NEWLY-DESIGNED SIS BLOCK COPOLYMER FOR IMPROVING DIE-CUT PERFORMANCE AND NEW EVALUATION METHOD FOR DIE-CUT PROPERTY

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1. Introduction :

Various types of styrenic block copolymers (SBCs) can be used as thermoplastic elastomers for hot melt pressure sensitive adhesives (HMPSA). Especially, Styrene-Isoprene-Styrene block copolymer (SIS), one of SBCs, is preferably used in HMPSA fields because it has several advantages as follows.

i) SIS is softer than other SBCs and can give a higher tackiness.

ii) SIS can be mixed with wide types of tackifiers.

iii) SIS contains less gels than other SBCs, such as Styrene-Butadiene-Styrene bock copolymer (SBS).

Historically, many types of SIS have been developed with various factors for modifying PSA performance or improving processability. [1] [2] [3]

For label application, SIS-based HMPSA is widely used all over the world. Especially, it is preferably used for food labels and frozen labels because it shows better low-temperature performances by utilizing soft property of SIS. Nowadays, several performances are required to HMPSA for label application from market as following.

i) Adhesive performance with wide temperature range (especially low-temperature performance) required accompanying increase in applications such as low-temperature food storage etc.

ii) Good anti-oil migration property

iii) Good die-cut performance required as label market size grows and high speed production is needed.

2. Background technology :

2.1. Low-temperature performance and anti-oil migration property :

It is not easy to improve low-temperature performance of SIS-based HMPSA within the range of conventional technology. To improve low-temperature performance, it is generally effective to decrease glass transition temperature (Tg) of HMPSA by increasing oil or adding liquid resin. However, there is a concern of oil migration by increasing oil. There is a concern of cost increasing by using liquid resin.

Besides, liquid resin makes it difficult to handle at production. If increasing oil is selected, good anti-oil migration property is required to HMPSA because oil migration makes display of a label dirty and adhesive performance of the HMPSA worse. Use of SIS with high styrene content is effective to inhibit oil migration, although it generally makes adhesives harder and its performances worse. From above, it is not easy to improve low-temperature performance of SIS-based HMPSA with conventional polymer structure. Good anti-oil migration property is often needed to achieve the low-temperature performance.

2.2. Die-cut performance :

In label production, labels are cut into predetermined shapes at die-cut process. The die-cut process can be divided into three sub-processes as shown in Figure 1. “1st process” is a die-cut process. At this process, a face layer and an adhesive layer on a release paper are cut by a cutting blade. To prevent a release paper from being cut, the adhesive layer is not completely cut, in other words, a thin adhesive layer remains uncut. “2nd process” is a cutting to stripping process. A partially cut label sheet is transported to a next process as it is in this process. It is important that the cut adhesive layer does not rejoin because a rejoined adhesive layer becomes hard to cut in next process. In “3rd process”, the both face layer and adhesive layer around a label body are removed from the release paper because they are unnecessary. At this time, the thin adhesive layer that is left without being cut in die-cut process is pulled and cut completely. This process is called a matrix stripping process.

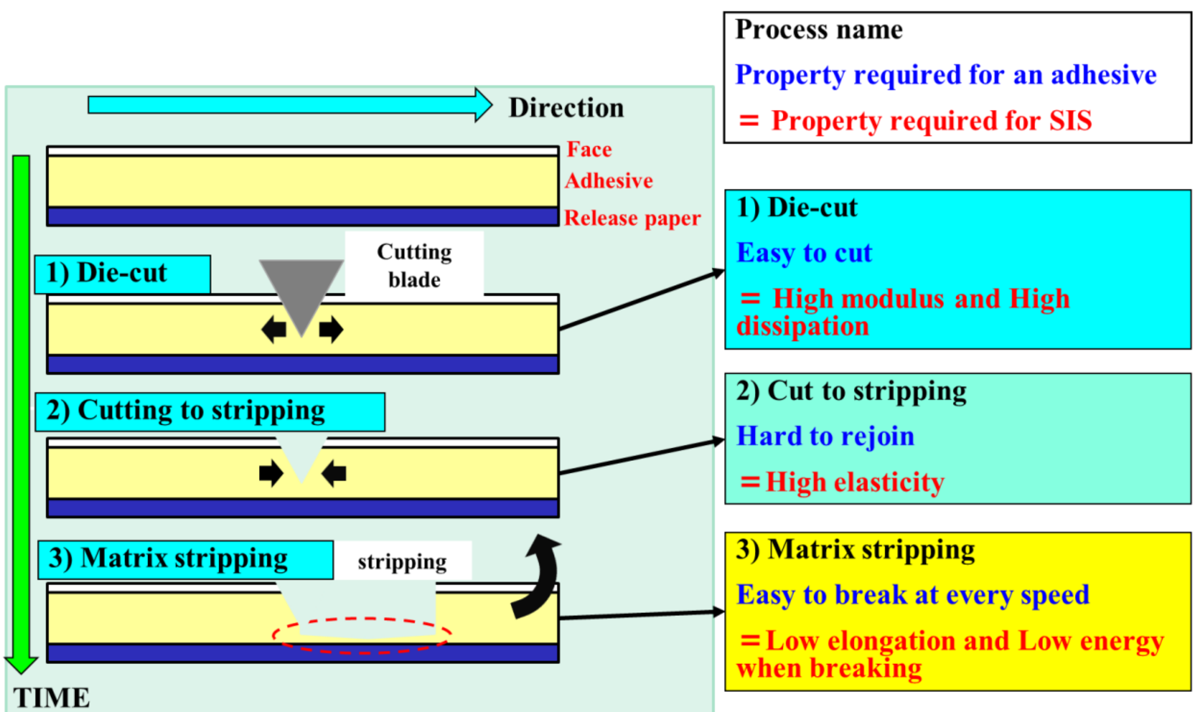


Figure 1 Die-cut process in label production

At die-cut process, an adhesive sometimes sticks to a cutting blade and there is a problem that a label sheet cannot be cut continuously. The problem often occurs when the adhesive formulation is changed in order to improve the adhesive performance of HMPSA. It is said that the die-cut performance of HMPSA can be predicted by the rheological properties (Figure 2) [4]. To increase the die-cut performance, it is preferred to use high modulus and high dissipating SIS as a base polymer.

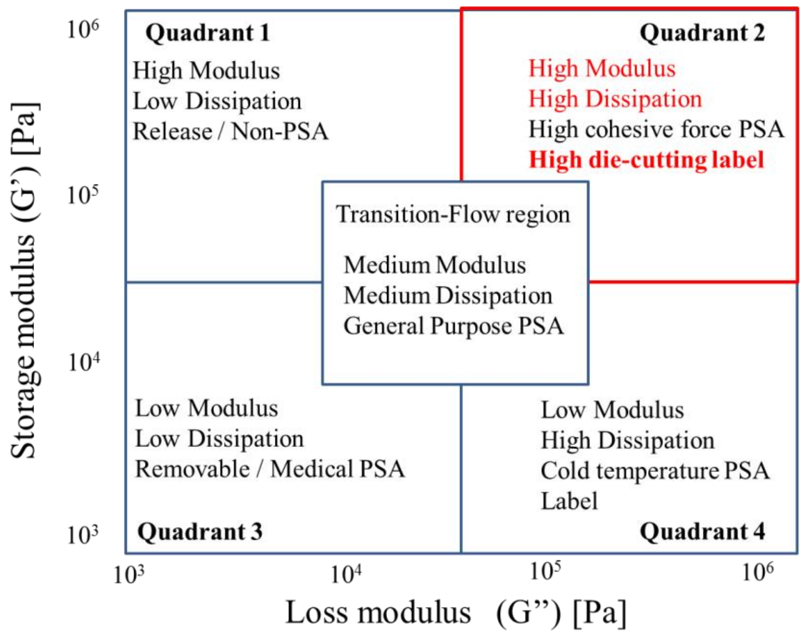


Figure 2 Viscoelastic Window (G' vs. G'')

Matrix stripping process is particularly important where high speed production is required. Regarding the processability, both lower elongation and lower tensile strength of SIS, that is, lower breaking energy (Figure 3) is needed to get good matrix stripping performance, when SIS is pulled at high speed.

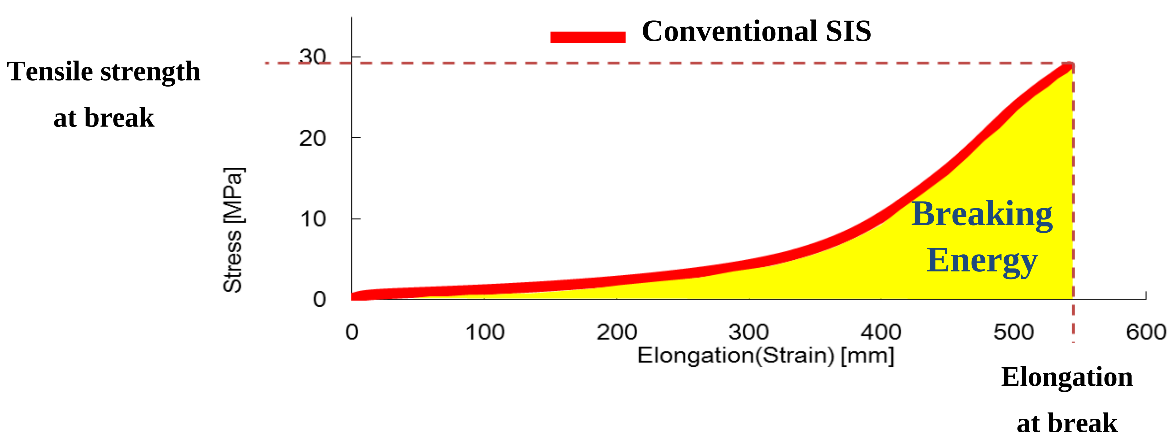


Figure 3 Image of breaking energy of SIS

If SIS is too easy to elongate, pulling a string of HMPSA is concerning issue that the adhesive stick to surface of a label face layer. As a result, it causes a problem that the adhesive on the face layer sticks to a back side of a release paper when a label sheet is rolled up. On the other hand, if a tensile strength of SIS is too high, an adhesive layer cannot be cut at matrix stripping process. Thereby, a label body is rolled up with an unnecessary matrix part and a yield gets worse.

This processability for matrix stripping process has not been explained by rheological properties, and any suitable evaluation method has not been found up in our study.

3. Purpose of this study :

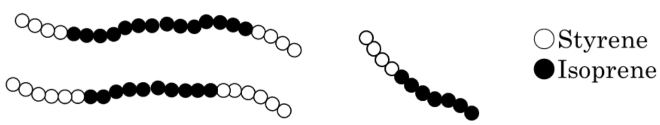
Purpose of this study is to develop a SIS block copolymer for HMPSA that can achieve both good adhesive performance and good die-cut performance for label application.

Table 1 shows correlation between each SIS designing factor and the physical or adhesive properties. Using SIS with high styrene content and high diblock content can improve a die-cut performance of HMPSA, because it give a high modulus and high dissipating HMPSA. However, such a design cannot minimize tensile strength and elongation of SIS. That is, it is impossible to achieve low breaking energy for good processability at matrix stripping process. For this reason, it is difficult to obtain HMPSA that is completely suitable for die-cut process.

In addition, if SIS with high styrene content is used to improve the die-cut performance, adhesive performances of a HMPSA tend to decrease as mentioned previously. It is difficult to achieve both good adhesive performance and preferable die cut performance when we merely adjust conventional SIS designing factors such as styrene content, SI diblock content, molecular weight, and number of arms etc. The purpose of this study paper is to solve this problem and to find a new SIS polymer design to be compatible both of performances.

Table 1 SIS designing factors for label application

SIS design factor	Physical Properties				Adhesive properties for Label			
	Tensile strength	Elongation	Modulus	Melt viscosity	Wettability	Oil migration	Cohesion	Die-cut performance
Styrene content	↗	↘	↗	↗	↘	↗	↗	↗
Molecular weight	↗	↘	↗	↗	→	→	↗	→
SI Diblock Content	↘	↗	↘	↘	→	→	↘	↗
Number of Arms	↗	↘	↗	↘	→	→	↗	→



SIS Tri-block SI Di-block

4. Results and discussions :

4.1. Idea for new SIS :

In order to solve the problem, it is considered necessary to introduce a SIS designing factor which is not known in common. We focused on the morphology of SIS. As mentioned, when SIS with high styrene content is used to improve die-cut performance, the breaking energy of the SIS increases. We thought that it might be due to the morphology of SIS.

Normally, SBC consists of polystyrene endblocks and the elastomeric midblock. They create a micro phase separation structure consisting of polystyrene domains and elastomeric matrix (Figure 4). The morphology of the two-phase structure depends on the ratio of endblock (polystyrene) and midblock (polyisoprene) (Figure 5). SBC of low styrene content forms a spherical structure of polystyrene domain. Their morphology can be observed by Transmission Electron Microscope (TEM). Generally, in the case of conventional SIS block copolymer containing polystyrene endblocks less than about 20% shows the spherical morphology. SIS with the spherical structure shows soft property. But in higher-styrene copolymers, a cylindrical or lamellar structure can be observed. They show harder property. If we controlled the morphology without restriction of styrene content, we could adjust mechanical properties of SIS and get new SIS polymer with small breaking energy even with high styrene content.

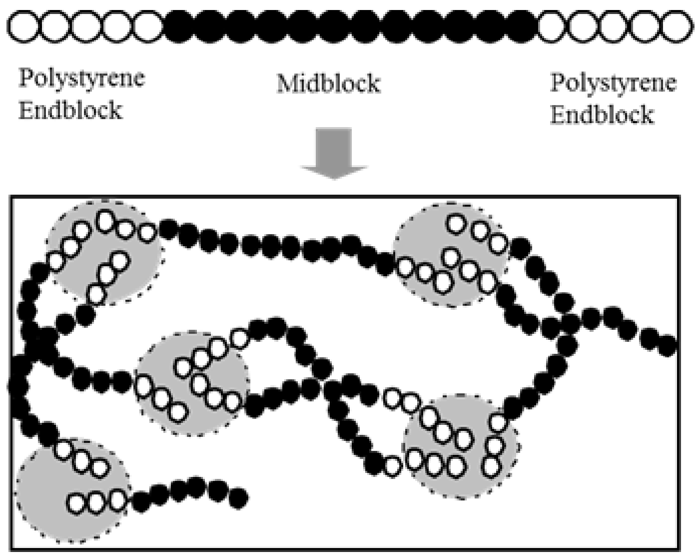


Figure 4　Image of SBC morphology (spherical styrene domain)

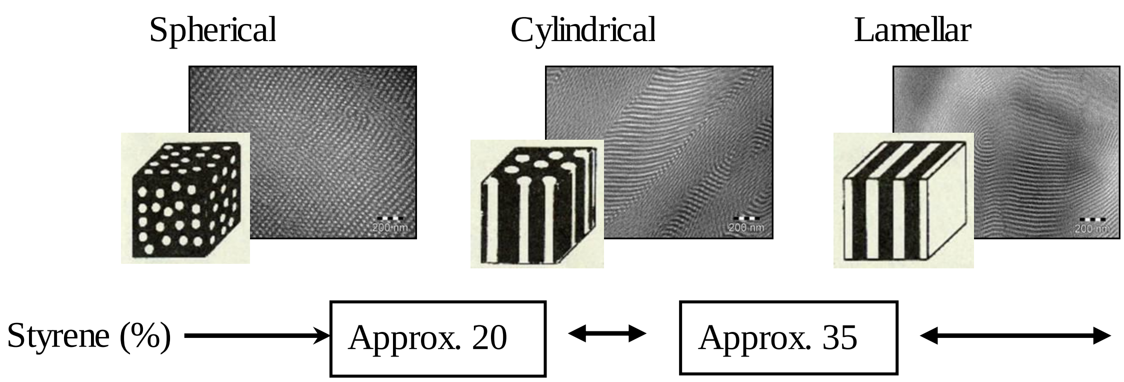


Figure 5　Typical morphology; conventional SIS block copolymers (TEM)

4.2. Asymmetric styrenic blocked SIS design :

We have studied new polymer design to form unique morphology. We reported a new key design factor “Asymmetric styrenic block’’ to control the morphology of SIS in PSTC2010.[5] Asymmetric styrenic blocked SIS block copolymer (hereinafter to as SIS’) is a triblock SIS copolymer with different polystyrene block length. A composition with asymmetric SIS’ and symmetric SIS block copolymer (hereinafter to as SIS) forms spherical structure and soft property even though it has high styrene content. The composition containing asymmetric SIS’ showed softer property than conventional symmetric SIS for the same styrene content (Figure 6).

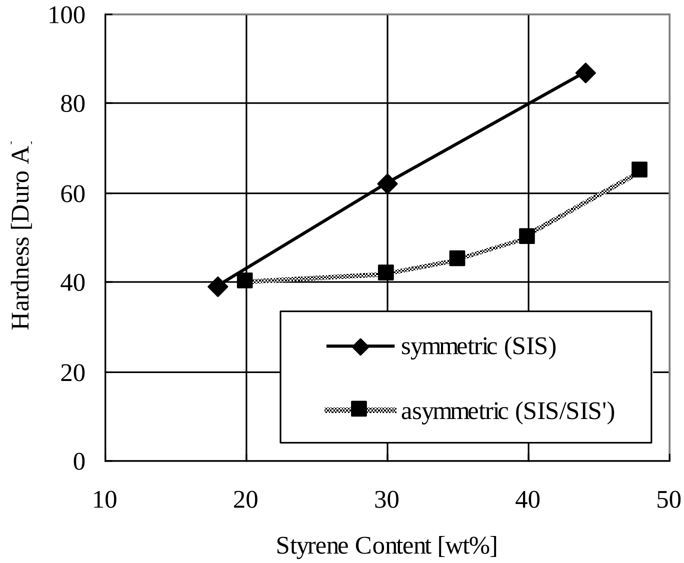


Figure 6 Hardness vs. styrene content.

In this study, to meet the requirements for label application, we studied a new composition with asymmetric SIS’. With our design concept, asymmetric SIS’ must be blended with SI diblock copolymer (hereinafter to as SI). An image of the new composition is shown in Figure 7. SI diblock copolymer gives high wettability to HMPSA and improves die-cut performance of die-cut sub-process.

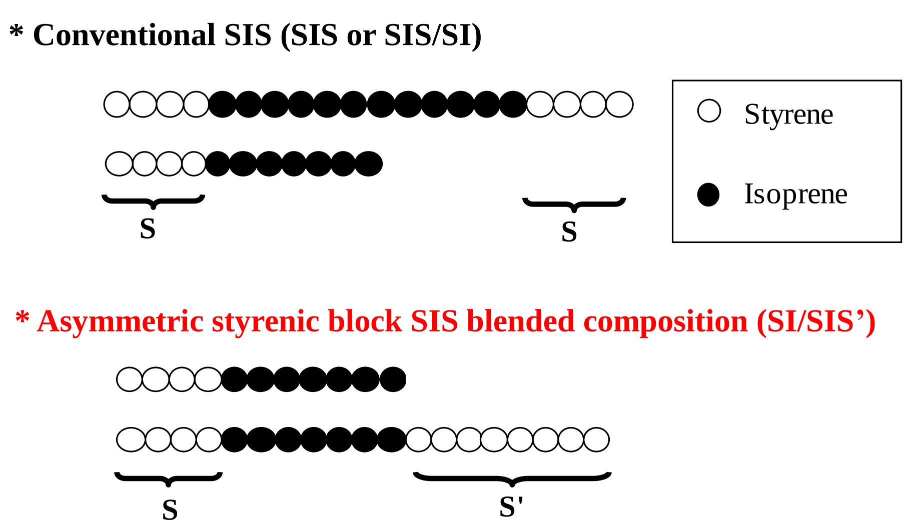


Figure 7 Designing concept of new asymmetric SIS’ composition for label application

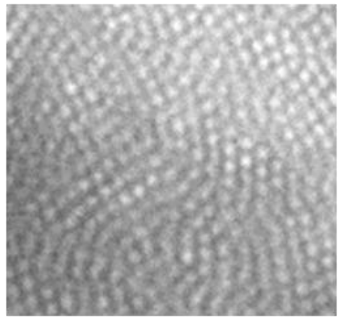
Then we developed a new prototype composition (SI and SIS' composition, QS-24). Table 2 shows polymer characteristics of QS-24 and conventional SISs for label application. This new composition has high styrene content (24%) and high SI diblock content (65%). However, QS-24 shows lower hardness than SIS-B that has the same styrene content. It indicates that the new composition containing asymmetric SIS' shows softer property than conventional SIS as we expected. It shows spherical structure by TEM although SIS-B shows cylindrical structure. (Figure 8)

Thus, we developed a new SIS composition for label application. It is expected not only to have high modulus and high dissipating property that comes from high styrene content and high diblock content, but also to show low breaking energy derived from spherical structure. That is, it is expected to show both high die-cut performance and good matrix stripping performance. In addition, it is expected to show good adhesive performance derived from its soft property and good anti-oil migration property derived from its high styrene content.

Table 2 Characteristics of conventional SIS and newly designed SIS composition

		SIS-A (Conventional)	SIS-B (Conventional)	**Prototype QS-24 (Asymmetric Styrenic SIS composition)**
Structure [1]		SIS/SI	SIS/SI	**SIS'/SI**
Styrene Content [2]	[%]	16	24	**24**
SI Diblock Content [3]	[%]	55	67	**65**
Hardness [4]	[Duro A]	26	34	**28**
Melt Flow Rate [5]	[g/10min]	12	20	**15**
Morphology [6]		Spherical	Cylindrical	**Spherical**

1) SI: Di-block copolymer, SIS: Tri-block copolymer, SIS': Asymmetric styrenic SIS
2) Abbe's refractometer
3) Gel Permeation Chromatography
4) ASTM D-2240 (Type A)
5) ASTM D-1238 (G condition 200degC)
6) TEM



Morphology of QS-24
(Styrene content = 24%)
Spherical structure

Figure 8 Morphology of new SIS composition (QS-24) with asymmetric SIS' structure

4-3. DMA study :

Figure 9 shows DMA charts of the conventional symmetric SIS and newly designed SIS composition, QS-24. Following three regions are generally confirmed in G' modulus curve of SIS.

(A) Decreasing of G' value due to a glass transition of polyisoprene block around -60 ˚C,

(B) Plateau region where SIS exhibits rubbery property,

(C) Decreasing of G' value due to a glass transition of polystyrene block around 100 ˚C,

In order to obtain good low temperature property, it is preferable that G' value drops sharply at region (A). Normally, this behavior depends on the styrene content and diblock content of SIS. It sharply decreases as the styrene content is lower and diblock content is higher.

The new composition QS-24 containing asymmetric SIS' shows interesting G' modulus curve. QS-24 shows sharp G' value drop compared to SIS-B having almost the same styrene content and diblock content. Although this is still under study, it is presumed that it is because QS-24 shows spherical structure and soft property whereas SIS-B shows cylindrical structure. Because QS-24 shows lower G' value at plateau region compared to SIS-B, G' value drops rapidly toward plateau region. This data shows that QS-24 exhibits softer property than conventional SIS, and suggests that high adhesive performance can be expected even at low-temperature.

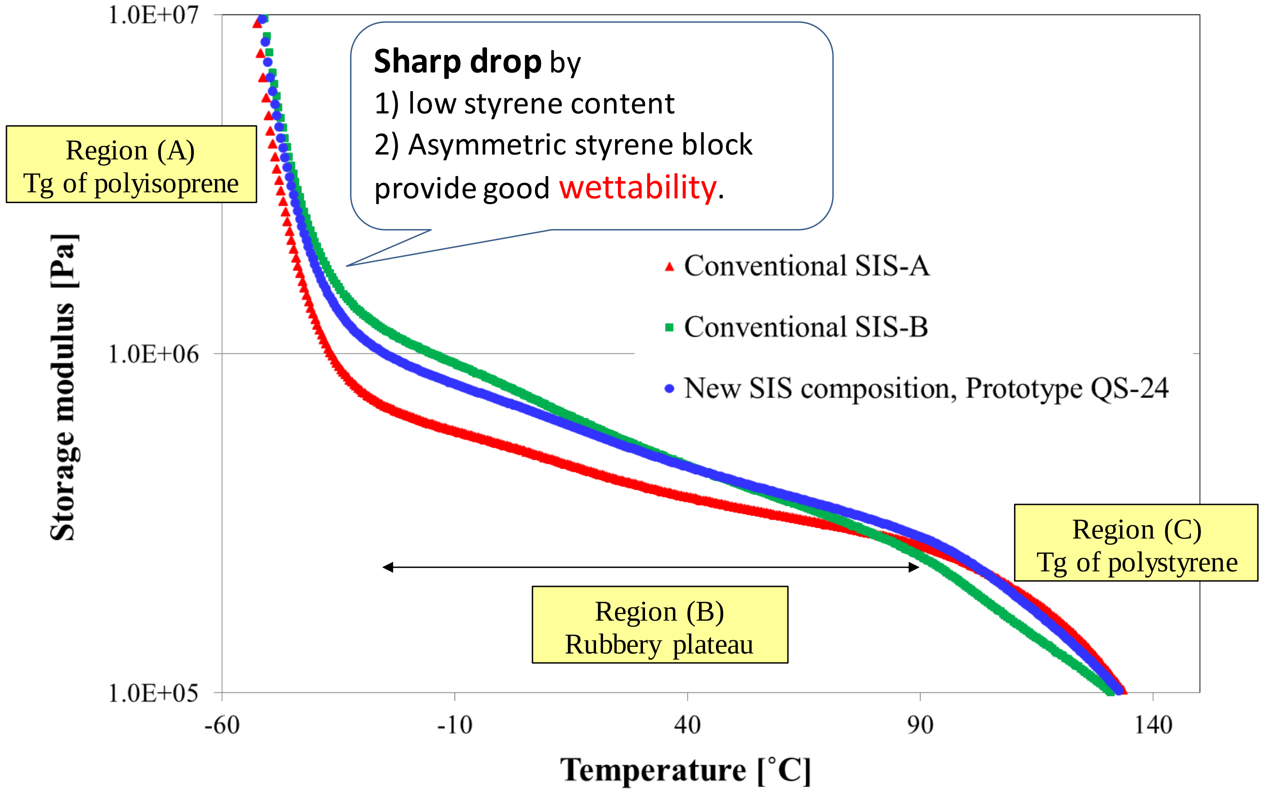


Figure 9 DMA curves of SIS block copolymers (10 rad)

4-4. Adhesive properties and anti-oil migration property :

Table 3 shows evaluation results of adhesive properties of the newly designed SIS composition (QS-24) and conventional symmetric SIS-A. Formulation-I (hereinafter to as F-I) is standard formulation, and Formulation-II (hereinafter to as F-II) is oil rich formulation. In F-I, SIS-A based formulation shows good tackiness because it has low styrene content and high diblock content. When compared in F-I, the QS-24 based formulation shows good tackiness as much as SIS-A based one.

This is considered to be because QS-24 shows soft property by forming spherical structure and suggests QS-24 is suitable for label application. Furthermore, it shows high holding power. It is considered to be due to relative high cohesive power derived from high styrene content. When QS-24 is formulated in oil rich formulation (F-II), the adhesive properties of F-II does not significantly decrease compared to that of F-I. Furthermore, Tg of the F-II is much lower than that of F-I. This result indicates that HMPSA formulation for low-temperature can be easily made by using newly designed SIS composition, QS-24.

In addition, it was confirmed that the QS-24 based HMPSA shows good anti-oil migration property. Figure 10 shows evaluation results regarding oil migration property of HMPSAs containing some types of SIS. QS-24 shows excellent anti-oil migration property almost equal to conventional SIS-B which has high styrene content. On the other hand, oil migration was remarkable in SIS-A with low styrene content. From this result, it was confirmed that QS-24 is suitable for oil rich formulation. Details of the oil migration test method are described in the appendices.

In conclusion, it was confirmed to be able to achieve both (1) good adhesive performance (especially good low-temperature performance can be expected.), and (2) good anti-oil migration property, by using newly designed SIS composition with asymmetric SIS, QS-24.

Table 3 Adhesive properties of conventional and newly designed SIS composition

		SIS-A (Conventional)		Prototype QS-24 (Asymmetric Styrenic SIS composition)	
Polymer Characteristies					
Structure and composition		SIS/SI		SIS'/SI	
Styrene Content	[%]	16		24	
SI Diblock Content	[%]	55		65	
Melt Flow Rate	[g/10min]	12		15	
Adhesive formulation 1)		I	-	I	II
Formulation type		standard	-	standard	Oil rich
Adhesive Properties					
Loop tack to SUS 2)	[N/25mm], @23 °C	20	-	20	17
Peel adhesion to SUS 3)	[N/m], @23 °C	650	-	580	530
Holding power to SUS 4)	[min.], @50 °C	90	-	280	160
Melt viscosity 5)	[mPa·s], @160 °C	16000	-	38000	30000
Tangent delta 6)					
Peak top	[°C]	2.0	-	4.9	-3.5

1) Formulation-I (Standard) : SIS / C5C9 Hydrocarbon Resin / Naphthenic oil = 100 / 150 / 50
Formulation-II (Oil rich) : SIS / C5C9 Hydrocarbon Resin / Naphthenic oil = 100 / 135 / 65
2) PSTC-16 Test method B (using loop tack tester, to Steel)
3) PSTC-101 Test method A, 180°Peel (to Steel)
4) PSTC-107 Procedure A (modified) (to Steel, 10X25mm, 1kg load)
5) Brookfield viscometer
6) By DMA, 10 rad.

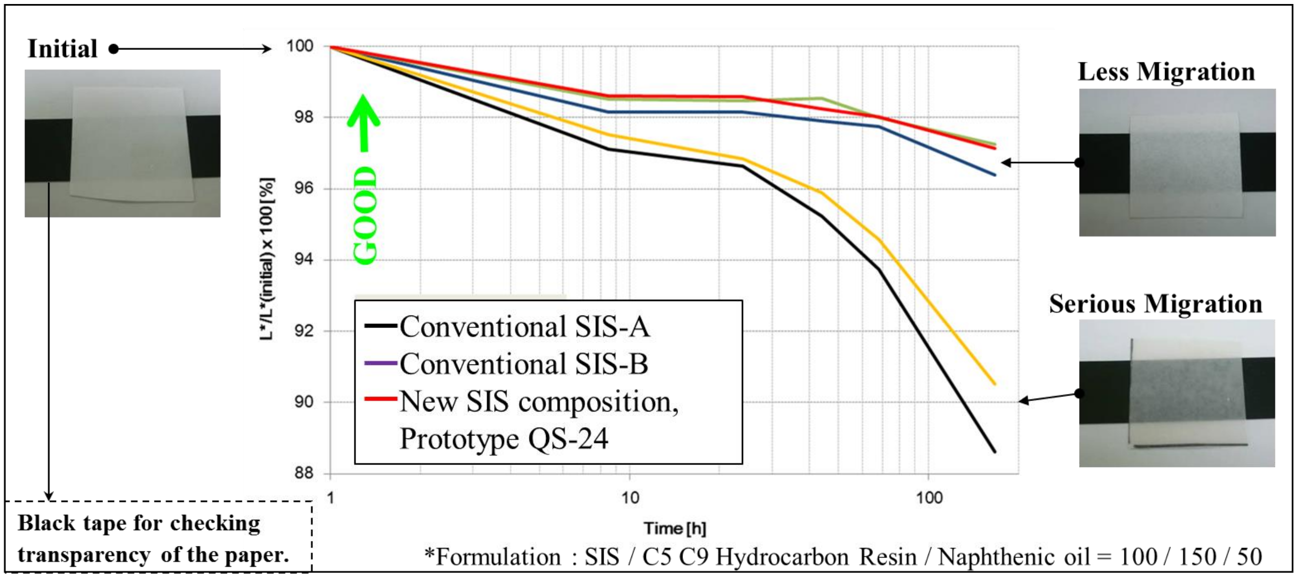


Figure 10 Oil migration test result of conventional SISs and a newly designed SIS composition

4.5. New evaluation method for die-cut property

Until now, we do not have an appropriate evaluation method for quantifying the matrix stripping property. For the reason, it is difficult to complete a design of new SIS with good matrix stripping property. Therefore, we tried to establish the new evaluation method. Matrix stripping process contains tensile break of a thin adhesive layer. As described previously, we thought that it is important that HMPSA has lower breaking energy. Therefore, we studied and developed a new alternative evaluation method using "High speed tensile test (HST) equipment (Figure 11). It can simulate the matrix stripping tensile break process with the maximum 100 (m/minute) speed like actual die-cut machine speed. Lower breaking energy shows better matrix-stripping performance in this test.

Figure 12 and Table 4 show HST test results of several SIS samples containing QS-24. Actually, there is high correlation between the breaking energy of SIS in this test and the actual die-cut speed in label production line.

By using this new evaluation method, we confirmed that newly designed asymmetric SIS compositions, for example QS-24, show quite lower breaking energy and better matrix stripping property than conventional SISs. Thus, we succeeded in developing SIS which has high styrene content but low breaking energy. The QS-24 based HMPSA shows both good die-cut performance as well as preferable matrix stripping performance.

Figure 11　High speed tensile test (HST) equipment

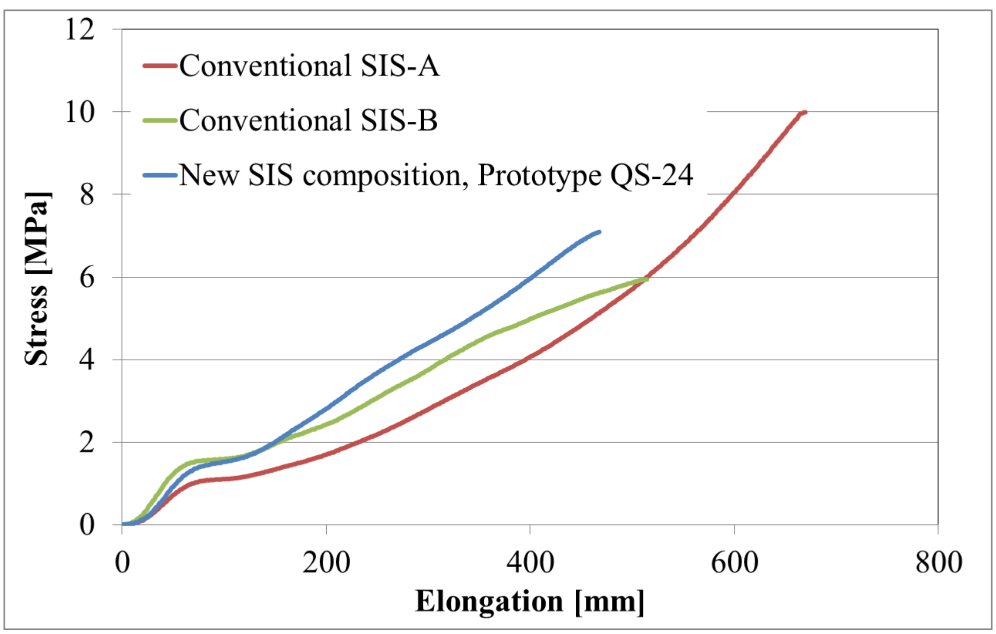


Figure 12　Results of HST test (23 ˚C)

Table 4 Results of HST test (23 ˚C)

	Tensile strength [MPa]	Elongation [mm]	Breaking Energy [N/mm]	Actual machine Speed Ranking
Conventional SIS-A	9.5	660	2530	3
Conventional SIS-B	6.0	520	1670	2
New SIS composition, Prototype QS-24	**6.8**	**460**	**1570**	**1**

5. Conclusion :

Asymmetric SIS composition shows unique morphology. Although it has high styrene content, it forms spherical structure and becomes soft material. We confirmed that we can obtain HMPSA satisfying all of requirements below for label application by using the asymmetric SIS composition.

i) Good adhesive performance (including low-temperature performance),
ii) Good anti-oil migration property,
iii) High speed die-cut performance

These can be achieved with a simple formulation without using any other special materials. We have completed the design of new SIS composition by developing a novel method for quantifying the matrix stripping property which was difficult to quantitatively evaluate in the past.

6. Appendices :

Anti-oil migration test method is as follows.
In this evaluation, firstly, each adhesive sample is coated on a transparent PET substrate. Next, the PSA sheet is pasted to a white copy paper. Subsequently, a load of 2 kg is applied per A4 size laminated sheet (the size is close to letter size). The sample with load applied is left in an oven at 80 °C. After a certain period of time, take the sample and measure lightness (L *) of the copy paper by color-difference meter.

“L*(after aging) / L*(Initial) ratio” value is an indicator of oil migration.

When there is little oil migration to the paper, the L* value hardly decreases from initial value, and L*(after aging) / L*(Initial) ratio is kept at almost 100%. When there is a lot of oil migration, the L* value of the paper significantly decreases and L*(after aging) / L*(Initial) ratio intensely decreases.

7. 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.

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[5] Sadaharu, H., “Newly designed SIS block copolymers for pressure sensitive adhesives (PSA)’’, PSTC Technical Seminar Proceedings, 2010

8. Acknowledgement :

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