

Effects of Miscibility on Probe Tack 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 in our previous articles. 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 probe tack. Probe tack values were measured at various rates of separation and temperatures to obtain master curves. In the case of miscible pressure sensitive adhesives (PSAs) at the condition of measurement, the peak position in the master curve of probe tack shifted to the lower velocity (higher temperature) as the tackifier content increased. On the contrary, immiscible PSAs had much smaller probe tack values than miscible ones and did not give manifest shift of peaks. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 771–776, 1998

Key words: natural rubber; tackifier; miscibility; pressure sensitive adhesive; probe tack

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 tapes and labels can be pasted and removed many times, and the adhesive is not left on the adherend in many cases. Because PSAs are very convenient, as described above, they are often used in many fields. PSAs are utilized not only in our daily life, such as cellophane tape and labels, but also in packaging, printing, medical, electrical, and automobile industries. Especially, natural-rubber

(NR)-based PSAs have a very long history and have been widely used. Recently, acrylic polymers and some kinds of block copolymers (SIS, SBS, etc.) come to be used more and more,¹ 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, rosin derivatives) with NR in order to improve its wettability to the adherend and to achieve rapid and effective bonding. At specific blend ratios, these rubber-resin blends become PSAs, while at other concentrations, they do not provide adequate performances as PSAs. It is necessary for obtaining PSAs of good performance to select proper tackifiers and their proper concentrations for NR. As

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Table I Tackifiers Used for Tack Measurements

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
	Petroleum	ESCOREZ 5320 ^b	75.2	395	Hydrogenated petroleum resin ^h
Completely immiscible	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 catalogs.

^h By IR and NMR measurements.

generally admitted, PSA performances, such as peel adhesion, tack, and shear creep resistance, depend strongly on viscoelastic properties of the PSAs.²⁻⁴ 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 miscibility, viscoelastic properties, and performances of PSAs systematically. However, there are a few studies about the effect of miscibility between components 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.^{5,6} 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. Measurement of tack is especially important to evaluate the PSA's ability to wet a surface of adherend and to form bonds instantaneously. Probe tack is the most general and easiest method to measure tack, and its values indicate the vertical force necessary to break bonds on the assumption of simple separation. In this article, effects of miscibility of PSA components on probe tack 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 tack measurements are listed in Table I.

PSA sheets for the probe tack 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 (dry state) by a knife spacer. 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 pressed to release coating paper using a 2-kg roller. The sheets were seasoned at 20 $^{\circ}\text{C}$ and 65% relative humidity (RH) for more than 14 days and cut into small tapes just before the measurement.

The measurement of probe tack was performed on a Polyken Tack Tester with a stainless steel probe of 5 mm diameter. This tester is designed to measure the maximum force required to break the adhesive bond between the probe and PSA. Measurements were carried out at 7 different temperatures (20, 30, 40, 50, 60, 80, and 100 $^{\circ}\text{C}$) just after the probe and specimen were heated to the test temperature for 5 min. As for the test temperature, 20 $^{\circ}\text{C}$, measurements were performed at 9 different rates of separation (0.01,

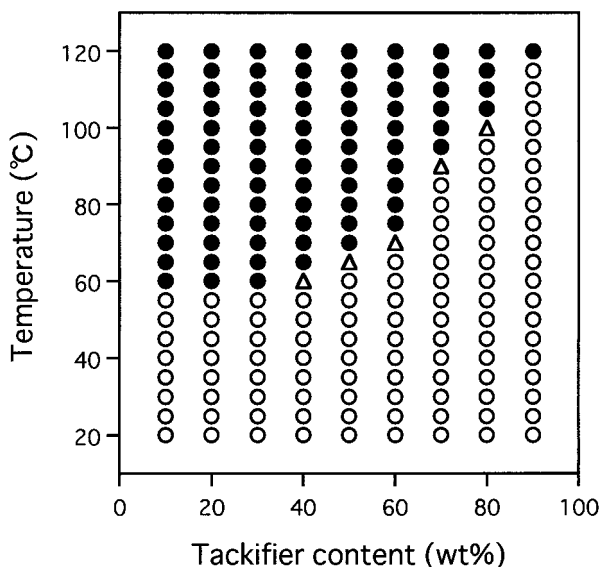


Figure 1 Phase diagram of the NR-ESCOREZ 5320 system: (○) transparent; (●) opaque; (△) semitransparent.

0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, and 5 cm/s); and at 30°C or higher temperatures, 3 separation rates (0.1, 1, and 5 cm/s) were adopted. The contact pressure was 100 gf/cm², and the dwell time was 1 s. Probe tack values reported here are the average of 5 measurements under the same conditions.

The glass transition temperatures (T_g s) of the blends were determined by DSC using a Perkin-Elmer DSC7. The first scan was run at a heating rate of 40°C/min from -120 to 150°C, followed by a rapid cooling, and then the second scan was run with the same conditions as the first scan. Since the T_g from the second scan was almost the same value as that from the first scan, T_g values were read from the easier thermogram to process data.

RESULTS AND DISCUSSION

The phase diagram of NR-ESCOREZ 5320 system is shown in Figure 1. Though this phase diagram is the LCST type with a critical temperature at 56°C, 2 days of isothermal heating (under 100°C) is at least required to induce phase separation in all of the blends. As the PSAs were heated for only 5 min just before the probe tack measurement, they still remained miscible. The probe tack values measured at various rates of separation and temperatures were plotted against reduced rates of separation at 20°C (stan-

dard temperature, T_s) using the time-temperature superposition principle, which was expressed by the WLF equation⁷ (eq. 1).

$$\log a_T = \frac{-C_1(T - T_s)}{C_2 + T - T_s} \dots \quad (1)$$

Here, T is the temperature at the tack measurement, T_s is the standard temperature (293.15 K), C_1 and C_2 are constants, and a_T is a shift factor. In this way, master curves of probe tack were obtained.

Figure 2 shows the master curves of probe tack of NR-ESCOREZ 5320 blends. In the range of experimental velocity, the maximum probe tack value of each curve increases as the tackifier content increases up to 60%. The NR-ESCOREZ 5320 blends containing 70% or more tackifier did not give tackiness at all. The peak (where the probe tack value is maximum at each tackifier content) shifts to lower rate of separation (higher temperature) as the tackifier content increases. This phenomenon is caused by the elevation in T_g with increasing tackifier content and is a common phenomenon in all the miscible PSAs, such as acrylic and polybutadiene-based PSAs.^{8,9} The peak shifts slightly at the low tackifier content, while the shift is remarkable at the tackifier content of 50 and 60%. The T_g s of NR-ESCOREZ 5320 blends are shown in Figure 3. All of the blends of NR-ESCOREZ 5320 system exhibit a single T_g , which is located between those of NR and ESCOREZ 5320, and the T_g increases with increasing tackifier content. This is an evidence that the blends of this system are miscible and only 1 phase exists at the condition of measurement. The T_g elevates about 28°C by blending 60% of ESCOREZ 5320 with NR.

The phase diagram of NR-Clearon K-4090 system was the LCST type with a critical temperature at 61°C; however, at least 2 days of isothermal heating (under 100°C) was required to induce phase separation in each blend. In master curves of probe tack of NR-Clearon K-4090 system, data points, which were measured at 80 and 100°C, were connected smoothly to the curve drawn by data points at or under 60°C. This result indicated that the blends still remained miscible at the condition of tack measurement. In contrast to the NR-ESCOREZ 5320 blend containing 70% of tackifier, the NR-Clearon K-4090 blend with the same tackifier content provided very large tack values (over 4000 gf/cm²) at 30–40°C at the ve-

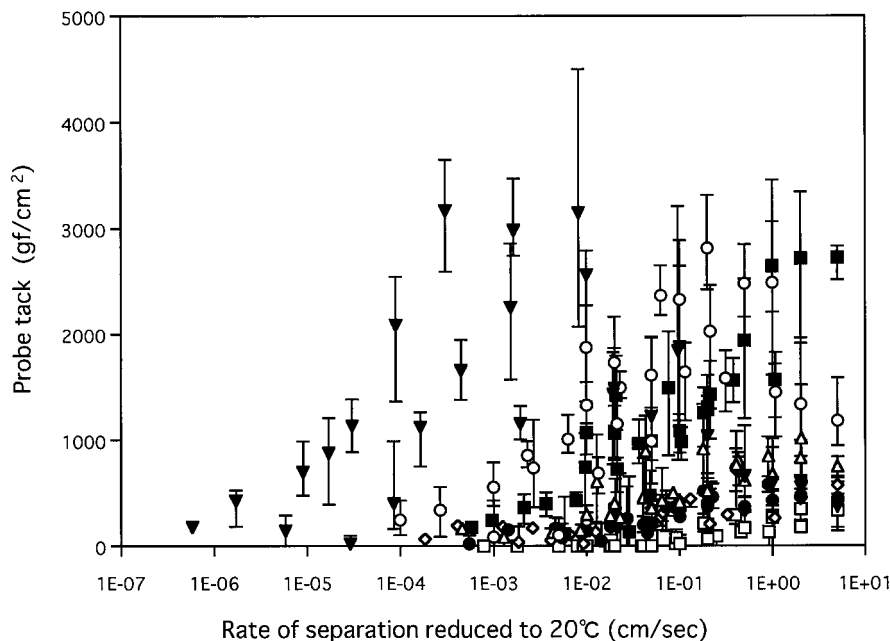


Figure 2 Master curves of the probe tack of NR-ESCOREZ 5320 blends. Tackifier content: (□) 0, (◇) 10, (●) 20, (△) 30, (■) 40, (○) 50, and (▼) 60%.

locity of 0.01–0.1 cm/s. In the NR-Clearon K-4090 system, the peak also shifted to lower rate of separation as the tackifier content increased. Though the shift was negligible or the peaks did not emerge in the range of experimental velocity at the low tackifier content, the shift of the peaks was remarkable at the tackifier contents of 50–60

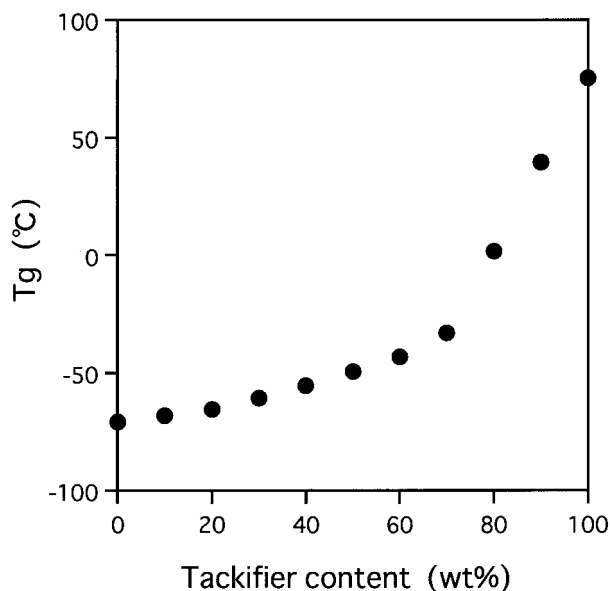


Figure 3 T_g -composition curve of NR-ESCOREZ 5320 blends (measured by DSC).

and 60–70%. Each blend of this system had only 1 T_g , which elevated with increasing tackifier content. The T_g -composition curves of NR-ESCOREZ 5320 (Fig. 3), and NR-Clearon K-4090 blends are concave. This concavity is generally found in polymer-polymer blends where a strong interaction between the segment pairs is expected to occur.^{10–12} In NR-Clearon K-4090 system, an increase in T_g became larger as the tackifier content increased. Though the T_g increased only 17°C by adding 50% of Clearon K-4090 to NR, it increased no less than 20°C from 50 to 70% of tackifier content. This can be a good explanation of the reason why the peak of probe tack shifted only slightly at the tackifier content less than 60%. The measured T_g values of the blends were in good agreement with those calculated from eq. (2), which was derived from the assumption of continuity of entropy before and after the glass transition.^{13,14}

$$\ln T_g = \frac{\phi_1 \Delta C p_1 \ln T_{g1} + \phi_2 \Delta C p_2 \ln T_{g2}}{\phi_1 \Delta C p_1 + \phi_2 \Delta C p_2} \quad (2)$$

Here, T_g is the glass transition temperature of a blend, T_{g1} is the T_g of NR = 202.3K, T_{g2} is the T_g of the tackifier (314.9K in the case of Clearon K-4090), and ϕ_1 and ϕ_2 are the weight fractions of NR and the tackifier, respectively. $\Delta C p_1$

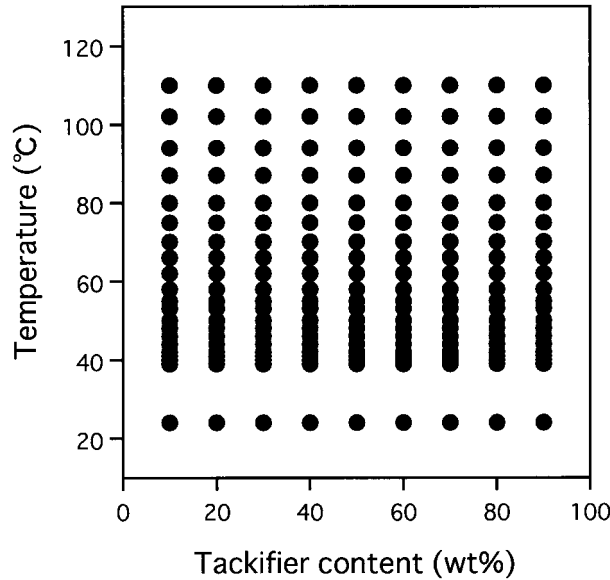


Figure 4 Phase diagram of NR-Polypale system: (●) opaque.

is the difference in specific heat of NR before and after the glass transition at constant pressure (0.543 J/gK), and ΔC_{p2} is that of the tackifier (0.184 J/gK).

In the NR-Clearon K-4090 system, the maximum probe tack value of each curve increased as

the tackifier content increased up to 70% in the range of experimental velocity similar to NR-ESCOREZ 5320 system. This may be attributable to an elevation in T_g and a decrease in the apparent viscosity that attain good wettability as the result of homogeneous mixing of NR with the tackifier at the molecular level.¹⁵ NR-Clearon K-4090 blends, whose tackifier contents were over 70%, provided no tackiness.

Similar results were obtained for NR-Estergum HP system about probe tack and T_g s. The NR-Estergum HP system was completely miscible: it was miscible at any experimental composition and temperature. In the probe tack of this system, the peak shifted toward lower velocity as the tackifier content increased. Though the peak shifted less than 1 order of velocity by mixing 50% of Estergum HP with NR, the peak shift of the blend containing 70% of Estergum HP was overwhelmingly conspicuous. This result probably reflected the T_g variations. Measured T_g s roughly agreed with the T_g values calculated from eq. (2). The tack values were as large as those of the two-blend systems.

Similar tendencies were seen in 2 other miscible blend systems (NR-Superester A-75 and NR-ESCOREZ 1102): a peak shift in the probe tack and a single T_g , depending on composition. T_g -composition curves of the 2 miscible NR-tackifier

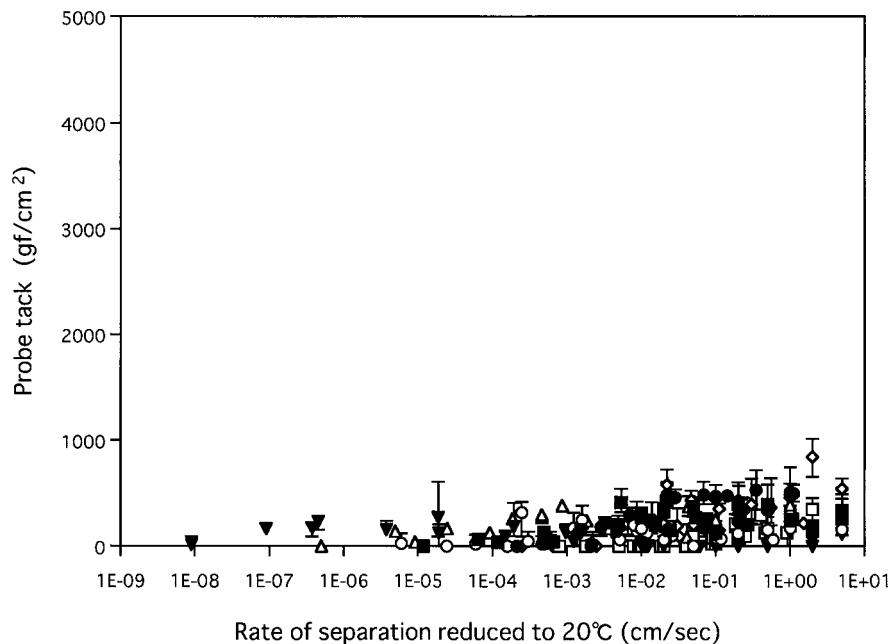


Figure 5 Master curves of the probe tack of NR-Polypale blends. Tackifier content: (□) 0, (◇) 10, (●) 20, (△) 30, (■) 40, (○) 50, and (▼) 60%.

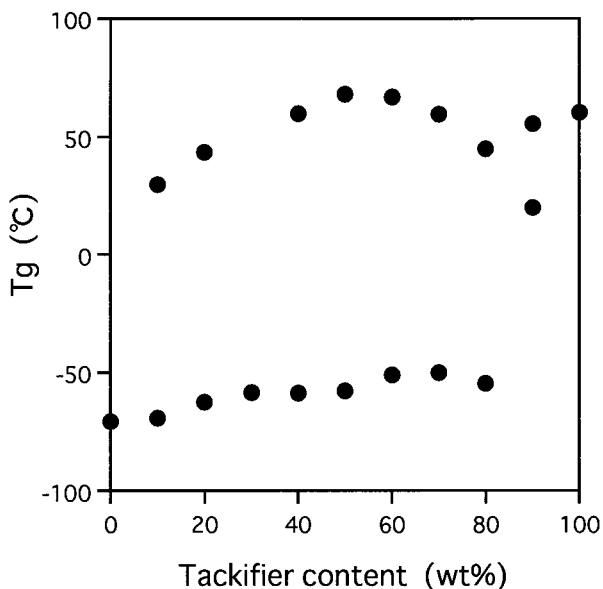


Figure 6 T_g -composition curve of NR-Polypale blends (measured by DSC).

systems were concave similar to 3 former systems.

The NR-Polypale system is completely immiscible, as shown in Figure 4. Figure 5 shows the master curves of probe tack of NR-Polypale blends. The probe tack values of NR-Polypale blends are much smaller than those of the miscible PSA systems and almost the same as those of NR itself. The change in tack values by composition and velocity shown in this figure seems to be within the experimental error. The shift of the peak toward lower velocity is not observed in this system. The T_g s of NR-Polypale blends are shown in Figure 6. Almost all the blends of NR-Polypale system have 2 T_g s, which indicate the existence of the following 2 phases: one is rich in NR, and the other is rich in Polypale. The variation in T_g of each phase is small and irregular. Indistinctness of the peak shift in the probe tack is due to the little change of T_g in spite of the increase in tackifier content.

The other immiscible blend system (NR-Kristalex 1120) showed similar results on probe tack and T_g s, as follows: the tack values of NR-Kristalex 1120 blends were as small as those of NR-Polypale blends. On the basis of these results, the tackifier-rich phase is considered to act as a filler

and not to improve wettability and mechanical properties of NR in immiscible PSAs.¹⁶

CONCLUSIONS

1. In the case of miscible PSAs, the peak of the probe tack shifted to the lower rate of separation (higher temperature) as the tackifier content increased, which was caused by elevation in T_g .
2. The probe tack values of immiscible PSAs were much smaller than those of the miscible ones, and the shift of the peak to a lower velocity was not observed.

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