Polymer Degradation and Stability 118 (2015) 178–187

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

NMR evaluation of polystyrene nanocomposites degraded by repeated extrusion processing

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ARTICLE INFO

Article history:
Received 27 August 2014
Received in revised form
18 March 2015
Accepted 27 March 2015
Available online 25 April 2015

Keywords:
Clay
Nanocomposites
NMR
Low field
Polymer degradation
Extrusion

ABSTRACT

Polystyrene nanocomposites with organoclay were prepared by melt extrusion in a twin screw extruder. After that, the samples were submitted to several cycles in the extruder to degrade them. The materials obtained before and after degradation cycles were analyzed by melt flow index measurements, X-ray diffraction and principally by nuclear magnetic resonance spectroscopy. The results showed the formation of nanomaterials with good dispersion and distribution containing low nanoparticle concentration and the nanostructured materials formed presented mixed morphology, composed of intercalated and exfoliated structures. The use of NMR spectroscopy allowed obtaining information on sample degradation with the increase of cycle times through the loss of structural organization and changes in the molecular dynamics of the materials through the T_1H relaxation data. All the results shed light on the behavior of the degradation process in the materials formed.

1. Introduction

Polymers in general are susceptible to changes in chemical structure and/or physical properties, due to external chemical or physical factors, leading to a decrease in their properties, such as loss of mechanical or chemical resistance, color change and surface roughness. This phenomenon is called degradation. The type of polymer and its first use, as well as the type of polymerization (type of catalyst, reaction conditions, etc.), influence the stability of the material and its susceptibility to certain types of degradation reactions [1,2].

Polymer nanocomposites are an important class of polymers that have wide application in a number of different industrial sectors. Therefore, organic–inorganic nanocomposite materials have been extensively studied in the past few decades. Inorganic nanoscale fillers are considered to be very important, including layered silicates (such as montmorillonite). The most commonly used organo-modification agents are carbon-chain alkyl ammonium salts. However, the molecular structure, such as alkyl chain length, number of alkyl chains and unsaturations, is also a determining factor of the thermal stability of polymer/MMT nanocomposites. Studies show that polymer degradation can be catalyzed by interaction with clay minerals due to the presence of acidic sites [3–6]. The reasons for the limited growth in the use of nanocomposites are the challenges to achieve dispersion of nanoparticles and their lower thermal and oxidative stability. To overcome these challenges, it is necessary to know the variables involved in the manufacturing process. The thermal stability of the organoclay component is of major importance, as many polymer composites are either melt-blended or intercalated at high temperatures to yield good distribution of filler in the nanoscale [7–9]. All the nanocomposite components may be subjected to high temperatures during preparation and in service. If the processing temperature is higher than the thermal stability of the organoclay, then decomposition occurs. This can affect the level of platelet exfoliation and perhaps interfacial bonding, which influence the physical and mechanical properties of the final nanocomposite [4,10,11].

Polystyrene is a thermoplastic widely used because of its low cost, transparency and good electrical properties. Polystyrene has become very important since it combines low cost with excellent processability, performance and productivity [8,12]. It is used in different areas of industry, such as for packaging, household items, cups and pens, and appliance parts. Some objects made by this

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http://dx.doi.org/10.1016/j.polymdegradstab.2015.03.022
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polymer are discarded very quickly. It is good to study ways to recycle this polymer and/or to degrade it because of the material's short useful life. The degradation mechanism of this polymer can generate a monomer when it is totally degraded.

Methods to differentiate between products of degradation reactions and structural changes in the polymer can be used to monitor the degradation process. The choice of the most appropriate method will depend on the properties of interest. Techniques are needed to characterize nanocomposites with nanoscale resolution. Traditionally this is done with transmission electron microscopy (TEM) and X-ray diffraction (XRD). XRD provides essential information on the structure of the nanocomposite; and allows quantification of changes in layered-silicate layer spacing. Other methods such as small-angle X-ray scattering and rheological measurements also serve to complement the XRD and TEM data [13–15]. New methods still need to be developed to complement these nanocomposite characterization techniques, especially methods that quantify the degree of nanodispersion of the layered silicate in the bulk polymer. Nuclear magnetic resonance (NMR) spectroscopy involves a set of techniques that allow studying different types of compounds due to the different information provided, without destroying the sample. Liquid NMR allows identifying changes in the chemical structure of the polymer due to degradation and the molecular weight loss. Solid-state NMR is widely used to study crystalline, amorphous materials and especially heterogeneous ones, focusing on evaluation of the intermolecular interactions, domain formation and molecular organization in the system [16,17]. Low-field NMR techniques, through measurements of proton relaxation times, can give enough information to understand the behavior of the polymerization process, chemical modifications and degradation process.

Van der Hart et al. developed NMR relaxometry as a means to characterize the morphology of MMT nanocomposites. They suggested that the use of T_1H (proton longitudinal relaxation time), as a relative measure of MMT dispersion, could be applied to different MMT nanocomposites. The method is based on measurement of T_1H. It uses two effects: (1) the paramagnetic character of this MMT, which directly reduces the T_1 H of nearby protons; and (2) spin diffusion, whereby this locally enhanced relaxation propagates to more distant protons. Clay minerals, in particular MMT-filled nanocomposites, often contain Fe^{3+} ions in small amounts (typically, 0–5 wt% as Fe_2O_3) substituting Al^{3+} in the octahedral plane. The important feature of the Fe^{3+} ion is that it is paramagnetic due to its unpaired electrons ($I = 5/2$). The paramagnetic Fe^{3+} ions inside clay can produce magnetic fluctuations and further perturb NMR parameters, such as significant line broadening, partial signal loss, and a notable shortening of the spin-lattice relaxation time for the neighboring nuclei on the clay surface. By building up the magnetization gradient around clay particles, the polarization will propagate from the neighboring nuclei into the remote ones via spin diffusion. Here, these paramagnetic Fe^{3+} ions act as powerful relaxation centers and greatly enhance the ^{1}H and ^{13}C spin-lattice relaxation of composites [18,19]. As a result, these changes in the nuclear spin-lattice relaxation are correlated with two important features of clay morphology: interfacial surface area and interlayer spacing [20,21].

Based on the above observations, this study had two objectives: to prepare polymeric nanocomposites of polystyrene and organoclay by melt processing; and to simulate the recycling process of these materials in a twin screw extruder to monitor the polymer degradation process. To do that, we decided to characterize the resulting materials using mainly nuclear magnetic resonance spectroscopic techniques, because this spectroscopy permits assessing the properties and hence the type of morphology obtained before and after the degradation process and also allows observing the extent to which the properties are affected by this processing, revealing the structure and morphology formed in the nanocomposites and in the degraded materials.

2. Materials and methods

2.1. Materials

The materials used to prepare the nanocomposites were polystyrene, supplied by Innova S.A., and Viscogel S7 (a montmorillonite organoclay), supplied by Bentec, containing dimethyl benzyl hydrogenated tallow ammonium as a surfactant.

2.2. Methods

2.2.1. Preparation of the nanomaterials

The polystyrene was milled to produce homogenous particles and increase their surface area, to facilitate dispersion of the nanoparticles during the melting process. After milling, the powdered polymer was used to formulate the nanocomposites. The polymer was mixed with the clay at a single concentration (5%).

The nanocomposites were denominated employ the following pattern: PSyz, where: PS- polystyrene, y-extrusion cycles z-clay percentage (Table 1).

The best processing conditions as well the concentration were determined by consulting the literature, followed by experimental tests. The materials were processed in an interpenetrating co-rotating twin-screw extruder, with screw diameter of 20 mm and L/D ratio of 36. The extruded materials were granulated in a pelletizer. The temperatures in the extruder processing zones varied from 150 °C to 190 °C (Zone 1–150 °C, Zone 2–170 °C, Zones 3 to 9–190 °C) and the rotation speed was 600 rpm. The degree of homogenization depended on the temperature and rotation speed. After the composite materials were obtained, they were subjected to different processing cycles in the twin-screw extruder, thus simulating the recycling process. The pure polymer composites were subjected to a total of ten reprocessing cycles. The samples were compared after each cycle to obtain information about the structure of the clay and the polymeric material's degradation process.

2.2.2. Characterization of the initial materials and nanocomposites

The polymer was analyzed by nuclear magnetic resonance through carbon-13 NMR solution to determine the chemical structure and its tacticity; by X-ray diffraction to evaluate the clay crystallinity profile; by NMR relaxometry to evaluate changes in polymer chains after degradation process; and by melt flow index (MFI) measurement. The starting materials and nanocomposites obtained were evaluated and characterized by the same techniques used to assess the PS, described below.

2.2.2.1. NMR analysis

2.2.2.1.1. Solution NMR. Carbon-13 NMR solution analyses were performed to characterize the molecular structure, microstructure (tacticity) and changes in them. These analyses were carried out in a Varian Mercury NMR spectrometer, with frequency of 300 MHz for the ^{1}H nucleus and 75.4 MHz for the ^{13}C nucleus, with single pulse scans at 90° at room temperature for ^{13}C analysis. Deuterated chloroform ($CDCl_3$) was used to dissolve the PS.

2.2.2.1.2. NMR ^{1}H NMR relaxometry experiments. To obtain information on the molecular dynamics of the PS samples and their nanocomposites, the proton spin-lattice relaxation times (T_1H) were determined by low-field NMR in the solid state using a Resonance Instruments Maran Ultra 23 spectrometer, operating at 23.4 MHz (for protons) and equipped with an 18 mm variable