PREPARATION AND DEGRADATION OF POLYMER FOAMING AGENT-BASED NANO PARTICLES

Il-Do Chung, Jae-Wook Jeong, Chang-Sik Ha, Won-Jeic Cho*
Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Korea
Received 24 August 2012

Abstract
New monomers, MAHSIH (methacryloyl toluenesulfonyl hydrazide) and MAHSBH (methacryloyl oxybis(benzenesulfonyl) hydrazide) containing foamingable sulfonylhydrazide functional group after decomposed by heating, were synthesized from p-toluenesulfonyl hydrazide (TSH) and 4,4'-oxybis(benzenesulfonyl) hydrazide (OBSH) with methacryloyl chloride, respectively, and used to obtain polymeric foaming agents (PFAs) followed by the preparation of their nanoparticles by using modified reverse microemulsion method. The structures of synthesized monomers and their PFAs were identified by FT-IR, and 1H-NMR spectroscopy. The decomposition temperatures of PFAs were determined to be 224 - 245°C and this temperature was decreased around 160°C by adding an activator such as surface treated nano silica to the polymer. The exothermic temperatures and heats determined by the decomposition of the PFAs were 260°C and 287 J/g for poly(MAOSIH), and 260°C and 447 J/g for poly(MAHSBH), respectively. Furthermore, the polymer incorporated with PFA showed better skin and inner cell structure as well as better mechanical properties than those added with low molecular weight foaming agents. The PFA nanoparticles showed much lower decomposition temperature at around 140°C and higher exothermic heat than its PFA.

Keywords: Polymeric foaming agent (PFA), nanoparticle, p-Toluenesulfonyl hydrazide (TSH), 4,4'-oxybis(benzenesulfonyl) hydrazide), decomposition temperature, gas evolution.

1. INTRODUCTION

A chemical foaming agent or chemical blowing agent is a chemical additive that can produce foam structures within a polymeric matrix. The types of foaming agents currently being produced can be divided into two classes: one consists of the inorganic types like ammonia and sodium bicarbonate. These foaming agents have been used extensively in open cell sponges to generate carbon dioxide. The other contains organic substances which decompose and evolve carbon dioxide, which are typically used in closed cell materials.

In the past decades, over thousand chemicals have been developed as foaming agents for polymers. Di-isono-benzene (DAB) was developed as the first commercial organic foaming agent in 1940s but because of its toxicity and staining properties, non-staining aliphatic compounds like 2,2'-azobisisobutyronitrile, azodicarbonamide and dimethoxyamine derivatives were developed as organic foaming agents. Since 1972, several sulfonyl hydrazides have been used as foaming agents for rubbers and plastics. Sulfonyl hydrazides with an asymmetric molecular configuration have been found useful only in rubber application, since in many other polymers, e.g., poly(vinyl chloride), they make a malodorous like odor. Among them, 4,4'-oxybis(benzenesulfonyl) hydrazide (OBSH) and p-toluenesulfonyl hydrazide (TSH) are widely used as foaming agent. The use of these low molecular weight organic foaming agents showed some drawbacks such as the lack of compatibility with polymers and the difficulty of cell size control of foams formed.

To improve the compatibility of low molecular weight foaming agent with polymers, the additional master batching process has been developed. However, this resulted in the increase of cost and ineffective method. Therefore, there is a strong requirement to develop a polymeric foaming agent (PFA) as an alternative which is expected to give better compatibility with polymers including ethylene vinyl acetate (EVA).

Recently, Cai and coworkers reported that poly(p-vinylphenylsulfonylhydrazide) (PVPSH) was grafted onto silane coupling agent pre-treated nano-silica via aqueous radical polymerization in order to promote dispersion of nano-silica in polypropylene (PP). It was reported that the melt blending of PVPSH grafted nano-silica with PP should result...
bubble-stretching effect to improve nano-particles dispersion in the PP matrix. We have reported the synthesis and evaluation of polymeric foaming agent based on TSH and OBSH, and showed better compatibility with polymers and mechanical properties than those added with low molecular weight foaming agents. Therefore, the objectives of this paper are to summarize and show what we have published for new PFA containing OBSH and TSH and their foaming behaviors as well as the effects of activator added to PFA. In this study, new monomers, MAOBH and MATSH, and their PFA were synthesized and characterized by FT-IR and 1H-NMR spectroscopies, then used them to obtain their nanoparticles. The decomposition and gas evolution of PFA were determined by using gas evolution measurement instrument (GEMI). TGA and DSC were also used to evaluate their decomposition and exothermic behaviors. The morphologies of polymer incorporated with foaming agents and their PFA were examined. The foaming performance was measured according to basic formulation based on ethylene-vinyl acetate copolymer (EVA). The mechanical properties of the EVA foam with foaming agents and their PFA were measured according to ASTM method.

2. EXPERIMENTAL

2.1. Materials

OBSH, TSH, as foaming agents and surface-treated urea, i.e., Cellex-A as a foaming activator were used as received from Kum Yang Co., Ltd., Korea. Triethylamine (TEA) was refluxed with acetic anhydride, washed with KOH, and finally vacuum distilled. AIBN received from Aldrich Co. was dissolved in chloroform and precipitated by adding an equal volume of methanol. All other reagents and solvents were purchased from commercial suppliers and purified by standard procedures. THF and sodium bicarbonate were used without further purification.

2.2. Measurements

The infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrophotometer. 1H-NMR spectroscopic measurement was recorded using FT-300 MHZ Varian Gemini 2000 spectrophotometer using DMSO-d6 solvent. The chemical shifts were assigned in ppm tetramethylsilane as the internal standard. The thermal decomposition temperature (Td) were examined with a thermo-gravity analysis instrument (TA Instrument, New Castle, USA, Q500) by scanning the samples from 100 to 900°C at a scanning rate of 10°C/min. under nitrogen gas. Gas evolution was measured by gas volume measurement instrument (GEMI) which was assembled by Kum Yang Co., Ltd., Korea. The tube containing 0.5 g of the samples was put into the oil bath and heated by increasing the temperature with constant speed, i.e., 5°C/min., from 100°C. Differential scanning calorimetry (DSC) was carried out in a Du Pont 900 Thermal Analyzer at a heating rate of 10°C/min in atmosphere. The morphologies of EVA incorporated with foaming agents were analyzed by scanning electron microscopy (SEM; JEOL JSM35-CF) after coated with gold prior to installation in the SEM chamber. Hardness of EVA foam samples incorporated with foaming agent was measured according to ASTM D2240 using automated hydraulic bade of hardness tester (Gotech Testing Machines Inc, GT-GS-MB) which was designed for adapting the hardness tester to retain the accurate, steady, and uniform force angle to the specimen and also avoid the test errors due to the uneven surface of it. The tensile strength, elongation at break, tear strength, and split tear of the foam sample were measured using Gotech Universal Testing Machine (GT-A170006 or A1700S) at cross-head speed of 200 mm/min at 25°C according to ASTM D3754. The compression set was determined when the foam samples were in between two flat metal plates and were subsequently compacted to 50% of the original thickness. Those were left in the oven at 60°C for 6 h and later allowed to recover at room temperature for 30 min. The recovered thickness of the foam was re-measured to obtain the percentage change in original thickness again according to ASTM D395.

The expansion ratios were calculated from the following equations:

Volumetric expansion ratio (%) = \[
\left(\frac{[t_1 \times t_2 \times t_3]}{[m_1 \times m_2 \times m_3]}\right) \times 100
\]

Area expansion ratio (%) = \[
\left(\frac{[t_1 \times t_2]}{[m_1 \times m_2]}\right) \times 100
\]

where, t1, t2, t3 indicate the length, width, and height of foam sheet, m1, m2, m3 indicate the length, width, and height of solid sheet before foaming, respectively.

2.3. Syntheses of monomers

Polymerizable foaming agents were prepared by the reaction of methacryloyl chloride (MAC) and their corresponding foaming agents. Briefly, for the synthesis of MAOBH, to a stirred solution of OBSH (25 g, 0.07 mol), TEA (0.5 mL, 0.0035 mol) and trace amount of hydroquinone (0.01 g) in THF (140 mL), MAC (8 mL, 0.0745 mol) was added dropwise, so that may not rapidly increase the reaction temperature over 40°C. After the addition was completed, sodium bicarbonate (5.8 g, 0.07
mol) in distilled water (20 mL) was added into the above solution which released CO₂ gas. During this process, the solution turned transparent with a phase separation in the flask. After the reaction was completed, the organic layer was separated, dried with Molecular Sieve#4, and finally evaporated to obtain pure MAOBSH in 91 % yield.

2.4. Syntheses of PFAs

For the synthesis of PFA from MAOBSH, a solution of MAOBSH (4 g, 9.36 mmol) and AIBN (0.06 g, 0.187 mmol) in THF (40 mL) was introduced into a dry Pyrex polymerization vessel. The vessel was sealed after degassed twice by purging with purified N₂ gas and placed into a water bath maintained at 70°C for 24 h. The PFA, poly(MAOBSH), was precipitated in excess diethyl ether, collected by filtration, washed twice with diethyl ether and then dried in a vacuum oven at 30°C until a constant weight.

2.5. Decomposition activation test

The effect of activator was determined by measuring the decomposition temperature (TD) and gas evolution after mixing PFA with the activator, Cellux-A by powder blending and sieving process at the mixing ratios at 90:10 and 80:20.

2.6. Evaluation of foaming behavior

PFAs and their related foaming agents were used after grinding and passing through a 200 mesh sieve to ensure that the particles are less than 74 μm in size. For the formulation of EVA with foaming agents, briefly, the EVA resin on rollers at room temperature, CaCO₃, titanium dioxide and stearic acid were added on the rolls and well-mixed. After 10 min, foaming agents and dicumyl peroxide (DCP) as a cross-linking agent were incorporated into the mixture, and allowed to mix for additional 3 min. After the sheeting of the mixture by the rolls was completely done, it was placed and heated in a press in a closed mold, whereby inflation and curing or vulcanization occurred for 0–20 min at 155–160°C under the pressure at 14.71 MPa. In order to evaluate the area expansion ratio as a function of foaming time, each solid sheet was placed into the mold and heated after cutting the sheets into the original size with both length and width of 2.3 cm.

3. RESULTS AND DISCUSSION

3.1 Identification of monomers and their polymers

For the characterization of OBSH and its PFA, the FT-IR spectrum (Fig. 1) of the polymer indicated characteristic absorption peaks at 1620 cm⁻¹ (stretching vibration of C=O), 1440 cm⁻¹ (CH₂ scissoring), 1400 cm⁻¹ (CH₃ scissoring) and the bands in OBSh unit showed at 1500 cm⁻¹ (stretching vibration of the aromatic C=C), 1150 and 1090cm⁻¹ (stretching vibration of O=O=O) and 900~790cm⁻¹ (out-of-plane vibration of aromatic =C-H) with the concurrent disappearance of vinyl group peak at 1680 cm⁻¹ (stretching vibration of vinyl C=C). 1H-NMR spectrum of PFA showed aromatic proton at 7.3~7.8 ppm, NH-NH at 9.9~10.4 ppm, CH₃ at 1.7 ppm and polymer backbone at 0.5~2 ppm with the concurrent disappearance of vinyl protons in monomer moiety at 5.4 and 5.6 ppm, respectively.

Fig. 1: FT-IR spectra of MAOBSH (a) and poly(MAOBSH) (b) (KBr).

3.2 Decomposition temperature and gas evolution

Figure 2 showed the gas evolution graph of foaming agent and its monomer and PFA as a function of decomposition temperature with constant heating rate of 5°C/min.

Fig. 2: Decomposition temperature and gas evolution graphs

The synthesized PFA, shown in Figure 2, has higher and slower decomposition temperatures than the corresponding OBSh and its monomer. This is attributed to the increasing of molecular weight as
well as the incorporation of methacrylate unit in monomer. The gas evolution of PFA was determined to be 74 ml/g at 760°C.

Table 1 shows the thermal decomposition behaviors of foaming agent and its monomer and PFA. As shown in Table 1, the PFA has showed higher decomposition temperature with the two-step decomposition behaviors at 245 and 293°C, as well as gradual weight loss behaviors compared with commercial OBSII and its monomers. This is attributed to the fact that the unstable sulfuric acid released from polymer backbone was formed at higher temperature.

<table>
<thead>
<tr>
<th>Table 1: Decomposition and Exothermic Behaviors</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGA (Decomposition)</td>
</tr>
<tr>
<td>1st point</td>
</tr>
<tr>
<td>OOBII</td>
</tr>
<tr>
<td>MAOBSII</td>
</tr>
<tr>
<td>PFA</td>
</tr>
</tbody>
</table>

DSC permits the determination of the exothermic heat which is generated at the decomposition point of the polymer blowing agent. As shown in Table 1, the synthesized polymer showed higher exothermic temperature at 25°C and lower exothermic heat of 287 J/g compared with foaming agent and its monomer.

From the thermal analyses by TGA and DSC, gradual and higher decomposition temperature of PFA makes it possible to decompose of foaming agent during mixing process before foaming.

3.3. Effect of decomposition activator and foaming performance

Figure 3 showed the effect of an activator such as surface treated urea with stearic acid on the decomposition of PFA depending on the amount added. In a pure state, PFA decomposed at temperature 245°C. However, the decomposition temperature of PFA was decreased as low as 160°C with the help of activator, and this value decreased with the increase of activator added even though it gradually decomposed. This is not surprising because this is one of the strongest activator for OBSII among others such as zinc oxide and zinc-p-toluenedisulfinate. In addition, this decomposition temperature goes well with that of foaming process, meaning that it makes an effective foaming process without any loss of foaming agent as well as additional heating.

3.4 Mechanical properties

As shown in Table 2, the mechanical properties of EVA incorporated with PFA has better mechanical properties such as elongation and compression set than OBSII with similar values of other properties. Especially, compression set is one of the key properties of the sponge for EVA shoe soles. These results were attributed to the gradual decomposition of PFA and the introduction of polymeric formation. Because the methacrylic polymers have a polar functional group, they have better miscibility with EVA during the mixing and better adhesion bonding.

<table>
<thead>
<tr>
<th>Table 3: Mechanical Properties of EVA Sponge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
</tr>
<tr>
<td>Hardness (shore A)</td>
</tr>
<tr>
<td>Specific gravity</td>
</tr>
<tr>
<td>Volumetric expansion</td>
</tr>
<tr>
<td>Tensile strength</td>
</tr>
<tr>
<td>Tear strength</td>
</tr>
<tr>
<td>Elongation</td>
</tr>
<tr>
<td>Split tear</td>
</tr>
<tr>
<td>Compression set</td>
</tr>
</tbody>
</table>

3.5 Morphological studies

As shown in Figure 4, the surface of SBR with PFA is homogeneous, clean and smooth, which indicates the better compatibility of PFA with SBR and other fillers compared to TSH, which showed rugged, not clean and tough, meaning the poor miscibility with SBR.

The gradual decomposition of PFA kept the surface clean and smooth even after foaming process. The cell structure of crosslinked area of SBR with PFA was as fine as TSH with improved compatibility between SBR and PFA. The nanoparticles of PFA were prepared by using AOT/n hexane reverse micro-emulsion method. Several TEM images of the particles were taken at magnification of 150,000. The size and number of reverse micelles which are dispersed in the bulk organic fluid largely is
Polymerizable MATSH, MAOBSH, and their PFAs, having sulfonylhydrazide functional group to be decomposed by heating, were synthesized and characterized. The synthesized PFAs showed higher decomposition temperature and gradual weight loss behaviors. In the foaming test, the EVA incorporated with PFA showed better surface and fine cell structure as well as mechanical properties such as elongation and compression set due to better compatibility and higher nucleation sites than commercial foaming agents. The PFA nanoparticles showed much lower decomposition temperature at around 140°C and higher exothermic heat than its PFA. This research describes a novel PFA which has several advantages such as no predecomposition of PFA during mixing process, controllable foaming temperature, and excellent compatibility with polymers, respectively. Future research will focus on the effect of particle size as well as the detailed morphological analysis such as cell size anisotropy and cell density, and so on.

REFERENCES


Preparation and degradation of...