



ELSEVIER

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytestPOLYMER
TESTING

ROGER BROWN

Material properties

Use of wollastonite in a thermoplastic elastomer composition



Hugo M. Tiggemann^a, Daiane Tomacheski^b, Fabrício Celso^b, Vanda F. Ribeiro^c,
Sônia M.B. Nachtigall^{a,*}

^a Chemistry Institute, Federal University of Rio Grande do Sul, 9500 Bento Gonçalves Avenue, Porto Alegre 91.501-970, Brazil

^b Feevale University, 2755 ERS239 Road, Novo Hamburgo 93.352-000, Brazil

^c Softer Brasil, 275 Edgar Hoffmeister Avenue, Campo Bom 93.700-000, Brazil

ARTICLE INFO

Article history:

Received 17 July 2013

Accepted 28 August 2013

Keywords:

Thermoplastic elastomer

Wollastonite

Nanocomposite

DMA

Morphology

ABSTRACT

Thermoplastic elastomer compositions (TPEs) based on wollastonite-filled SEBS/PP/oil blends were prepared and characterized. The development of new TPEs with improved mechanical strength may broaden their applications, especially for soft goods. Wollastonite is a natural filler that combines high thermal stability with low health hazard in comparison to other fibrous inorganic fillers. Morphological, thermal and mechanical properties of the composite materials were studied by transmission electron microscopy (TEM), thermogravimetry (TGA), tensile tests and dynamic mechanical analysis (DMA). The results indicate that the filler was mainly distributed as nanoparticles in the PS domains, improving the mechanical resistance of the materials even at low concentration (2 phr).

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Thermoplastic elastomers (TPEs) are materials that show elastomeric behavior but can be processed and recycled as thermoplastics [1]. This unique combination of mechanical properties and easy processing allows the preparation of objects with complex shapes and smooth surfaces using common plastic processing equipment. Triblock copolymers are the main type of commercialized TPEs, typical examples being styrene-butadiene-styrene (SBS) and styrene-ethylene/butylene – styrene (SEBS). These copolymers combine the mechanical resistance of dispersed styrenic phases with the elastomeric character of a polybutadiene or poly(ethylene-butadiene) matrix. SBS and SEBS copolymers are never used in their pure form due to their poor processing properties and high cost [2]. To obtain a satisfactory balance of properties and improved processing, they must be compounded with oils, fillers or

other polymers. Mineral oils are added to lower hardness and to improve processability [3]. Often, 20–40 wt% SEBS is blended with PP or PE to make stiffer compounds. SEBS-PP-oil blends have been commercialized since the early 1990s [4]. The plasticizer molecules lower the cohesive forces between the polymer chains, increasing chain mobility. If the oil is paraffinic in nature, it can be located in both phases (elastomer and PP), hence affecting the rheological and mechanical properties of both components. Sengupta and Noordemeer published a relevant study relating properties and morphology of SEBS-PP blends containing a high amount of oil (140 phr, as is usual in commercial formulations) [4]. A particular feature of such TPE compounds is that co-continuous morphologies can be obtained over a wide composition range. According to Veenstra [5], the elastic moduli of blends with co-continuous morphologies are significantly higher than the moduli of the same blends with a droplet/matrix morphology if the minor phase is the component with the highest modulus.

Various fillers and reinforcements have been introduced into thermoplastic elastomers to enhance processability, permeability, mechanical and thermal properties, as well as

* Corresponding author. Tel.: +55 51 3308 7208.

E-mail addresses: sonia.nachtigall@ufrgs.br, sonianachtigall@hotmail.com (S.M.B. Nachtigall).

to reduce material costs [5,6]. Wollastonite is a naturally occurring acicular white mineral, which shows high aspect ratio [10]. Some research works indicate that wollastonite is an effective and low-cost filler which can improve the tensile modulus, stiffness, hardness and strength of polymers [7]. Other key characteristics of wollastonite are thermal stability, low water absorption and relatively little health hazard [8].

The purpose of the present work was to study the effect of using wollastonite as filler in a thermoplastic elastomer composition based on a SEBS/PP blend containing a high amount of processing oil. The goal of the study was to investigate the morphological, thermal and mechanical properties of the materials using transmission electron microscopy (TEM), thermogravimetry (TGA), tensile tests and dynamic mechanical analysis (DMA).

2. Experimental

2.1. Materials

The TPE compound used in this study was based on polypropylene (PP, from BRASKEM S.A., MFI 1.5 g/10 min at 230 °C), styrene-ethylene/butylene-styrene copolymer (SEBS, from TAIPOLE, 31 to 34% styrene), oil (NYPAR303, from Nynas, 64% paraffinic and 36% naphthenic) and an antioxidant (Sunox1010, from Sunny, melting temperature between 110 and 125 °C). Unmodified wollastonite (Nyad M325) from Nyco was used as filler.

2.2. Methodology

2.2.1. Wollastonite characterization

The filler particle size was determined by laser diffraction using a CILAS 1180 analyser. TGA analysis was performed using a TA Instruments QA50 thermal analyser, under nitrogen, from 20 to 1000 °C, with a heating rate of 20 °C/min. SEM analysis was done using a JEOL JSM 6060 microscope. For this, the sample was spread over a conductive tape and then gold-metalized.

2.2.2. Preparation and characterization of the composites

A 100/35.5/157.7 phr (SEBS/PP/oil) composition was used as polymer matrix in all materials. Wollastonite (0, 2, 5 and 7 phr) was added as filler. The components were well mixed at ambient temperature and left resting until the plasticizer was absorbed. Melt mixing was performed in a mixer, Haake Rheomix 600, at 180 °C and 100 rpm for 10 minutes using roller rotors. The products were pressed in a mold 2 mm thick, at 180 °C and 620 kPa for 1 minute.

TGA of composite samples (10–15 mg) were performed from 20 to 700 °C, using the same conditions as for wollastonite. Specimens for TEM were ultramicrotomed at –130 °C (Ultramicrotome EMC CXL) and analysed in a JEOL microscope JEM-1200, with acceleration tension of 80 kV. Tensile tests were performed at ambient temperature according to DIN 53,504, with samples cut from pressed plaques. A Universal Testing Machine EMIC DL 2000 with an extensometer was used. The speed was 200 mm/min and the load cell capacity was 1000 N.

3. Results and discussion

3.1. Wollastonite characterization

The SEM images of wollastonite (Fig. 1) shows the typical acicular morphology of this filler. However, different particle sizes were found in this sample which reflects its tendency to easily fracture.

Wollastonite showed low weight loss up to 1000 °C (Fig. 2). The 5.5 wt% weight loss observed can be attributed to water and to a small amount of calcite impurity (calcium carbonate) [9].

3.2. Preparation and characterization of the composites

The TPE compound used as matrix in the preparation of the composites followed a typical commercial formulation, containing high level of oil (157.7 phr) and a considerable amount of PP (35.5 phr). This material can be characterized as a very soft TPE compound with 37 Shore A hardness. The addition of wollastonite slightly increased hardness. The composition containing 7 phr wollastonite showed hardness 39 in the Shore A scale, allowing its use in the same applications as the TPE matrix.

3.2.1. Thermal degradation behavior

Fig. 3 shows the thermal degradation curves of the TPE blend and its components. It could be seen that the plasticizer oil started to degrade at the lowest temperature. It showed a one single degradation step, with maximum at 392 °C. According to the producer, this oil is composed of naphthenic and paraffinic oils where the naphthenic content is probably responsible by the onset of the degradation process. Both polymers (PP and SEBS) degraded at a similar temperature range. However, SEBS showed its maximum degradation rate at somewhat lower temperature (449 °C against 465 °C for PP). This behavior reflects the higher thermal stability of the PP chains, which are fully saturated and homogeneous. The thermal degradation of SEBS in nitrogen has been ascribed to the chain scission at the boundary of the PS-olefin phases [10].

A close look at the decomposition curves of the SEBS/PP/oil blend shows that the degradation of each component was accelerated by the presence, and possibly degradation, of the others. Diffusion of active species across phase boundaries, or direct reaction at the boundaries, probably occurred, indicating an extensive degree of phase dispersion.

The introduction of inorganic fillers in polymeric matrices may inhibit or accelerate the degradation process. An increase in the thermal stability is the more usual effect and has been related to the decrease in oxygen diffusion in the material [11]. However, faster matrix degradation has been observed in some systems. This can be caused by photodegradation induction, decomposition of modifiers or absorption of antioxidants by the fillers [12]. Fig. 4 shows the TG and DTG curves of the TPE containing different levels of wollastonite, obtained under nitrogen. It was observed that the degradation profile of the TPE did not change with the filler addition since the temperature of maximum degradation rate of each step remained

Download English Version:

<https://daneshyari.com/en/article/5206340>

Download Persian Version:

<https://daneshyari.com/article/5206340>

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