Mechanical Properties of Acrylic Block Copolymer PSAs

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Abstract
The styrene block copolymer (SBC) is widely used as a main component polymer of a pressure sensitive adhesive. A non-solvent coating is possible for this pressure sensitive adhesive by using an extruding machine. However, the SBC pressure sensitive adhesive has the following disadvantage.
(1) Since SBC is a non-polar polymer, the tackifier that can be used is restricted.
(2) The heat resistance of a pressure sensitive adhesive is bad because of a styrene domain.
The acrylic block copolymer (MAM) is marketed in order to eliminate these disadvantages. Since the methacrylate forms the domain, the softening point of MAM is higher than SBC about 10°C. However, MAM is also a block polymer, the temperature dependency of an adhesive property is severe.
Then, we studied the temperature / peel speed dependability of the MAM pressure sensitive adhesive. As for the used pressure sensitive adhesive, an acrylic oligomer and a rosin derivative tackifier are blended with a MAM polymer. Investigation was accomplished by using the rolling tack tester. Activation energy was calculated by Arrenius-plot method with changing rolling rate and temperature.
From the investigations, it becomes clear that the activation energy of these pressure sensitive adhesives is about 34 Kcal/mol. Moreover, activation energy decreased with the amount of tackifiers.

Keywords:
acrylic block copolymer, tackifier, oligomer, rolling tack, time-temperature superposition, shift factor, activation energy,
1. Introduction
PSA tapes are used in various applications such as electrical insulation, surface protection, nameplate adhesives, medical care, and household uses. Usually, they are used for the purpose of long term holding or securing in position in each field. Accordingly, the adhesion of the tape should be evaluated over the time schedule suitable for each application purpose and service condition. The actual measurement, however, is commonly made over a shorter time range than the actual service time due to the limitations of the testing apparatus or a measuring time limit. Moreover, in order to enhance the reproducibility of the test data, the tests are conducted at one point under the strictly limited, specific conditions typically regarding the shape of test specimens, temperature and rolling rate.

However, if the adhesion was measured over the time expanded to the length of multi orders to obtain data in a time spectrum, the properties of the tape could be safely predicted for a longer time range or very short time range corresponding to the actual application conditions through extrapolation from the actual measurement into the shorter or longer time area. Eventually, the total characteristics of a PSA tape may be perceived with the aid of one spectrum.

The test method for adhesion, such as 180° peel force, also includes another problem in that measurement is carried out in the presence of the backing. In the case of double-coated tapes, a test specimen is lined with polyester film or similar for measurement. Conventional studies made concerning the effect of the backing on adhesion, prove that the adhesion is greatly affected by thickness and Young's modulus of both the adhesive and the backing.

For such reasons, it is difficult to define the original characteristics of PSA tape from the measurement of the velocity spectrum of adhesion because the effect of the backing on adhesion depends on the peeling rate.

Therefore, in order to analyze the original characteristics of the pressure-sensitive adhesive, it is necessary to evaluate the properties of the adhesive alone, and then to evaluate them using a PSA tape to include the effect of the backing.

For these purposes, the rolling friction or rolling adhesive moment of the pressure-sensitive adhesive or a PSA tape is determined over a wide range of rolling rates by rolling a ball or cylinder in contact with the adhesive surface.

The rolling tack of acrylic block copolymer PSAs over a wide range of rolling rates and temperature were measured by using the cylinder tack tester, and the activation energy of the rolling tack for different adhesive compositions was investigated. This paper reports the relation between the velocity spectrum of the rolling tack and the activation energy of acrylic block copolymer PSAs.

2. Experimental

2.1 Cylinder Type Rolling Tack Tester

figure 1 is a schematic diagram of the rolling tack tester. The rolling cylinder for measuring the rolling adhesive moment is adjusted to be neutral (0) in weight with the aid of the balance weight fixed just past
the fulcrum. The cylinder can then be loaded as required by additional weights. The PSA tape is applied to a flat table with the surface to be measured facing out, and the flat table is pulled at a constant rate. The cylinder loaded with an additional weight is placed on the adhesive face. The cylinder is rotated on the adhesive by pulling the flat table. At this time, the rolling tack of the cylinder generated by adhesion is detected by the load cell. The rolling cylinder is made of stainless steel (SUS 304), 20mm width, 10mm diameter, and its surface roughness Ra equal to about 0.5µm. This study of the rolling tack is conducted by rolling a steel cylinder, 10mm in diameter, 20mm in width, to which a weight of 100 g is added, at temperatures of 25, 40, 60, 80°C and at a rate ranging from 0.1 to 300 mm/s.

2.2 Glass Transition Temperature (Tg) of Pressure-Sensitive Adhesives
Glass transition temperatures of pressure-sensitive adhesives were calculated by tan δ temperature spectrum. Tan δ was measured at 10 Hz and 0.25% strain by using Viscoelastic Spectrometer Model DVA-200 (ITK Co. Ltd).

2.3 Materials
The materials used for this research are shown in Table 1. Mixtures of triblock acrylic copolymer (MAM) and diblock acrylic copolymer (MA) are used for PSA base polymer.

· Acrylic Block Copolymer
MAM and MA are acrylic block copolymers, which were developed by Kuraray Co., Ltd\(^{12}\). These polymers are polymerized by using a unique anionic living polymerization system. In this living anionic polymerization system, the acrylic block copolymers were sequentially polymerized. The SEC curve is showed in figure 2. The first PMMA block and the diblock copolymer have very narrow molecular weight distribution, even in the triblock copolymer (Mw/Mn=1.1-1.3). In the final triblock copolymer, any diblocks or MMA portions have not been detected. The TEM photo of Figure 2 also shows that MAM has a well-defined structure. The sample was stained with phosphotungstic acid. The micro phase separation is very clear and the sample shows cylindrically ordered dark PMMA micro domains with an approximate size of diameter 10-20nm in light PBA matrix.

2.4 Test Specimens
As shown in Table 2, using 8 kinds of MAM/MA/oligomer/Tackifier PSAs, transfer type adhesives of 50 µm in thickness were prepared as test specimens for measuring rolling tack.

3. Results and Discussion
3.1 Analysis Method
Figure 4 shows the rolling tack velocity spectrum of PSA-1 at temperatures of 25, 40, 60, and 80°C. The abscissa axis indicates the rolling rate and the ordinate axis indicates the rolling tack. As shown in figure 4, the rolling tack of the PSA-1 simply increases at rolling rates over 300 mm/s. The stick-slip phenomenon was not seen in the range of these pulling rate and temperature. The peak tack value was
shown on condition of 300mm/s and 25°C, and the value was 2.8N/20mm.

**· Time-Temperature Superposition**

Accordingly, it follows that the time-temperature superposition principle usually applicable to the mechanical properties of amorphous high polymers like rubber will also be applicable to the rolling tack of pressure-sensitive adhesives. Figure 5 presents the master curve of the rolling tack drawn by shifting the tack value at each temperature shown in figure 4 with reference to the 25°C curve and superpositioning them.

The shift factor in this process is shown as white circles in figure 6.

Supposing that the shift factor is to be an Arrehnius type, activation energy $\Delta H$ is calculated from equation (2). Calculated $\Delta H$ of PSA-1 was 22.2 kcal/mol.

$$\ln a_T = \frac{\Delta H}{R} \left( \frac{1}{T} - \frac{1}{T_g} \right)$$ 

$$\Delta H = 2.303R \frac{d \log a_T}{d \left( \frac{1}{T} \right)}$$

The adhesion is a composite of interfacial chemical behavior where the pressure-sensitive adhesive face wet the adherend, and viscoelastic behavior where the peel force is distributed by deformation of the pressure-sensitive adhesive bulk. Here, as for the viscoelastic properties, the time-temperature superposition principle is applicable to those properties because the adhesive is an amorphous high polymer. As shown in figure 7 and mentioned before, the principle is applicable to the rolling tack; consequently it follows that the viscoelastic properties of the adhesive make a great contribution to adhesion.

**· Activation Energy Calculated from WLF Equation**

The broken line in figure 6 is obtained from the Williams, Landel, and Ferry time-temperature superposition principle, where the shift factor $a_T$ is given by equation (3)

$$\log a_T = \frac{-C_1(T - T_g)}{C_2 + T - T_g}$$

where $C_1$ and $C_2$ being constants. For simplicity, the glass transition temperature $T_g$ of the adhesives is employed here as a reference temperature, so that $C_1$, $C_2$ take the values 17.4 and 51.6°C.

Measured $T_g$ of PSA-1 is –27.3°C, from the equation (3) and (2), calculated $\Delta H$ of PSA-1 was 29.3 kcal/mol.

**· Reduced Temperature**

On the basis of this shift factor, the rolling rate equivalent to each set temperature for the rolling tack at a rolling rate of 5 mm/s was obtained and is shown in figure 7. Thus, it is found that the rolling rate of 100 mm/s corresponds to 0°C at a rolling rate of 5mm/s.

According to the results mentioned above, it can be said that the rolling tack over a wide temperature
range from -10°C to 100°C are available from the velocity spectrum of the rolling tack over rolling rates ranging from 0.1 to 300 mm/s at temperatures of 25, 40, 60, and 80°C. 

3.2 Rolling Tack of PSA Containing a Tackifier (PSA-6)

Figure 8 shows the rolling tack velocity spectrum of PSA-6 at temperatures of 25, 40, 60, and 80°C. As shown in figure 8, the rolling tack of the PSA-6 shows the complicated behavior. The stick-slip phenomenon of this pressure sensitive adhesive appeared in the peculiar pulling rate range at a given measurement temperature. The peak tack value was shown on condition of 3mm/s and 25°C, and the value was 7.5N/20mm.

Figure 9 presents the master curve of the rolling tack drawn by shifting the tack value at each temperature shown in figure 8 with reference to the 25°C curve and superpositioning them. Calculated $\Delta H$ from equation (2) of PSA-6 was 34.1 kcal/mol.

From figure 9, it becomes clear that the stick-slip phenomenon of this PSA appears in the velocity range from 0.02 to 4mm/s at 25°C. The stick-slip phenomenon has taken place at very low velocity. It is a very unique pressure sensitive adhesive.

3.3 Rolling Tack and Activation Energy

Figure 10 shows the 2D counter plot of the peak value of rolling tack of PSAs. From the figure 10, it becomes clear that the tack value depends on the amount of tackifier greatly. It has maximum in 10% of oligomer. If the amount of oligomer increases further, a tack value will decrease.

Figure 11 shows the 2D counter plot of activation energy $\Delta H$ of PSAs.

The relation between activation energy $\Delta H$ and rolling tack is shown in figure 12. The correlation coefficient is 0.96; consequently, from the fact that the activation energy and rolling tack show high correlation, this activation energy makes a great contribution to the rolling tack.

4. Conclusion

Using the acrylic block copolymer pressure-sensitive adhesives, the rolling tack is determined by the cylinder type rolling tack tester over rolling rates ranging from 0.1 to 300 mm/s, at temperatures of 25, 40, 60, and 80°C. As a result, the following have been made clear:

1. The time-temperature superposition principle usually applicable to the mechanical properties of amorphous high polymers like rubber will also be applicable to the rolling tack of pressure-sensitive adhesives. Furthermore, the effect of temperature over a wide temperature range from -10°C to 100°C can be predicted from the profile of the velocity spectrum of the rolling tack.

2. The correlation coefficient between activation energy $\Delta H$ and rolling tack is 0.96; consequently, from the fact that the activation energy and rolling tack show high correlation, this activation energy makes a great contribution to the rolling tack.
Literature Cited
2) TEST METHODS FOR PRESSURE SENSITIVE TAPES PSTC-3.
3) D. Satas and F. Egan, Adhesive Age, 9, [8], 22(1966).
Figure 1. Cylinder Type Rolling Tack Tester

Table 1. Materials

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<tr>
<th>Copolymer MAM</th>
<th>PMMA/PBA/PMMA</th>
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<td>Tackifier</td>
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Figure 2. SEC trace of MAM, MA and the precursors

Figure 3. Morphology of MAM
Table 2. Test Specimen

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![Graph](image-url)  

**Figure 4.** Rolling Tack Velocity Spectrum of PSA-1 at Various Temperatures
Figure 5. Time-Temperature Superposition of PSA-1

Figure 6. Shift Factor of PSA-1 Evaluated from Rolling Tack
Figure 7. Reduced Temperature of PSA-1

Figure 8. Rolling Tack Velocity Spectrum of PSA-6 at Various Temperatures
Table 3. Test Results

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Figure 9. Time-Temperature Superposition of PSA-6 and Reduced Temperature
Figure 10. 2D Counter Plot of Peak Value of Rolling Tack

Figure 11. 2D Counter Plot of Activation Energy $\Delta H$
Figure 12. Activation Energy $\Delta E$ vs. Peak Value of Rolling Tack