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In-Line Monitoring and Spectral Analysis of Polymer Blend Dispersion in Microcompounder

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ABSTRACT

Microcompounders are the most common compounding machines for making polymer composites. The torque rheometry is an effective tool for predicting the processing characteristics of thermoplastic polymers. It provides continuous monitoring of torque and temperature data during compounding which is a measure of processability. In this work, we have studied the influence of processing parameters on the dispersion degree of an anthracene derivative (**AMA**) in a polystyrene matrix with respect to the rheological, structural, and optical properties. The chemical structure of the synthesized **AMA** as a tracer was confirmed by ¹H NMR and thermal properties were examined by DSC. In addition, a blend of polystyrene and AMA was spin-coated on a glass substrate to investigate oxidation stability confirmed by UV measurement. By using microcompounder, the polymer blend with the **AMA** tracer was mixed and it was visually indicated by fluorescent images. **KEYWORDS**

Microcompounders; extrusion; tracers; fluorescent images; monitoring

1. Introduction

Hot-melt extrusion (HME) is one of the most widely used processing techniques for the plastic, pharmaceutical, and food industries [1-3]. It is a fully continuous manufacturing technology in which raw materials are converted into products by forcing the formulation through a die under various controlled conditions. Process monitoring systems equipped in the HME provide information on die temperatures, feed rate or throughput, screw speed, torque and drive amperage, melt pressure, and viscosity [4,5]. Classical process control based on measurements of these parameters is in many cases not sufficient to explain process variations in material properties and to monitor the extrudate quality attributes. Non-destructive in-line monitoring equipment such as UV-vis absorption, photoluminescence, FT-IR, and Raman spectroscopy are useful tools for product screening and quantitative as well as qualitative analysis of HME formulations [6-10]. Furthermore, the use of spectroscopic methods in manufacturing provides important information on a molecular level because of the use of superposed information about the chemical composition by monitoring the wavelength-dependent absorption spectra. Wang et al. applied the UV-vis spectroscopy technique to monitor the

CONTACT Namchul Cho C chon7@sch.ac.kr; Tae-Dong Kim C tdkim@hnu.kr Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl. © 2019 Taylor & Francis Group, LLC 76 🛞 W. T. OH ET AL.

process-induced degradation of poly-L-lactic acid during extrusion [11]. Gilmor et al. developed an in-line color monitoring system with the fiber-optic reflection probe inserted into the die of a single-screw extruder [12]. Carneiro et al. determined the residence time distribution (RTD) along a kneading block via in-line monitoring of the light emission of a perylene fluorescent tracer in a slit die attached to a single-screw extruder and at several locations along a corotating twin-screw extruder [13]. Due to providing information on the mixing history of the melt, fluorescent in-line monitoring is the one of powerful tools to determine the RTD of a formulation and to measure accurate melt temperatures. Here, we present synthesis and characterization of an anthracene derivative (AMA), 9,10-bis({5-phenyl-[1,1'-biphenyl]-3-yl})anthracene, as a fluorescent tracer blended with a polystyrene for HME. Because the anthracene molecules have been utilized for the use of blue host materials in light-emitting diodes applications, it can be a good candidate for the fluorescent tracers. They are also known that the 9,10-disubstitution on anthracene improves their photochemical stability [14]. A lab-scale microcompounder composed with RheoComp® BIM Series has been utilized and in-line monitored in the extrusion barrel as function of the process settings in order to evaluate the material behavior.

2. Experimental details

2.1. Materials

All reagents were purchased from commercial sources and solvents were purified by distillation prior to use. All reaction containers were flame dried under vacuum before use.

2.1.1. 3,5-(diphenyl)bromobenzene

To a solution of 1,3,5-tribromobenzene (12.0 g, 0.030 mol) in 30 mL of dry tetrahydrofuran (THF) was added 0.1 g of bis(triphenylphosphine)palladium (II) chloride under nitrogen. After the solution was purged with nitrogen for 5 minutes, a solution of phenylmagnesium bromide, which was freshly prepared from 12.6 g (0.080 mol) of bromobenzene in 15 mL of dry THF with 2.0 g of magnesium in 10 mL of dry THF, was added through an addition funnel at room temperature. The reaction mixture was stirred overnight. Then it was quenched by slowly adding 15 mL of 0.5 N HCl with stirring. The solvents were removed via a rotary evaporator. The residue was dissolved in hexane and washed with 0.1 M HCl followed by water. After removal of solvents, crude residues were purified chromatography on silica gel using hexane as an eluent. After drying, 3.6 g of pure 3,5-(diphenyl)bromobenzene was collected, yielding 30.0%. ¹H NMR (CDCl₃, ppm): $\delta = 7.71$ (s, 3H), 7.60 (d, 4H), 7.45 (t, 4H), 7.37 (t, 2H).

2.1.2. 9,10-bis({5-phenyl-[1,1'-biphenyl]-3-yl})anthracene (AMA)

A solution of 3,5-(diphenyl)bromobenzene (5.0 g, 0.016 mol) in 50 mL of THF was cooled to -78 °C under nitrogen, and *t*-BuLi (1.7 M in pentane, 11.8 mL, 0.020 mol) was added dropwise during 10 minutes. After 30 minutes, B(OMe)₃ (2.0 g, 0.019 mol) was added, and the mixture was stirred at -78 °C for 30 minutes and then at room temperature for 3 hours. The mixture was poured into 2 N HCl solution and stirred for

overnight to produce a solid. The resulting white precipitate was dried to give a 3.5 g of 3,5-(diphenyl)phenylboronic acid. Then, 3,5-(diphenyl)phenylboronic acid (3.5 g, 0.013 mol) and 9,10-dibromoanthracene (2.0 g, 0.006 mmol) were dissolved in 50 mL of THF and 40 mL of 2M aqueous potassium carbonate. After the reaction mixture was degassed four times, 0.5 g of tetrakis(triphenylphosphine)palladium was added and vigorously refluxed under flowing nitrogen for 48 hours. When the reaction mixture was cooled down to room temperature, it was poured into 100 mL of methanol and deionized water (9:1). After the crude product was purified by flash chromatography with hexane/methylene chloride (5:1), 1.3 g of 9,10-bis({5-phenyl-[1,1'-biphenyl]-3-yl})anthracene was obtained (yield: 56%). ¹H NMR (CDCl₃, ppm): $\delta = 8.03$ (s, 2H), 7.85 (d, 4H), 7.78-7.72 (m, 12H), 7.51-7.43 (m, 12H), 7.35 (m, 4H). EI+ -Mass: 635, Anal. calcd for C50H34: C 94.6, H 5.40; found: C 94.76, H 5.27%.

2.2. Characterization

¹H NMR spectra (300 MHz) were taken on a Varian 300 spectrometer. UV-vis spectra were obtained on a Perkin-Elmer spectrophotometer. Elemental analyses were performed on a Vario EL Elemental Analysis Instrument (Elementar Co.). Differential scanning calorimetry (DSC) was performed on a TA instruments Q50 at a ramping rate of 10 °C/min. Visualization experiment with a batch internal mixer for microcompounding was carried out by RheoComp® BIM Series. Scanning electron microscopy (SEM) was used to characterize the morphology of the extruded polymer mixer.

3. Results and discussion

The structure and synthetic route of **AMA**, which is a fluorescent tracer for polymer extrusion are shown in Scheme 1. 3,5-(diphenyl)bromobenzene is synthesized from 1,3,5-tribromobenzene by reacting with a Grignard reagent of phenylmagnesium bromide. 3,5-(diphenyl)phenylboronic acid, then, is obtained from lithiated 3,5-(diphenyl)bromobenzene and trimethylborate. The Suzuki coupling reaction was employed for the



Scheme 1. Synthetic routes of a fluorescent tracer, AMA



Figure 1. DSC curve for AMA



Figure 2. (a) UV-vis absorption spectra of **AMA** (1.0 wt%) blended with PS in thin films (b) the absorption intensity (401 nm) changes of the film as a function of time annealed at $170 \,^{\circ}$ C in air



Figure 3. In-line monitoring in the extrusion barrel composed with RheoComp® BIM Series with a function of the time versus torque power at $180 \,^{\circ}$ C.

synthesis of **AMA** between 9,10-dibromoanthracene and 3,5-(diphenyl)phenylboronic acid. The resulting intermediates and **AMA** were characterized by ¹H NMR, UV-vis absorption spectroscopy, HR-MS, and EA analysis.

The AMA is soluble in common organic solvents such as acetone, ethyl acetate, tetrahydrofuran, toluene, and chlorinated solvents due to the bulky phenyl groups. For an example, measured quantitative solubility of AMA in chlorobenzene solvent at $25 \,^{\circ}$ C was found to be 36 mg/mL. The thermal property of AMA was determined by DSC in air atmosphere at $10 \,^{\circ}$ C/min of heating rate. Upon heating, one endothermic peak at $231 \,^{\circ}$ C indicating the transition to the isotropic melt was observed (Figure 1). It is generally known that anthracene molecules undergo a reaction with oxygen when they exposed to the air at high temperature to give endoperoxides. The endoperoxides have a bridge structure with an oxygen molecule, which bonds to anthracene at the C-9, C-10 positions. Therefore, the 9,10-disubstituted anthracene derivatives can provide improved photochemical stability by protecting these active core sites from oxygen.

The oxydation properties have been investigated by UV-vis absorption spectra recorded at regular intervals enabling a determination of absorption-time profiles. The absorption spectra of a thin film for the blend of 1.0wt% of **AMA** in polystyrene (PS) are shown in Figure 2(a). Before heating, the film has absorption at 359, 378, and 401 nm corresponding to the intrinsic absorption of anthracene molecules. There is slightly reduced absorption intensity remained over 95% after annealing at 170 °C in air condition for 300 sec (Figure 2(b)). These results indicate that **AMA** has remarkable thermal and chemical stability even in atmospheric air condition.



AMA/PS mixed for 5min

(a)



AMA/PS mixed for 10min

(b)

Figure 4. SEM images of AMA/PS composites mixed for (a) 300 and (b) 600 seconds.

The melt mixing has been performed in a lab-scale microcompounder composed with RheoComp® BIM Series. The optimized amount of **AMA** was added in 1.0% by weight in the mixing batch at 100 °C. Then, the processing temperature was increased to 180 °C and kept at that temperature to ensure proper viscosity for the mixing while at the same time minimizing degradation of both the **AMA** and PS. The rotational screw speed was set at 100 rpm. Figure 3 shows in-line monitoring in the extrusion barrel as function of the process settings. The initial toque was increased to ~180 Nm due to high viscosity of the mixture during rising temperature. The toque power started to rapidly decrease at 100 seconds. As shown in the inserted picture at 350 seconds, there is still remained fluorescent tracers especially in the barrel inlet. However, we could not observe these agglomerated tracers after 600 seconds.

Figure 4 shows the SEM micrographs of AMA/PS composites obtained by two mixing times from the RheoComp® BIM extruder. The surface morphology of the sample collected after 5 min was found to be inhomogeneous which the AMA was quite agglomerated and not well dispersed in PS matrix. In Figure 4(a) it is clearly indicated that phase separation between AMA and PS occurred in circled areas. However, the AMA aggregates were completely disappeared after 10 min of mixing. (Figure 4(b)).

4. Conclusion

We have successfully developed a fluorescent tracer, **AMA**, for predicting the HME processing characteristics of a polystyrene in a lab-scale microcompounder composed with RheoComp® BIM Series. A blend of polystyrene and **AMA** was spin-coated on a glass substrate to investigate oxidation stability confirmed by UV measurement. We have found that the **AMA** has remarkable thermal and chemical stability in atmospheric air condition proper to use HME. By using microcompounder, the polymer blend with the **AMA** was mixed and it was visually indicated by fluorescent images during the material process. We have observed that the mixture has well dispersed after being last for 600 seconds at 180 °C.

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