Influence of Molecular Structure of Star S-SBR on Its Properties

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ABSTRACT: Star S-SBR can be produced in one step by a kind of new anion polymerization technology in which modified naphthalene lithium acted as the initiator and $SnCl_4$ acted as the coupling agent. The influence of the molecular structure of star S-SBR on its mechanical and dynamic properties was studied. The results showed that Star S-SBR, with styrene (St) content of 20–25% and vinyl (Bv) content of 45%, and molecular weight for one arm (MW/arm) of 8 ten thousand, has good mechanical properties, low rolling resistance and high wet grip. The end of the S-SBR molecular chain was coupled by a coupling agent, which resulted in low internal friction loss. The bound rubber content of star S-SBR-carbon black compound was larger than that of linear S-SBR compound. Experiments showed that the Sn—C key in star S-SBR broke easily under shear action and formed a free group, and the free group bonded immediately with the active group on the surface of a carbon black particle. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2311–2315, 2003

INTRODUCTION

Sn-coupled S-SBR is a kind of rubber used for high performance tire tread[1] because it exhibits excellent low dynamic heating, high wet grip performance and favorable mechanical properties. Because Sn-coupled S-SBR is a rubber with an overall balance of low rolling resistance and wet grip performance, it has been rapidly developed in recent years.[2]

The favorable properties of Sn-coupled S-SBR stem from its chemical composition, monomer unit order and distribution, and the unique structure of an end-molecular chain coupled with $SnCl_4$. The wet grip performance can be attributed to the chemical structure units, which contribute slow relaxation to the macromolecule. The low rolling resistance of rubber is related to its chemical composition monomer unit, which contributes small space resistance and low internal friction loss among molecular chains.

Many studies have been carried out in order to examine rolling resistance and wet grip.[3,4] The results of these studies showed that large values of the loss factor (tgδ) in the temperature range from -25–0°C can be correlated to high wet grip, and small values of tgδ in the temperature range from 50–60°C correlatives to low rolling resistance. Therefore, balance of these two characteristics may be achieved by designing the ideal macromolecular structure.

We adopted a new method (patent applied for)[5,6] which contains a new anion catalysis polymerization system and synthetic technology, and allows fully coupled S-SBR (star S-SBR) to be produced in one step. This new method is different from the traditional method of producing coupled S-SBR by anion polymerization. Our method has many advantages, such as low cost, high efficiency, controlled macromolecular structure and regulated coupling degree of S-SBR.

In order to find the optimal molecular structure of star S-SBR, the relationship between its chemical and mechanical properties was studied. Chemical properties examined include: chemical composition, coupled structure, and one arm molecular weight. Mechanical properties include: dynamic heating , dynamic properties, dynamic compression permanent set, and content of bound rubber.

Based on the characteristics of quick relaxation of the molecular chain and low friction loss among the molecular chains, the microstructure and molecular weight for one arm of star S-SBR were mapped.

EXPERIMENTAL

Materials

SBR-1500 was provided by the organic synthetic factory of Ji Lin Chemical Company in China. Cis-BR was provided by Beijing Yanshan Synthetic Rubber Factory in China.

Star_S-SBR was produced in our laboratory. The samples were produced by adopting anion polymer-

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ization technology in which modified naphthalene lithium acts as the initiator and $SnCl_4$ acts as the coupling agent.

Other used materials are common in the rubber processing industry.

Methods

The dynamic mechanical properties of Star S-SBR were measured by MAK-04 viscoelastometer. The temperatures conditions were: -25, 0, 50°C. The frequency was 11Hz, and the deformation amplitude was 0.5%.

The temperature rise (ΔT) in compression fatigue was determined by a YS-25 compression fatigue machine produced in China. The room temperature was 50°C, the load was 1.01 MPa, and the stroke was 6 mm.

The content of bound rubber was determined by immersion test, in which about 0.5 g (W_1) of S-SBR carbon black compound was placed into a small cubic container made of copper net and then immersed in a toluene / tetrahydrofuran blend solution for three days. It was then filtered, and the remainder was dried and weighed (W_2). The percentage of rubber contained in the compound ($X\%$) was calculated by the following equation:

$$\text{wt }\% = 1 - [(W_1 - W_2)/(W_1 \times X\%)]$$

Other properties were measured according to the state standards in China.

Sample and composition

Analysis of the samples revealed the following vinyl (Bv) and styrene (St) compositions. Samples 1–5 (S_1–S_5) had a Bv content of 45% and an St content of 15.6, 17.8, 20.7, 22.5, 25.6% respectively. Samples 6–10 (S_6–S_{10}) had an St content of 22.4% and Bv contents of 33.1, 40.3, 44.1, 50.4, 56.2% respectively. Samples 11–14 (S_{11}–S_{14}) had an St content of 20.7%, a Bv content of 45%, and molecular weight for one arm (MW/arm) of 6, 7, 8, and 9 ten thousand.

The composition of the samples was: Rubber 100; ZnO 3.0; stearic acid 1.0; DM 1.2; D 0.6; 4010NA 1.0; paraffin wax 1.0; HAF 50; liquid coumarone-indene resin 5.0 Phr.

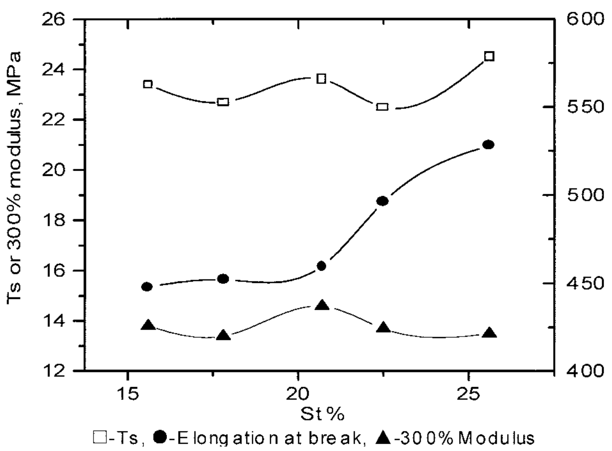

Figure 1 The effect of St content on the mechanical properties of S-SBR.

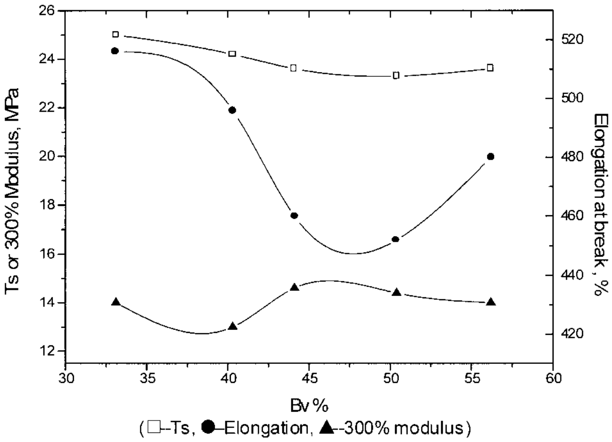

Figure 2 The effect of Bv content on the mechanical properties of S-SBR.

RESULTS AND DISCUSSION

Mechanical properties

The influence of St and Bv contents and the MW/arm on the mechanical properties of Star S-SBR is shown in Figure 1, 2, and 3, respectively.

Figure1 shows that with an increasing content of styrene, the tensile strength (Ts) and elongation at break of S-SBR increase, but the Ts increases only slightly, and the 300% modulus does not change remarkably. The results show that star S-SBR in which the styrene content falls in the range of 20–25% exhibits higher mechanical properties than star S-SBR in which less styrene is present.

As shown in Figure 2, an increasing content of Bv in Star S-SBR causes the Ts and the elongation at break to decrease and the 300% modulus to increase slightly. The sample with Bv content of about 45% provides the optimal mechanical properties of those tested.

Each macromolecular chain of star S-SBR generally contains four to six arms and forms a star model structure. Figure 3 shows that increasing the MW/arm causes the Ts and the elongation at break to first increase and later decrease. The bigger MW/arm value is, the more complicated processing becomes. A MW/Arm value of 8 ten thousand is ideal for good mechanical and processing properties.

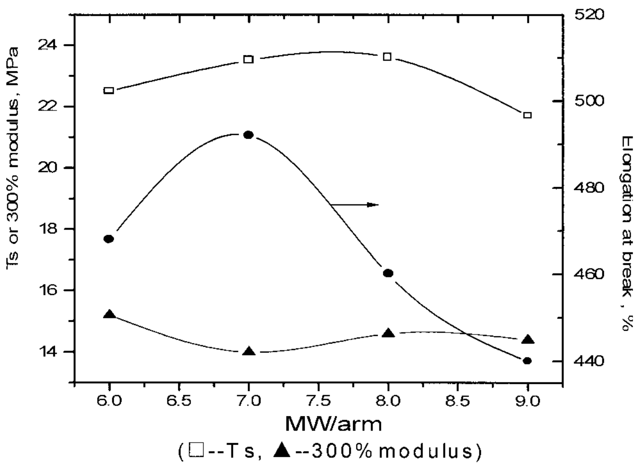

Figure 3 The effect of MW/arm on the mechanical properties of S-SBR.

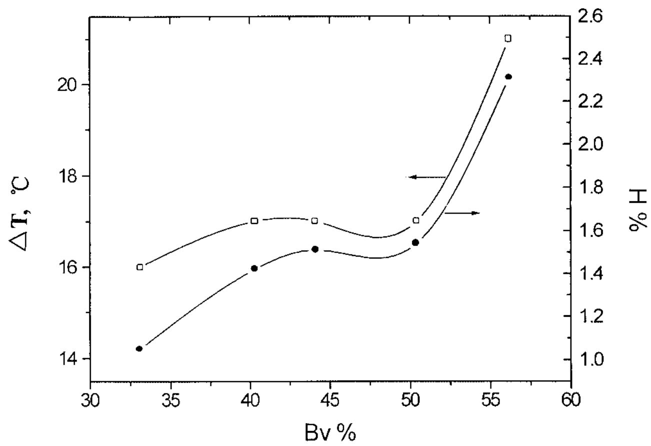

Figure 5 The effect of Bv % on ΔT and H% (St % = 20.7%).

Dynamic properties

Dynamic heating (δT) and compress permanent set (H %)

Figures 4 and 5 show that with increasing St % and Bv %, ΔT and H % first increase slightly in the range of St % from 15.6–22.5% and Bv % from 33.1–45%. With higher St and Bv contents, ΔT and H % increase sharply for St content >22.5% and Bv content >45%. This is because increasing the content of St and Bv makes the space resistance of molecular chain movement increase, and then internal friction resistance among molecular chains becomes bigger.

Figure 6 presents ΔT and H % of star S-SBR as a function of MW/arm. Values of ΔT and H % decrease with increasing values of MW/arm. From this, it can be concluded that large MW/arm values make star S-SBR lose internal friction resistance produced by molecular end groups and relax quickly. However, large MW/arm values would make star S-SBR processing difficult, so a suitable value to prevent difficulty in processing is 8 ten thousand.

Rolling resistance and wet grip

With increasing St %, Bv % and MW/arm, the tgδ of the samples at 50°C does not change remarkably. Only when St % and Bv % are 25.6% and 56.2% respectively does the tgδ of the sample increase slightly. This shows that the star S-SBR behaves with low rolling resistance in our study range.

With increasing St % and Bv %, the tgδ of S-SBR at 0 and -25°C increases, especially as St % and Bv % reach values larger than 21% and 45%. In this range, tgδ (0, −25°C) increases remarkably (Fig.7 and 8). This indicates that high levels of St and Bv could improve wet and ice grip of star S-SBR.

With increasing MW/arm, tgδ (50, 0, −25°C) changes slightly (Fig. 9). This shows clearly that the wet and ice grip of star S-SBR are not influenced by MW/arm in our study range.

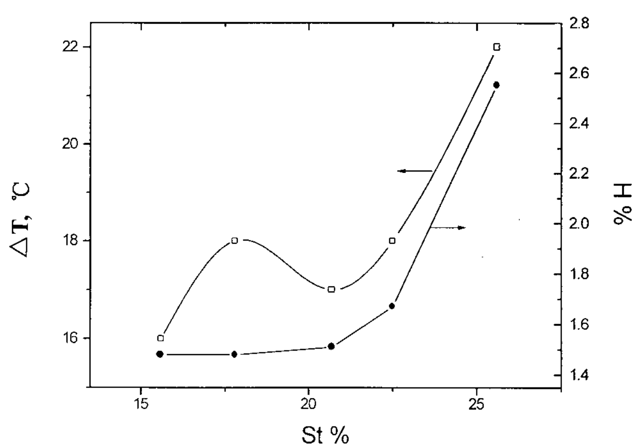

Figure 4 The effect of St % on ΔT and H% (Bv % = 45%).

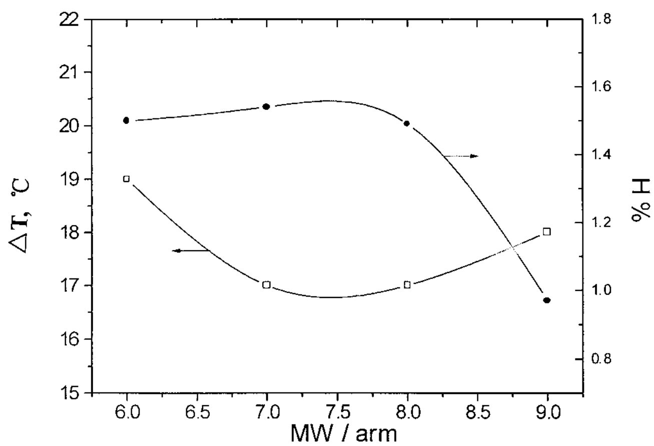

Figure 6 The effect of MW/arm on ΔT and H% (St % = 20.7%; Bv % = 45%).

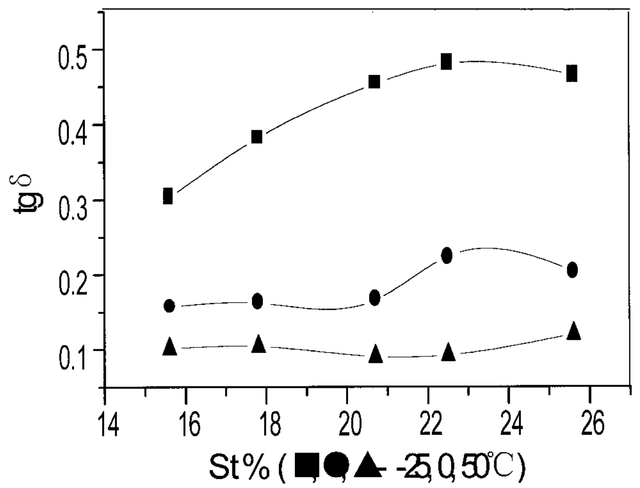

Figure 7 The relation of St % to tgδ (Bv% = 45%).

As mentioned above, for the purpose of balancing mechanical properties, reducing rolling resistance while enhancing wet and ice grip performance, the optimal polymer would have an St content of 21–25%, a Bv content of about 45% and a MW/arm of 8 ten thousand.

Properties of four kinds of rubber for tire tread

The properties of four kinds of rubber for tire tread are list in Table I. In a comparison of star S-SBR to linear S-SBR and E-SBR the mechanical properties show hardly any difference, but the ΔT and tgδ at 50°C for star S-SBR are lowest, and the tgδ at 0 and −25°C is highest. Star S-SBR (sample S_3) has low rolling resistance and high wet and ice grip performance.

The bound rubber content of star S-SBR is larger than that of linear S-SBR. This shows that the Sn—C bond contained in the star S-SBR molecular chain

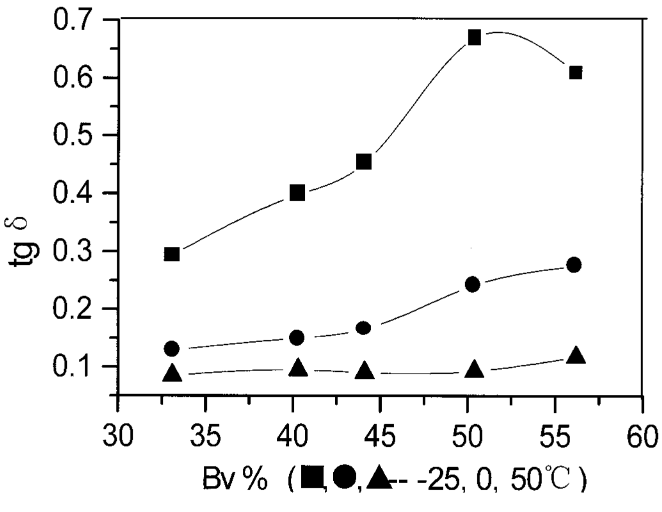

Figure 8 The relation of Bv % to tgδ (St % = 20.7%).

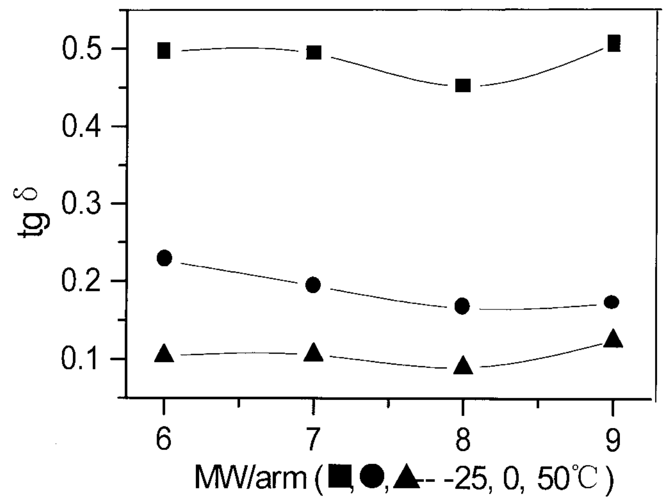

Figure 9 The relation of MW/arm to tgδ (St % = 20.7%; Bv % - 45%).

breaks easily under shear action to form a free group, which immediately bonds to an active group on the surface of carbon black.[8]

The Ts, 300% modulus, elongation at break, tear strength and tgδ (0, −25°C) of star S-SBR are higher than those of cis-BR. At 50°C, the tgδ values of both kinds of rubber are similar. That is to say, star S-SBR has the same low rolling resistance as cis-BR, and the same wet and ice grip performance as E-SBR. Thus star S-SBR is a kind of ideal tread tire, combining the best mechanical properties of the other two kinds of rubber.

TABLE I
Properties of Four Kinds of Tread Rubber

Sample properties	S-SBR (linear)	Star-S-SBR (coupled)	E-SBR (SBR-1500)	Cis-BR (BR900)
St%	22.4	20.7	23.5	—
Bv%	42.4	44.1	—	—
Hardness	67	66	65	60
300% Modulus (Mpa)	12.5	14.6	10.6	9.7
Tensile strength (Mpa)	23.3	23.6	25.4	17.2
Elongation (%)	528	460	548	400
Tear strength (kN/m)	49	47	47	45
Bound rubber content (%)	8	12.5	—	—
Built-up heat (°C)	26	17	25	20
Loss factor, tg δ 11 Hz				
−25°C	0.363	0.453	0.295	0.109
0°C	0.154	0.166	0.167	0.107
50°C	0.139	0.090	0.149	0.097

CONCLUSION

Star S-SBR, with St and Bv contents of 21–25% and 45% respectively and MW/arm of 8 ten thousand, shows favorable mechanical properties, low rolling resistance and high wet and ice grip.

The bound rubber content of star S-SBR is larger than that of linear S-SBR because the Sn—C bond contained in coupled S-SBR breaks easily under shear action, and the free group produced bonds immediately to an active group on the surface of the carbon black particle.

Compared to cis-BR and E-SBR, star S-SBR has the same low rolling resistance as cis-BR and the same wet and ice grip performance as E-SBR. Therefore, star S-SBR is an ideal rubber for high performance tire tread.

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