radial architecture and butadiene or isoprene mid-blocks were used in this study. The extensive analyses of morphological, mechanical, thermal and dynamic mechanical properties of block copolymer/layered silicate nanocomposites containing variable amount of organomodified montmorillonite as well as different types of block copolymers provide the supporting data for both the experimental endeavor and theoretical explanation.

## 2. Experimental

### 2.1. Materials

Dellite 67G (D67G), a montmorillonite organically modified by cation exchange reaction with high content of dimethyl dihydrogenated tallow ammonium chloride, provided by Laviosa Chimica Mineraria, was used as received.

The following thermoplastic elastomers (TPE) were used:

- Radial styrene–butadiene–styrene block copolymer (SBS-R) with 32% polystyrene, $M_n$ = 198,000, MFI < 1 g/10 min (190 °C/5 kg) (Europrene Sol T 161 C).
- Linear styrene–butadiene–styrene block copolymer (SBS-L) with 31.8% polystyrene, $M_n$ = 89,000, MFI = 6.46 g/10 min (190 °C/5 kg) (Europrene Sol T 166).
- Linear styrene–isoprene–styrene block copolymer (SIS-19) with 19.11% polystyrene, $M_n$ = 115,000, MFI = 11.38 g/10 min (190 °C/5 kg) (Europrene Sol T 9113).
- Linear styrene–isoprene–styrene block copolymer (SIS-30) with 29.68% polystyrene, $M_n$ = 89,000, MFI = 6.00 g/10 min (190 °C/5 kg) (Europrene Sol T 9326).

Number average molar mass ($M_n$) was in-house measured by size exclusion chromatography (SEC) in tetrahydrofuran (THF) against polystyrene standards.

### 2.2. Nanocomposites preparation

Nanocomposites with different content of organically modified layered silicate were obtained in dynamical conditions, by melt intercalation method, using a Brabender Plastograph, at 170 ± 5 °C and 100 rpm for 15 min. The obtained nanocomposites were marked as TPE/XD67G where TPE represents one of the thermoplastic elastomers mentioned above and X represents the concentration of Dellite in nanocomposites.

### 2.3. Characterization

#### 2.3.1. X-ray diffraction

The basal spacing, $d_{001}$, was determined by X-ray diffraction (XRD) on a DRON diffractometer, using the Co K$\alpha$ radiation source ($\lambda$ = 1.79021 Å) filtered with Fe for K$\beta$ component removing, in Bragg–Brentano system. The samples were scanned at a scanning rate of 0.02°/5 s from the $2\theta$ value of 1.5° to 12° and 0.05°/5 s from $2\theta$ value of 12° to 37°. The samples were analyzed in reflection mode. The $d$-spacing ($d$) of the interlayer gallery of nanocomposites was calculated from the Bragg equation:

$$d = \lambda/(2\sin\theta_{\max}) \tag{1}$$

An overall accuracy of ±0.1% for the $d$-spacing was estimated.

#### 2.3.2. Characterization of mechanical properties

Tensile properties of nanocomposites, tensile modulus at 300% elongation and tensile strength at break were determined according to ISO 37 on specimens type 1 (5 specimens for each test) using an Instron Testing Machine 3382 with video extensometer. A modified Zwick Testing Machine 1454R connected to a computer was used for determining the elongation at break. The experiments were performed at room temperature with a cross-head speed of 2 mm/min for elastic modulus and 100 mm/min for tensile strength determination. Hardness was determined using a Durometer Hardness Tester type Shore A from Zwick according to ISO 868. Specimens for the characterization of mechanical properties were stamped from pressed plates.

#### 2.3.3. Thermal characterization

Differential scanning calorimetry (DSC) was performed on a DSC Q2000 from TA Instruments under helium flow (50 mL/min). The samples weighting between 8 and 15 mg, in form of small disks of 4.5 mm in diameter and 0.8–1.2 mm thickness, were placed in aluminum pans. The heating rate was 10 °C/min in a temperature range between −110 and 150 °C. Glass transition ($T_g$) was determined as the midpoint of the heat capacity jump.

#### 2.3.4. Dynamic mechanical analysis

Dynamic mechanical thermal analysis of nanocomposites was undertaken with TA-Q800 Dynamic Mechanical Analyzer at a constant frequency of 1 Hz with oscillation amplitude of 20 μm. This last value was chosen in order to stay in the linear viscoelastic region of each sample. The storage modulus, loss modulus, and loss factor ($\tan\delta$) were recorded as a function of temperature from room temperature (RT) to 160 °C with a heating rate of 3 °C/min. The oscillation mode is like a deformation-controlled one, the sample dimensions in shear having nominal values – 10 mm length × 2 mm thickness × 10 mm width and in bending 60 mm × 3 mm × 12 mm.

#### 2.3.5. AFM investigation

The morphology of SBS and nanocomposites surface was investigated using atomic force microscopy (AFM). MultiMode 8 from Bruker (Germany) operating in Peak Force QNM mode was used in this study. Topographical and peak force error images as well as the elastic modulus of the samples were acquired using a silicon tip (Bruker) with the nominal radius of 8 nm, cantilever length of 225 μm, and a resonant frequency of 90 kHz. The images (256 × 256) were recorded on pressed plates and analyzed using the AFM software NanoScope version 1.20.

## 3. Results and discussion

### 3.1. XRD analysis

XRD patterns at low angles of SBS/10 wt.% D67G nanocomposites are shown in Fig. 1 and the $d$-spacings, half-maximum breadths ($\beta_{001}$ and $\beta_{002}$) and the area of each peak ($S_{001}$ and $S_{002}$) are shown in Table 1. It can be seen from the values of $d_{001}$ and $d_{002}$ and the aspect of the diffraction patterns that homogeneous nanocomposites having ordered lamellar structure were obtained (Table 1, Fig. 1a). The reflections at high angles in nanocomposites as compared to D67 (Fig. 1b) pointed out an order in the structure and orientation of the silicate layers also confirmed by the smaller values obtained for the half-maximum breadth, $\beta_{001}$. The basal spacing increased with about 3.5 Å, from 33.90 Å for Dellite 67G

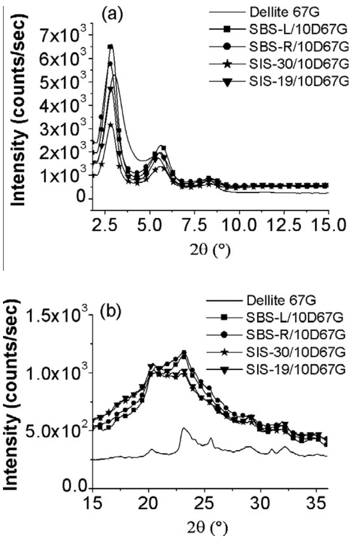

**Fig. 1.** X-ray diffraction patterns of block-copolymer/Dellite 67G nanocomposites. (a) From $2\theta$ value of 1.5° to 12°, at a scanning rate of 0.02°/5 s; (b) from $2\theta$ value of 12° to 37°, at a scanning rate of 0.05°/5 s.