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# Development of a new styrenic elastomer using renewable monomer

*Kuraray has been developing and manufacturing liquid rubber such as liquid isoprene rubber (LIR), liquid butadiene rubber (LBR) and styrenic elastomers Septon and Hybrar utilizing novel living anionic polymerization technology. We recently commercialized a new acrylic thermoplastic elastomer (Kurarity) to the market. Most recently we introduced liquid farnesene rubber (LFR) using β-farnesene, a renewable conjugated diene monomer which was successfully developed and is now under testing as a tire additive. Here we introduce hydrogenated styrene farnesene copolymer (HSFC) developed from β-farnesene and our living anionic polymerization and hydrogenation technology detailing its basic properties and promising application development.*

## 1 New styrenic elastomer using β-farnesene

β-farnesene has two unique features:

- First β-farnesene is synthesized from renewable resources. β-farnesene is produced from the fermentation of sugar extracted from sugarcane and is based on an innovative microbial engineering technology from bioscience company Amyris, Emeryville, CA, USA [1]. Amyris' industrial production platform is located in Brazil and they have expanded the use of β-farnesene related chemicals to applications such as jet fuel and cosmetic ingredients.
- Second is its characteristic chemical structure **(fig. 1)**. It has a chemical structure corresponding to its isoprene trimer which possesses an anionically polymerizable conjugated diene structure. The chemical structure of β-farnesene and HSFC is shown in **figure 1.**

When we polymerize β-farnesene using the anionic polymerization method, polymerization proceeds with conjugated diene moiety and poly-β-farnesene 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.

In **figure 2,** various properties of HSFC are shown in comparison to conventional HSBC. HSFC shows high flowability, excellent softness, good permanent elongation, and compression set. Temperature dependence of loss tangent (loss factor) tan δ measured by viscoelasticity measurement is shown in **figure 3.**

Septon and Hybrar have tan δ curves having their peak at glass transition temperature. The tan δ curve of HSFC also has it peak at the glass transition temperature. However, HSFC shows a high tan δ value 0.5 at 0 °C which is different from Septon.

We assume that these features derive from its highly branched structure. That is, HSFC possesses higher molecular weight between the cross-linking points compared to polybutadiene, polyisoprene or its hydrogenated forms. Therefore, HSFC shows low hardness and low 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.

Next we will introduce the high adhesiveness and good elastic recovery of HSFC along with potential applications.

## 3 Typical properties and applications of HSFC

### 3.1 Adhesives

Adhesives are a main field of application for styrenic elastomers. It is well known that SIS (combined with tackifiers and plasticizers) is used to produce hot melt adhesives. In applications requiring improved tempera-

**Fig. 1:** Chemical structure of β-farnesene and HSFC

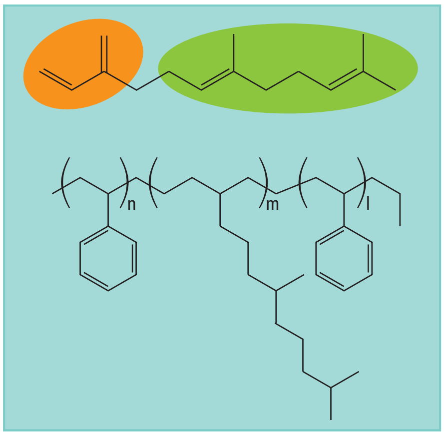



**Fig. 2:** Comparison of HSBC and HSFC in basic properties

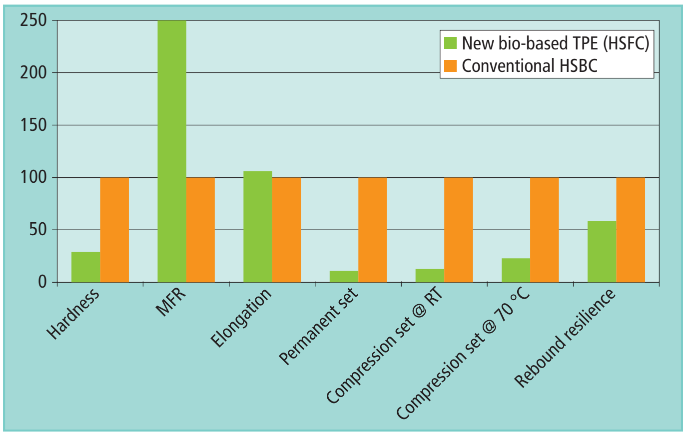
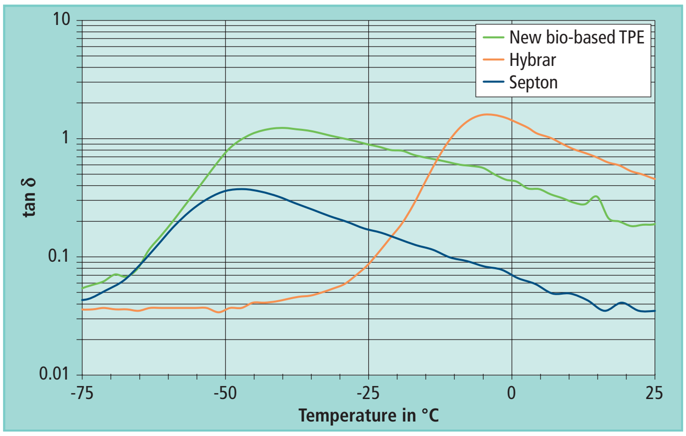



**Fig. 3:** Temperature dependence of loss tangent



ture 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 (plus small amounts of tackifier and polyolefin compound) are used in the adhesive. HSFC shows good adhesiveness and tackiness without adding tackifier or plasticizer.

### 3.2 Gel

Due to the high softness of HSFCs gel applications are also promising **(tab. 1).** Conventional HSBCs and plasticizers such as paraffinic oil are used for cushioning materials. Usually 3 – 10 parts of plasticizer should be added to each part of 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 deteriorates softness, surface tackiness and the appearance of the gel products. HSFC has higher softness than HSBC. Therefore, it requires less plasticizer to meet target hardnesses.

The properties of gel compounds produced from HSFC and Septon 4055 are shown in **table 2.** Gels of similar hardness are prepared by adjusting the amount of paraffinic oil then 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 Septon compounds. However, HSFC can reduce oil bleeding (oil retention; 99.3 %) due to lower oil addition.

Two cycle stress-strain curves of HSFC and Septon 2002 are shown in **figure 4.** Samples having 25 mm width and 150 mm length are punched out from compression molded 0.5 mm thick sheets and measured by a tensile tester. Although maximum stresses are different in HSFC and Septon, HSFC shows excellent elastic recovery due to its low hysteresis loss ($1^{st}$ cycle 15 %, $2^{nd}$ cycle 10 %). 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 from its high flowability which may also contribute to the low hysteresis loss.

**Tab. 1:** Adhesive properties of HSFC and Septon compounds

| | | Unit | HSFC KL-SF904 | KL-SF904/TF [1] 80/20 wt% | Septon/TF [1] 80/20 wt% |
|---|---|---|---|---|---|
| Peel strength [2] | to PMMA | N/25 mm | 11.2 | 14.9 | 13.7 |
| | to SST | N/25 mm | 8.1 | 13.3 | 11.2 |
| | to PE | N/25 mm | 0.5 | 2.8 | 0.2 |
| Ball tack | | Ball no. | 5 | 6 | 5 |
| SAFT [3] | | °C | 145 | 132 | 159 |

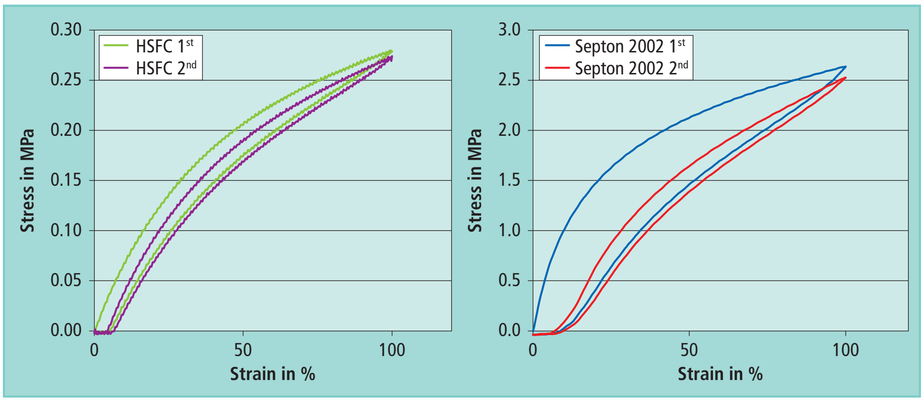
[1] Tackifier Arkon P-125 (Arakawa Chemical Industries, Ltd.)
[2] 180° peel, 23 ±1 °C, RH 50 ±5 %, peel speed 300 mm/min
[3] Shear adhesive failure temperature, to SST, 25 × 25 mm, 0.5 kg, ramp rate 0.5 °C/min

**Tab. 2:** Properties of HSFC gel compounds

| | Unit | HSFC/oil* 100/100 wt% | S4055/oil* 100/400 wt% |
|---|---|---|---|
| Hardness | Shore OO | 23 | 32 |
| MFR (160 °C, 2.16 kg) | g/10 min | 2.0 | 2.7 |
| Compression set (40 °C, 22 h) | % | 13 | 15 |
| Oil retention (168 h) | % | 99.3 | 95.0 |

* Paraffinic oil PW-32 (Idemitsu Kosan Co., Ltd.)

**Fig. 4:** Two cycle stress-strain curves of HSFC and Septon 2002




## 4 Summary

After the development of living anionic polymerization, a variety of styrenic elastomers were produced by changing the monomer ratio and/or chain structure. Today, we produce a differentiated structured elastomer HSFC by utilizing β-farnesene, a newly developed renewable monomer. We have shown a variety of differentiated features of HSFC such as softness, high flowability, high damping, adhesiveness, and low hysteresis loss. We expect HSFC will continue to produce new market value to meet developing customer needs.

## 5 References

[1] S. Schofer, D. McPhee, N. Moriguchi, Y. Yamana, B. Chapman, K. Hirata, Y. Uehara, R. Boehm: Biofene, a renewable monomer for elastomer materials with novel properties. Polymer development, characterization, and use in elastomer formulations. RFP Rubber Fibres Plastics, vol. 9, no. 4, Nov 2014, 235 – 239.

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