DEVELOPMENT OF A NEW STYRENIC ELASTOMER USING RENEWABLE MONOMER

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Abstract

Utilizing a new renewable monomer called β-farnesene, a new hydrogenated styrene farnesene copolymer (HSFC) with a unique chemical structure and differentiated properties has been developed. β-farnesene is produced from the fermentation of sugar extracted from sugarcane and is based on an innovative microbial engineering technology. When β-farnesene is polymerized using anionic polymerization method, polymerization proceeds with conjugated diene moiety and poly-β-farnesene possesses a highly condensed, long alkyl side chain. This unique chemical structure results in differentiated features that conventional hydrogenated styrenic block copolymers (HSBC) do not have. In comparison to HSBC, HSFC exhibits higher flowability, good adhesion, lower hardness without plasticizer, good permanent and compression set and improved damping properties over a wide temperature range. With this property set, HSFC lends itself to applications such as adhesives, gels, low hardness compounds and non-wovens. It is expected that HSFC will continue to expand and produce new market value to meet developing needs

Introduction

The latest advancement in farnesene polymer technology has been the introduction of liquid farnesene rubber (LFR) using β-farnesene, a renewable conjugated diene monomer which has been successfully developed and is now under testing as a tire additive. Complimentary to this, a hydrogenated styrene farnesene copolymer (HSFC) has been developed from β-farnesene and living anionic polymerization and hydrogenation technology and is introduced here due to its differentiated properties and promising application development.

New Styrenic Elastomer

β-farnesene has two unique features. First, β-farnesene is synthesized from renewable resources and second it has a characteristic chemical structure. β-farnesene is produced from the fermentation of sugar extracted from sugarcane and is based on an innovative microbial engineering technology. The use of β-farnesene related chemicals to applications such as jet fuel and cosmetic ingredients. β-farnesene has a chemical structure corresponding to its isoprene trimer which possesses an anionically polymerizable conjugated diene structure. (Ref. 1) The chemical structure of β-farnesene and HSFC is shown in Figure 1. When β-farnesene is polymerized using the anionic polymerization method, polymerization proceeds with conjugated diene moiety and poly-β-farnesene formed possesses a highly condensed, long alkyl side chain. HSFC has hydrogenated poly-β-farnesene in its soft segment and it shows a differentiated feature from the original structure that conventional thermoplastic elastomers do not have.

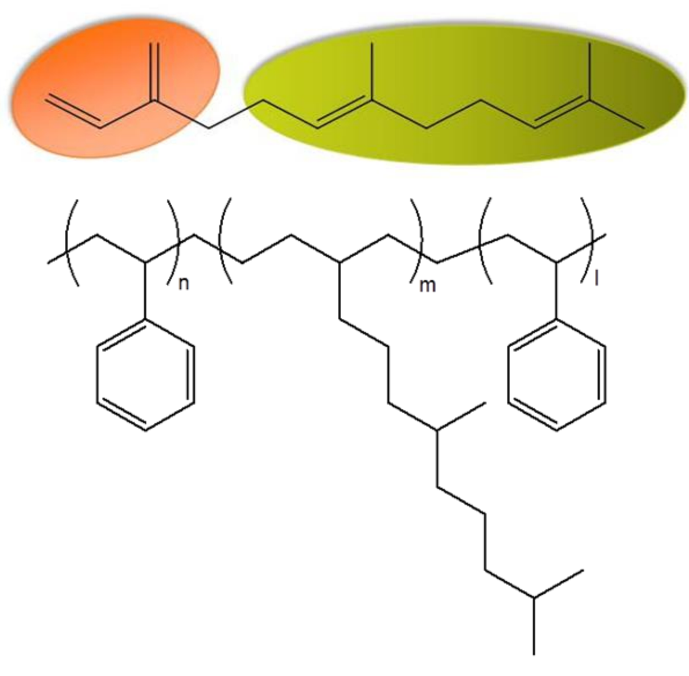

Figure 1. Chemical structure of β-farnesene and hydrogenated styrene farnesene copolymer (HSFC)

In Figure 2, various properties of HSFC are shown in comparison to conventional hydrogenated styrenic block copolymers (HSBC). HSFC shows high flowability, excellent softness, good permanent elongation set and compression set. The temperature dependence of loss tangent (loss factor) tan δ measured by viscoelasticity measurement is shown in Figure 3. The conventional HSBC and high vinyl HSBC have tan δ curves having their peak at the glass transition temperature. The tan δ curve of HSFC also has its peak at the glass transition temperature. However, HSFC shows a high tan δ value of 0.5 at 0 deg. C which is different than that of the conventional HSBC. (Ref. 2) We assume that these features are derived from the highly branched structure of the HSFC. It possesses higher molecular weight between the cross-linking points compared to poly-butadiene, poly-isoprene or its hydrogenated forms. Therefore, HSFC has lower hardness and lower viscosity due to its low cross-link density. Furthermore, the high molecular mobility of the farnesene segment may induce improved damping properties across a wide temperature range.

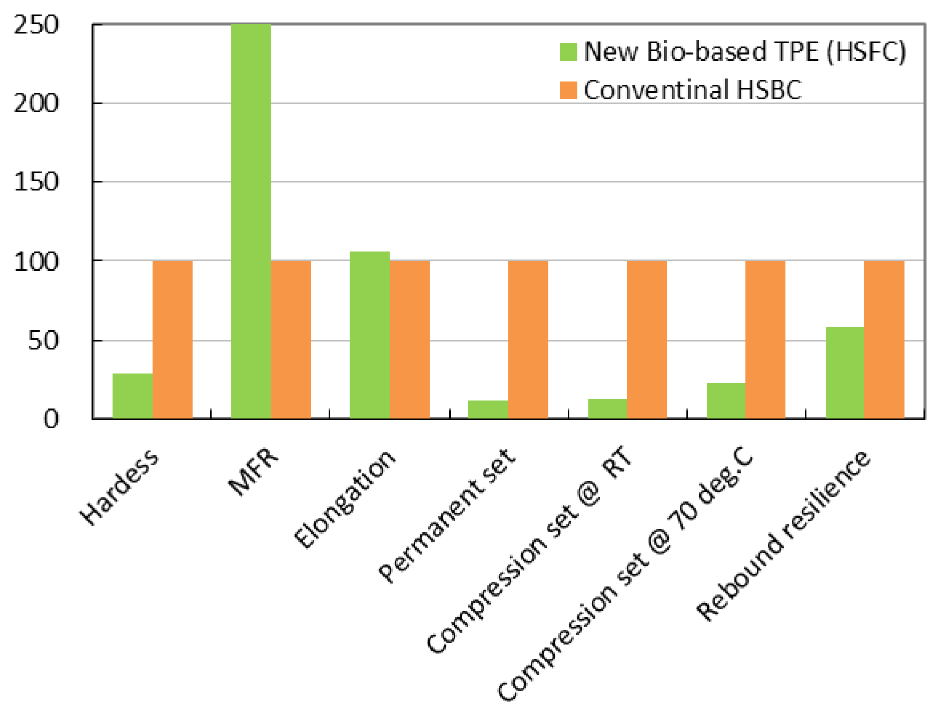

Figure 2. Comparison of HSBC and HSFC in basic properties

In the next section, adhesive properties and good elastic recovery of HSFC along with its potential applications will be discussed.

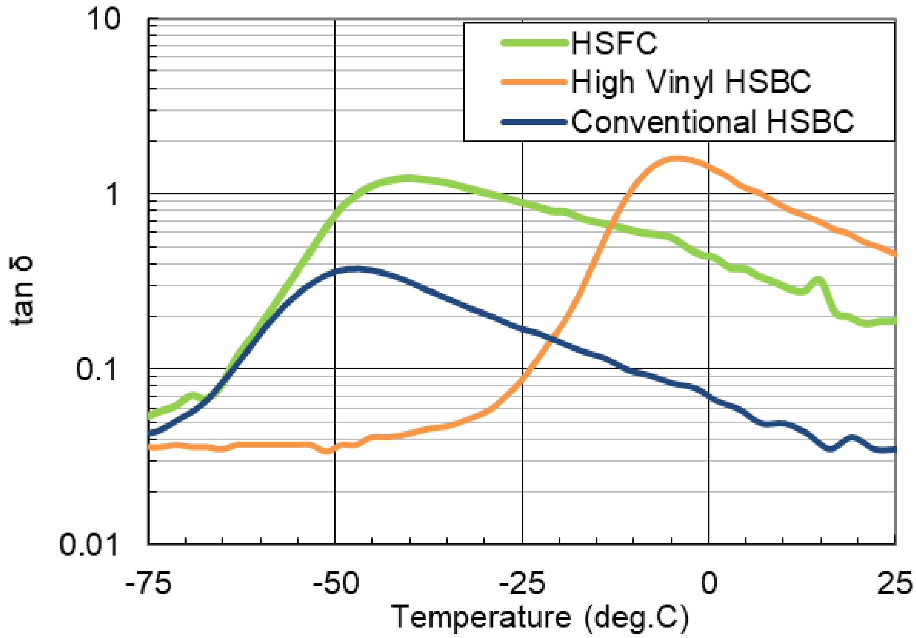

Figure 3. Temperature dependence of loss tangent of HSFC compared to HSBCs

Properties and Applications

One of the main applications of styrenic elastomers is in adhesives. It is well known that SIS combined with tackifiers and plasticizers is used to produce hot melt adhesives. In applications which require improved temperature or weather resistance, SEPS, SEBS, or SEEPS are typically used. In the specific case of protective films used for vehicles, electronics, or industrial parts, SEPS or SEBS with small amounts of tackifier and polyolefin compounds are used in the adhesive. HSFC shows good adhesive properties and tackiness without the addition of a tackifier or a plasticizer.

Table 1. Adhesive properties of HSFC and HSBC compounds

		unit	HSFC	HSFC/TF[*1]	Conventional HSBC/TF[*1]
				80/20 [wt%]	80/20 [wt%]
Peel strength[*2]	to PMMA	N/25mm	11.2	14.9	13.7
	to SST	N/25mm	8.1	13.3	11.2
	to PE	N/25mm	0.5	2.8	0.2
Ball tack		(Ball No.)	5	6	5
SAFT[*3]		deg. C	145	132	159

*1 Tackifier: Hydrogenated hydrocarbon resins

*2 180° peel, 23±1deg.C, RH 50±5%, peel speed 300mm/min

*3 Shear Adhesive Failure Temperature: to SST, 25×25mm, 0.5kg, ramp rate 0.5 deg. C/min

Gel applications are also promising for HSFC due to its high softness. Conventional HSBC and plasticizers such as paraffinic oil are used for cushioning materials. Usually 3 to 10 parts of plasticizer are added to each part of the conventional HSBC to obtain the required softness and moldability. With the appropriate type of plasticizer, HSBC shows good oil retention. However, with higher oil compositions, the plasticizer can bleed out which affects softness, surface tackiness and the appearance of the gel products. HSFC has higher softness than HSBC. Therefore, it requires less plasticizer to meet the target hardness.

The properties of gel compounds produced from HSFC and SEEPS are shown in Table 2. Gels of similar hardness are prepared by adjusting the amount of paraffinic oil and mixing them in a Brabender mixer. The oil retention property is measured by covering the gel with filter paper and then measuring the oil transfer weight loss after one week. HSFC gel compounds show equivalent MFR and compression set to SEEPS compounds. However, HSFC can reduce oil bleeding (oil retention; 99.3%) due to the addition of lesser oil.

Table 2. Properties of HSFC and HSBC gel compounds

	unit	HSFC/Oil*	Conventional HSBC/Oil*
		100/100 [wt%]	100/400 [wt%]
Hardness (Shore OO)		23	32
MFR (160deg.C, 2.16kg)	g/10min	2.0	2.7
Compression set (40deg.C, 22hrs)	%	13	15
Oil retention (168hrs)	%	99.3	95.0

* Paraffinic oil

Two cycles of stress-strain curves of HSFC and HSBC (SEPS) are shown in Figure 4. Samples that are 25 mm wide and 150 mm long were punched out from 0.5 mm thick compression molded sheets and measured by a tensile tester. Although maximum stresses are different in HSFC and other elastomers, HSFC shows excellent elastic recovery due to its low hysteresis loss (15 % in 1st cycle and 10 % in 2nd cycle). The hysteresis loss of elastomers is affected by morphology of the styrene segment at micro phase separation. The styrene domains of HSFC possess spherical microstructure which results in low hysteresis loss. The HSFC sheet has lower residual stress due to its high flowability which may also contribute to the low hysteresis loss.

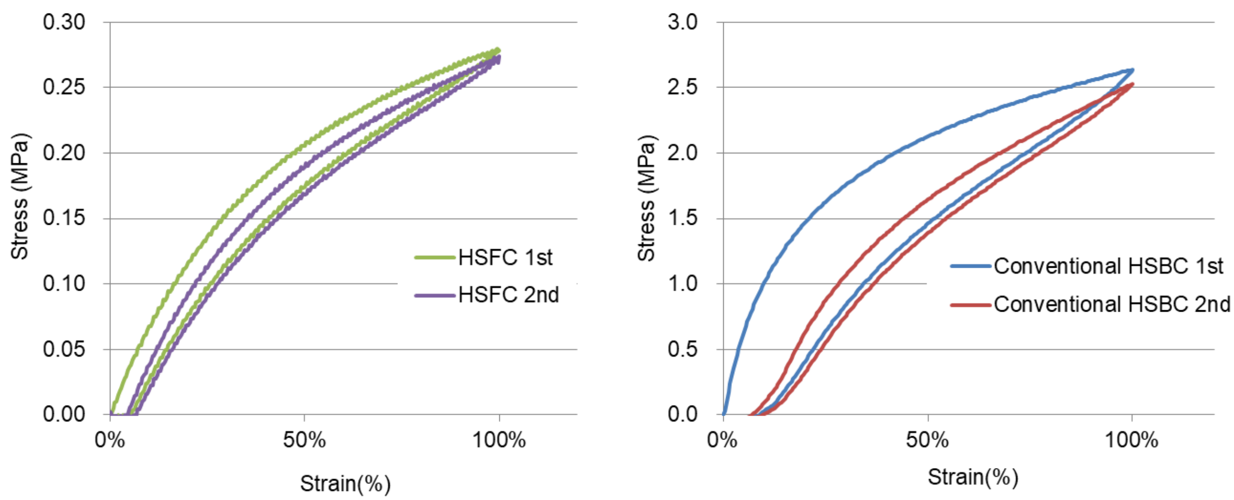

Figure 4. Two cycles of stress-strain curve of HSFC and conventional HSBC (SEPS) showing their hysteresis losses

Summary

After the development of living anionic polymerization, a variety of styrenic elastomers were produced by changing the monomer ratio and/or the chain structure. A structured elastomer, a hydrogenated styrene farnesene copolymer (HSFC) is introduced by utilizing β-farnesene which is a newly developed renewable monomer. A variety of differentiated features of HSFC such as softness, high flowability, high damping, adhesiveness, and low hysteresis loss have been confirmed.

References

1. S. J. Schofer, D. J. McPhee, N. Moriguchi, Y. et. Al. Rubber World, 25, August 2014.

2. K. Hirata, N. Moriguchi, H. Sasaki, et. al. Rubber World, 19, September 2016.