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Decomposition kinetic and mechanism of syndiotactic polystyrene nanocomposites with MWCNTs and nanodiamonds studied by TGA and Py-GC/MS

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ABSTRACT

In the present work, syndiotactic polystyrene (sPS) based nanocomposites containing 3 wt% of multi-walled carbon nanotubes (MWCNTs) and nanodiamonds (NDs) were prepared using the melt-mixing technique. Transmission electron microscopy (TEM) micrographs verified a good dispersion of the nanoparticles in the polymeric matrix, which resulted in a slight improvement of the mechanical properties of the nanocomposites. The addition of MWCNTs promotes the formation of β-type crystals while in sPS and sPS/NDs α-type crystals are mainly formed. From the thermogravimetric analysis experiments a substantial enhancement of sPS thermal stability was found, caused by the addition of nanofillers, especially from NDs. The temperature corresponding to a mass loss of 0.5% was found 295 °C for sPS, 352.4 °C for sPS-MWCNTs and 370.7 °C for sPS-NDs nanocomposites. The analytical method of Py-GC/MS was also used for further characterization of the samples. The main chain fragments collected from sPS pyrolysis were styrene monomers, dimers and trimers, while the three pyrolization temperatures applied (390, 420 and 500 °C) indicated some variations in intensity of decomposition fragments. The decomposition temperature as well as the nanoparticle addition (NDs or MWCNTs) affected the intensity of the recorded fragments but did not induce a change on the decomposition mechanism of sPS.

1. Introduction

Syndiotactic polystyrene (sPS) is a semicrystalline polymer synthesized from styrene monomer, like the amorphous polystyrene, but using a single-site catalyst, such as metallocene [1]. sPS differs from atactic or isotactic polystyrene due to the fact that the phenyl rings regularly alternate from side to side and this regular structure allows sPS to crystallize. Due to this semicrystalline nature, sPS products exhibit enhanced properties such as high melting point, good chemical and moisture resistance, high degree of dimensional stability, low specific gravity, good dielectric properties and superior mechanical strength, compared to amorphous polystyrene [2,3]. Thus, an increasing interest in the sPS is observed [4,5] even though sPS polymer has poor impact strength and low surface energy, similar to traditional atactic polystyrene. The main applications of sPS can be found in: photographic films, insulation films for electric and electronic products, heat-resistant dishes, especially for microwave ovens, food packaging films, car parts exposed to chemicals and high temperature, machine parts working at high temperature, appliances and equipment used in medicine and dentistry, resistant to sterilization with overheated steam, etc.

The development of sPS nanocomposites could further enhance the desirable properties of sPS [6]. Montmorillonite (MMT) nanoclay is frequently used as an appropriate filler to fabricate high-performance sPS nanocomposites [7] while its effect on the crystallization kinetics as well as the polymorphic and thermal behaviour of sPS/MMT nanocomposites has also been reported [8–11]. The fabrication method of sPS/clay nanocomposites has been found to influence the microstructure and final mechanical properties, especially tensile strength [12,13]. In the case of nanocomposites exhibiting intercalation structure, the stepwise mixing method yielded more obvious intercalation structure than the simultaneous mixing method so that the former method resulted in higher tensile strength. On the other hand, the nanocomposites exhibiting exfoliated structure did not reveal any differences in the mechanical properties between the two fabrication methods [12]. Exfoliated nanocomposites showed better mechanical properties than intercalated ones because of the

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uniformly dispersed clay layers [13]. The presence of MMTs favours the formation of α-form sPS crystals and enhances the rigidity of the sPS matrix [14].

Carbon nanotubes and nanofibers (CNF) have been also used to fabricate sPS nanocomposites [15–18]. It was found that CNFs can serve as nucleation sites for sPS crystallization, and they improve the electrical conductivity of sPS. Emphasis was also given on the effect of multi-walled carbon nanotubes (MWCNTs) on sPS crystallization [19,20] while it was found that the incorporation of MWCNTs reduced the electrical resistivity of sPS by 10 orders of magnitude [21].

Besides the enhancement of the physical properties of sPS, one of the major problems which should be solved is its low thermal stability. Due to its high melting point (270 °C), the required melt processing temperature of sPS is higher than 300 °C, which is near to the polymer decomposition temperature and this causes a major problem in the processability of the polymer. The addition of nanofillers has been found to improve the thermal stability of polymers [22,23]. In the present research, except MWCNTs, nanodiamonds (NDs) which represent a carbon form that combines all the benefits of nanoscale-fillers with the well-known superior diamond properties including exceptional hardness and elastic modulus were selected.

The aim of the present study is to enhance the physical properties as well as thermal stability of sPS with the addition of MWCNTs and NDs. Both nanoparticles have high thermal and electrical conductivity, thus their addition to sPS (besides the improvement of the mechanical properties) could lead to nanocomposites with high conductivity properties. The thermal stability of the prepared nanocomposites was studied using thermogravimetric analysis and pyrolysis-gas chromatography/mass spectroscopy (Py-GC/MS). Two types of measurements were carried out at Py-GC/MS: evolved gas analysis (EGA) and single shot pyrolysis (SS). The recorded chromatographs show various peaks, corresponding to mass spectra and chemical structures appropriate to evaluate the decomposition mechanism of sPS.

2. Experimental

2.1. Materials

Syndiotactic polystyrene (sPS) was kindly supplied by Dow Chemicals with stereoregularity at 99% and average molecular weight $M_w = 2.1 \times 10^5$. Purified multi-walled carbon nanotubes (MWCNTs) used in this work were synthesized by chemical vapour deposition (CVD) process and the average outer diameter is 10–25 nm, they were purchased from Timesnano Chengdu Organic Chemicals Co., Ltd. (China). Nanodiamonds (NDs) of cubic diamond phase and average primary particle size of 4.0 nm were purchased from NanoDiamond S.A.

2.2. Nanocomposites preparation

sPS nanocomposites containing 3 wt% of MWCNTs and NDs were prepared by melt mixing in a Haake-Buchler Rheomixer (model 600) with roller blades and a mixing head with a volumetric capacity of 69 mL. Prior to melt-mixing the nanoparticles were dried by heating in a vacuum oven at 130 °C for 24 h. The two components were physically premixed before being fed in the rheomixer. In order to achieve a better dispersion of the nanoparticles in sPS a RETSCH planetary ball mill (model S100) was used. The sPS flakes along with the proper amount of nanoparticles (MWCNTs or NDs) were fed into the ‘C’ type stainless steel grinding jar with a capacity of 25 mL. Five steel spheres were also added as a grinding medium. The milling was set at 500 rpm for a period of 3 h. Melt blending was performed after ball milling at 270 °C and 30 rpm for 15 min. During the mixing period the melt temperature and torque were continuously recorded. Each nanocomposite after preparation was milled and placed in a desiccator to prevent any moisture absorption.

2.3. Mechanical properties

Measurements of tensile mechanical properties of the prepared nanocomposites were performed on an Instron 3344 dynamometer, in accordance with ASTM D638, using a crosshead speed of 5 mm/min. Relative thin sheets of about 300 ± 25 μm were prepared using an Otto Weber, Type PW 30 hydraulic press connected with an Omron E5AX Temperature Controller, at a temperature of 280 ± 5 °C. The moulds were rapidly cooled by immersing them in water at 20 °C. In order to measure the mechanical properties from these sheets, dumb-bell-shaped tensile test specimens (central portions 5 mm × 0.5 mm thick, 22 mm gauge length) were cut in a Wallace cutting press. The values of Young’s modulus, yield stress, elongation at break and tensile strength at the break point were determined. For the notched Izod impact tests a Tinius Olsen apparatus was used under ASTM D256. The specimens were prepared in a similar way as described before. Prior to the measurements, the samples were conditioned at 25 °C in a 50 ± 5% relative humidity environment for 48 h. At least five specimens were tested for each sample and the average values are reported.

2.4. Transmission electron microscopy (TEM)

TEM images were obtained on a JEOL JEM-2100 instrument equipped with a LaB6 filament, operating at 200 kV. TEM specimens were prepared by supporting thin sections (80–100 nm) of samples onto 200 mesh holey carbon copper grids.

2.5. Differential scanning calorimetry (DSC)

Thermal behaviour of the nanocomposite materials was studied using a Perkin-Elmer Pyris Diamond DSC differential scanning calorimeter. The instrument was calibrated with high purity indium and zinc standards. Samples of about 5 mg were used. The samples were heated up to 300 °C with a heating rate 20 °C, remained at this temperature for 1 min, quenched (cooling rate 300 °C/min) to 20 °C and rescanned again until 300 °C with heating rate 20 °C/min. The recorded thermograms of this second scan were used. A Perkin-Elmer Intracooler II was used to allow the DSC to achieve high and constant cooling rates.

2.6. Wide angle X-ray diffractometry (WAXD)

WAXD study of sPS nanocomposites, in the form of thin films, were performed over the range 2θ from 5 to 60°, at steps of 0.05° and counting time of 5 s, using MiniFlex II XRD system from Rigaku Co. The films have been prepared as described before for mechanical properties and are crystallized at 200 °C for 6 h.

2.7. Thermogravimetric analysis

Thermogravimetric analysis was carried out with a SETARAM SETSYS TG-DTA 16/18 instrument. Samples (5.0 ± 0.3 mg) were placed in alumina crucibles. An empty alumina crucible was used as reference. sPS nanocomposites were heated from ambient temperature to 550 °C in a 50 mL/min flow of N_2 at heating rates of 5, 10, 15 and 20 °C/min. Continuous recordings of sample temperature, sample weight and heat flow were taken.