Chemical modified technology of BR, S-SBR and TPE in Japan

Iwakazu Hattori[1], Hiroshi Takino[1] and Yoichiro Hibiya[1]
ETIC Inc.[1], Nanakubo Bldg. 3F, 1-11-11 Toranomon,
Minato-ku, Tokyo, 105-0001, Japan
E-mail: i_hattori@elastec-intel.jp

1. Introduction

The Kyoto Protocol was adapted at the third conference of the United Nations Framework Convention on Climate Change in December 1997. It was known that one of the causes for the abnormal weather is the increase of greenhouse gas emissions such as carbon dioxide and methane. The protocol requires industrialized nations to reduce those emissions by certain percent from 1990 levels during 2008 to 2012. For example, Japan is required to reduce carbon dioxide by 6 %, and EU is required to reduce it by 8%.

Although the effect of global environmental improvement based on CO_2 reduction of the Kyoto Protocol is doubted, at present, a much larger CO_2 reduction plan than the Kyoto Protocol is being seriously discussed not only in the United Nations Framework Convention on Climate Change, but also the United Nations Security Council and the Summit, as well as international conference such as the Asia-Pacific Economic Cooperation.

Matters related to this, such as reduction in rolling resistance of tires, use of light-weight materials, improvement of recyclability, bio fuels, and technology to correspond to bio materials are some of the important themes for the rubber industry. In 2010, in order to make it easier for the consumers to understand, labeling regulation which is the tire manufacturers' voluntary control for low rolling resistance (AAA, AA, A, B, C) and Wet Grip (a, b, c, d) of tires came into effect. The values of the tires sold in Japan based on the tire labeling regulation[1] are as shown in Table 1. Although the details of the technology are not made public, the basic technology for obtaining low fuel consumption tires such as AAA and AA is the use of terminal modified S-SBR, high dispersion method of carbon black as well as mastering of silica compounds.

In this report, authors would like to introduce this basic technology of chemical modified S-SBR, modified SEBS which is a hydrogenated polymer of SBS produced by similar technology to chemical modified S-SBR, and high *cis* BR.

Table 1: Type of Tire based on Tire Labeling Regulation in Japan[1]

Tire Maker	Type of Tire	Tire Size	Rolling Resistance	Wet Skid Resistance	Filler, Polymer
Goodyear	EfficientGrip	185/65 R15 88H～205/60 R16 92H	A	b	Silica, Special Rubber
Dunlop	ENASAVE 97	185/65 R15 88H～195/55 R16	AA	b	Silica, Epoxy-NR
	ENASAVE RV503	175/65 R14 82H～225/45 R19	A	c	?, Modified SBR
	ENASAVE EC202	145/65 R13 69S～215/55 R17 94V	A	c	?, Multi modified SBR
Bridgestone	**ECOPIA EP100S**	185/65 R15 88H、195/65 R15 91H **2 Sizes**	**AAA**	c	C.B., **Modified SBR** (Nano Pro-Tec)
	ECOPIA EP100	155/65 R13 73H～225/45 R18 91W	AA～A	c	C.B., **Modified SBR**
	ECOPIA EX10	155/65 R13 73S～245/45 R19 98W	AA～A	b	**Silica**, **Modified SBR**
Yokohama	BluEarth AE-01	145/80 R13 75S～215/60 R16 95H	A	c	**Silica**, High Mw SBR
	DNA Earth-1	155/65 R13 73S～245/35 R20 95W	A	b～c	**Silica**, ibid SBR+NR
Michelin	Primacy LC	195/60 R15 88V～245/45 R19 98Y	A	c	**Full Silica, ?**
	ENERGY SAVER	185/55 R14 80H～215/60 R16 99H XL	A	c	**Full Silica, ?**
Toyo Tire	**SUPER ECO WALKER**	195/65 R15 91H **One Size**	**AAA**	c	**Silica, Super Active SBR**
	ECO WALKER	155/65 R13 73S～215/55 R17 94V	A	c～d	CB+**Silica**, **ibid SBR**

2. Trend of Chemical Modified S-SBR

In this part, author would like to introduce industrialization or chemical modified S-SBR technology which may lead to breakthrough for industrialization. Trends of these S-SBRs are shown in Figure 1.

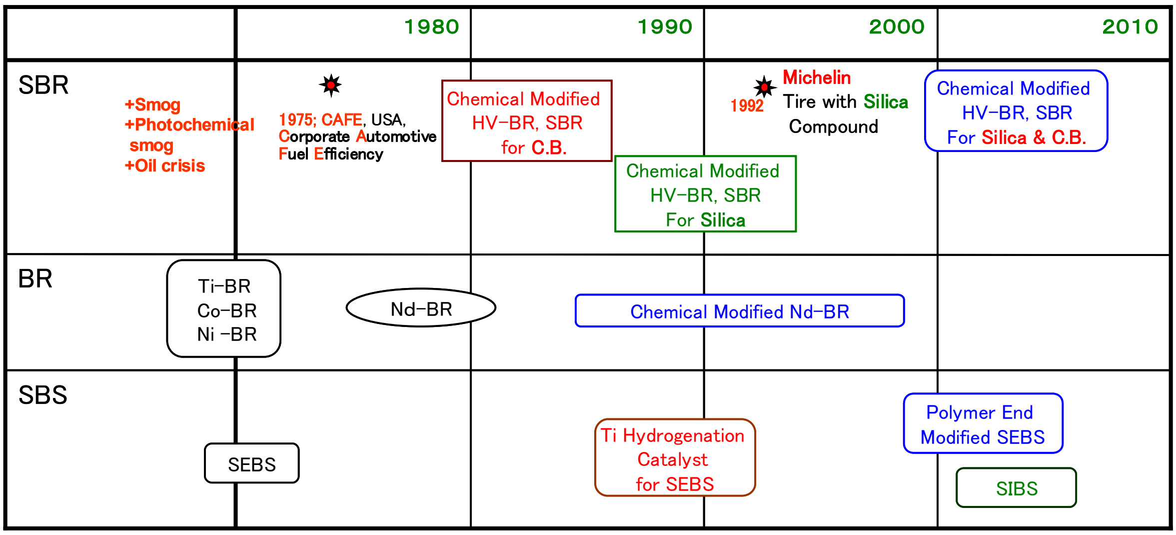

Figure 1: Technical Trend of Polydiene

2.1 Chemical Modified S-SBR

Tires which are the largest application of rubber, are also related to the prevention of global warming up, and because of the severe fuel consumption regulations for vehicles in Japan, Europe, and the United States, studies were advanced on reinforcing and dispersing carbon black particles with even smaller particle size so that low rolling resistance and wet grip on wet road surface will coexist, has been the trend since the oil shock in the latter half of the 1970s. Against such requirements, in the 1980s, among various types of synthetic rubber, solution SBR (S-SBR) which allows modification of the chain at both ends became the center of research[2]. Starting from around 1990, S-SBR remained as the basic rubber, but the center of research moved to silica compounds in spite of problems such as cost and processability, because they realized low rolling resistance and good wet grip in comparison with carbon black. Both silica and carbon black required stronger reinforcement, and in early part of the 2000s, an excellent S-SBR was developed. Morikawa[3] and others studied several types of S-SBR that introduced functional group having high compatibility with silica at initial point of polymerization, chain end, and both ends of SBR. In case primary amino group and alkoxysilyl group are introduced to the terminating end, it was reported that the rubber bound to silica and carbon black increased, and tan δ near room temperature which corresponds to the rolling resistance of the tires, and wear resistance were improved.

Hayashi[4] and others analyzed the polymerization behavior of 1, 1-diphenyl ethylene derivatives, and by merely changing the amount of monomer addition and the number of times, proposed a method for introducing functional groups to not only one end or both ends, but also to an arbitrary position in the S-SBR polymer chain.

2-2. Chemical Modified High *cis* -1,4 BR

Unlike S-SBR, it was considered for a long time that transition metal catalysts used for the production of high *cis* BR had no living polymerization property, and chain end modification cannot be done. However, when the polymerization behavior of Nd-BR having pseudo living polymerization property was analyzed, it was made clear that chain end modification[5] was possible in the case of high *cis* BR as well, and industrialization of BR which is believed to be an application of this technology is reported by Tadaki[6]. This BR has improved processability and abrasion resistance.

2.3 Chemical Modified SEBS

SEBS excels in heat resistance, weatherability, and recycling properties. It can modify polyolefins, and it is already used in automotive parts.

However, since SEBS has no modifying effect on polar polymers such as polyamide and polyester, it was made into a functional group by adding maleic anhydride to the side chains of SEBS by radical reaction. In this case, compatibility with polyamide will be improved, but since the number of functional groups and molecular crosslinking caused by side reactions cannot be controlled, there was the problem of the flow becoming extremely bad after the modification. Thus, after producing SBS, functional groups that will become –COOH, -NHR, and –OH were introduced to the end of the chains, then hydrogenated. As a result, modified SEBS was developed. Modification of polylactic acid and PET, and nanocompositing of clay have been reported.[7] Although details are unknown, it is said that modified SEBS[8] with excellent performance as compatibleness agent for PET / PP has been developed.

References

1. Car Watch H/P: http://car.watch.impress.co.jp/docs/special/20100709_379272.html
2. Gomu Gizyutsu Forum Ed.: “Gomu Kougyou niokeru Gizyutsu Yosoku”, Posty Corp., Tokyo (1990)
3. A. Morikawa, T. Sone, M. Shibata, and T. Tadaki: Preprint of IRC 2005 Yokohama, Paper No. 26-S1-I-01 (2005)
4. M. Hayashi, K. Inagaki, A. Imai, and A. Hirao,: *Nippon Gomu Kyokaishi*, **78**, 91 (2005)
5. I. Hattori, F. Tsutsumi, M. Sakakibara, and K. Makino: *J. Elastomers Plastics*, **23**, 135 (1991)
6. T. Tadaki: *Nippon Gomu Kyokaishi*, **76**, 441 (2003)
7. K. Kato, M. Fujiwara, and Y. Araki,: *JETI*, **54** (12), 85 (2006)
8. I. Hattori: *Settyaku no Gizyutsu*, **25** (2) 12 (2005)