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ORIGINAL PAPER

Synthesis and characterization of polymeric foaming agent containing sulfonyl hydrazide moiety

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Abstract New monomer, methacryloyl toluenesulfonylhydrazide (MATSH) containing foamable sulfonylhydrazide functional group after decomposed by heating, was synthesized from *p*-toluenesulfonylhydrazide (TSH) with methacryloyl chloride, and used to obtain poly(MATSH) as a polymeric foaming agent (PFA) in dry THF at 70 °C using AIBN as an initiator. The structures of synthesized MATSH and poly(MATSH) were identified by FT-IR and ^{1}H-NMR spectroscopies. The decomposition temperature of poly(MATSH) was determined to be 224 °C and this temperature was decreased into around 160 °C by adding an activator such as surface-treated urea to polymer. The exothermic temperature and heat determined by the decomposition of the polymer were 260 °C and 447 J/g. The amount of gas evolution for poly(MATSH) measured at decomposition temperature was 90 mL/g. Furthermore, the polymer incorporated with PFA showed better skin and fine cell structure as well as better mechanical properties such as elongation and compression set due to better compatibility of the developed PFA with polymers than those added with TSH.

Keywords Polymeric foaming agent (PFA) · *p*-Toluenesulfonylhydrazide (TSH) · Decomposition temperature · Gas evolution · Mechanical property

Introduction

Chemical foaming agent or chemical blowing agent is a chemical additive that is able to evolve gas through thermal decomposition and produces cellular structures within structures in a polymeric matrix. The main reason for manufacturing foamed plastics and rubbers is their greatly reduced density, which lowers the weight of the finished material and decreases costs. There are also additional improved properties gained

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from the cellular structure such as improved heat and sound insulation, dielectric properties, higher shock absorption, higher rigidity of integral materials, prevention of sink parts in heavy-section injection molded parts, and decorative effects.

In the past 70 years, over a thousand chemicals have been suggested as foaming agents for polymers. Diazoaminobenzene (DAB) was developed as the first commercial organic foaming agent in 1940s but because of its toxicity and staining properties, non-staining aliphatic compounds such as 2,2′-azobisisobutyonitrile, derivatives of azodicarboxylic acid, and dinitrosopentamethylene tetramine were developed as organic foaming agents [1–3]. Since 1952, several sulfonyl hydrazides have been used as foaming agents for rubbers and plastics [4–7]. 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 mercaptan-like odor. Among them, 4,4′-oxybis(benzenesulfonyl hydrazide) (OBSH) and *p*-toluenesulfonylhydrazide (TSH) are widely used as foaming agents [8, 9]. The use of these low molecular weight organic foaming agents displayed 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 polymeric foaming agent (PFA) as an alternative which is expected to be better compatible with polymers such as SBR and EVA.

Recently, Cai et al. [10] reported that poly(*p*-vinylphenlysulfonylhydrazide) (PVPSH) was grafted onto silane coupling agent pre-treated nano-silica via aqueous radical polymerization to promote dispersion of nano-silica in polypropylene (PP). It was reported that the melt blending of PVPSH grafted nano-silica with PP should arouse bubble-stretching effect to improve nanoparticles dispersion in the PP matrix [10–12].

The objectives of this study are to synthesize new PFA containing sulfonyl hydrazide, to evaluate its foaming behaviors as well as the effects of activator added to PFA. In this study, new monomer, MATSH, and its PFA were synthesized and identified by FT-IR and ^{1}H-NMR spectroscopies. The decomposition and gas evolution of poly(MATSH) were determined by gas evolution measurement instrument (GEMI). TGA and DSC were also used to evaluate their decomposition and exothermic behaviors. The morphologies of polymer incorporated with TSH and its PFA were examined. The foaming performance was measured according to basic foaming formulation based on SBR. The mechanical properties of the EVA foam with PFA were measured according to ASTM method.

Experimental section

Materials

TSH as a foaming agent 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 vaccum distilled. Azobisisobutyronitrile (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.

Measurements

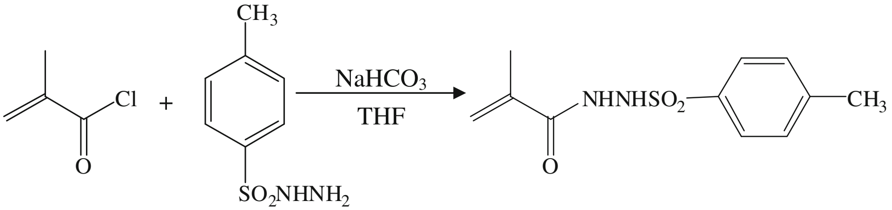
The infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrophotometer. ^{1}H-NMR spectroscopic measurement was recorded using FT-300 MHZ Varian Gemini 2000 spectrophotometer using DMSO-d_6 solvent. The chemical shifts were assigned in ppm tetramethylsilane as the internal standard. The thermal decomposition temperatures (T_d) were examined with a thermo-gravity analysis instrument (TA Instrument, New Castle, USA, Q500) by scanning the samples from 100 to 800 °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 were 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 SBR incorporated with foaming agents were analyzed by scanning electron microscopy (SEM; JEOL JSM35-CF) after being coated with gold before installation in the SEM chamber. Hardness of EVA foam sponges 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 forcing 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 sponge were measured using Gotech Universal Testing Machine (GT-A170006 or AI700S) 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 compressed 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 foams was remeasured to obtain the percentage change in original thickness according to ASTM D395. The expansion ratio was calculated from the following equation:

$$\text{Expansion ratio }(\%) = [(t_1 \times t_2 \times t_3)/(m_1 \times m_2 \times m_3)] \times 100,$$

where t_1 is the length of foam sheet, t_2 is the width of foam sheet, t_3 is the height of foam sheet, m_1 is the length of mold, m_2 is the width of mold, and m_3 is the thickness of mold, respectively.

Synthesis of MATSH

MATSH was prepared by the reaction of methacryloyl chloride (MAC) and TSH, as shown in Scheme 1. In brief, to a stirred solution of TSH (25 g, 0.134 mol), TEA



Scheme 1 Reaction scheme for synthesis of MATSH

(0.5 mL, 0.0035 mol) and trace amount of hydroquinone (0.01 g) in THF (140 mL), MAC (15.3 mL, 0.134 mol) was added dropwise, so that may not rapidly increase the reaction temperature over 40 °C. After the addition was completed, sodium bicarbonate (11.3 g, 0.134 mol) in distilled water (10 mL) was added into the above solution. 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 MATSH in 92% yield.

Synthesis of PFA

A solution of MATSH (2 g, 9.36 mmol) and AIBN (0.03 g, 0.099 mmol) in THF (40 mL) was introduced into a dry Pyrex polymerization vessel. The vessel was sealed after degassed twice by purging with purified N_2 gas and placed into a water bath maintained at 70 °C for 48 h. The PFA, poly(MATSH), was precipitated in excess diethyl ether, collected by filtration, and then dried in a vacuum oven at 30 °C until a constant weight.

Decomposition activation test

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

Evaluation of foaming behavior

The polymers incorporated with TSH and its PFA were prepared and shown in Table 1. For the formulation of SBR with foaming agents, briefly, to the SBR resin on rollers at room temperature, talc, process oil, 2-mercaptobenzothiazole (M) and dibenzothiazyl disulfide (DM) as accelerators, stearic acid, and Cellex-A were added on the rolls and well mixed. After 10 min, foaming agents and sulfur as vulcanization 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 150 kgf/cm^2.

Table 1 Formulation and processing conditions of polymer with TSH and its PFA

	Ingredients (PHR)	SBR sponge		EVA sponge	
Formulation	SBR1501	100	100	–	–
	EVA (VA 20%)	–	–	100	100
	Talc (filler)	40	40	–	–
	Process oil	10	10	–	–
	Sulfur	1	1	–	–
	M	1	1	–	–
	DM	0.5	0.5	–	–
	Stearic acid	1	1	1	1
	$CaCO_3$	–	–	10	10
	DCP	–	–	1	1
	Cellex-A	2	2	2	2
	TSH	6	–	6	–
	PFA	–	6	–	6
Processing conditions	Mixing process: by 2-open roll mills (5″ × 12″L) for 15 min				
	Compression molding: mold size (100 × 150 × 10 mm)				
	Curing and foaming conditions: 160 °C for 0–20 min under pressure at 150 kgf/cm^2				

Results and discussion

Identification of MATSH and its polymer

The FT-IR spectrum (Fig. 1) of the polymer indicated characteristic absorption peaks at 1730 cm^{-1} (stretching vibration of C=O), 1440 cm^{-1} (CH_2 scissoring), 1400 cm^{-1} (CH_3 scissoring), 1590 cm^{-1} (stretching vibration of the aromatic C=C), 1150 and 1090 cm^{-1} (stretching vibration of O=S=O), and 900–790 cm^{-1} (out-of-plane vibration of aromatic =C–H) with the concurrent disappearance of vinyl group peak at 1600 cm^{-1} (stretching vibration of vinyl C=C).

As shown in Fig. 2, ^{1}H-NMR spectrum of poly(MATSH) showed aromatic proton at 7.3–7.8 ppm, NH–NH at 9.3–9.7 ppm, CH_3 in TSH at 1.7 ppm, CH_3 in MAC at 1.2 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.

Exothermic decomposition and gas evolution

Figure 3 showed the gas evolution graph of foaming agent and its monomer and polymer as a function of decomposition temperature with constant heating rate of 5 °C/min. As shown in Fig. 3, the synthesized PFA has higher and slower decomposition temperatures than the corresponding foaming agent and monomer. This is attributed to the increasing of molecular weight as well as the incorporation of methacrylic unit in moiety. The gas evolution of PFA was determined to be 90 mL/g at 260 °C.

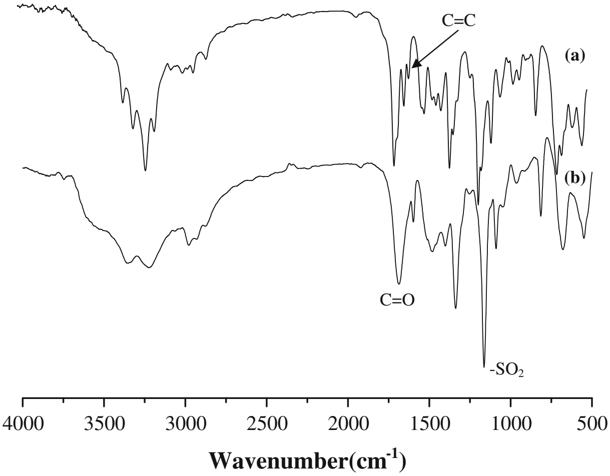


Fig. 1 FT-IR spectra of MATSH (*a*) and poly(MATSH) (*b*) (KBr)

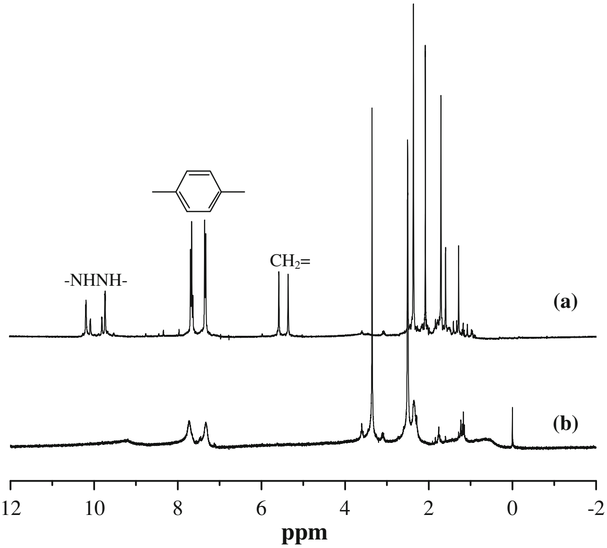


Fig. 2 ^{1}H-NMR spectra of MATSH (*a*) and poly(MATSH) (*b*) (DMSO-d_6)

Table 2 shows the thermal decomposition behaviors of foaming agent and its monomer and polymer. As shown in Table 2 and Fig. 4, the PFA has showed higher decomposition temperature with the two-step decomposition behaviors at 224 and 370 °C, as well as gradual weight loss behaviors compared with commercial foaming agent and its monomers. This is attributed to the fact that the unstable toluenesulfenic acid released from polymer backbone was formed at higher temperature. The decomposition mechanism of poly(MATSH) would be expected to be as follows [13]. As shown in Scheme 2, poly(MATSH) was expected to be

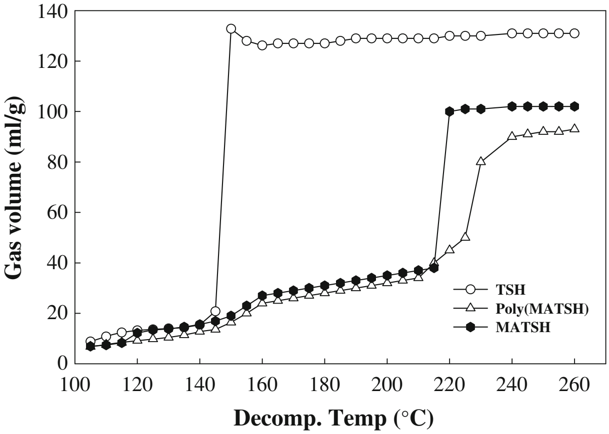


Fig. 3 Decomposition temperature and gas evolution graphs of TSH, MATSH, and PFA

Table 2 Decomposition and exothermic behaviors

	TGA (decomposition)		DSC (exothermic heat)	
	1st point (°C)	2nd point (°C)	Temp. (°C)	Calory (J/g)
TSH	196	370	176	1036
MATSH	215		231	375
PFA	224		260	447

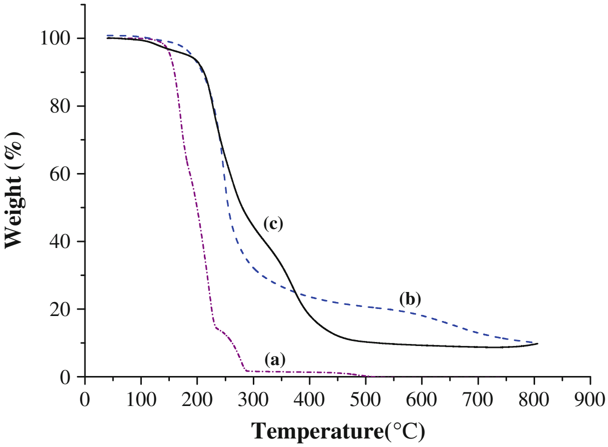
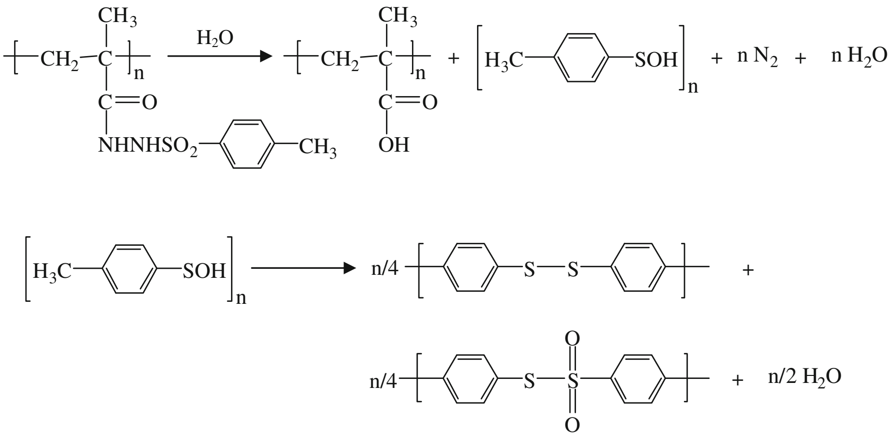


Fig. 4 TGA thermograms of TSH (*a*), MATSH (*b*), and poly(MATSH) (*c*)

decomposed into polymethacrylic acid and toluenesulfenic acid with the evolution of nitrogen gas, which is the major foaming gaseous product. The formed toluenesulfenic acid would be stabilized by disproportionation to give a polymeric disulfide and a thiosulfonate which are compatible to the polymer matrix.



Scheme 2 Proposed decomposition mechanism of poly(MATSH)

DSC permits the determination of the exothermic heat which is generated at the decomposition point of the polymer blowing agent. As shown in Table 2, the synthesized polymer showed higher exothermic temperature at 260 °C and lower exothermic heat compared with foaming agent and its monomer.

From the thermal analyses by TGA and DSC, gradual and higher decomposition temperature of PFA makes no predecomposition of foaming agent during mixing process before foaming.

Effect of foaming performance

Figure 5 showed the effect of activator such as surface-treated urea with stearic acid on the decomposition of poly(MATSH) depending on the amount added. In a pure state, poly(MATSH) decomposes at temperature 224 °C. However, the decomposition temperature of poly(MATSH) was decreased as low as 160 °C with the help of activator, and this value decreased with the increase of activator added even

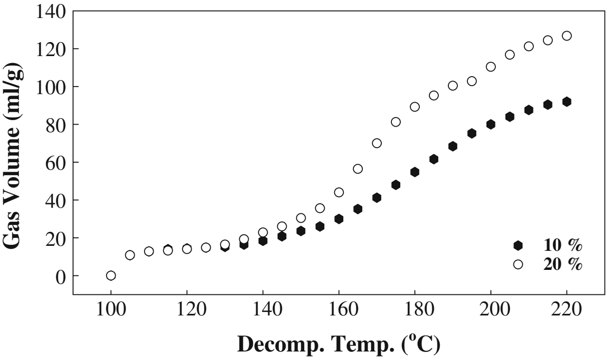


Fig. 5 Decomposition activation graph of poly(MATSH) with surface treated with urea

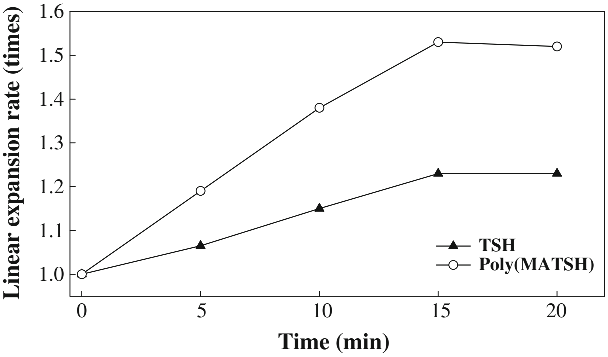


Fig. 6 Linear expansion graph of SBR sponge incorporated with TSH and poly(MATSH)

Table 3 Mechanical properties of EVA sponge

	Unit	TSH	PFA
Hardness (shore C)	–	29	28
Specific gravity	g/cm^3	0.12	0.11
Volumetric expansion	%	430	434
Tensile strength	kg/cm^2	13.83	13.71
Tear strength	kg/cm^2	5.91	5.95
Elongation	%	305	370
Split tear	kg/cm^2	2.63	2.63
Compression set	%	88.2	81.21

though it gradually decomposed. 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 any additional heating.

The foaming performance of poly(MATSH) on SBR compression molding with different times, shown in Fig. 6, compared with TSH, showed better initial foaming, higher expansion rate, and higher thermal stability. Especially, it showed 20% higher expansion rate than TSH in spite of the incorporation of the methacrylic unit in poly(MATSH). This is attributed to the strong interaction between PFA and activator as well as the methacrylic polar group in poly(MATSH), which makes the vulcanization speed and decomposition activation faster despite of the gradual decomposition of PFA.

Mechanical properties

As shown in Table 3, the mechanical properties of EVA incorporated with PFA has better mechanical properties such as elongation and compression set than TSH 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.

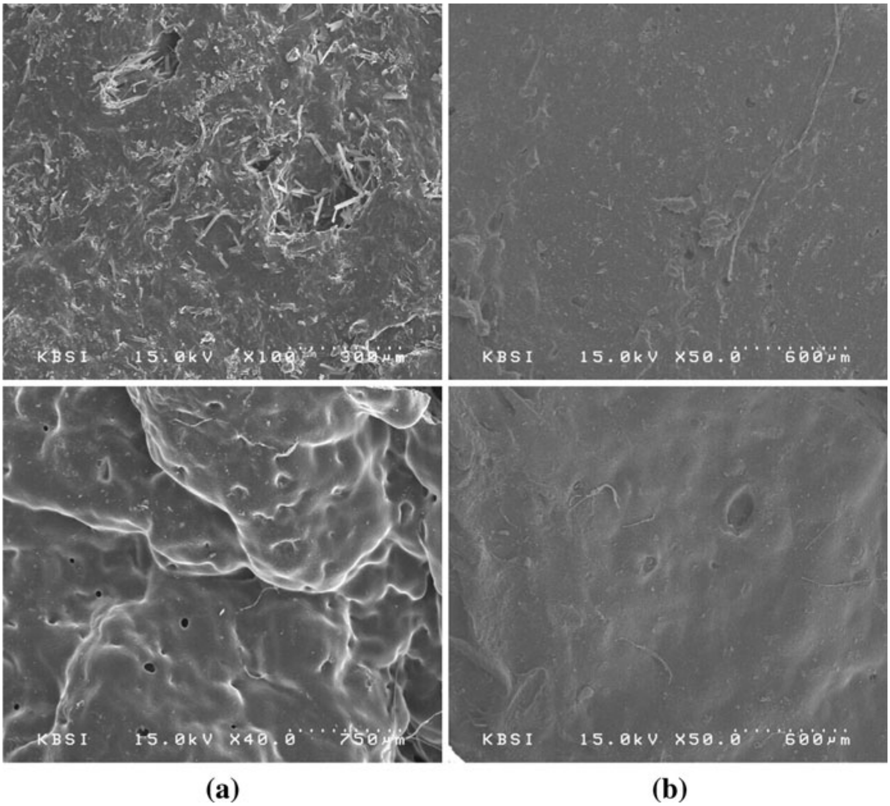


Fig. 7 SEM images of the surface area of SBR sponges incorporated with TSH (*a*) and PFA (*b*) [*upper*; before foaming, *bottom*; after foaming]

Because the methacrylic polymers have a polar functional group, they have better miscibility with EVA during the mixing and better adhesion bonding.

Morphological studies

As shown in Fig. 7, 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 crossed area of SBR with PFA was as fine as TSH with improved compatibility between SBR and PFA (Fig. 8).

Conclusions

New monomer, MATSH, and its PFA, poly(MATSH) having sulfonylhydrazide functional group decomposed by heating, were synthesized and characterized. The

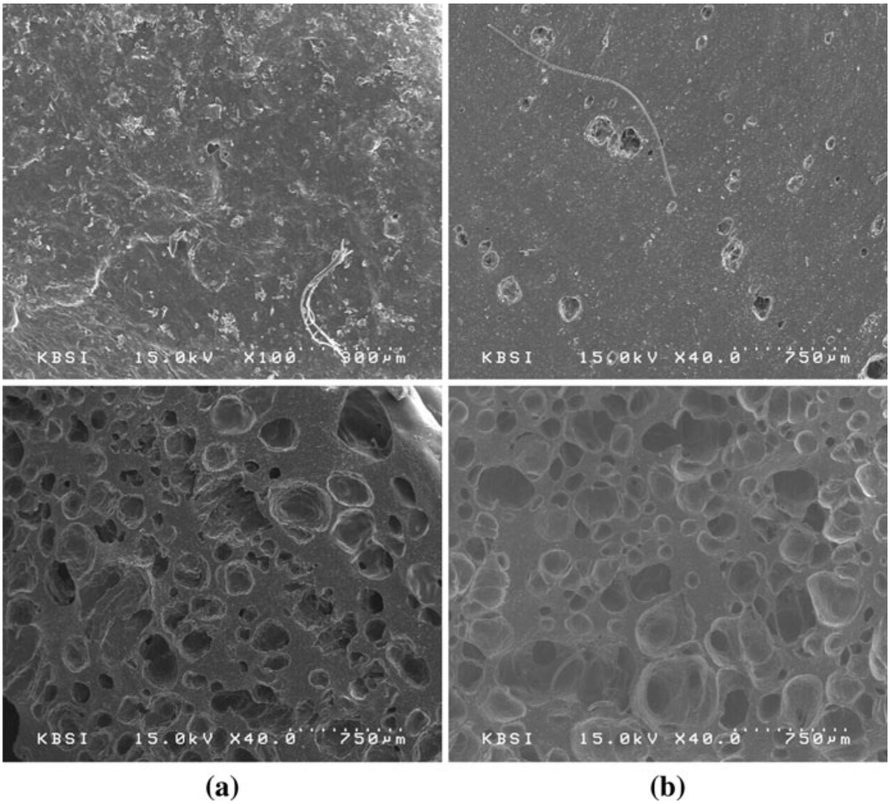


Fig. 8 SEM images of the cross area of SBR sponges incorporated with TSH (*a*) and PFA (*b*) [*upper*; before foaming, *bottom*; after foaming]

synthesized PFA showed higher decomposition temperature and gradual weight loss behaviors. In the foaming test, the SBR 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 than TSH. 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.

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