

A conductive foam: Based on novel poly(styrene-*b*-butadiene-co-styrene-*b*-styrene) tri-block copolymer filled by carbon black

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ABSTRACT: In this article, a conductive foam based on a novel styrene-based thermoplastic elastomer called poly(styrene-*b*-butadiene-co-styrene-*b*-styrene) tri-block copolymer S(BS)S was prepared and introduced. S(BS)S was particularly designed for chemical foaming with uniform fine cells, which overcame the shortcomings of traditional poly(styrene-*b*-butadiene-*b*-styrene) tri-block copolymer (SBS). The preparation of conductive foams filled by the carbon black was studied. After the detail investigation of cross-linking and foaming behaviors using moving die rheometer, the optimal foaming temperature was determined at 180°C with a complex accelerator for foaming agent. Scanning electron microscopy (SEM) images shown that the cell bubbles of conductive foam were around 30–50 μm. The conductivity of foams was tested using a megger and a semiconductor performance tester. SEM images also indicated that the conductivity of foams was mainly affected by the distribution of carbon black in the cell walls. The formation of the network of the carbon black aggregates had a contribution to perfect conductive paths. It also found that the conductivity of foams declined obviously with the foaming agent content increasing. The more foaming agent led to a sharp increasing of the number of cells (from 2.93×10^6 to 6.20×10^7 cells/cm³) and a rapid thinning of the cell walls (from 45.3 to 1.4 μm), resulting in an effective conductive path of the carbon black no forming. The conductive soft foams with the density of 0.48–0.09 g/cm³ and the volume resistivity of 3.1×10^3 – 2.5×10^5 Ω cm can be easily prepared in this study. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41644.

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INTRODUCTION

Generally speaking, polymer foams are produced by a process involving nucleation and growth of gas bubbles in a polymer matrix. Nanoparticles incorporated into the polymer foams offer several potential benefits and have been discussed briefly in a recent review article.¹ Conductive polymer foam is one of the important polymer foams. Compared with ordinary materials, polymer foams have many inherent advantages, such as low density, low thermal conductivity, good sound isolation, high specific strength, and impact resistance, which have been widely used in various fields, including aerospace, atomic energy, electric and petrochemical industry, and so on.^{2–7} In short, polymer foams have many meaningful applications in modern industry.

Carbon black and carbon fibers are the most commonly used conductive components. The reason for this is that these two

fillers have a much great tendency to form a conductive network due to their chain-like or grapes-like aggregate structures.⁸ Many scientists^{9,10} studied carbon black filled conductive composites, and they found that the conductivity of composites was influenced by the distribution of carbon black particles in the resin, which direct determined the current conductivity in the composites. According to the literature, the studies of conductive polymer foams were mostly focused on polyurethane (PU),^{11–15} polystyrene (PS),^{16,17} polypropylene (PP),¹⁸ polystyrene-*b*-ethylene-butylene-*b*-polystyrene (SEBS) and their blends with polystyrene (PS),¹⁹ and ethylene-vinyl acetate copolymer (EVA).²⁰ As everyone knows, poly(styrene-*b*-butadiene-*b*-styrene) tri-block copolymer (SBS) is the representative of styrene-based thermoplastic elastomers, which has advantages of good skid resistance, air permeability, low temperature resistance, and rebound resilience.^{21–23} Unfortunately, traditional SBS has no

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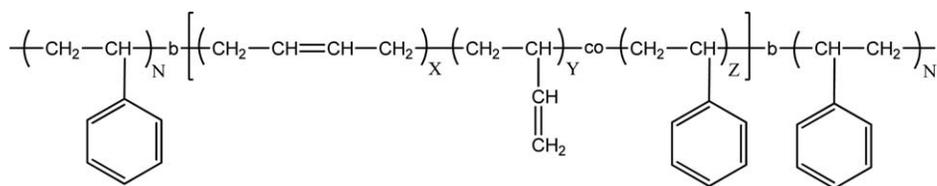


Figure 1. Molecular structure of S(BS)S. N and X + Y + Z represent the polymerization degrees of hard and soft blocks, respectively.

capacity of chemical foaming with uniform fine cells, and therefore, it has been no reports of conductive foams based on SBS so far.

Here, poly(styrene-*b*-butadiene-*co*-styrene-*b*-styrene) tri-block copolymer (S(BS)S) which is a new styrene-based thermoplastic elastomer is introduced. This styrene-based tri-block copolymer is synthesized using active anionic polymerization. Figure 1 illustrates the molecular structure of S(BS)S, which has polystyrene blocks at both ends and poly(butadiene-*co*-styrene) block in the middle. However, poly(butadiene) is the middle block in traditional SBS, which is different from S(BS)S. S(BS)S is specially designed for chemical foaming with uniform fine cells to overcome the shortcomings of SBS. In addition, its mechanical properties are similar with traditional SBS (see Table I).

In this study, the preparation of conductive soft foams based on S(BS)S tri-block copolymer and the carbon black was investigated. The influence of the conductive filler together with the cell size on the conductivity of foams was also studied. The carbon black was used as conductive filler owing to the low cost, the large loading, and the easy dispersion contrasted with CNTs.^{24–30} The cross-linking and foaming behaviors were investigated using moving die rheometer (MDR). The shape and size of the cell bubbles, as well as the distribution of carbon black in the cell walls, were observed via scanning electron microscopy (SEM). The conductivity of foams was tested using a megger and a semiconductor performance tester. The conductive soft foams with the density of 0.48–0.09 g/cm³ and the volume resistivity of 3.1×10^3 – $2.5 \times 10^5 \Omega \text{ cm}$ can be easily prepared in this study. Conductive soft foam of styrene-based thermoplastic elastomers which has many potential applications was provided.

EXPERIMENTAL

Materials

S(BS)S (TVA301) that was synthesized via active anionic polymerization was supplied by Baling Petrochemical of Sinopec. It contained 30 wt % styrene repeat unit at both ends (hard blocks), and 47 wt % butadiene and 23 wt % styrene in the middle of the molecular chain (soft blocks). The weight-average

Table I. Comparison of Mechanical Properties Between S(BS)S and a Traditional SBS

	S(BS)S	SBS	Method
Tensile strength (MPa)	14.20	16.20	ISO 37
Elongation (%)	720	750	ISO 37
Hardness (Shore A)	78	76	ISO 7619-1

molecular weight of S(BS)S used here was 14,000 g/mol with a polydispersity index $\bar{M}_w/\bar{M}_n = 1.03$ (GPC, tetrahydrofuran as a mobile phase). The comparison of mechanical properties between S(BS)S and a traditional SBS is shown in Table I. The weight-average molecular weight of this SBS was 13,000 g/mol, and it also contained 30 wt % styrene repeat unit at both ends (hard blocks). Azodicarbonamide (yellow powder, foaming agent) was produced by Ningxia Risheng Chemicals Group. Dicumyl Peroxide (DCP, cross-linker) was bought from Shanghai Chemical Reagent Company. Carbon black (Ensaco350G) was obtained from Timcal Belgium S.A., Switzerland. All other ingredients, such as zinc oxide (ZnO), zinc stearate, and stearic acid (the lubricant), were analytical grade, kindly supplied by Chengdu Kelong Reagent.

Sample Preparation

The S(BS)S tri-block copolymer was mixed with ingredients according to the formulations (expressed in phr) in Table II using an laboratory two-roll mill at 90°C. In Table II, the number in the symbol of C0–C20 represented the amount of carbon black. For example, the amount of carbon black was 20 phr for C20. Similarly, the number in the symbol of A1–A12 represented the amount of azodicarbonamide (in phr). S(BS)S was first milled for 2 min, and then ZnO, zinc stearate, and stearic acid were added. After that, azodicarbonamide was added along with carbon black. Mixing was kept for another 3 min to ensure the homogeneous distribution of ingredients. Finally, the cross-linker DCP was added. The sheets of mixed compounds (with thickness of 0.6 mm) were taken out of the two-roll mill, and stored at room temperature for 24 h before foaming.

The soft foams were prepared from the sheets of mixed compounds by the molding method via a plate vulcanizing machine. The sheets were first cut to 6.0 cm × 10.0 cm × 0.6 cm, and then were placed into a metal mold. The closed metal mold together with sheets was placed into the plate vulcanizing machine whose temperature of both upper and lower plates was 180°C. The plate vulcanizing machine was closed quickly, and a pressure of 10 MPa was applied to the metal mold. The sheets of mixed compounds in the mold (10 MPa) were kept about 5–8 min at 180°C. The melted and cross-linked sheets foamed immediately after opening the plate vulcanizing machine. So the soft foams based on S(BS)S were gained.

Measurements

Differential Scanning Calorimetry. The decomposition behavior of the azodicarbonamide (chemical foaming agent) was studied using differential scanning calorimetry (DSC) (NETZSCH 204 F1). The experiments were performed from 60 to 240°C at 20°C/min. To prevent from the interference of the oxidation, the

Table II. Formulations of the Mixed Compounds of S(BS)S Before Foaming

Ingredients (phr)	Samples													
	C0	C3	C5	C7	C10	C12	C15	C20	A1	A3	A6	A9	A12	
S(BS)S	100	100	100	100	100	100	100	100	100	100	100	100	100	
DCP	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	
ZnO	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	
Zinc stearate	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	
Stearic acid	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	
Azodicarbonamide	3	3	3	3	3	3	3	3	1	3	6	9	12	
Carbon black	0	3	5	7	10	12	15	20	20	20	20	20	20	

samples were protected by high-purity nitrogen (50 ml/min) during measurements.

Moving Die Rheometer. The foaming and cross-linking behaviors of mixed compounds were measured by a MDR (Model GT-M2000-FA, Gotech) according to the method of ASTM D 5289. The MDR was equipped with a pressure sensor at the upper die. The pressure (in the mold) of mixed compounds during foaming and cross-linking can be detected conveniently by MDR. Each of the measurements was lasted for 10–15 min with 1° switch angle.

Scanning Electron Microscopy. The soft foams were first frozen in liquid nitrogen, and then were immediately fractured to produce a clean and intact surface with a minimum deformation. The fracture surfaces were sputtered with a thin layer of gold. The morphology was observed using SEM (JSM-5900LV) with 20 kV.

Volume Resistivity. The volume resistivity of soft foams which was higher than $10^{10} \Omega \text{ cm}$ was measured using a megger (ZC36, Shanghai Precision Scientific Instrument). For the vol-

ume resistivity of soft foams lower than $10^{10} \Omega \text{ cm}$, the measurements were performed by a Keithley semiconductor performance tester (4200-SCS, Keithley Instruments), and the test voltage was 10 V.

RESULTS AND DISCUSSION

Foams Preparation

Accelerators for Foaming Agent. In this study, the chemical foaming method was used to prepare soft foams. The foaming agent and the crosslinker used were azodicarbonamide (AC) and dicumyl peroxide (DCP), respectively. In the chemical foaming of polymers, it generally agrees that the decomposition of foaming agent and the cross-linking induced by the cross-linker happen simultaneously. On one hand, the decomposition of foaming agents produces plentiful gas to generate the nucleus cells which continue to grow up. On the other hand, the cross-linking reaction enhances the melt strength of polymers to prevent gas from escaping and keeps the cells stable. So, it requires that the decomposition temperature of foaming agents is compatible with the cross-linking reaction. The azodicarbonamide starts to release gas around 215–221°C. At this temperature, the decomposition half-life of DCP is 1–2 s. It indicates that the

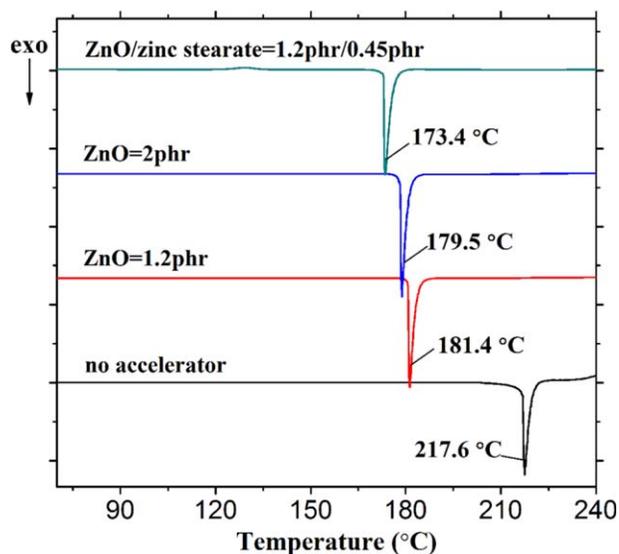
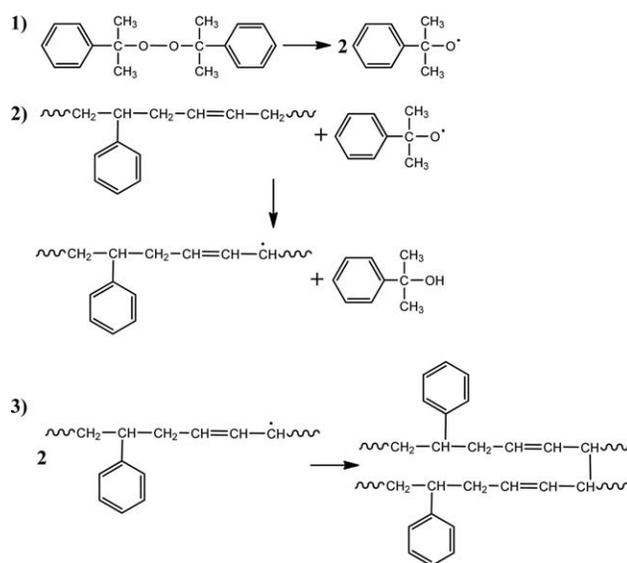
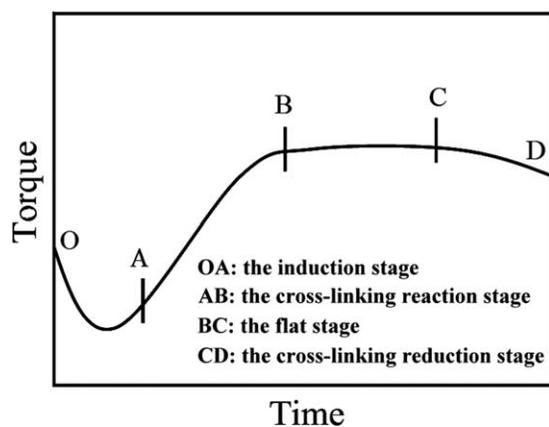


Figure 2. DSC curves of azodicarbonamide with no accelerator, ZnO = 1.2 phr, ZnO = 2 phr, and ZnO/zinc stearate = 1.2 phr/0.45 phr. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 1. Scheme of the cross-linking reaction of S(BS)S induced by DCP.



Scheme 2. A typical cross-linking curve.

cross-linking processing of S(BS)S will complete before the full decomposition of azodicarbonamide, resulting in the melt strength of S(BS)S being too high to foam. Therefore, it is necessary to reduce the decomposition temperature of azodicarbonamide.

Here, the accelerators for azodicarbonamide decomposition were used to expect to reduce the decomposition temperature. In general, ZnO, stearic acid salts, the carbonate, and the phosphate can be used as the decomposition accelerators. Tai and Wang reported that adding ZnO not only lowered the decomposition temperature of azodicarbonamide but also promoted its decomposition rate.³¹ Some researchers found that the decomposition temperature of azodicarbonamide was reduced by adding zinc stearate.^{32,33} In this study, two accelerators, including ZnO and ZnO/zinc stearate (the complex accelerator), were evaluated using DSC. As shown in Figure 2, the decomposition temperature (releasing gas) of the pure azodicarbonamide is up to 217.6°C. However, the decomposition temperature reduces to 181.4°C after 1.2 phr of ZnO is added. The reduction of the decomposition temperature is less obvious when the

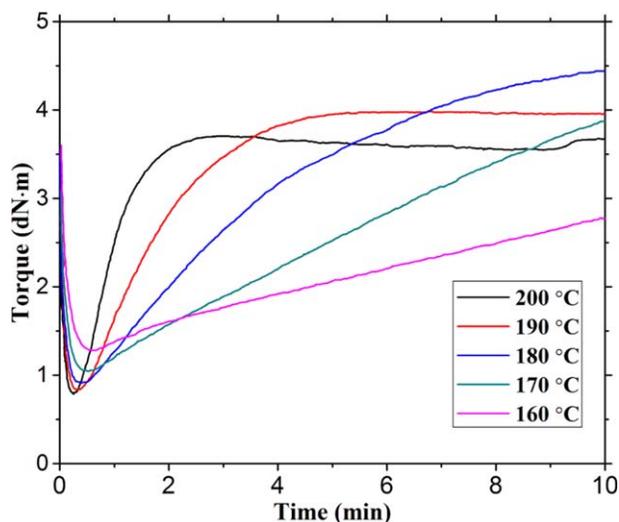
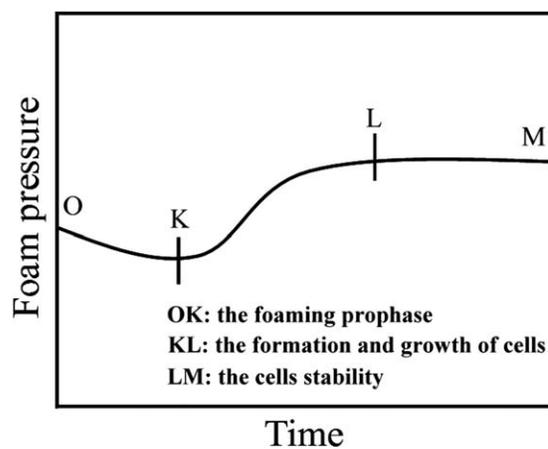


Figure 3. Cross-linking curves of the mixed compound of S(BS)S (C15 in Table II) at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 3. A typical foaming curve.

amount of ZnO increases from 1.2 phr (181.4°C) to 2 phr (179.5°C). Surprisingly, the decomposition temperature is reduced to 173.4°C when 1.2 phr ZnO and 0.45 phr zinc stearate are used simultaneously. Around 173°C, the decomposition half-life of DCP is about 1 min, which is suitable to obtain an effective crosslinking for S(BS)S.

Cross-Linking Reaction. Scheme 1 is the scheme of cross-linking reaction of S(BS)S induced by DCP. This reaction can be divided into three steps: (1) the decomposition of DCP produces free radicals; (2) the free radicals produced by DCP capture the α -H (next to the double bonds) in BS blocks of S(BS)S, and the free radicals of the S(BS)S backbone are generated; (3) the free radicals of S(BS)S link to each other to generate a cross-linked network.

The cross-linking reaction can obviously enhance the melt strength of polymers, which can be reflected as the shear torque increasing in a rheometer. So, a moving die rheometer (MDR) was used to measure the degree of cross-linking in this study. The greater the torque is, the higher the degree of cross-linking

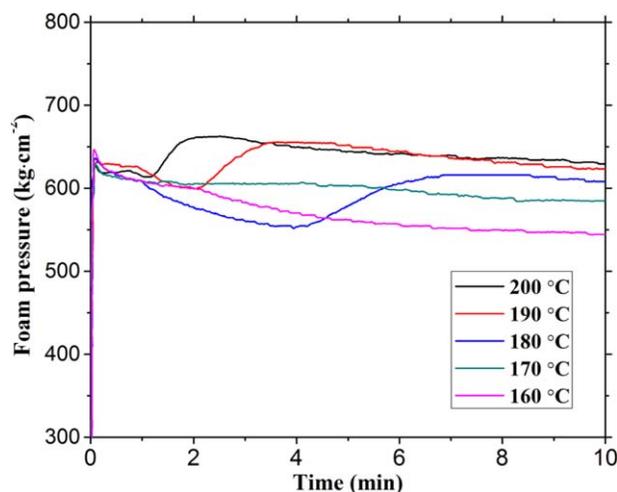


Figure 4. Foaming curves of the mixed compound of S(BS)S (C15 in Table II) at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

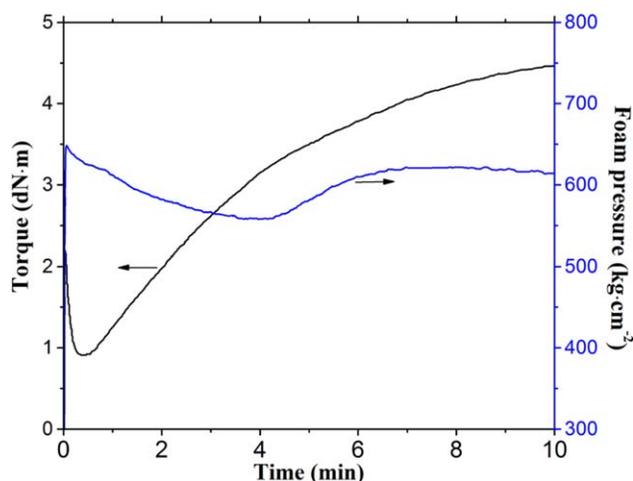


Figure 5. Cross-linking curve and the foaming curve of the mixed compound of S(BS)S (C15 in Table II) at 180°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is. According to cross-linking process, a cross-linking (vulcanization) curve can be divided into four stages (Scheme 2).

1. The induction stage (OA). It starts from S(BS)S placing in MDR and end with a minor cross-linking appearing;
2. The cross-linking reaction stage (AB). In this period, the free radicals of S(BS)S link to each other, and the torque of MDR increases rapidly. The slope of the cross-linking direct represents the rate of the cross-linking reaction;
3. The flat stage (BC). The cross-linking reaction completes, and the torque keeps unchanging;
4. The cross-linking reduction stage (CD). The cross-linked bonds degrade under a high temperature, and the torque decreases slightly with the time increasing.

An ideal cross-linking curve is such a curve that the induction stage (OA) and the flat stage (BC) are long enough to guarantee

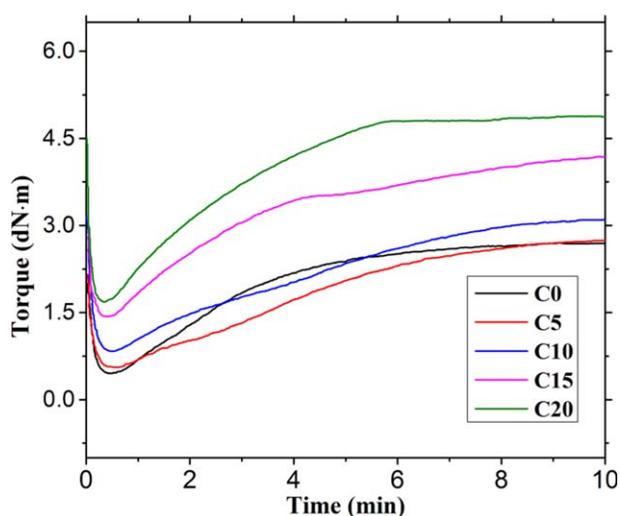


Figure 6. Cross-linking curves of the mixed compound of S(BS)S with different amount of conductive carbon black. The temperature is 180°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

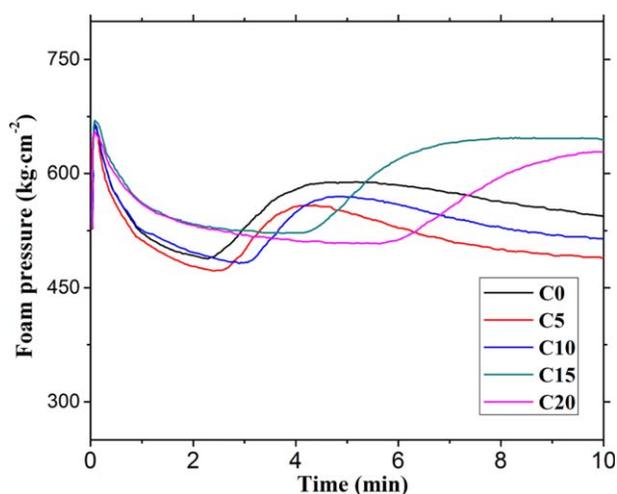


Figure 7. Foaming curves of the mixed compound of S(BS)S with different amount of conductive carbon black. The temperature is 180°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the security of production in processing, while the cross-linking reaction stage (AB) is as short as possible (a high rate of cross-linking reaction), resulting in a higher efficiency and a lower consumption of energy. The cross-linking reduction stage (CD) is always unexpected.

The cross-linking curves of the mixed compound of S(BS)S (C15 in Table II) are shown in Figure 3. The cross-linking curves change greatly at different temperatures. The induction stage gradually reduces with the temperature increasing. The cross-linking reaction stage obviously becomes short, and the slope of curves in this stage shows a significant increasing as the temperature increases from 160 to 200°C. It is noted that no flat stage presents when the temperatures are 160 and 170°C, which means that the rate of cross-linking is slow, and the

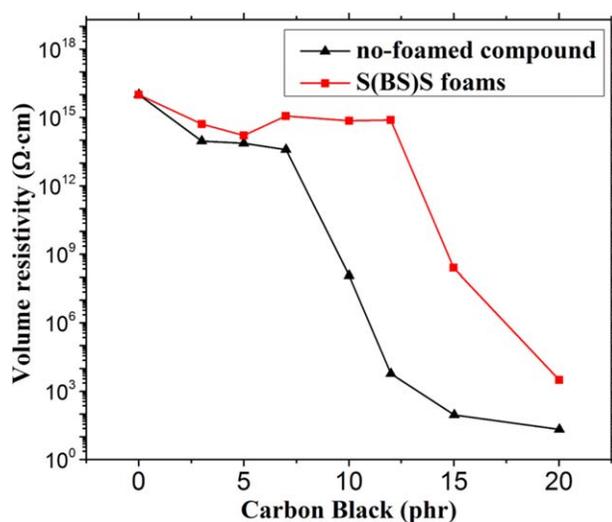


Figure 8. Volume resistivity of S(BS)S foams (azodicarbonamide content is 3 phr) and no-foamed mixed compound with different amount of conductive carbon black. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

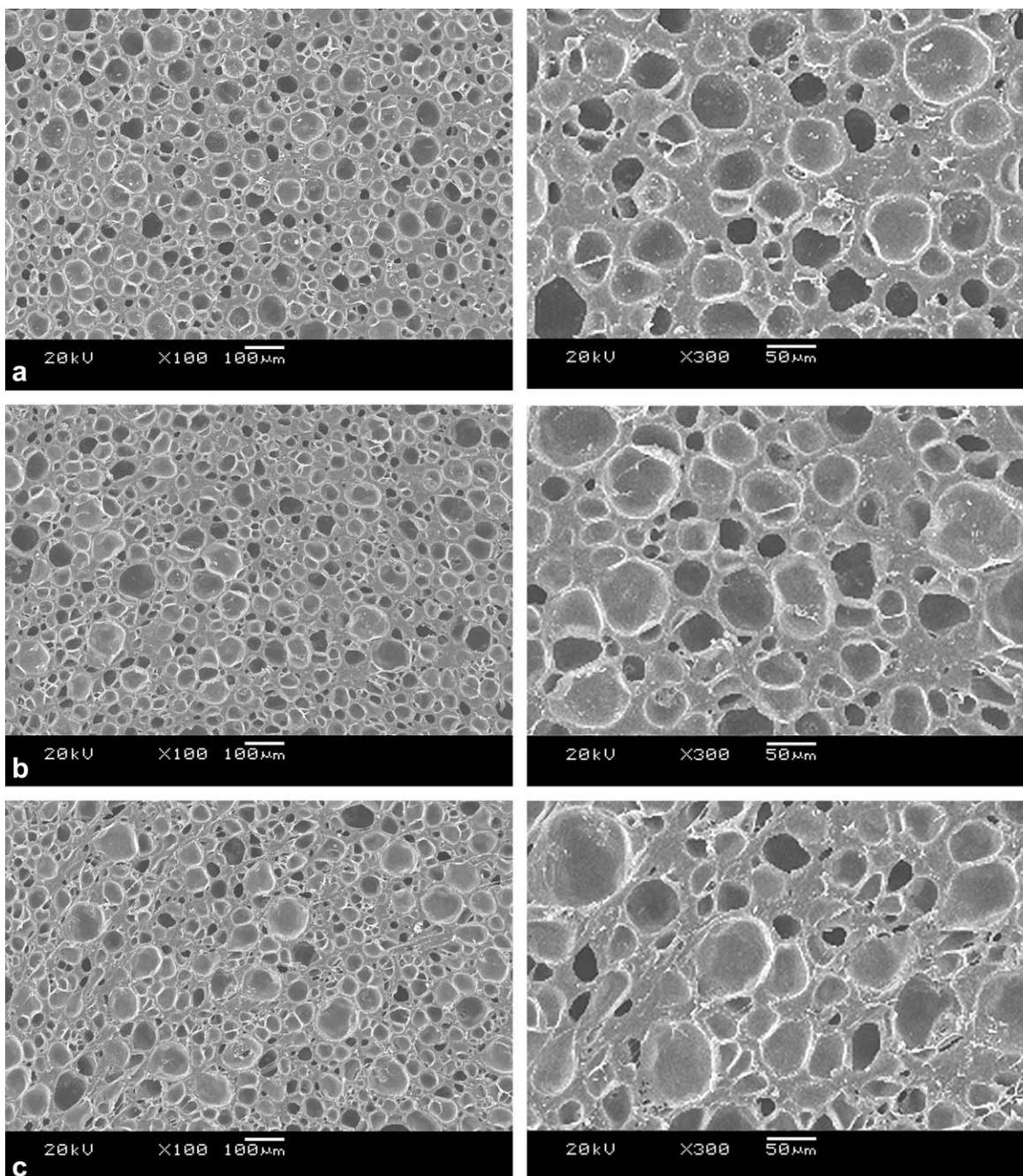


Figure 9. SEM images of the cells and cell walls of S(BS)S foams with different carbon black content. (a) C0 (0 phr); (b) C5 (5 phr); (c) C10 (10 phr); (d) C15 (15 phr); (e) C20 (20 phr).

reaction does not complete at a given time (10 min). At 180°C, the torque reaches an equilibrium value at approximate 10 min, showing an initial point of the flat stage. At 190°C, the rate of cross-linking is faster, and the flat stage is long enough. However, the induction stage is too short to control. At 200°C, it shows a cross-linking reduction stage after 4 min. So, 180°C is the best cross-linking temperature for the mixed compound of S(BS)S.

Foaming Behaviors. In the chemical foaming, the formation of foams can be divided into three stages, including the formation

of cells, the growth of cells, and the stability of cells. A scheme of the typical foaming curve is shown in Scheme 3. OK is the stage of the foaming prophase. It begins from the mixed compound of S(BS)S putting into in MDR, and the mixed compound softens under heating. KL is the stage of the formation and growth of cells. The foaming agent begins to release gas, which makes the polymer melt expanded, resulting in the pressure of foamed mixed compound increases gradually. LM represents the stage of the cells' stability. The volume of gas solved in the polymer melt does not increase again after the complete

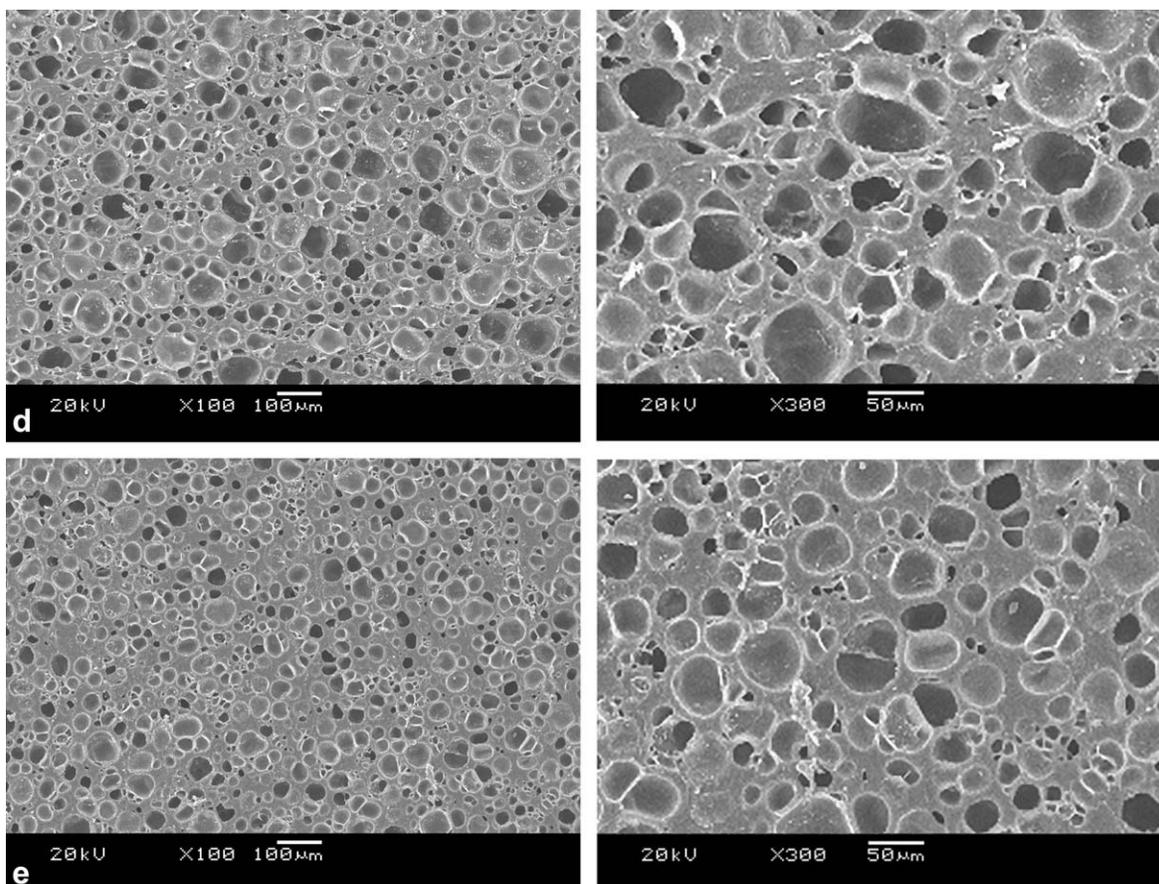


Figure 9. (Continued)

decomposition of foaming agent, and therefore, the pressure keeps unchanged.

The foaming curves of the mixed compound of S(BS)S (C15 in Table II) at different temperatures are shown in Figure 4. It can be observed that only the stage of the foaming prophase presents when temperature are 160 and 170°C. It indicates that azodicarbonamide does not break down and no gas was released at these two temperatures. In the range of 180–200°C, the stage of the formation and growth of cells, together with the stage of the cells stability, can be clearly observed. The stage of the foaming prophase is significantly shortened with the temperature increasing, indicating the reduction of the decomposition time of azodicarbonamide. Figure 4 also illustrates a higher temperature can shorten the time of the formation and growth of cells.

Chemical Foaming Temperature. In the chemical foaming, if the decomposition of azodicarbonamide is obviously prior to the cross-linking reaction, the gas in bubble cells escapes due to the low melts strength of polymer melts, causing the failure of foaming. If the decomposition of azodicarbonamide is lag behind the cross-linking reaction, a very high melts strength still prevents the bubble cells from growing up, although the escaping of gas is suppressed. This also brings a failure. A successful foaming needs the cross-linking reaction accompanied by the decomposition of azodicarbonamide. That is to say, the proper

melts strength benefits to the growth and stability of the bubble cells. Through comparison of the results in Figures 3 and 4, as shown in Figure 5, we found that the cross-linking curve and the foaming curve at 180°C are fully compatible. So, the temperature at 180°C is the best foaming temperature for the mixed compound of S(BS)S.

Influence of Carbon Black on Foaming. The above discussions are based on the mixed compound of C15 (in Table II), whose amount of carbon black is 15 phr. Because the amount of carbon black will certainly affect the conductivity of the foams,

Table III. Tensile Properties of S(BS)S Foams (According to ISO 1798)

Samples	Tensile strength (MPa)	Elongation (%)
C0	1.60 ± 0.08	270 ± 27
C5	2.03 ± 0.10	261 ± 26
C10	2.51 ± 0.13	258 ± 26
C15	3.14 ± 0.16	240 ± 24
C20	3.70 ± 0.19	223 ± 22
A1	5.41 ± 0.27	202 ± 20
A3	3.80 ± 0.19	228 ± 23
A6	1.82 ± 0.09	275 ± 28
A9	0.32 ± 0.04	320 ± 32
A12	0.06 ± 0.01	331 ± 33

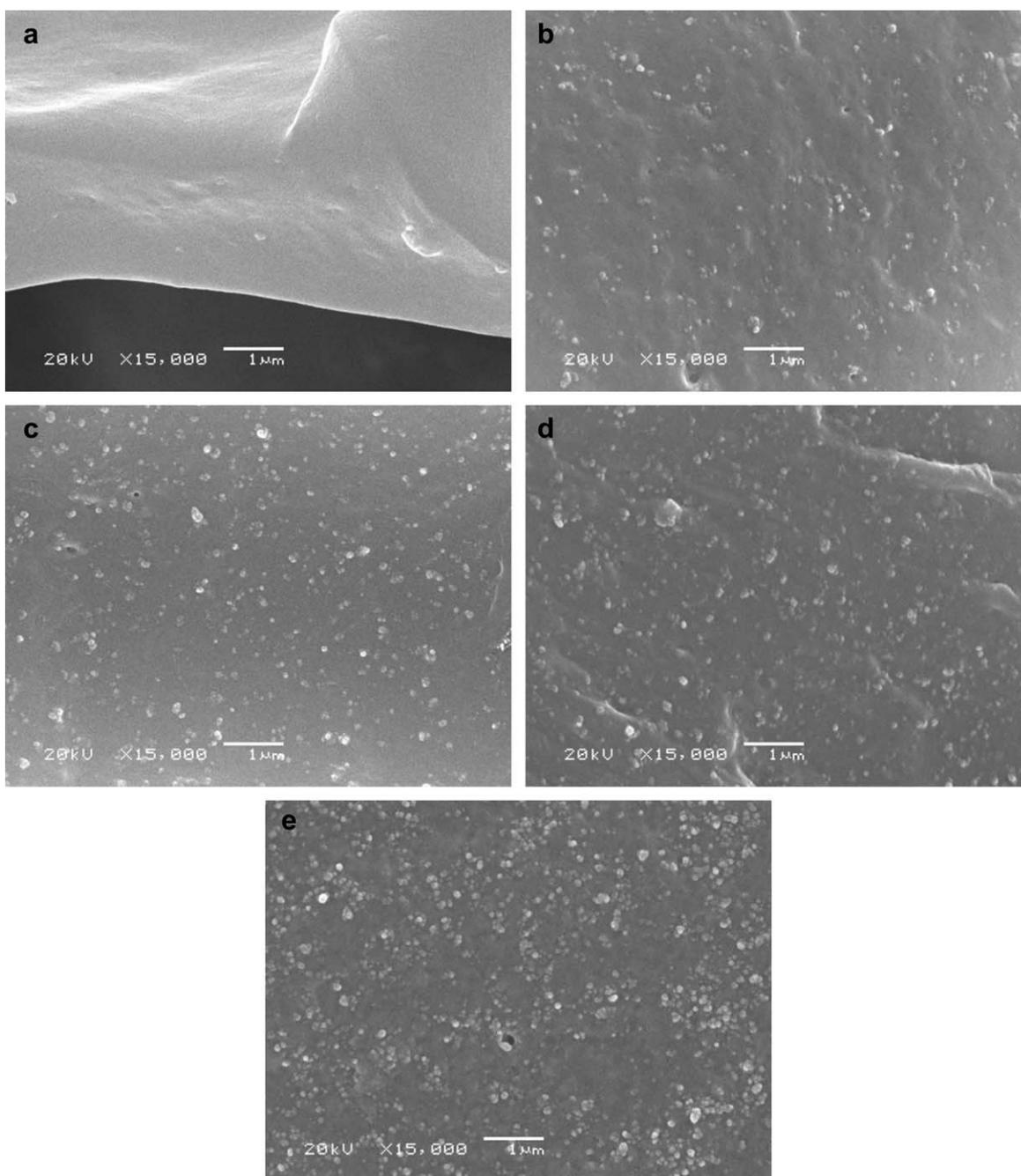


Figure 10. SEM images of the distribution of carbon blacks aggregates in the cell walls with different carbon black content. (a) C0 (0 phr); (b) C5 (5 phr); (c) C10 (10 phr); (d) C15 (15 phr); (e) C20 (20 phr).

we also want to learn the influence of the amount of carbon black on the cross-linking reaction and the foaming behavior. Figure 6 shows the cross-linking curves of the mixed compound of S(BS)S with the different amount of the conductive carbon black. It can be observed that the shape of the cross-linking curves is similar. All the curves show the cross-linking reaction stage when the amount of carbon black is from 0 to 20 phr. At the same time, there is no obvious change for the slope of the curves within the cross-linking reaction stage. It indicates that the change of the carbon black content does not significantly change the rate of the cross-linking reaction. In

Figure 6, however, the torque of the curves is different at a specific time. There has a nonlinear increasing of the torque when the carbon black contents are 10, 15, and 20 phr, whereas a little difference in the case of 0 and 5 phr. The torque measured by MDR characterizes the melt viscosity of the polymer melts. As everyone knows, ultrafine inorganic fillers can enhance the viscosity of the polymer melt apparently. So this is also the main reason of the torque increasing after adding the carbon black. As shown in Figure 6, the effect of increasing viscosity presents suddenly when the carbon black content is above 15 phr.

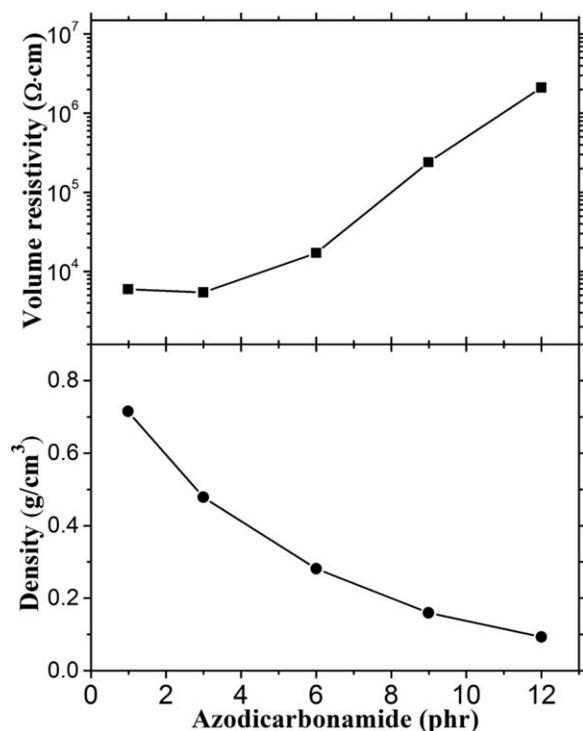


Figure 11. Volume resistivity of S(BS)S foams (carbon black content is fixed at 20 phr) with different azodicarbonamide contents.

The foaming curves with the different amount of carbon black are also measured, and the results are shown in Figure 7. Surprisingly, the adding of the carbon black can prolong the initial decomposition time of azodicarbonamide. The initial decomposition time is extended from 2.4 to 6.0 min with the carbon black content increasing from 0 to 20 phr. An obvious time increasing can be observed when the carbon black content is above 15 phr. Besides, the stage of the formation and growth of cells in foaming curves are also prolonged when the amount of carbon black is above 15 phr. This stage is around 2.0 min when the carbon black contents are 0, 5, and 10 phr. However, the stage is extended to 4.1 and 5.0 min when the contents are 15 and 20 phr, respectively. As mentioned above, a good foaming requires the cross-linking reaction accompanied by the decomposition of foaming agent. Carbon black is the ultrafine inorganic filler which probably absorbed and diluted the accelerator (ZnO/zinc stearate) of azodicarbonamide, resulting in prolonging the initial decomposition of azodicarbonamide and the stage of the formation and growth of cells. Carbon black can also apparently enhance the viscosity of the polymer melt, and high melts viscosity prolongs the time on the stage of cells formation and growth. So, to obtain good foams, a more carbon black content in the compound requires a longer foaming time. Therefore, it can be inferred that the total foaming time is different for C0–C20. In the actual production, the total foaming time for C0–C10 needs about 7 min, and at least 9 min is required for C15. The total foaming time of C20 is more than 10 min.

Conductivity of Foams

Influence of Carbon Black on Volume Resistivity. The volume resistivity curves of conductive foams, as well as the no-foamed mixed compound, with different carbon black content are

shown in Figure 8. It can be observed that the volume resistivity decreases with the amount of conductive carbon black increasing. For S(BS)S foams, the volume resistivity is around $10^{14} \Omega \text{ cm}$ when the carbon black content is from 3 to 12 phr. However, the volume resistivity declines from 7.87×10^{14} to $3.15 \times 10^3 \Omega \text{ cm}$ when the carbon black increases from 12 to 20 phr, showing a sharp decreasing of 11 orders of magnitude. It obviously indicates that an insulator–conductor transition exists with the carbon black content changing, which can be described by the percolation threshold. Generally speaking, the reason of this insulator–conductor transition occurring is that the conductive path is suddenly formed by many of the adjacent carbon black particles.³⁴ As shown in Figure 8, the percolation threshold of S(BS)S foams is around 15–20 phr. For the no-foamed mixed compound, however, it is observed that the volume resistivity exhibits a nonlinear sharp decreasing of 10 orders of magnitude when the carbon black is from 7 to 12 phr. This shows that no-foamed mixed compound has a percolation threshold of 12 phr approximately, which is lower than that of S(BS)S foams. It also can be observed that the volume resistivity of S(BS)S foams is always higher than that of the no-foamed mixed compound. This phenomenon can be probably explained from the existence of the cells in foams.¹⁶ Since the conductive paths formed by carbon black in cell walls is seriously deteriorated due to the existence of the cells.

Cell Structure of Foams and Distribution of Carbon Black.

The cell structure of the foams, as well as the distribution of carbon black, was investigated by SEM. The SEM images of the cell structure are shown in Figure 9. As the carbon black content increases from 0 to 20 phr, all the cells exhibit a closed-cell structure. There exists no orientation of cells, and the morphology of cells is mainly round with a deformation. The average thickness of cell walls does not change obviously except for Figure 9(e), which is possibly ascribed to the high melt intensity of C20. The average diameter of cells in Figure 9 was calculated using software. The average diameter of cells is 51.1, 51.8, 50.7, 42.4, and 37.6 μm when the carbon black is 0, 5, 10, 15, and 20 phr, respectively. The average size of cells has no change with the carbon black content increasing from 0 to 10 phr, whereas it reduces to 42.4 μm , and 37.6 μm in the case of 15 phr, and 20 phr, respectively. In a foaming process, the average size of cells is finally determined by the stage of cells formation and growth. Carbon black can apparently enhance the viscosity of the polymer melt, and a high melts viscosity prolongs the time on the stage of cells formation and suppresses cells growth. In Figure 7, it can be clearly observed that the initial decomposition time of foaming agent, as well as the stage of cells the formation and growth, has not changed much when the carbon black contents are 0, 5, and 10 phr, resulting in the unchanged average size of cells in Figure 9(a–c). However, that of 10 and 15 phr carbon blacks obviously prolonged, and therefore, a smaller average size of cells is observed in Figure 9(d,e). The tensile test for the foams shown in Figure 9 was conducted according to ISO 1798 method, and the tensile properties are listed in Table III. For C0–C15, the tensile strength gradually enhances from 1.60 to 3.70 MPa with the carbon black content increasing from 0 and 20 phr, and the elongation decreases from 270% to 223%.

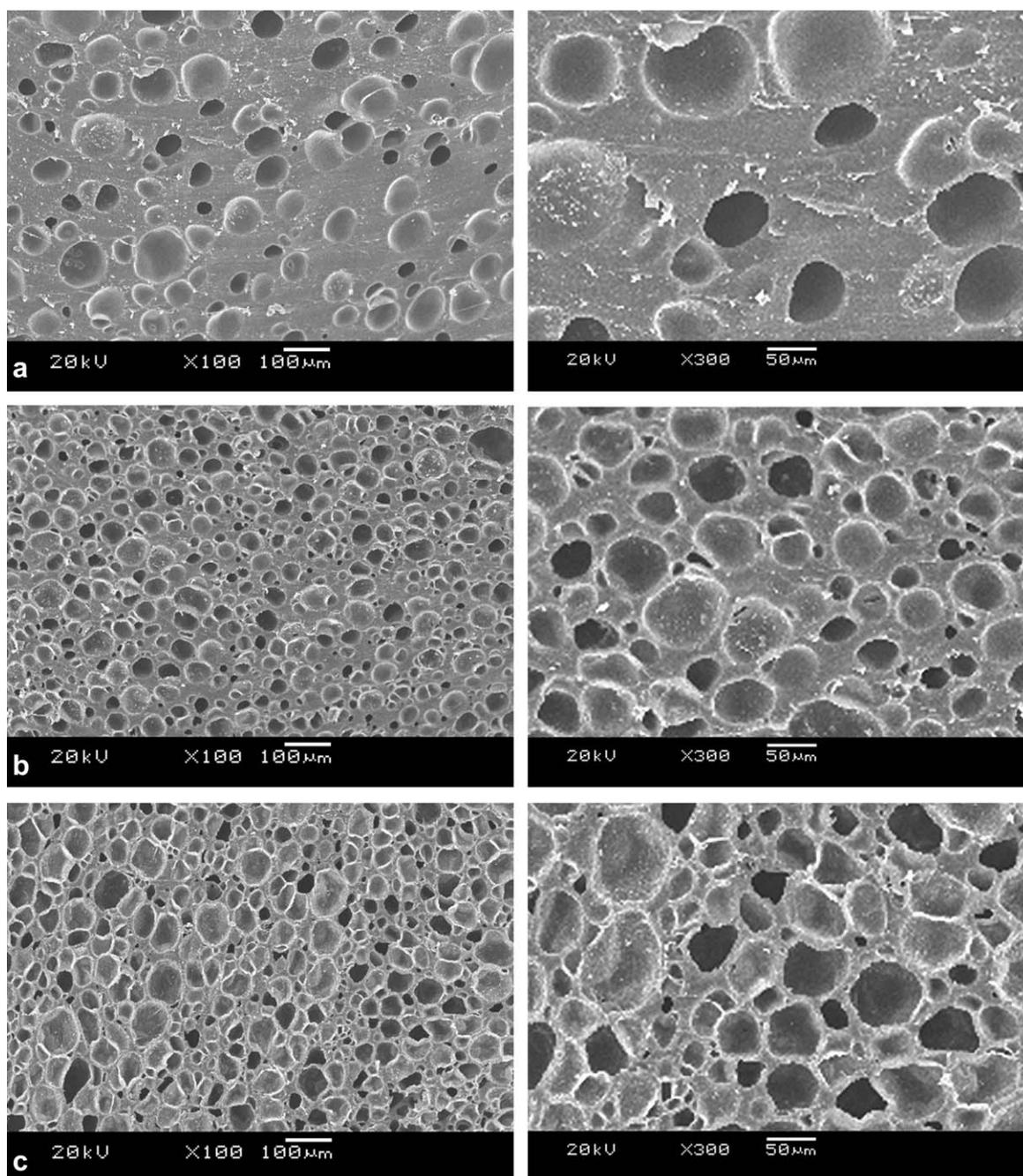


Figure 12. SEM images of cells and cell walls of S(BS)S foams with different azodicarbonamide content. (a) A1 (1 phr); (b) A3 (3 phr); (c) A6 (6 phr); (d) A9 (9 phr); (e) A12 (12 phr). Carbon black content is fixed at 20 phr.

Aggregate is the smallest unit of carbon black, and therefore, the distribution of carbon black aggregates in the polymer matrix determined the electrical properties.³⁵ The distributions of carbon black aggregates in the cell walls are shown in Figure 10. The carbon black content is 0, 5, 10, 15, and 20 phr from Figure 10(a–e). From Figure 10(b–e), the bright particles are the carbon black aggregates dispersed. In Figure 10(b), the average diameter of aggregates in the cell walls was around 70 nm according to statistical calculations, and the distances between the carbon black are too long to form conductive paths throughout the polymer matrix. With the carbon black content

increasing to 10 phr, as shown in Figure 10(c), the carbon black aggregates still exist in isolation, but their distance is closer from each other. Figure 10(d) shows that the carbon black aggregates begin to touch each other, and the prototype of conductive paths generates when the carbon black content is above 15 phr. According to the tunneling theory,³⁶ the conductive paths are formed when the distance between the conductive particles reduces to the level that the electrons can migrate by thermal shocking. In Figure 10(e), the perfect conductive paths in the cell walls are generated when the carbon black content reaches to 20 phr.

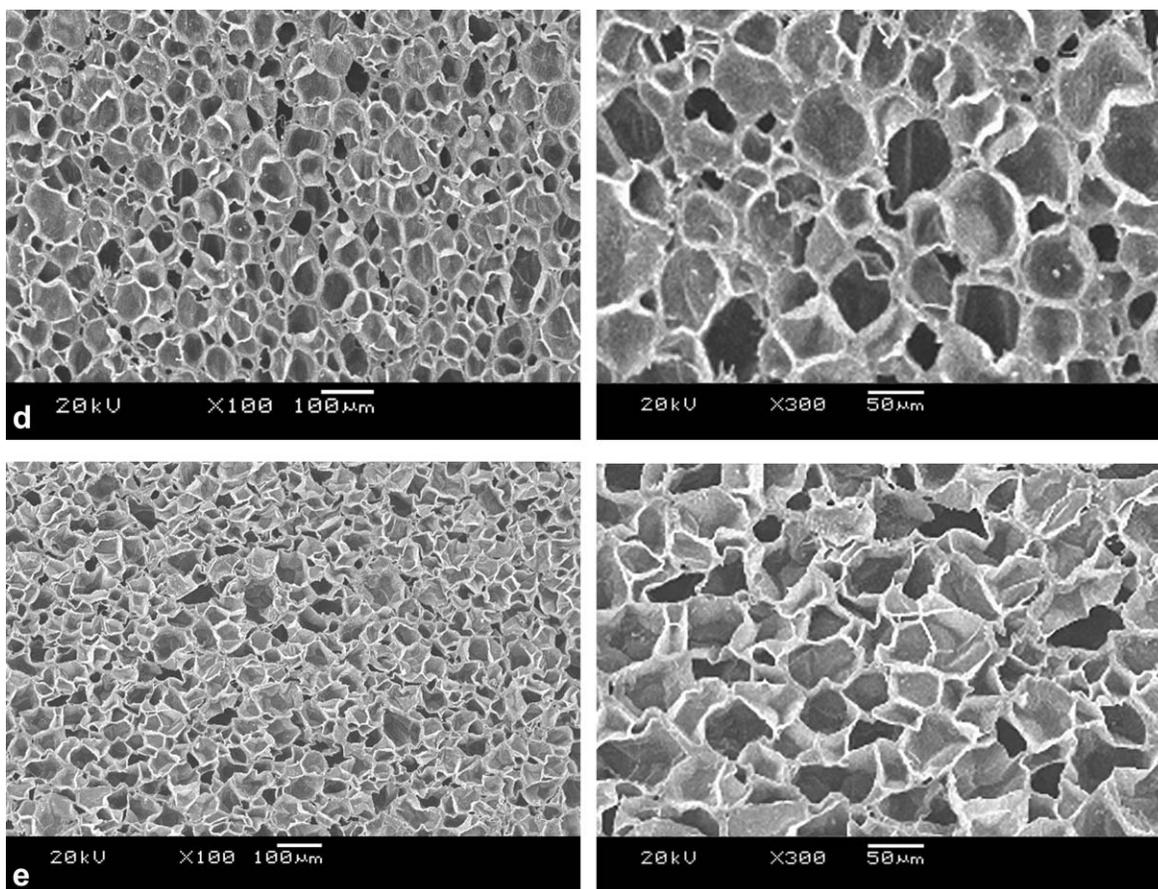


Figure 12. (Continued)

Influence of Azodicarbonamide on Volume Resistivity and Cell Structure. In the chemical foaming, the foaming agent generally has a great impact on the foam density and the cell size. In this study, the foaming agent is azodicarbonamide, and the influence of the foaming agent content on the density and the volume resistivity of S(BS)S foams was also investigated. The results are shown in Figure 11. The formulations of S(BS)S foams follow A1 to A12 in Table II. In these formulations, the carbon black content is fixed at 20 phr.

It can be observed that the density of S(BS)S foams gradually decreases with the azodicarbonamide content increasing from 1 to 12 phr, and the volume resistivity obviously enhances. The foam density and volume resistivity are 0.71 g/cm^3 and $6.02 \times 10^3 \Omega \text{ cm}$ when the azodicarbonamide content is 1 phr, respectively. Increasing the azodicarbonamide to 3 phr, the foam density reduces to 0.48 g/cm^3 , and the volume resistivity remains unchanged. Further increasing the azodicarbonamide to 6 phr, the foam density falls down from 0.48 to 0.28 g/cm^3 . The volume resistivity is $1.7 \times 10^4 \Omega \text{ cm}$, and there is only a slight decreasing in conductivity. The volume resistivity suddenly increases approximately 1 order of magnitude when the azodicarbonamide content is 9 phr. Finally, the foam density falls down to 0.09 g/cm^3 when the azodicarbonamide content increasing to 12 phr, and the volume resistivity increases again by 1 order of magnitude. The experiments of the samples of 15 phr carbon blacks with various contents of azodicarbonamide

were also performed. However, their volume resistivity is much higher than that of the samples containing 20 phr carbon blacks. The formulations and the volume resistivity of the samples with 15 phr carbon blacks are listed in Supporting Information Table S1 and Figure S1.

Figure 12 shows the SEM images of the cell structure with different azodicarbonamide content. In Figure 12(a), it can be observed that a very small number of cells exists due to the insufficient amount of the foaming agent (1 phr), and these cells dispersed in the polymer matrix as the island structure. In Figure 12(b), the azodicarbonamide content increasing to 3 phr, the cells whose number obviously increases (per unit volume) still dispersed as the island structure. As shown in Figure 12(a,b), we can clearly observe two phases, including the cells' phase and the polymer phase. With the azodicarbonamide content increasing to above 6 phr, the number of the cells per unit volume sharply increases. However, we can no longer distinguish the polymer phase in Figure 12(c–e), because the polymer phase converts to the cell walls. After statistical calculations, it also learned that the average diameter of cells is reduced from 59.5 to $30.4 \mu\text{m}$ with the azodicarbonamide content increasing from 1 to 12 phr. The number of cells per unit volume enhances from 2.93×10^6 to $6.20 \times 10^7 \text{ cells/cm}^3$. In addition, the average thickness of the cell walls decreases from 45.3 to $1.4 \mu\text{m}$. There are also some changes for the shape of the cells. The shape of cells is almost round when the azodicarbonamide

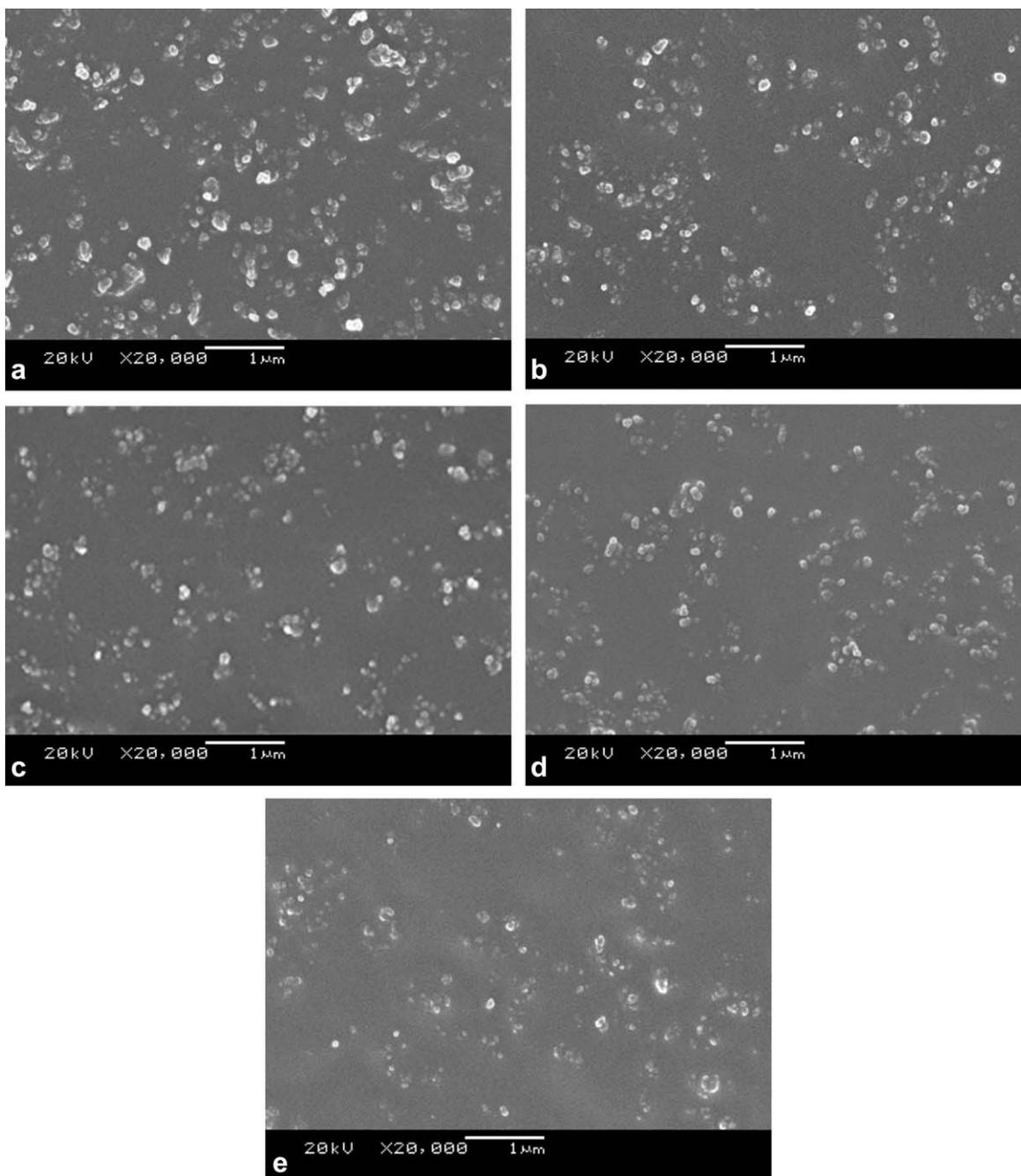


Figure 13. SEM images of the distribution of carbon blacks aggregates in the cell walls with different carbon black content. (a) A1 (1 phr); (b) A3 (3 phr); (c) A6 (6 phr); (d) A9 (9 phr); (e) A12 (12 phr). Carbon black content is fixed at 20 phr.

contents are 1 phr [Figure 12(a)], 3 phr [Figure 12(b)], and 6 phr [Figure 12(c)]. With the azodicarbonamide content increasing to 9 phr [Figure 12(d)] and 12 phr [Figure 12(e)], the shape of cells changes from the round to the polygonal.

For S(BS)S foams, the carbon black can only be dispersed in the polymer matrix or the cell walls. The distributions of carbon black aggregates in the cell walls are shown in Figure 13 (corresponding to Figure 12). So, the sharp increasing of cells per unit volume and thinning of the cell walls certainly affect the distribution and the concentration of the carbon black in the polymer.

Therefore, the conductive performance is greatly affected, resulting in the volume resistivity increasing from 6.02×10^3 to $2.11 \times 10^6 \Omega \text{ cm}$ in Figure 11. The main reason can be probably explained that the cell walls gradually transform from the three-dimensional (3D) to the two-dimensional (2D) with the sharp increasing the number of cells per unit volume,¹³ resulting that the carbon black cannot form an effective conductive path. From the SEM images with magnitude of 300 in Figure 12, it can be clearly observed that the cell walls gradually transform from a “body” to a “sheet,” and then to a “film,” and this proves a

process from 3D to 2D. The tensile test for the foams shown in Figure 12 was also conducted (Table III). For A1–A12, the tensile strength gradually decreases from 5.41 to 0.06 MPa when the azodicarbonamide content increases from 1 and 12 phr. If the cell walls present as a “body,” the tensile strength will be higher. If the cell walls present as a “film,” the tensile strength will be lower. Thus, tensile properties are the indirect evidence to prove a process of the cell walls from 3D to 2D. A similar phenomenon was also reported by Li and coworkers¹³ that the density of CNTs/PU foams decreased with increasing in expansion ratio, and the cell walls became thinner. The CNTs content in the walls was reduced, which decreased the conductive paths and caused the conductivity of the foam worse. As discussed above, the influence of the azodicarbonamide content on conductivity is performed by the combination of the number of cells per unit volume and the thickness of the cell walls.

CONCLUSIONS

In this study, a new styrene-based thermoplastic elastomer called S(BS)S was introduced. This styrene-based tri-block copolymer was specially designed for chemical foaming with uniform fine cells, which overcame the shortcomings of traditional SBS.

The preparation of conductive foams based on S(BS)S filled by the carbon black was studied in detail. It was concluded that a complex accelerator of ZnO/zinc stearate (1.2 phr/0.45 phr) was the best for foaming agent (azodicarbonamide). The decomposition temperature of azodicarbonamide is reduced to from 217.6 to 173.4°C. The cross-linking reaction and foaming behaviors of the mixed compound of S(BS)S were investigated. The optimal foaming temperature was determined at 180°C according to the investigation of cross-linking and foaming curves at different temperatures. We found that the carbon black content has a great impact on foaming behaviors, that the initial decomposition time of azodicarbonamide and the stage of the formation and growth of cells were both prolonged, resulting in a more foaming time for the formulation with more carbon black.

The influence of the amount of the conductive carbon black, the distribution of carbon black in cell walls, and the cell structure on the conductivity of foams was also studied in detail. The results shown that the conductivity of foams was mainly affected by the distribution of carbon black in the cell walls when the foaming agent content was fixed. The formation of the network of the carbon black aggregates had a contribution to perfect conductive paths. It also found that the conductivity of foams declined obviously with the foaming agent content increasing when the carbon black content was constant. This was because the more azodicarbonamide content led to a sharp increasing of the number of cells per unit volume and a rapid thinning of the cell walls, resulting in an effective conductive path of the carbon black no forming.

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REFERENCES

1. Lee, L. J.; Zeng, C.; Cao, X.; Han, X.; Shen, J.; Xu, G. *Compos. Sci. Technol.* **2005**, *65*, 2344.
2. Zeng, C.; Hossieny, N.; Zhang, C.; Wang, B. *Polymer* **2010**, *51*, 655.
3. Rodríguez-Pérez, M.; Campo-Arnáiz, R.; Aroca, R.; De Saja, J. *Polymer* **2005**, *46*, 12093.
4. Xin, Z. X.; Zhang, Z. X.; Pal, K.; Byeon, J. U.; Lee, S. H.; Kim, J. K. *Mater. Des.* **2010**, *31*, 589.
5. Thirumal, M.; Khastgir, D.; Singha, N. K.; Manjunath, B.; Naik, Y. *J. Appl. Polym. Sci.* **2008**, *108*, 1810.
6. Park, K.-Y.; Lee, S.-E.; Kim, C.-G.; Han, J.-H. *Compos. Sci. Technol.* **2006**, *66*, 576.
7. Bush, S.; Ademosu, O. *Colloids Surf. Physicochem. Eng. Aspects* **2005**, *263*, 370.
8. Zhang, W.; Dehghani-Sanij, A. A.; Blackburn, R. S. *J. Mater. Sci.* **2007**, *42*, 3408.
9. Cheah, K.; Simon, G. P.; Forsyth, M. *Polym. Int.* **2001**, *50*, 27.
10. Gubbels, F.; Blacher, S.; Vanlathem, E.; Jérôme, R.; Deltour, R.; Brouers, F.; Teyssie, P. *Macromolecules* **1995**, *28*, 1559.
11. Peng, M.; Zhou, M.; Jin, Z.; Kong, W.; Xu, Z.; Vaddillo, D. J. *Mater. Sci.* **2010**, *45*, 1065.
12. Xiang, Z. D.; Chen, T.; Li, Z. M.; Bian, X. C. *Macromol. Mater. Eng.* **2009**, *294*, 91.
13. Xu, X. B.; Li, Z. M.; Shi, L.; Bian, X. C.; Xiang, Z. D. *Small* **2007**, *3*, 408.
14. Wang, T.; Yin, J.; Zheng, Z.; Mao, Z. *J. Appl. Polym. Sci.* **2012**, *125*, E278.
15. Yoshioka, M.; Nishio, Y.; Saito, D.; Ohashi, H.; Hashimoto, M.; Shiraishi, N. *J. Appl. Polym. Sci.* **2013**, *130*, 622.
16. Yang, Y.; Gupta, M. C.; Dudley, K. L.; Lawrence, R. W. *Adv. Mater.* **2005**, *17*, 1999.
17. Yang, Y.; Gupta, M. C.; Dudley, K. L.; Lawrence, R. W. *Nano Lett.* **2005**, *5*, 2131.
18. Ding, J.; Shangguan, J.; Ma, W.; Zhong, Q. *J. Appl. Polym. Sci.* **2013**, *128*, 3639.
19. Sharudin, R. W. B.; Ohshima, M. *J. Appl. Polym. Sci.* **2013**, *128*, 2245.
20. Park, K. W.; Kim, G. H. *J. Appl. Polym. Sci.* **2009**, *112*, 1845.
21. Wen, G.; Zhang, Y.; Zhang, Y.; Sun, K.; Fan, Y. *Polym. Test.* **2002**, *21*, 295.
22. Leblanc, J. L. *J. Appl. Polym. Sci.* **1977**, *21*, 2419.
23. Ma, R.; Zhang, Z.; Zhang, L. *J. Appl. Polym. Sci.* **2006**, *102*, 729.
24. Naficy, S.; Garmabi, H. *Compos. Sci. Technol.* **2007**, *67*, 3233.

25. Al-Saleh, M. H.; Sundararaj, U. *Eur. Polym. J.* **2008**, *44*, 1931.
26. Probst, N.; Grivei, E. *Carbon* **2002**, *40*, 201.
27. Reffae, A. S.; El Nashar, D.; Abd-El-Messieh, S.; Abd-El Nour, K. *Mater. Des.* **2009**, *30*, 3760.
28. Gupta, S.; Ou, R.; Gerhardt, R. A. *J. Electron. Mater.* **2006**, *35*, 224.
29. Li, H.; Xiao, H.; Ou, J. *Compos. Sci. Technol.* **2008**, *68*, 2114.
30. Aljaafari, A. *Mater. Des.* **2010**, *31*, 3207.
31. Tai, H.-J.; Wang, J. *J. Cell. Plastics* **1997**, *33*, 304.
32. Zhang, B. S.; Lv, X. F.; Zhang, Z. X.; Liu, Y.; Kim, J. K.; Xin, Z. X. *Mater. Des.* **2010**, *31*, 3106.
33. Mao, Y.; Qi, R. *J. Appl. Polym. Sci.* **2008**, *109*, 3249.
34. Xiao, H.; Li, H.; Ou, J. *Sens. Actuators A: Phys.* **2010**, *160*, 87.
35. Balberg, I. *Carbon* **2002**, *40*, 139.
36. York, R. L.; Slowinski, K. J. *Electroanal. Chem.* **2003**, *550*, 327.