NEWLY DESIGNED SIS BLOCK COPOLYMER FOR HIGH TEMPERATURE PERFORMANCE

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1. Introduction

There are various types of styrenic block copolymers (SBC). These thermoplastic elastomers can be used for hot melt pressure sensitive adhesives (HMPSA). [1-5] Styrene-Isoprene-Styrene block copolymer (SIS) is preferably used in HMPSA fields because it has several advantages as follows.

i) SIS is softer than other styrenic block copolymers and can give an aggressive tackiness.
ii) SIS can be used with various type of tackifiers.
iii) SIS contains less gel polymer than the other styrenic block copolymers, such as SBS.
iv) SIS can be used in hot melt process (as well as other SBCs). Hot melt process is lower cost process and can give lower VOCs in final product than solvent-based process.

However, SIS has the disadvantage regarding to the high temperature performance (as well as other SBCs). This disadvantage result from the glass transition temperature (Tg) of styrene domain. This disadvantage and hot melt processability that is one of the advantage of SIS are in a trade-off relationship for the reason mentioned below. Styrenic end-block gives hard domain and physical crosslink. Therefore, SIS gives an elastomeric state in the room temperature. However, in higher temperature over Tg of styrenic hard domain, SIS transfer from an elastomeric state to a melt state. As a result of this state change, modulus of SIS is significantly going down and SIS gives poorer PSA performance.

Generally, in the high temperature application, for example, masking tape and wire harness tape for automotive application, solvent based natural rubber or acrylic systems are preferably used. However, the solvent-based system gives lower processability than the hot melt system regarding to process speed, running cost and so on. In addition, recently some action has been taken to strengthen restriction of VOC components and solvent free process.

In these backgrounds, we have focused on developing newly designed SIS which has not only high temperature performance but also hot melt processability (**Figure 1**).

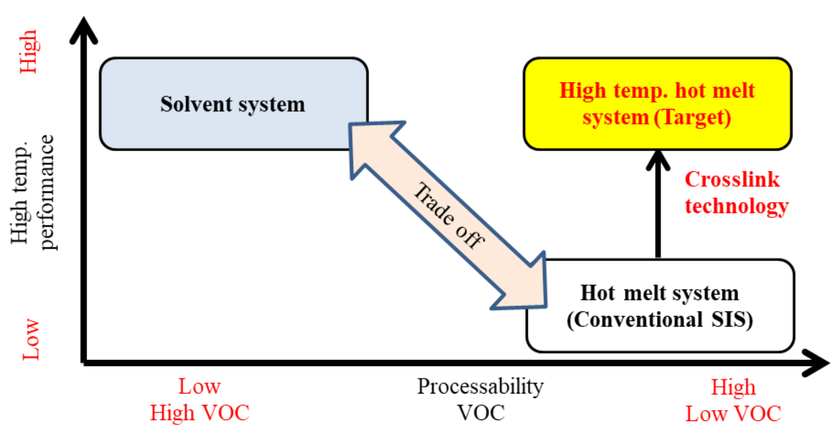


Figure 1. Property image of each adhesive system and target

2. Crosslinkable SIS

To meet the requirements and eco-friendly backgrounds, we have developed newly designed SIS. This newly designed SIS has crosslinkable function. This polymer can give applicability for hot melt system. In addition, by subsequent curing system, this crosslinkable SIS based adhesive gives significantly improved high temperature performance (**Figure 2 and 3**).

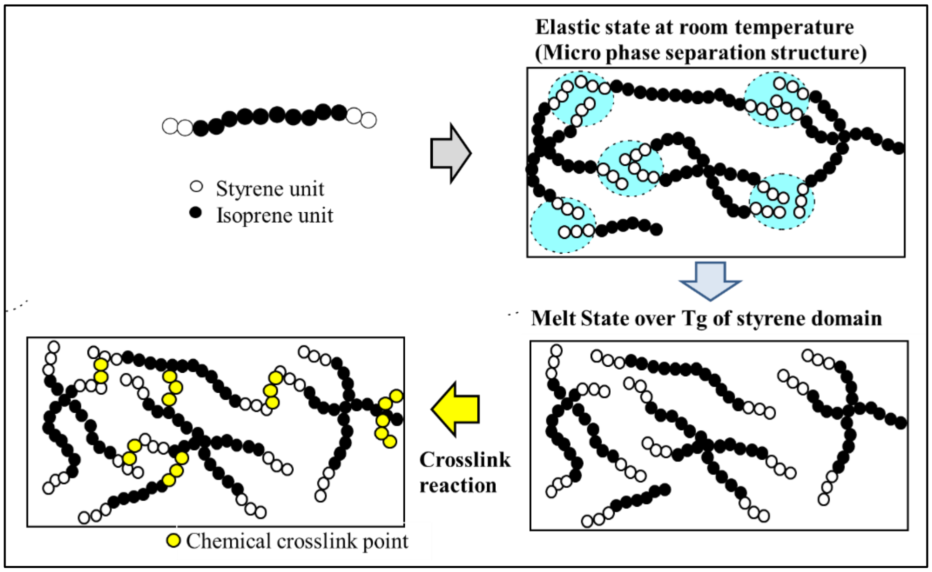


Figure 2. Image of state change and crosslink reaction

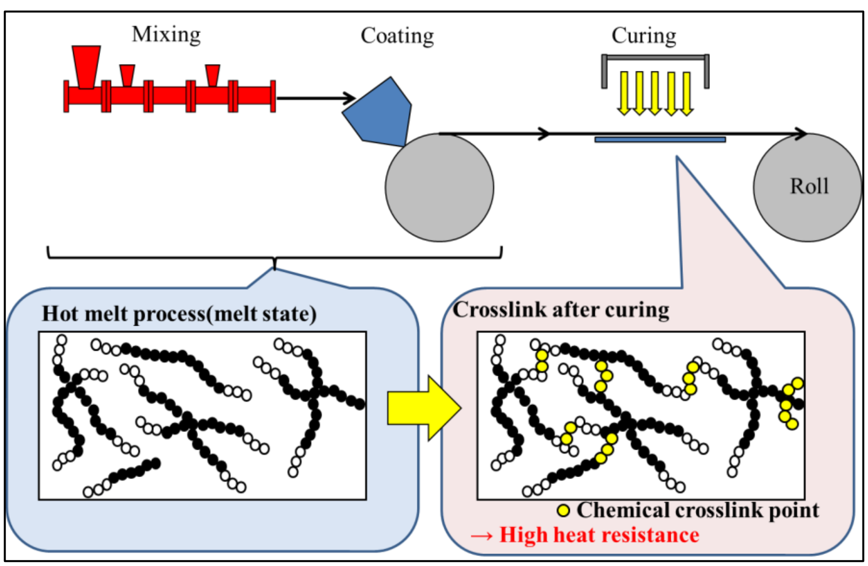


Figure 3. Process image: Hot melt mixing/coating, followed by curing

3. Crosslinkable SIS generation 1

At first, to develop crosslinkable SIS, we applied and modified a star polymer technology that is a traditional technology in SBCs field (Crosslinkable SIS 1, **Figure 4**). As expected, this crosslinkable SIS 1 based adhesive gives the almost same high temperature performance after curing as solvent system adhesive that is a targeted heat resistance type of tape. However, crosslinkable SIS 1 shows lower tackiness than before curing (**Figure 5**).

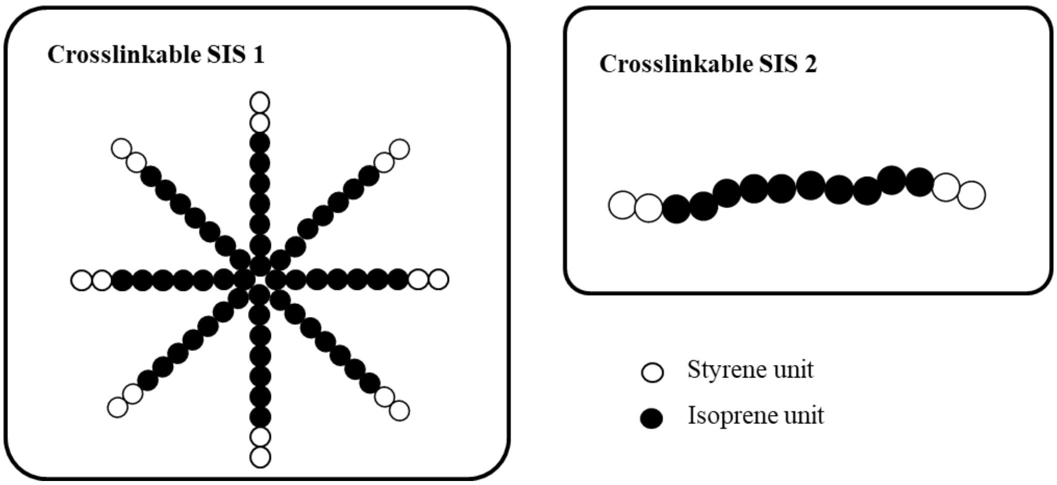
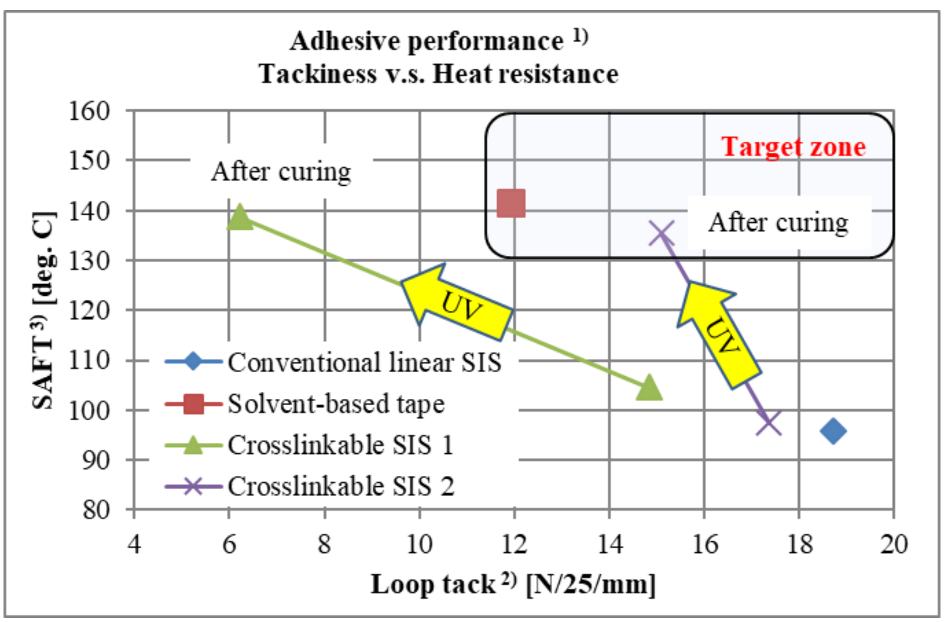


Figure 4. Image of crosslinkable SIS block copolymers



1) Rubber Composition / C5 hydrocarbon resin / naphthenic oil = 100 / 100 / 10.
2) PSTC-16 (to Steel, 25*25mm)
3) PSTC-17 (to Steel, 10*25mm, 0.5kg load, 0.5deg.C/min).

Figure 5. Adhesive performance of crosslinkable SIS block copolymers

In general, the multi-armed SIS block copolymer gives poorer tackiness than the linear SIS block polymer because of restricting isoprene chain free movement. Crosslinkable SIS 1 is not only multi-armed polymer itself but also gives hyper-armed polymer after curing. This is the reason why crosslinkable SIS 1 shows poorer tackiness after curing.

4. Crosslinkable SIS generation 2

Secondly, we developed crosslinkable SIS 2 to overcome loss of tackiness issue after curing about Crosslinkable SIS 1. We applied the new modification technology to Crosslinkable SIS 2 (**Figure 3**). This polymer has the conventional linear SIS structure and crosslinkable modification, which keep isoprene chain free movement after curing. This interesting feature results in keeping aggressive tackiness that is one of the most important advantage of SIS.

These two types of polymer characteristics are in **Table 1**. In addition, adhesive properties of the two polymer compositions are in **Figure 5** compared with conventional SIS and solvent-based tape.

Table 1. Characteristic of crosslinkable SIS block copolymers

name		Conventional linear SIS	Crosslinkable SIS 1	Crosslinkable SIS 2
Structure		Linear	Star	Linear
Styrene Content [1]	[%]	14	19	15
SI Diblock Content [2]	[%]	26	15	-
Melt Index [3]	[g/10min.]	10	11	11

1) Abbe's refractometer
2) Gel Permeation Chromatography
3) ASTM D-1238(G condition 200deg.C, 5kg)

Conventional SIS shows good tackiness performance but lower heat resistance (lower shear adhesion failure temperature (SAFT) performance). This is the disadvantage of conventional SIS (hot melt system). At the higher temperature over Tg of styrene domain, physical crosslink of styrene domain become weak and adhesive made from conventional SIS form a melt state. This is the reason why conventional SIS gives lower SAFT performance.

Solvent-based adhesive gives higher heat resistance than conventional SIS and moderate tackiness. This property is a target one.

Crosslinkable SIS 1 gives higher SAFT value but lower tackiness after curing above mentioned. These two adhesive properties are in a tradeoff relationship.

On the other hand, Crosslinkable SIS 2 gives not only the almost same SAFT value as Crosslinkable SIS 1 and solvent-based adhesive but also higher tackiness than Crosslinkable SIS 1 (or the same tackiness as conventional SIS). Crosslinkable SIS 2 eliminates the trade off relationship between heat resistance (SAFT) and tackiness and achieves target properties.

The dynamic mechanical analysis (DMA) supports above results. DMA curve of adhesives before curing are in **Figure 6**. Storage modulus of Crosslinkable SIS 1 and 2 gradually drop over around 80 degree C. At high temperature, adhesive lose the modulus and change to melt state.

On the other hand, DMA curve of crosslinkable SIS adhesives after curing keep higher storage modulus than adhesive before curing at high temperature (**Figure 7**).

In addition, crosslinkable SIS 2 adhesive shows lower storage modulus than crosslinkable SIS 1 around Tg of isoprene block. This result implies that crosslinkable SIS shows higher wettability than crosslinkable SIS 2. This is the reason why crosslinkable SIS gives higher tackiness.

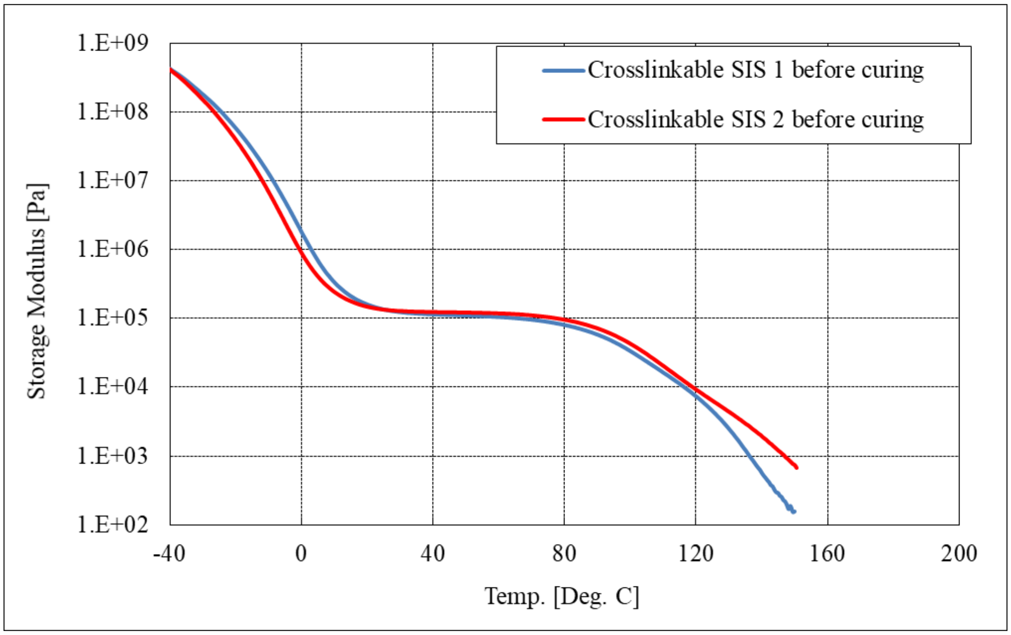


Figure 6. DMA curves of adhesives before curing (at 10 rad./s.)

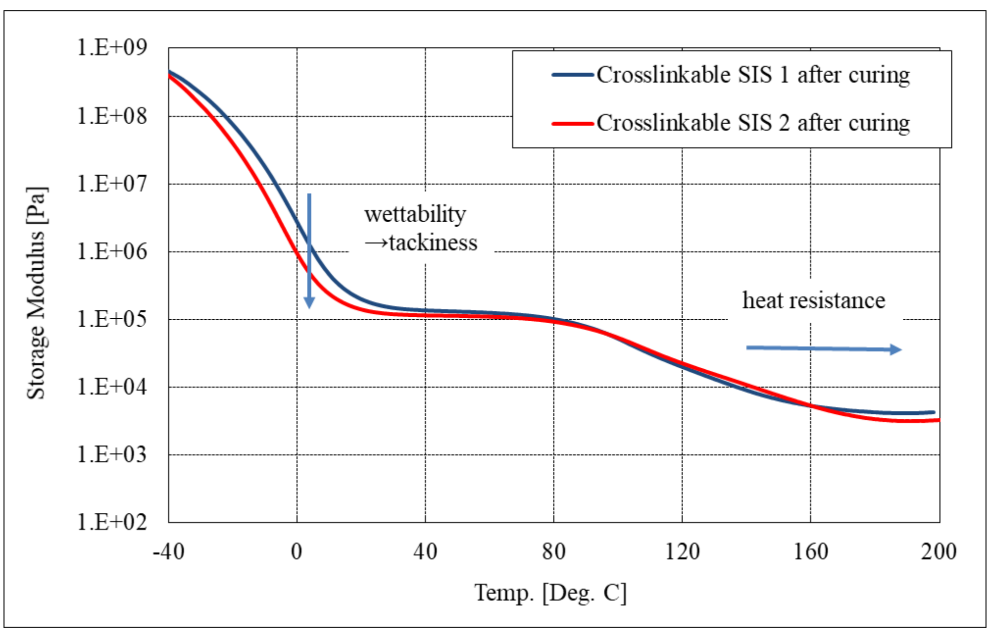


Figure 7. DMA curves of adhesives after curing (at 10 rad./s.)

5. Conclusion

In conclusion, we developed newly designed crosslinkable SIS 1 and 2.

At first, we applied and modified a star polymer technology that is a traditional technology in SBCs field (Crosslinkable SIS 1). Crosslinkable SIS 1 based adhesive gives the almost same high temperature performance after curing as solvent system adhesive. However, crosslinkable SIS 1 shows lower tackiness than before curing.

Secondly, we developed crosslinkable SIS 2 to overcome loss of tackiness issue after curing about Crosslinkable SIS 1. We applied the new modification technology to Crosslinkable SIS 2. This polymer has the conventional linear SIS structure and crosslinkable modification, which keep isoprene chain free movement after curing. This newly designed SIS block polymer gives the targeted high temperature performance without loss of aggressive tackiness and hot-melt processability that are the advantages of conventional SIS.

6. Literature Citations:

1. Komatsuzaki, S., "Application of Radial SIS polymers to Hot Melt Pressure Sensitive Adhesives", TAPPI Hot Melt Symposium, 1999.
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7. **Acknowledgement**

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