

Effects of Miscibility on Peel Strength of Natural-Rubber-Based Pressure-Sensitive Adhesives

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ABSTRACT: Natural rubber (NR) was blended in various ratios with 29 kinds of tackifier resins, which were prepared from rosin, terpenes, and petroleum. Miscibilities of all the blend systems were illustrated as phase diagrams. From these blend systems, we selected 7 systems having typical phase diagrams [completely miscible, completely immiscible, and lower critical solution temperature (LCST) types] and carried out measurements of peel strength. Peel strength was measured at the angle of 180° at 20°C over the wide range of pulling rates. In the case of pressure-sensitive adhesives (PSAs), which showed phase diagrams of the completely miscible or LCST type, the peak positions in the pulling rate–peel strength curves shifted to the lower velocity as the tackifier content increased. On the contrary, completely immiscible PSAs had a smaller peel strength than miscible ones and did not give manifest shift of peaks. In most of the adhesives, the fracture mode changed from cohesive failure to interfacial failure (between adhesive and adherend), slip-stick failure, and glassy failure (between the tape and adhesive) as the pulling rate increased. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 777–784, 1998

Key words: natural rubber; tackifier; miscibility; pressure-sensitive adhesive; peel strength

INTRODUCTION

Pressure sensitive adhesive (PSA) tapes can paste on various adherends under light pressure in a very short time without heating or heavy pressure. The bonds formed are strong enough to use for temporary adhesion. Removable PSA tapes and paste-removable pastes can be pasted and removed many times, and the adhesive is not left on the adherend.¹ Because PSAs are very convenient, as described above, they are often

used in many fields. PSA products, such as tapes and labels, are utilized not only in the packaging, printing, medical, electrical, and automobile industries² but also in our daily life. Especially, natural-rubber (NR)-based PSAs have been widely used, and they have a very long history. Recently, acrylic polymers and some kinds of block copolymers come to be used more and more,³ but NR is still used in the greatest deal of all of the PSAs in Japan and cannot be completely replaced by acrylic polymers.

Because NR alone is not sufficient to provide the required adhesion and tack, it is necessary to blend tackifier resins (for example, aliphatic or aromatic hydrocarbons, polyterpenes, and rosin

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Table I Tackifiers Used for Measurements of Peel Strength

Phase Diagram	Raw Materials	Commercial Names of Tackifiers	T_g ($^{\circ}\text{C}$) ^e	M_n ^f	Main Components
Completely miscible	Rosin or terpenes	Estergum HP ^a	54.4	685	Pentaerythritol ester of hydrogenated rosin ^g
		Superester A-75 ^a	46.6	682	Disproportionated rosin esterified by glycerol, diethyleneglycol ^g
LCST	Petroleum	ESCOREZ 1102 ^b	50.3	1283	Aliphatic resin, polymerized C5 ^h
	Rosin or terpenes	Clearon K-4090 ^c	41.8	793	Hydrogenated terpene resin ^g
Completely immiscible	Petroleum	ESCOREZ 5320 ^b	75.2	395	Hydrogenated petroleum resin ^h
	Rosin or terpenes	Polypale ^d	60.2	442	25% Polymerized rosin ^g
	Petroleum	Kristalex 1120 ^d	68.1	873	Polymer from pure aromatic monomer ^g

^a Offered by Arakawa Chemical Industry Co., Ltd. (Osaka, Japan).

^b Offered by TONEX Co., Ltd. (Kawasaki-shi, Japan).

^c Offered by Yasuhara Chemical Co., Ltd. (Fuchu-shi, Hiroshima, Japan).

^d Offered by Hercules Co., Ltd. (Wilmington, DE, U.S.A.).

^e By differential scanning calorimetry (DSC) measurements.

^f By gel permeation chromatography measurements.

^g Quoted from catalog.

^h By infrared and nuclear magnetic resonance measurements.

derivatives) with NR in order to improve its wettability to the adherend and to achieve rapid and effective bonding. At specific blend ratios, the rubber-resin blends become PSAs, while at other concentrations, they do not have adequate performances as PSAs. It is necessary for obtaining PSAs with good performance to select proper tackifiers and their proper concentrations for NR. As generally admitted, PSA performances, such as peel adhesion, tack, and shear creep resistance, depend strongly on viscoelastic properties of the adhesives.⁴⁻⁶ Moreover, miscibility between the components is one of the key factors in proper selection because it has a great influence on practical performances of PSAs. Therefore, it is very important to clarify the relationship between miscibilities, internal structures, viscoelastic properties, and performances of PSAs systematically. However, there are few studies about the effect of miscibility on PSA performances.

We investigated miscibilities between NR and 29 kinds of tackifiers, which were prepared from rosin, terpenes, and petroleum, and illustrated the miscibilities as phase diagrams.^{7,8} We selected 7 blend systems having typical phase diagrams [completely miscible, completely immiscible, and lower critical solution temperature

(LCST) types] among them and measured the probe tack and peel strength.

We reported the effects of miscibility of NR-tackifier blends on probe tack in the previous article.⁹

Peel strength is important and the most basic index to evaluate the force of adhesion. In this article, effects of miscibility of PSA components on peel strength are discussed.

EXPERIMENTAL

Natural rubber (NR) was blended with each tackifier in toluene solutions in 9 different solute weight ratios (9:1-1:9). The tackifiers used for measurements of peel strength are listed in Table I.

PSA sheets for the peel strength tests were prepared by coating these solutions on corona-treated polyethylene terephthalate (PET) film of 25 μm thickness, using our laboratory coating device. The thickness of the PSA layer was adjusted to 20 μm by a film thickness gauge. The PSA sheets thus obtained were air-dried at room temperature for 48 h and then dried in a vacuum oven at 40 $^{\circ}\text{C}$ for 48 h. Dried PSA sheets were

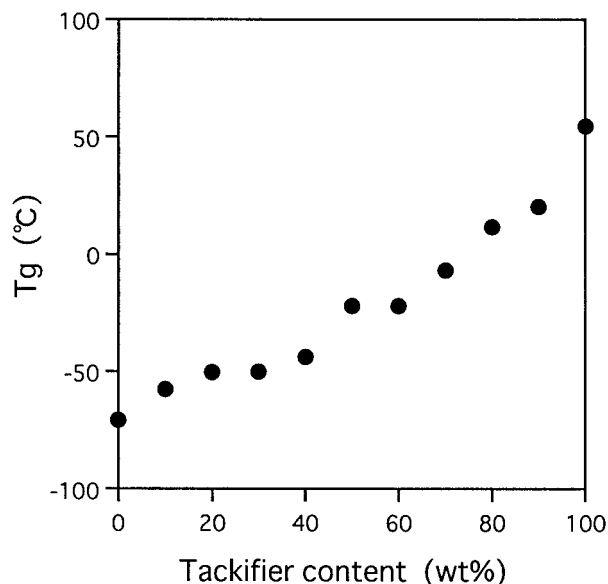


Figure 1 Tg-composition curve of NR-Estergum HP blends.

pressed onto release coating paper using a 2-kg roller. The sheets were seasoned at 20°C and 65% RH for more than 14 days and then cut into strips with a width of 1 cm. In this study, aluminum plates were used as adherends, which were cleaned with toluene beforehand. The PSA tape was pressed on the aluminum plate by the 2-kg roller passing over twice. The specimens were seasoned at 20°C and 65% RH for at least a month before measurements. The 180° peel strength of the PSA tapes was measured by Pulling cylinder tack tester (Sun Science Co., Ltd.) at the pulling rate of 0.5–14000 mm/min at 20°C.

The glass transition temperatures ($T_{g,s}$) of the blends were determined by DSC as described previously.⁹

RESULTS AND DISCUSSION

NR-Estergum HP blends were miscible at any temperature and tackifier content in the experimental range; that is, this blend system was completely miscible. And each blend of this system exhibits single Tg, depending on the tackifier content, as shown in Figure 1, which is an evidence of miscibility of this system. Peel strength of NR-Estergum HP blends is plotted against the pulling rate in Figure 2. The peak position of the peel strength curve shifts to the lower pulling rate as the tackifier content increases. This tendency is

not so clear in the region of tackifier content under 40%, whereas the peak shifts an order of magnitude from the tackifier content of 60 to 70%. Aubrey and Sherriff⁴ showed that the peak shift in the peel force of NR-based PSAs became rapidly larger as the tackifier content increased in the figures. The maximum peel strength of this system is about 700 gf/cm. The NR-Estergum HP blends containing 80 and 90% of tackifier did not show any stickiness (peel strength 0). The peeling modes of these PSAs are depicted in Figure 3. PSAs of this system give cohesive failure (in the bulk of the adhesive) and slip-stick failure (alternate failure of adhesive and glassy) over the wide range of pulling rate. The region of adhesive failure (failure between the adhesive and adherend) is small.

The phase diagram of NR-Clearon K-4090 system was the LCST type with a critical temperature at 61°C,⁷ but all of the blends were miscible at 20°C. These blends also showed single Tgs. The peel strength of NR-Clearon K-4090 blends is shown in Figure 4. At the tackifier content over 40%, there is a peak in the range of experimental velocity, and the peak tends to shift to the lower velocity as the tackifier content increases. The blends containing 10–40% tackifier probably have the maxima of peel strength at the higher velocity than the experimental range. In the low velocity region, there is an inclination that the peel strength becomes larger with increasing

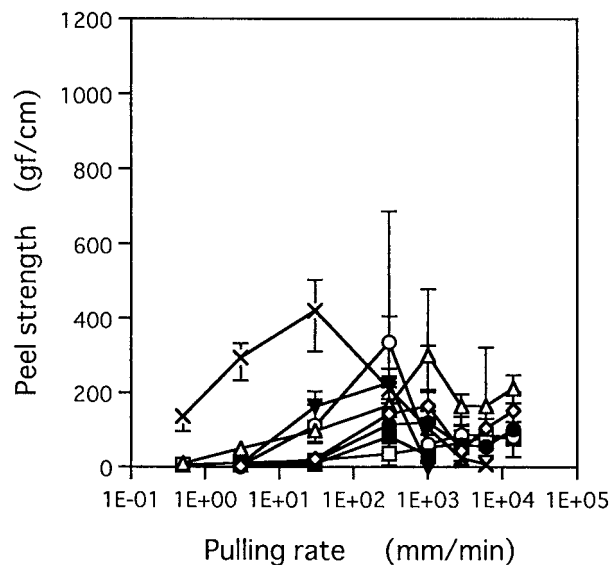


Figure 2 Peel strength of NR-Estergum HP blends at 20°C. Tackifier content: (□) 0%, (◇) 10%, (●) 20%, (△) 30%, (■) 40%, (○) 50%, (▼) 60%, and (×) 70%.

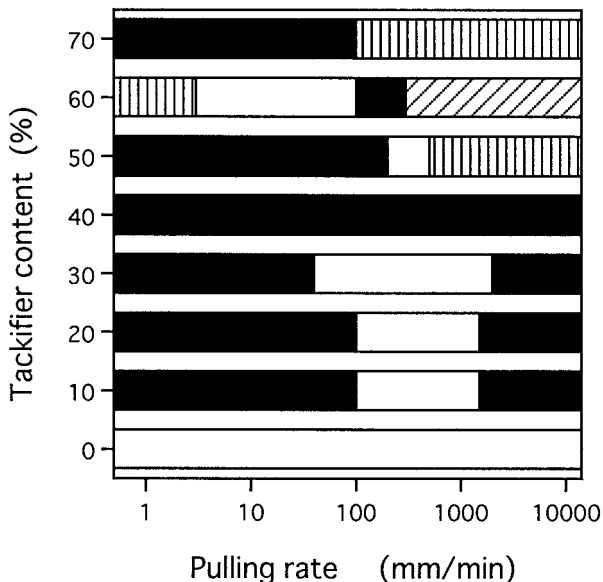


Figure 3 Peeling modes of NR-Estergum HP blends. ■, Cohesive failure; □, adhesive failure (between the adhesive and the aluminum); ▨, slip stick; ▩, glassy failure (between the tape and the adhesive).

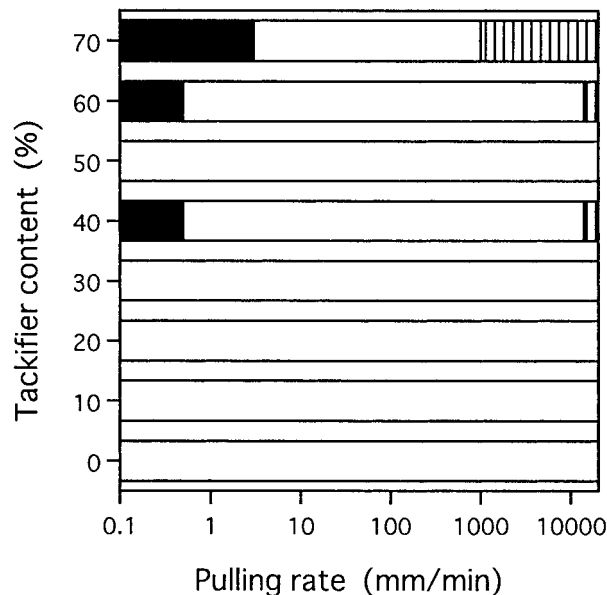


Figure 5 Peeling modes of NR-Clearon K-4090 blends. ■, Cohesive failure; □, adhesive failure (between the adhesive and the aluminum); ▨, slip stick; ▩, glassy failure (between the tape and the adhesive).

tackifier content. The maximum peel strength of NR-Clearon K-4090 system is larger than that of NR-Estergum HP system. The fracture modes of NR-Clearon PSAs are shown in Figure 5. The PSAs of this system show a wide range of interfacial failure (adhesive failure), which is a desir-

able feature as PSAs. The fracture mode generally changes from cohesive failure to adhesive, slip-stick, and glassy failure (fracture between the tape and the adhesive) as the pulling rate increases.⁴ The region of interfacial failure tends to be smaller as the tackifier content increases. For the blend containing 70% of Clearon K-4090, the peaks of the peel strength at 3 and 1000 mm/min in Figure 4 correspond to the transition from cohesive to adhesive failure and that from adhesive to slip-stick failure, respectively. The blend containing 60% of the tackifier has a peak at 6000 mm/min, which is perhaps attributable to the transition from adhesive failure to slip-stick failure.

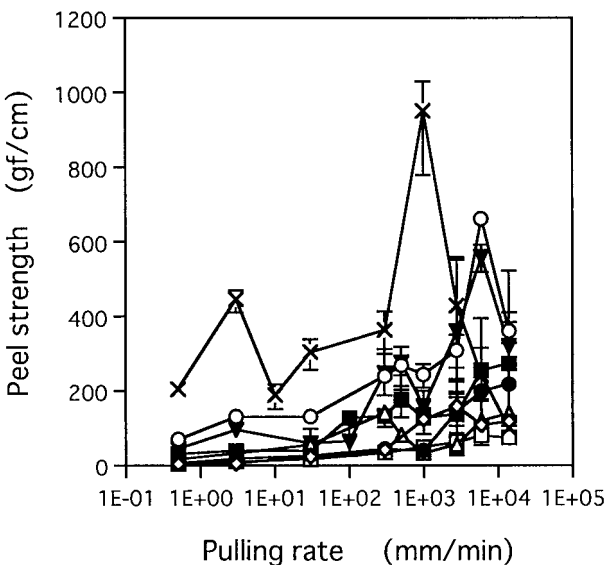


Figure 4 Peel strength of NR-Clearon K-4090 blends at 20°C. Tackifier content: (□) 0%, (◇) 10%, (●) 20%, (△) 30%, (■) 40%, (○) 50%, (▼) 60%, and (×) 70%.

The NR-ESCOREZ 5320 system had a phase diagram of the LCST type with a critical temperature at 56°C,^{8,9} though the blends were miscible at 20°C. These blends also showed single T_gs. The peel strength-pulling rate curves of NR-ESCOREZ 5320 blends are shown in Figure 6. In this PSA system, too, the peak is apt to shift to the lower velocity, and the peel strength in the low pulling rate region becomes larger as the tackifier content increases. The peak shift toward a lower velocity with increasing tackifier content is the characteristic of all the miscible PSAs, which is attributable to the elevation in T_g.¹⁰ The

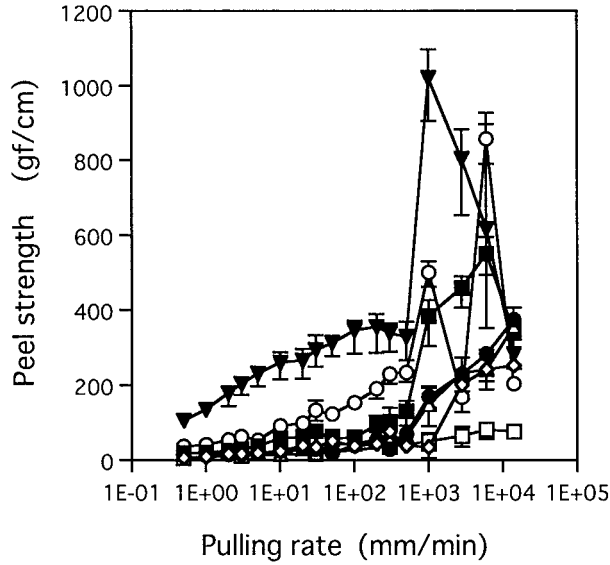


Figure 6 Peel strength of NR-ESCOREZ 5320 blends at 20°C. Tackifier content: (□) 0%, (◇) 10%, (●) 20%, (△) 30%, (■) 40%, (○) 50%, (▼) 60%.

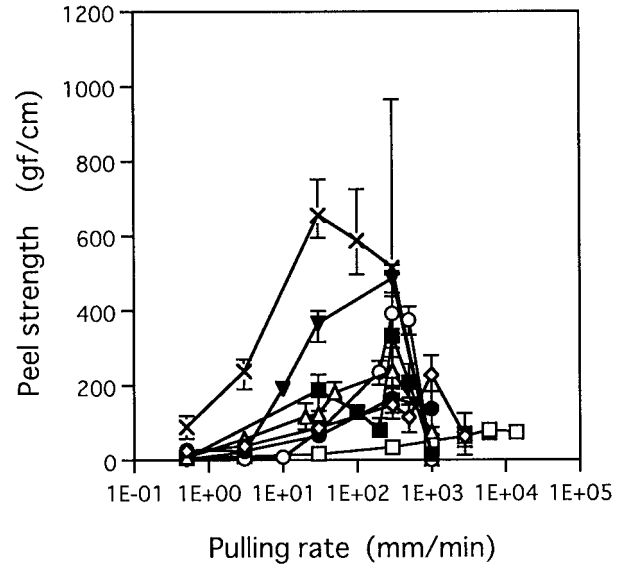


Figure 8 Peel strength of NR-ESCOREZ 1102 blends at 20°C. Tackifier content: (□) 0%, (◇) 10%, (●) 20%, (△) 30%, (■) 40%, (○) 50%, (▼) 60%, and (×) 70%.

blends containing 70% or more of ESCOREZ 5320 had no stickiness. The fracture modes of NR-ESCOREZ 5320 PSAs is shown in Figure 7. All of the PSAs of this system give interfacial failure except for the blend containing 60% of the tacki-

fier at the velocity over 6000 mm/min. NR-ESCOREZ 1102 system gave a phase diagram of the LCST type with a critical temperature of 83°C, therefore miscible at the condition of peel tests. Peel strength and fracture modes of NR-ES-

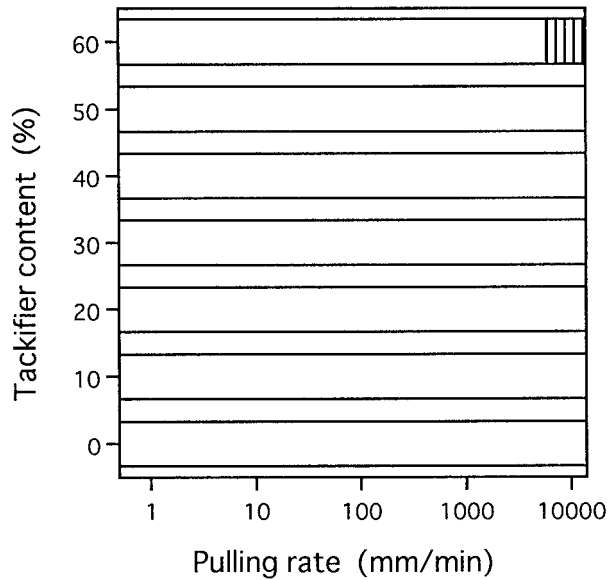


Figure 7 Peeling modes of NR-ESCOREZ 5320 blends: ■, Cohesive failure; □, adhesive failure (between the adhesive and the aluminum); ▨, slip stick; ▩, glassy failure (between the tape and the adhesive).

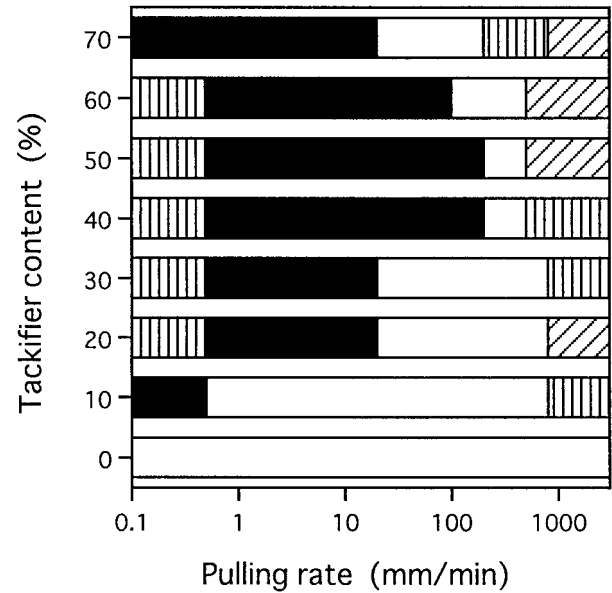


Figure 9 Peeling modes of NR-ESCOREZ 1102 blends: ■, Cohesive failure; □, adhesive failure (between the adhesive and the aluminum); ▨, slip stick; ▩, glassy failure (between the tape and the adhesive).

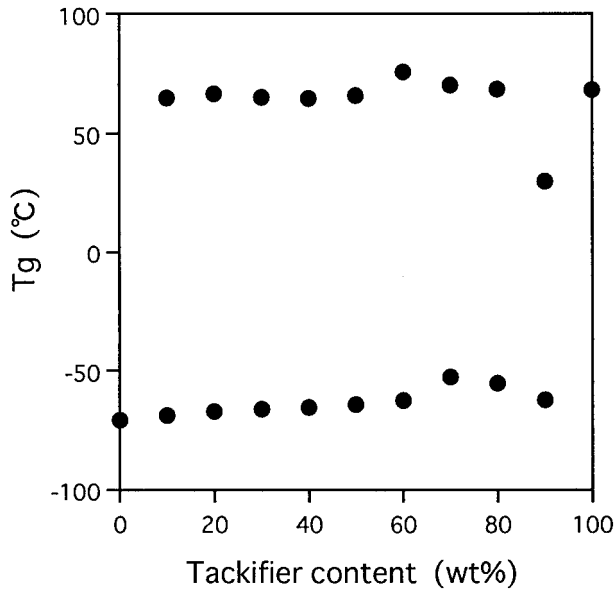


Figure 10 Tg-composition curve of NR-Kristalex 1120 blends.

COREZ 1102 system are shown in Figures 8 and 9. The peel strength of these blends (tackifier content 30-70%) gradually increases with an increasing velocity until 30-500 mm/min but suddenly drops to near 0 gf/cm at 1000 mm/min. The cause of this characteristic phenomenon is the transition from interfacial failure to slip-stick or glassy failure. As shown in Figure 9, NR-ES-

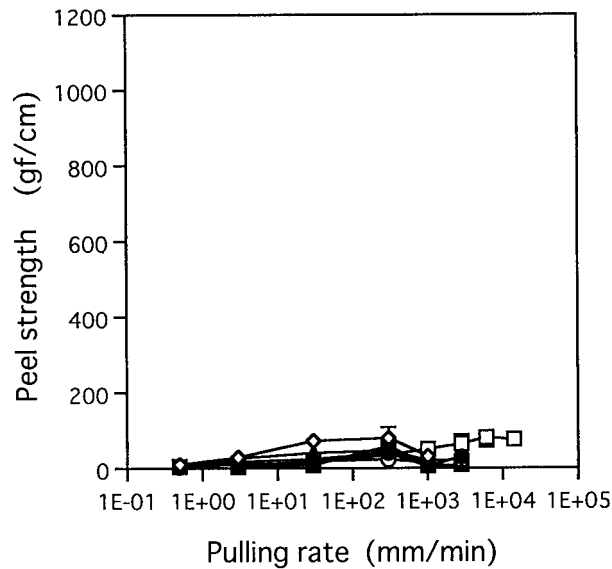


Figure 11 Peel strength of NR-Kristalex 1120 blends at 20°C. Tackifier content: (□) 0%, (◇) 10%, (●) 20%, (△) 30%, (■) 40%, (○) 50%.

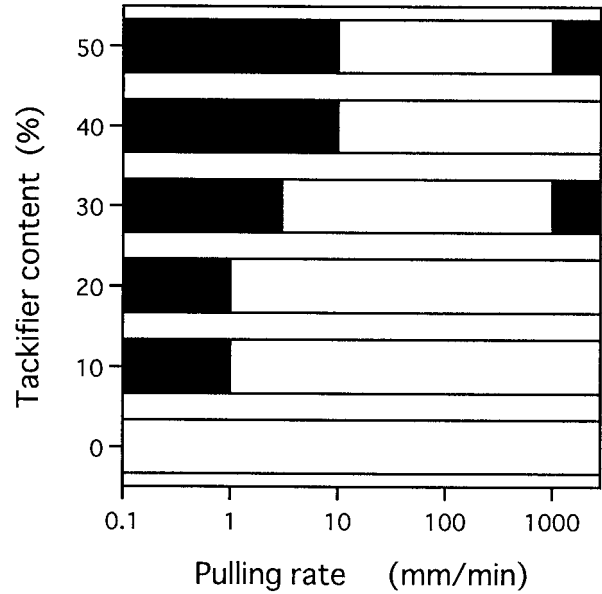


Figure 12 Peeling modes of NR-Kristalex 1120 blends: ■, Cohesive failure; □, adhesive failure (between the adhesive and the aluminum); ▨, slip stick; ▩, glassy failure (between the tape and the adhesive).

COREZ 1102 blends show slip-stick failure in the low-velocity region (lower than 1 mm/min) as well as in the high-velocity region (over 300 mm/min) and have a wide cohesive-failure region. It is very interesting that slip-stick failure was observed in

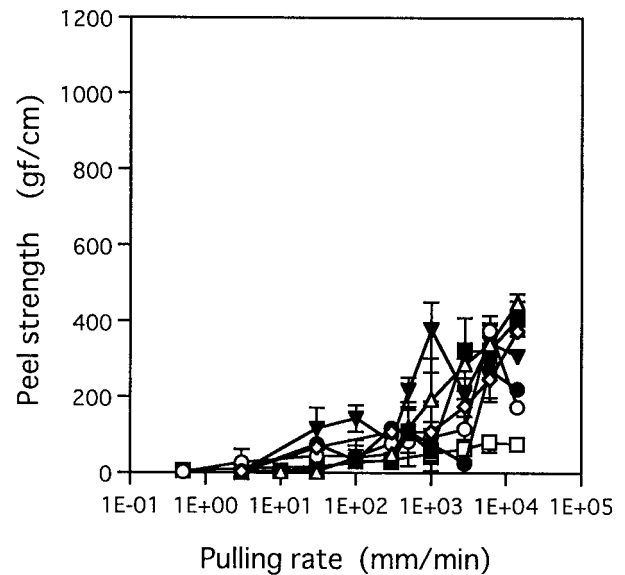


Figure 13 Peel strength of NR-Polypale blends at 20°C. Tackifier content: (□) 0%, (◇) 10%, (●) 20%, (△) 30%, (■) 40%, (○) 50%, (▼) 60%.

the lower velocity region than cohesive failure in NR-ESCOREZ 1102 system. The cause or reason for this result is unknown so far.

If the peeling modes of these 4 PSA systems are compared with each other, one may perceive that the PSAs, which show phase diagrams of the LCST type with a rather low critical temperature, exhibit interfacial failure over the wide velocity region and that the PSAs having phase diagrams of a completely miscible or LCST type with high T_c have a wide cohesive failure region. We cannot think of any reason why such a difference in the fracture mode is observed, and we do not know whether the difference is universal or not. To discuss this problem, we must perform measurement of peel strength for many other blend systems. There are reports that the best PSA properties were obtained at the composition and at the temperature where the transition from miscible to immiscible was about to take place.^{11,12}

NR-Kristalex 1120 system was completely immiscible; it was immiscible at any temperature and blend ratio of experiment.⁸ All of the blends of this system were pure white; and in the blends containing 40% or more of Kristalex 1120, phase separation structures, such as stripes, were clearly seen with naked eyes. When these blends were observed under an optical microscope, many spherical or dot-like particles of dispersed phase were seen. The T_g -composition curve of NR-Kristalex 1120 system is shown in Figure 10. In each blend of this system, 2 distinct and almost constant T_g s are observed, which are near the T_g s of NR and Kristalex 1120, respectively. Peel strength of NR-Kristalex 1120 blends are shown in Figure 11. The peel strength of these blends is much smaller than that of the miscible PSAs described above. And the maximum peel force is obtained at the pulling rate of 300 mm/min in every blend of this system (except tackifier 0%), irrespective of composition, which is in contrast with the peak shift of miscible blends. The peel strength of this system tends to diminish as the tackifier content increases. The peeling modes of NR-Kristalex 1120 blends are shown in Figure 12. The velocity range of interfacial failure is rather wide and tends to decrease with increasing tackifier content in this system. The tape specimens of NR-Kristalex 1120 blends were sometimes peeled from the adherend forming a membrane instead of fine filaments.

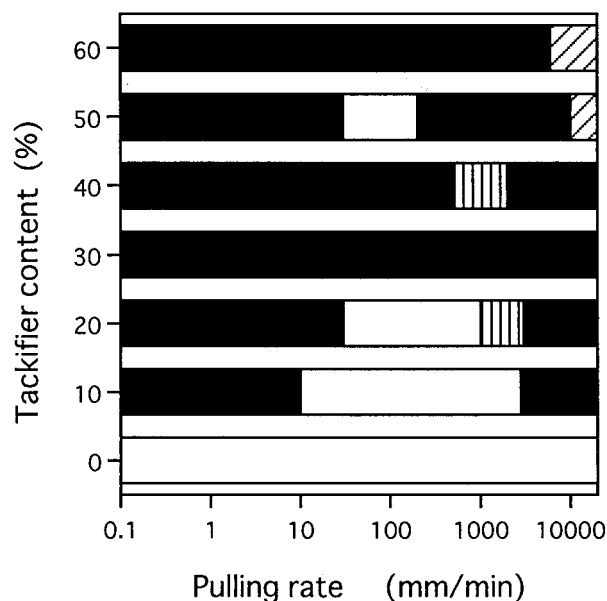


Figure 14 Peeling modes of NR-Polypale blends: ■, Cohesive failure; □, adhesive failure (between the adhesive and the aluminum); ▨, slip stick; ▩, glassy failure (between the tape and the adhesive).

NR-Polypale system was also completely immiscible.^{7,9} This system showed the phase diagram and T_g -composition curve similar to those of NR-Kristalex 1120 system. The peel force of NR-Polypale blends is shown in Figure 13. The peel strength of these blends is smaller than that of the miscible ones and is apt to increase with increasing velocity as a whole. The shift of the peak position is not observed. The region of cohesive failure is very wide in NR-Polypale blends, as shown in Figure 14.

As mentioned above, in the case of immiscible PSAs, peel strength is generally smaller than that of miscible PSAs, and the peak in the peel force curve does not shift to the lower velocity. Therefore, it is considered that the tackifier resin acts as a filler in the immiscible PSAs and that, essentially, does not change the mechanical properties of the matrix phase.^{10,13}

CONCLUSIONS

1. In the case of miscible PSAs, the peak positions in the pulling rate-peel strength curves shifted to the lower velocity as the tackifier content increased.
2. Immiscible PSAs had smaller peel strength

than miscible ones and did not exhibit apparent shift of peaks.

3. In most of the PSAs, the fracture mode changed from cohesive failure to interfacial, slip-stick, and glassy failure as the pulling rate increased. And the velocity range of interfacial failure tended to decrease as the tackifier content increased.

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