# NEWLY DESIGNED SIS BLOCK COPOLYMERS FOR PRESSURE SENSITIVE ADHESIVES (PSA)

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## 1. Introduction

Styrenic block copolymers (SBCs) are widely used for hot melt pressure sensitive adhesives (HMPSAs). Styrene-Isoprene-Styrene block copolymers (SISs) are preferably used in HMPSA, because of their high aggressive tack, good compatibility with various tackifiers, and good processability.

Historically, SIS have been developed with various structures for adjusting PSA performance and its processability [1, 2 and 3].

In other applications, SBCs can also be used for elastic films such as diaper films. For elastic films, high modulus and high elasticity are required of SBCs. However these two requirements have a trade-off relationship. We have recently developed newly-designed SIS block copolymers with high modulus and high elasticity to introduce a new design factor. They have a unique morphology (micro segregated structure). Although they are high-styrene content type of SIS (30% or more), the morphology forms a spherical structure by Transmission Electron Microscope (TEM).This means that they are soft polymers with high styrene content.

This unique morphology could have various advantages for HMPSA, such as good converting performance and broader temperature performance.

## 2. SIS for Elastic Films

Styrenic block copolymers (SBCs) are thermoplastic and elastomeric materials. SBCs are also used in film applications [4] other than PSA applications. The advantages of Styrene-Isoprene-Styrene (SIS) are softness and low gel content. This implies that some excellent elastic films can be produced with SIS by the extrusion process. But SIS has poor durability under sunlight and UV light compared with other SBCs (SEBS, SEPS), which means that SIS is suitable for the films in disposable application fields such as diapers and napkins.

A conventional SIS block copolymer which is widely applied to HMPSAs, SIS-A, can provide soft elastic films or sheets by extrusion (Figure 1). It can promote elasticity that shows excellent recovery properties (low tension set) (Table 1).

The soft, natural rubber-like film can be accepted in some fields. For the other applications, however, it has some problems because it is too soft. A polymer which shows higher modulus and high elasticity would be required.

In order to raise modulus, it is thought that higher styrene content in SIS block copolymers is preferable. SBCs with higher styrene content do show high modulus (SIS-B and SIS-C). On the other hand, they also show higher tension set values. Higher styrene polymers give poorer elasticity and recovery properties. There is a trade-off between high modulus and high elasticity (Figure 2).

## 3. Asymmetric styrene block

### 3-1. Morphology of styrenic block copolymers

The modulus and elasticity of SBCs depend on the morphology. SBCs consist of polystyrene endblocks and elastomeric midblocks. They create a two-phase structure consisting of polystyrene domains and elastomeric matrix (Figure 3).

The morphology of the two-phase structure depends on the ratio of endblock (polystyrene) to midblock. An SBC of low polystyrene content forms a spherical structure of polystyrene domain. In the PSA applications, they are commonly used.

Their morphology can be observed by Transmission Electron Microscope (TEM). Generally, conventional SIS block copolymers containing polystyrene endblocks less than about 20% show spherical morphology. But in higher-styrene copolymers, cylindrical or lamellar morphology can be observed (Figure 4).

The spherical structure seems to have elasticity, and generally higher-styrene copolymers give high modulus. Higher-styrene copolymer (styrene content around >20%) forms cylindrical or lamellar structure. These structures give high hardness and less elasticity, like a plastic material.

### 3-2. Asymmetric styrene block design

Conventional polymers, described in Paragraph 2, can not give higher modulus and higher elasticity by introducing conventional polymer designs (styrene content, molecular length, linear or radial structure and diblock).

We studied new polymer design to find a unique morphology to meet these requirements. Eventually, we found a key design factor “Asymmetric styrene block”. Asymmetric styrene blocked SIS is a triblock SIS copolymer with different styrene length.

An asymmetric styrene blocked SIS itself is very rigid. And with our design concept, asymmetric styrene blocked SIS block copolymer (hereinafter to as SIS’) must be blended with a symmetric SIS block copolymer (hereinafter to as SIS) to get elasticity (Figure 5). A new composition (SIS and SIS’composition, QS-48) has been designed and developed (Table 2).

Although the styrene content of the newly designed polymer (QS-48) is quite high, 48%, QS-48 has low hardness compared to symmetric SIS block polymers (styrene content = 44%). It shows high modulus and excellent elasticity and recovery properties (low tension set). Figure 6 shows its properties as an extruded sheet.

QS-48’s excellent performance may be attributable to its unique morphology and high styrene content. Figure 7 shows TEM image of QS-48. Conventional symmetric SIS with high styrene content (>40%) forms lamellar structure, but QS-48 shows spherical morphology while its styrene content is quite high (48%).

It is believed that spherical morphology gives elastic performance and high styrene content gives high modulus. QS-48 could be suitable for elastomeric film application.

Unexpectedly, SIS and SIS’ compositions (SIS/SIS’) are quite a bit softer than symmetric SIS block copolymers (SIS**)** with the same styrene content (Figure 8). Generally, SISs with low styrene content are commonly used for PSA applications, because these SISs are softer.

If this assumption is correct, SIS/SIS’ compositions with high styrene content, would show unique performance for PSA application.

## 4. Newly-designed polymer compositions in hot melt adhesives

### Symmetric / Asymmetric (SIS/SIS') compositions

We prepared three samples with different styrene content including QS-48 for hot melt adhesives. The polymer characteristics and adhesive properties are shown in Table 3.

In the results, QS-48 based PSA gives poor tackiness and high holding power, this means that it would still be hard. But the adhesive viscosity shows extremely low at low temperature (Figure 9).

In manufacturing hot melt adhesive products, SIS based adhesives are easily degradated and oxidized at higher temperatures during the mixing process and the coating or converting process. In order to prevent degradation of the polymers at high temperature, HMPSAs with lower adhesive viscosity are required.

In general, the adhesives-based conventional SIS block polymers with low adhesive viscosity could give poor holding power. But QS-48-based PSA has the advantage of processability (low adhesive viscosity) without losing holding power.

This asymmetric styrene blocked technology implies that it is possible to have low adhesive viscosity without losing holding power. This phenomenon is still under discussion, but it seems that "high styrene" and "spherical morphology" give unique characterization.

But the technology has certain limitations. In accordance with lower styrene content, the compositions lose this unique characterization. QS-20-based PSA (styrene content = 20%) shows quite similar performance and a dynamic mechanical analysis (DMA) curve to symmetric SIS-based PSA (SIS-B styrene content = 19%) (Table 3 and Figure 10). In this study, the technology could have favorable polymer structure range (around 30% styrene content). QS-30 has well-balanced PSA performance and low adhesive viscosity.

In the Tangent delta curves in DMA charts (Figure 11), temperature that peaks from 0 to 10 $^{o}$ C corresponds to glass transition temperature (Tg) of polyisoprene blocks. The Tg of QS-30 based PSA is lower than SIS-E based PSA, while the two polymers (QS-30 and SIS-E) have the same styrene content (30%) (Figure 12). It is apparent that asymmetric SIS (SIS') seems to affect isoprene/styrene phase separation and compatibility with tackifiers. This suggests that this technology would provide good low temperature performance.

## 5. Conclusion

Asymmetric styrene blocked SIS compositions (SIS's) have a unique morphology. They are soft polymers with high styrene content.

This unique morphology could have various advantages for HMPSA as well as film applications. SIS/SIS' compositions give low adhesive viscosity without losing adhesive performance and have possibility to give good low temperature performance (low Tg).

## Literature Citations:


1. Komatsuzaki, S., "Application of Radial SIS polymers to Hot Melt Pressure Sensitive Adhesives", TAPPI Hot Melt Symposium, 1999.
2. Ishiguro, M., "The Effect of SI Diblock on Carton Sealability of Packaging Tape", PSTC Technical Seminar Proceedings, 1995.
3. Matsubara, T., "Newly designed SIS block copolymers containing homo-polyisoprene", PSTC Technical Seminar Proceedings, 2004.
4. Richard Schmidt, "Styrenic Block Copolymers in Adhesive for Co-extruded films'', PSTC Technical Seminar Proceedings, 2008.

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**Table 1.** Properties; Conventional SIS based extruded sheets (1mm)

| | | SIS-A (Commercial) | SIS-B (Commercial) | SIS-C (Experimental) |
|---|---|---|---|---|
| Structure | | Radial/Linear | Linear | Linear |
| Styrene Content [1)] | [%] | 14 | 19 | 35 |
| Melt Flow Rate [2)] | [g/10min.] | 9 | 12 | 14 |
| Hardness [3)] | [Duro A] | 36 | 40 | 80 |
| Modulus;@100% (MD) [4)] | [MPa] | 0.3 | 1.6 | 3.9 |
| Modulus;@100% (TD) [4)] | [MPa] | 0.3 | 0.6 | 1.2 |
| Tension Set (TD) [5)] | [%] | 2 | 3 | 9 |

1) Abbe's refractometer
2) ASTM D-1238 (G condition 200$^{o}$C)
3) ASTM D2240 (Type A)
4) ASTM D412 (Method A: Tensile speed 500mm/min.)
5) ASTM-D412 (200% elongation)

**Figure 1.** Image of die-out

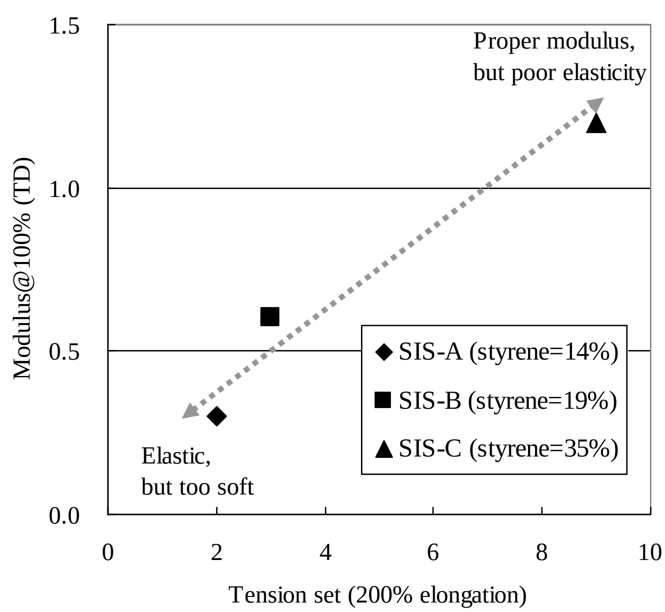


**Figure 2.** Trade-off between modulus and elasticity (Conventional SIS)

**Figure 3.** Image of morphology (spherical styrene domain)


**Figure 4.** Typical morphology; conventional SIS block copolymers (TEM)

**Figure 5.** Design concept for asymmetric styrene block SIS blend composition

**Table 2.** Characteristic of SIS block copolymers

| | | Prototype QS-48 (asymmetric styrene SIS composition) | SIS-D (Commercial) |
|---|---|---|---|
| Structure and composition | | SIS/SIS' | Linear SIS |
| Styrene Content | [%] | 48 | 44 |
| Melt Flow Rate | [g/10min.] | 15 | 40 |
| Hardness | [Duro A] | 65 | 90 |

1) Abbe's refractometer
2) ASTM D-1238 (G condition 200°C)
3) ASTM D2240 (Type A)
4) ASTM D412 (Method A: Tensile speed 500mm/min.)
5) ASTM-D412 (200% elongation)

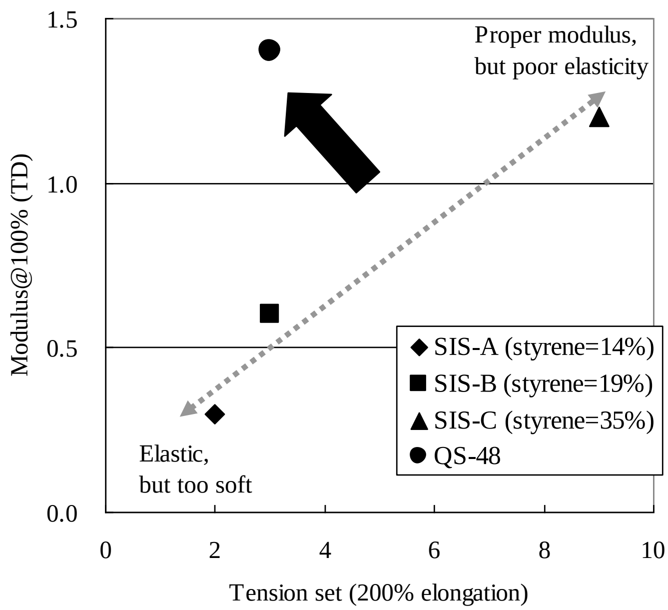


**Figure 6.** Position; QS-48

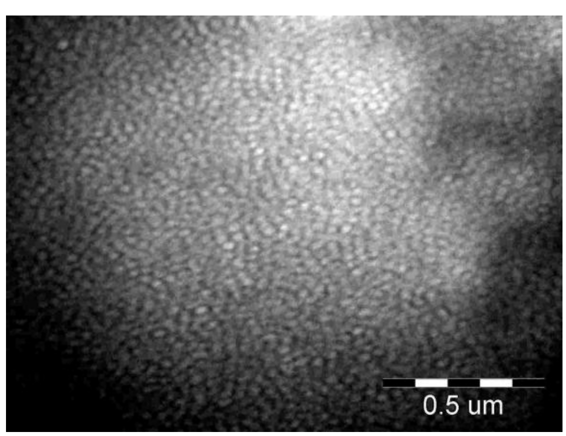

**Figure 7.** QS-48 (Styrene = 48%) ; TEM observation

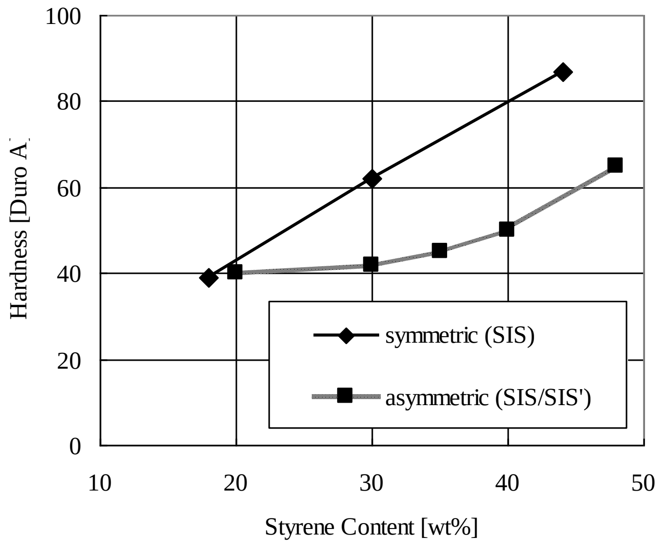


**Figure 8.** Hardness vs. styrene content

**Table 3.** Characteristics and adhesive properties of prototype compositions

| | | Prototype QS-48 | Prototype QS-30 | Prototype QS-20 | SIS-E | SIS-B | SIS-F |
|---|---|---|---|---|---|---|---|
| | | (asymmetric styrene SIS composition) | | | (Commercial) | | |
| Structure and composition | | SIS/SIS' | SIS/SIS' | SIS/SIS' | Linear SIS | Linear SIS | Linear SIS/SI |
| Styrene Content | [%] | 48 | 30 | 20 | 30 | 19 | 14 |
| SI Diblock Content | [%] | 0 | 0 | 0 | 0 | 0 | 26 |
| Melt Flow Rate | [g/10min.] | 15 | 7 | 8 | 14 | 10 | 10 |
| Hardness | [Duro A] | 65 | 42 | 40 | 62 | 40 | 35 |
| Adhesive properties[1)] | | | | | | | |
| Loop tack to polyethylene[2)] | [N],@23$^{o}$C | 0.63 | 8.5 | 10.0 | 9.0 | 8.3 | 11 |
| Peel adhesion to steel[3)] | [N/m],@23$^{o}$C | 650 | 600 | 600 | 550 | 550 | 580 |
| Holding power to steel[4)] | [min.],@40$^{o}$C | 2000 | 1500 | 800 | 1500 | 1000 | 400 |
| Tangent dalta[5)] | | | | | | | |
| Peak top | [$^{o}$C] | 7.5 | -1.0 | -1.0 | 7.5 | 1.5 | 0 |

1) Rubber Composition / C5-C9 hydrocarbon resin / naphthenic oil = 100 / 150 / 50.
2) Finat-9 Contact: 1sec.
3) PSTC-1 180$^{o}$ Peel (to Steel, 10*25mm).

4) PSTC-7 (to Steel, 10*25mm, 2kg load).
5) At 10rad./s.

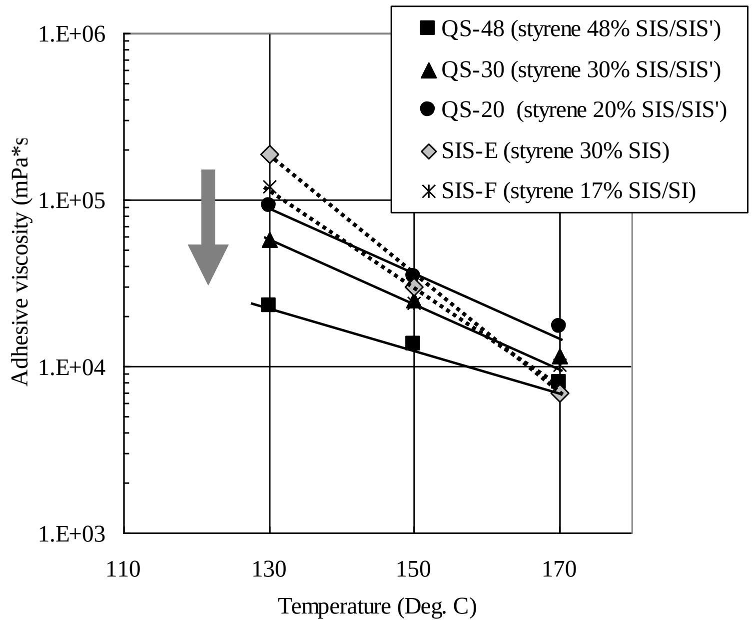


**Figure 9.** Adhesive viscosity

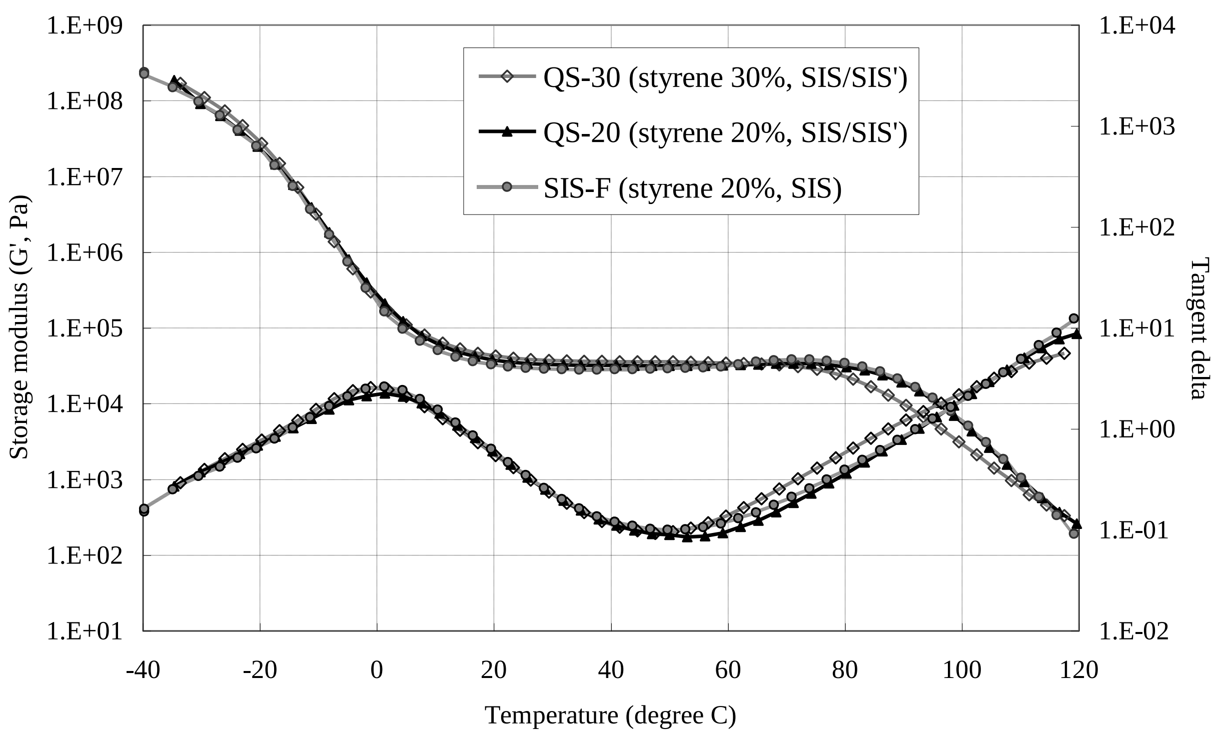


**Figure 10.** DMA curves of adhesives (Styrene content ≧30%) (at 10 rad./s.)

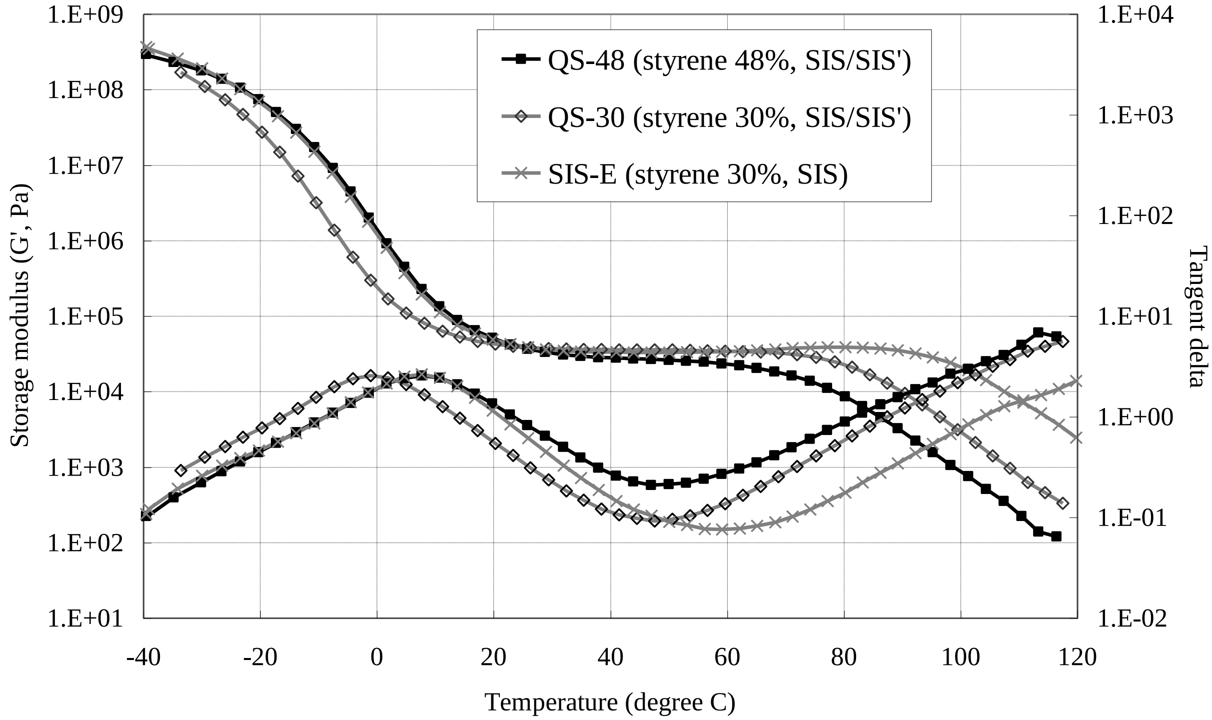


**Figure 11.** DMA curves of adhesives (Styrene content ≦30%) (at 10 rad./s.)

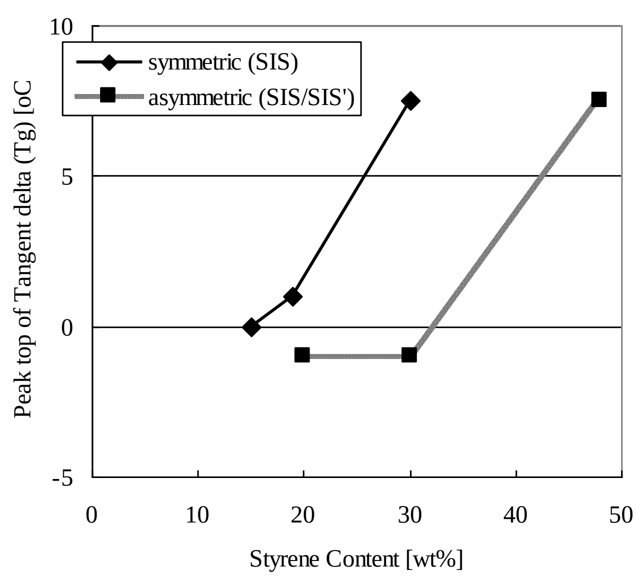


**Figure 12.** Glass transition temperature of PSAs
(Rubber Composition / C5-C9 hydrocarbon resin / naphthenic oil = 100 / 150 / 50)