

# Miscibility Between Natural Rubber and Tackifiers. I. Phase Diagrams of the Blends of Natural Rubber with Rosin and Terpene Resins

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**ABSTRACT:** Natural rubber (NR) was blended in various ratios with 17 kinds of tackifiers, which were prepared from rosin and terpenes. The blends were heated to various temperatures (20–120°C) in order to investigate their miscibility. The blends were visually observed for transparency or opacity at each temperature and further observed under an optical microscope for any existence of phase-separated structure. Miscibility of the blends is illustrated as phase diagrams in this article. Phase diagrams of all blends investigated in this study were classified into four types: completely miscible, lower critical solution temperature, upper critical solution temperature, and completely immiscible. The miscible range of a blend system tends to become smaller as the molecular weight of a tackifier increases. The data also indicate that the esters of hydrogenated rosin and of disproportionated rosin show comparatively good miscibility with NR whereas polymerized rosin and its esters have poor compatibility with NR in most cases. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2191–2197, 1997

**Key words:** natural rubber; tackifier; miscibility; rosin; terpene resin

## INTRODUCTION

Pressure sensitive adhesives (PSAs) consist mainly of elastomeric polymers and oligomeric resins (tackifiers). Blends of natural rubber (NR) and tackifiers have been widely used as PSAs in various fields of industry and also in our daily life for over 100 years. Since NR alone is not sufficient to provide the required balance between adhesion and tack, lower-molecular-weight tackifier resins (e.g., aliphatic or aromatic hydrocarbons, polyterpenes, rosin derivatives) have been blended with NR in order to improve its ability to wet the surface sufficiently and to form a bond of preferable

strength upon contact. The selection of proper tackifiers for NR dominates the performance of PSAs. Miscibility of the blends is one of the key factors in proper selection because it has a great influence on practical performances of PSAs. It is very important to clarify systematically the relationship between miscibilities, internal structures, viscoelastic properties, and performances of PSAs. Miscibility between NR and tackifiers has been extensively studied by Wetzell and Alexander,<sup>1</sup> Sherriff and colleagues,<sup>2,3</sup> Toyama and associates,<sup>4</sup> Fukuzawa,<sup>5</sup> and Class and Chu.<sup>6</sup> However, there have been few studies on phase diagrams of NR/tackifier blends. In this study, miscibilities between NR and various tackifiers prepared from rosin and terpenes were investigated by visual observation and illustrated as phase diagrams.

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## EXPERIMENTAL

Natural rubber (Mooney viscosity = 63.4,  $M_n$  = 299,000) was furnished by Uni Industry Co., Ltd. (Shimotsuga-Jun, Tochigi, Japan). Tackifiers employed in this study were furnished by Arakawa Chemical Industry Co., Ltd. (Osaka-shi, Osaka, Japan), Hercules Co., Ltd. (Wilmington, DE), and Yasuhara Chemical Co., Ltd. (Fuchushi, Hiroshima, Japan), and are listed in Table I.

NR and tackifiers were dissolved in toluene to prepare 5 and 50 wt % solutions, respectively. The two solutions were blended in nine different solute weight ratios (9 : 1 to 1 : 9). After examining the solutions for uniformity and transparency, we prepared filmy samples by coating them on slide glasses, or dropping them on slide glasses to form circles of 1 cm diameter. To remove their solvent, the samples were air-dried at room temperature for 24 h and then dried in a vacuum oven at 40°C for 48 h. After drying, the films dropped onto slide glasses were maintained at 20°C for 24 h to attain phase equilibrium, and then were placed on various spots of the Temperature-Gradient Phase Diagrammer (TGPD-1; Sun Science Co., Ltd., Setagaya, Tokyo, Japan), which is designed to maintain the desired temperature gradient for a long time. The films were visually observed at the interval of 24 h. This method will be called the "hot-plate method." On the other hand, the films coated on slide glasses were maintained at 20°C for 24 h and visually examined for transparency or opacity. In some cases they were observed under an optical microscope to determine whether any phase-separation structure could be seen at a fixed temperature. The same procedures were repeated by raising the temperature in a stepwise manner by 5°C at 24-h intervals up to 100 to 120°C in an air-circulation oven. Hereafter, this method will be called the "oven method." At first, miscibilities of all the blend systems were examined by the hot-plate method, and some systems were further examined by the oven method as reexamination. Essentially the same results were obtained from the same system by the two methods: the same type of phase diagrams and similar critical temperatures.

Molecular weights of NR and tackifiers were measured by gel permeation chromatography at 35°C with a refractive index detector (Shodex RI-71). For the measurement of molecular weight of NR,  $\mu$ -styragel columns (Waters Co., Ltd., Milford, MA) with pore sizes of  $10^5$ ,  $10^4$ , and  $10^3$  nm were used; for tackifiers, A-802 and KF-801

columns (Shodex Co., Ltd., Minato, Tokyo, Japan) were used. The solvent used was tetrahydrofuran (solvent grade) with a flow rate of 2 mL/min in the case of NR and 1 mL/min in the case of tackifiers. Molecular weights were obtained from calibration curve of polystyrene standards. The glass transition temperatures ( $T_g$ s) of tackifiers were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC7. The first scan was run at a heating rate of 40°C/min from 20°C to 150°C followed by a rapid cooling, then the second scan was run with the same conditions as the first scan. The data from the second scan are reported here as  $T_g$ s of tackifiers.

## RESULTS AND DISCUSSION

Various tackifiers of rosin derivatives are prepared from abietic acid by the series of chemical reactions shown in Figure 1.<sup>7</sup> Most of the tackifiers made from rosin have two sharp peaks partly overlapping in the molecular weight distribution curves, especially in the case of Polypale (Fig. 2). On the other hand, terpene resins have a broad peak, and sometimes with small shoulders, as shown in Figure 3. These findings indicate that tackifiers are mixtures of molecules with different molecular weights.

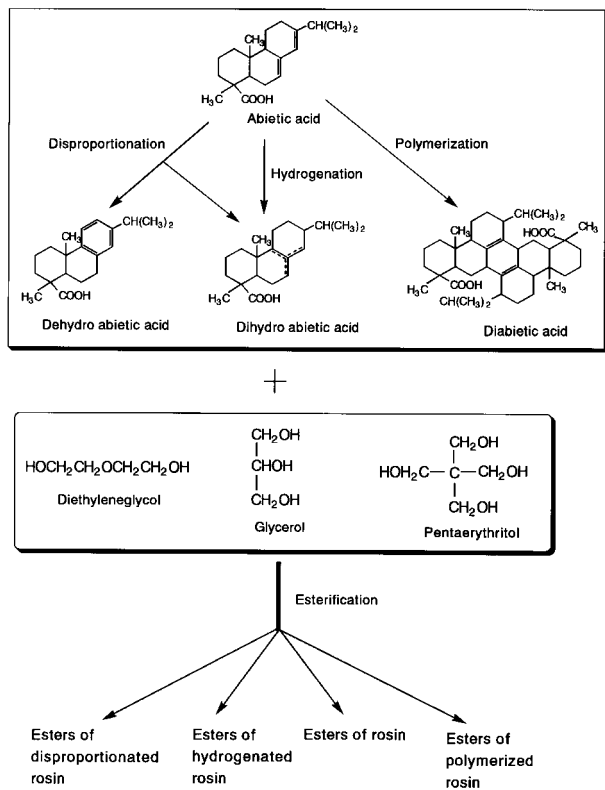
Phase diagrams of blends of NR/rosin derivatives are Figures 4 to 7, and phase diagrams of NR/terpene resins appear in Figures 8 and 9.

As shown in Figure 4, NR/Foral 85 system is miscible over the entire composition and temperature ranges studied, i.e., the phase diagram is the completely miscible type. The blends of NR and Foral 105 also showed a completely miscible-type phase diagram. The main components of Foral 85 and Foral 105 are esters of perhydrogenated rosin (tetrahydro rosin containing few C=C bonds). NR/Estergum H, Estergum HP, and Hercolyn D systems were completely miscible. These tackifiers are esters of partially hydrogenated rosin. Therefore it can be concluded that NR shows good miscibilities with esters of hydrogenated or perhydrogenated rosin in general. Aubrey and Sherriff<sup>3</sup> found that the pentaerythritol ester of hydrogenated rosin was known to be incompletely compatible with NR. Also according to them, several workers who used viscoelastic measurements and electron microscopy reported that phase separation occurred at resin concentrations of more than 40% in the NR/pentaerythritol ester of a hydrogenated rosin (Pentalyn H) system. Sherriff and co-

**Table I Characteristics of Tackifiers Used in This Study**

Basis	Commercial Names of Tackifiers	$M_n^a$	$M_w^a$	$T_g$ (°C) <sup>b</sup>	Softening	Phase Diagram	Main Components <sup>c</sup>
					Point (°C) <sup>c</sup>		
Tackifiers made from rosin <sup>d</sup>	Superester A-75 <sup>e</sup>	682	822	46.6	75	Miscible	Disproportionated rosin esterified by glycerol, diethyleneglycol
	Superester A-100 <sup>e</sup>	756	846	61.5	100	Miscible	Glycerol ester of disproportionated rosin
	Superester A-115 <sup>e</sup>	784	1,102	71.4	115	Miscible	Pentaerythritol ester of disproportionated rosin
	Superester A-125 <sup>e</sup>	1,093	2,469	81.7	125	LCST	Pentaerythritol ester of disproportionated rosin, including some fumaric acid
	Estergum H <sup>e</sup>	705	856	44.2	72	Miscible	Glycerol ester of hydrogenated rosin
	Estergum HP <sup>e</sup>	685	948	54.4	92	Miscible	Pentaerythritol ester of hydrogenated rosin
	Hercolyn D <sup>f</sup>	197	241	-34.0		Miscible	Methyl ester of hydrogenated rosin
	Foral 85 <sup>f</sup>	682	839	45.1	82	Miscible	Glycerol ester of perhydrogenated rosin
	Foral 105 <sup>f</sup>	715	976	57.2	104	Miscible	Pentaerythritol ester of perhydrogenated rosin
	Estergum AAG <sup>e</sup>	921	1,199	75.7	87.5	Immiscible	Glycerol ester of rosin
	Pencil AD <sup>e</sup>	785	1,222	61.0	101.5	Miscible	Pentaerythritol ester of gumrosin
	Pencil C <sup>e</sup>	1,102	1,963	91.6	125	UCST	Pentaerythritol ester of 25% polymerized rosin
	Polypale <sup>f</sup>	442	600	60.2	102	Immiscible	25% polymerized rosin
	Tackifiers made from terpene	Clearon K-4090 <sup>g</sup>	793	1,419	41.8	89	LCST
YS polystar T130 <sup>g</sup>		765	1,132	78.7	131	Miscible	Terpene phenolic copolymer (phenol 25%)
YS resin A-800 <sup>g</sup>		548	812	51.9	80	Miscible	$\alpha$ -pinene resin
YS resin TO-105 <sup>g</sup>		838	1,421	54.6	105	LCST	Aromatic modified terpene resin

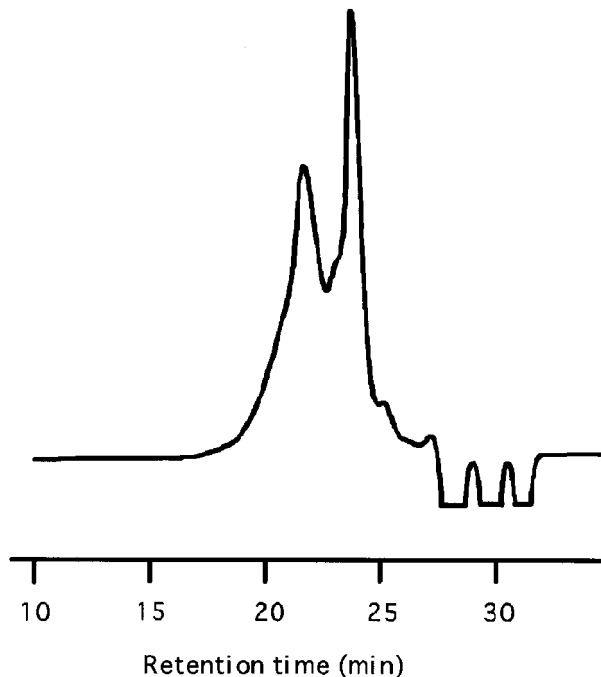
<sup>a</sup> By GPC measurements.<sup>b</sup> By DSC measurements.<sup>c</sup> Quoted from catalogues.<sup>d</sup> Main component of rosin is abietic acid.<sup>e</sup> Offered by Arakawa Chemical Industry Co., Ltd.<sup>f</sup> Offered by Hercules Co., Ltd.<sup>g</sup> Offered by Yasuhara Chemical Co., Ltd.



**Figure 1** Methods of preparing tackifiers from abietic acid.

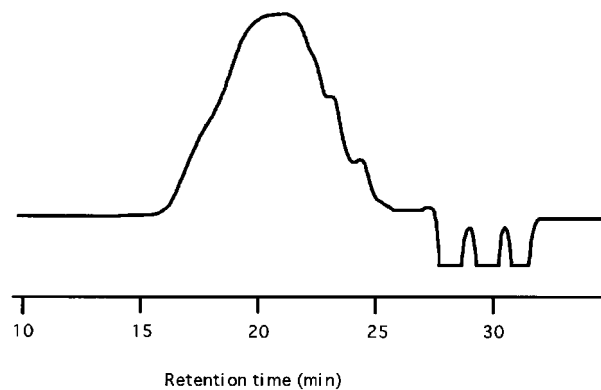
workers<sup>2</sup> reported that the NR/Pentalyn H system separated into two phases at resin concentrations over 60% on the basis of measurements by dilatometry. But Aubrey and Sherriff<sup>3</sup> did not detect phase separation by their viscoelastic analysis of the NR/Pentalyn H system. We also did not detect phase separation of the blends of NR with pentaerythritol ester of hydrogenated rosin (Estergum HP) by the phase diagram approach, despite the differences of methods and commercial names of tackifiers. Miscibility of blends should be investigated essentially by a thermodynamic approach at the equilibrium, and for this purpose the phase-diagram method seems appropriate.

Tackifiers of the Superester A series are esters of disproportionated rosin. The blends of NR and Superester A-75 gave a phase diagram of completely miscible type similar to Figure 4. Phase diagrams of NR/Superester A-100 and NR/Superester A-115 systems were also completely miscible. However, the NR/Superester A-125 system gives a phase diagram of lower critical solution temperature (LCST) type whose critical temperature ( $T_c$ ) is 70°C (Fig. 5). As shown in Table I, the number average molec-

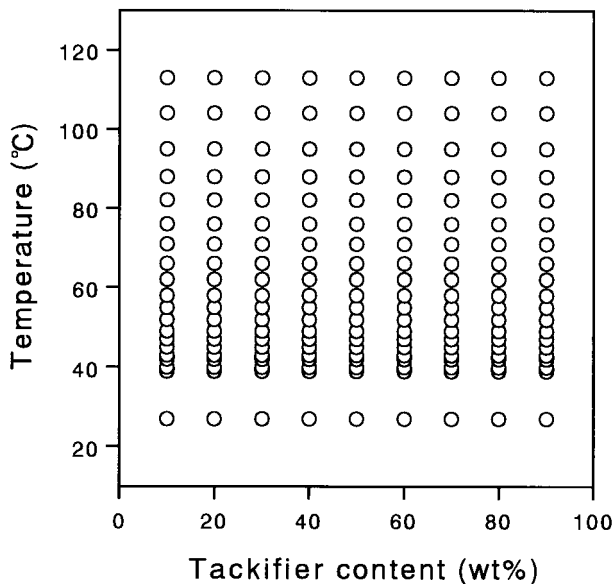


**Figure 2** Molecular weight distribution curve of Polypale.

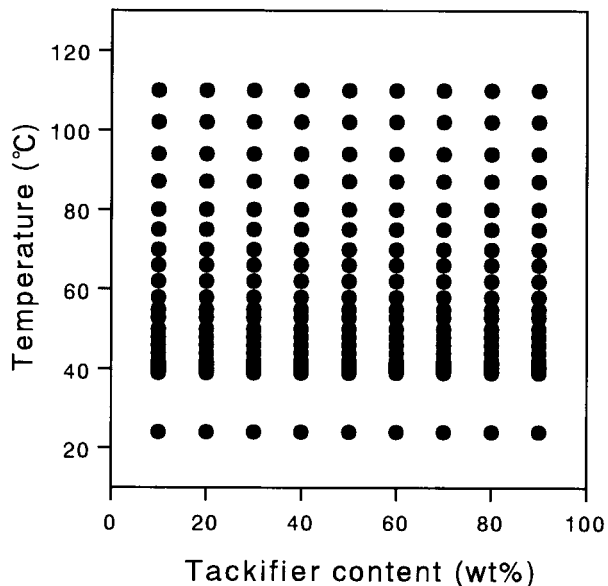
ular weights ( $M_n$ ) of Superester A-75, A-100, and A-115 are in the range of 600 to 800 whereas  $M_n$  of Superester A-125 is over 1,000. Thus it can be considered that the miscible range of a blend system becomes narrower as the molecular weight of a tackifier increases. This phenomenon is understood thermodynamically. Kim and Mizumachi<sup>8</sup> investigated miscibilities between poly(butylacrylate-co-acrylic acid) and Superesters, and found that miscibility was poorer as the alcoholic part of an ester became bulkier. Class and Chu<sup>9</sup> studied the influence



**Figure 3** Molecular weight distribution curve of Clearon K-4090.



**Figure 4** Phase diagram of NR/Foral 85 system (hot-plate method): (○) transparent; (●) opaque; (△) semi-transparent.

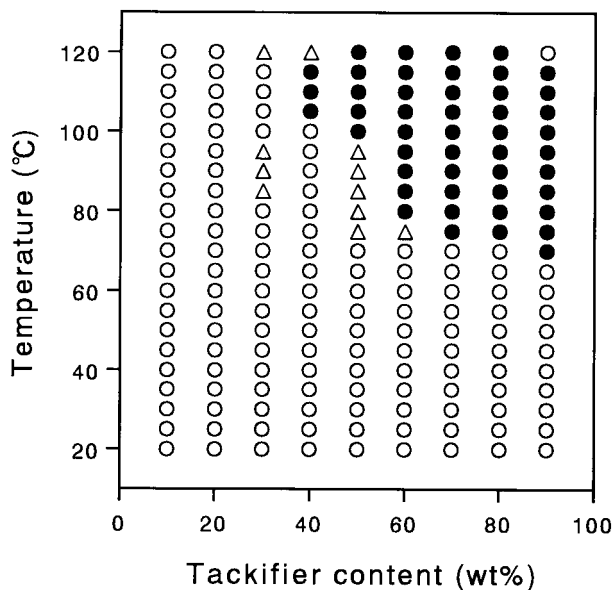


**Figure 6** Phase diagram of NR/Polypale system (hot-plate method): (○) transparent; (●) opaque; (△) semi-transparent.

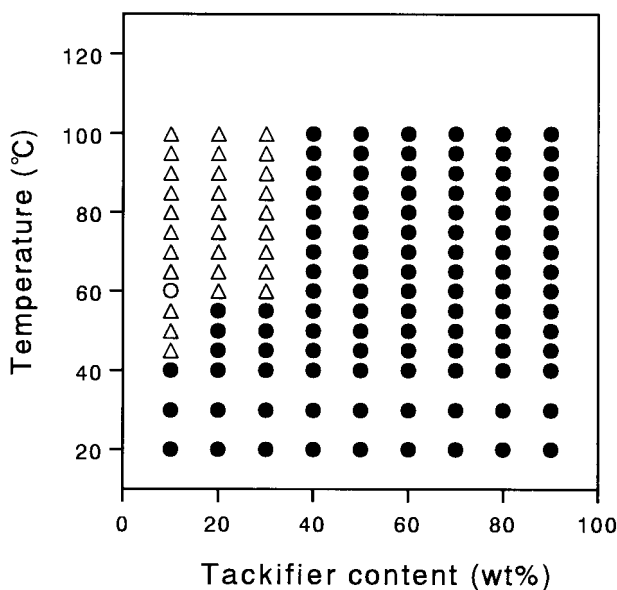
of tackifiers' molecular weight on miscibility between styrene-butadiene rubber and polystyrene resins, and reported that incompatibility was evident at weight average molecular weights over 1,000.

Blends of NR and Polypale are completely im-

miscible, as shown in Figure 6. In some of these blends, phase-separation structures were clearly seen even with the naked eye. NR/Pencil C system provides a phase diagram similar to an upper critical solution temperature type in which blends are slightly cloudy at the higher temperatures in the range of tackifier content under 40% (Fig. 7).



**Figure 5** Phase diagram of NR/Superester A-125 system (oven method): (○) transparent; (●) opaque; (△) semitransparent.

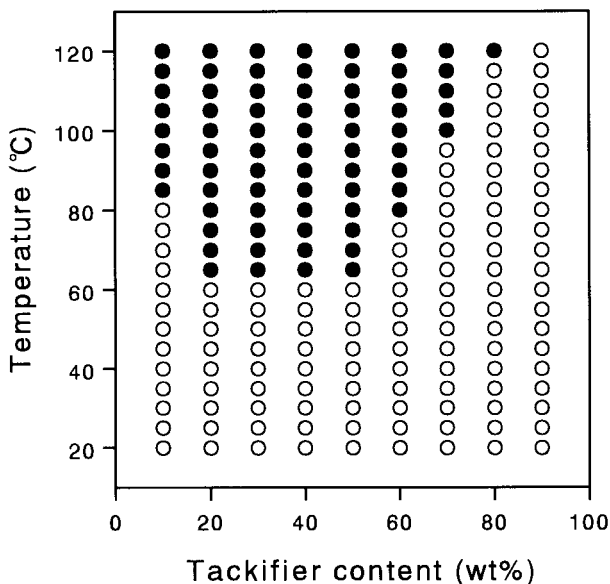


**Figure 7** Phase diagram of NR/Pencil C system (oven method): (○) transparent; (●) opaque; (△) semi-transparent.

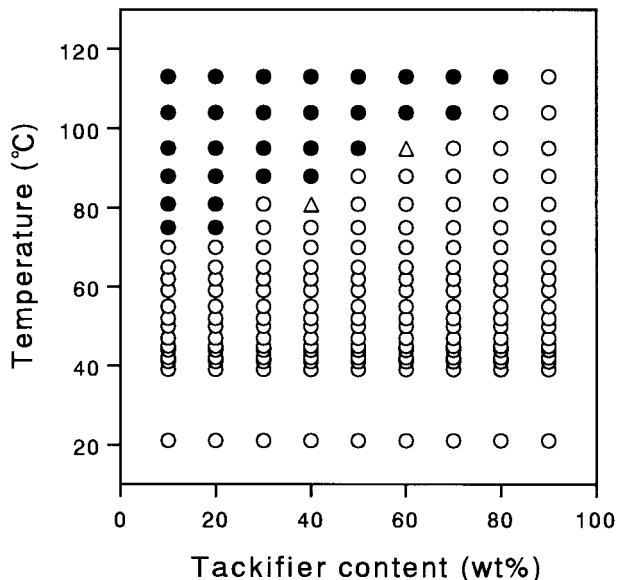
The main components of Polypale and Pencil C are partially polymerized rosin and ester of partially polymerized rosin, respectively. Pencil C has a large molecular weight, but the molecular weight of Polypale is the second-smallest of all the tackifiers. Therefore it has turned out that polymerized rosin and its esters generally show poor miscibility with NR.

Though both Estergum AAG and Pencil AD are esterified rosin, their miscibilities with NR were completely different: the NR/Estergum AAG system was completely phase-separated, similar to the case shown in Figure 6, whereas the NR/Pencil AD system was completely miscible. This difference is probably attributable to the differences in molecular weight of the tackifiers.

The phase diagram of the NR/Clearon K-4090 system is a typical LCST type in which  $T_c$  is 61°C (Fig. 8). Clearon K-4090 consists mainly of hydrogenated terpene resin. YS polystar T130 (terpene phenolic copolymer) and YS resin A-800 ( $\alpha$ -pinene resin) showed complete miscibility with NR. The NR/YS resin TO-105 (aromatic modified terpene resin) system gives a phase diagram of LCST type (Fig. 9). Akiyama and Miyako<sup>10</sup> described  $\beta$ -pinene resins as fairly miscible with NR whereas  $\alpha$ -pinene resins were not, although no experimental data were shown. They studied the miscibility of polybutadiene (PBD)/pinene resin blends by DSC and measurement of cloud points, and reported that PBD/ $\alpha$ -pinene resins showed



**Figure 8** Phase diagram of NR/Clearon K-4090 system (oven method): (○) transparent; (●) opaque; (△) semitransparent.



**Figure 9** Phase diagram of NR/YS resin TO-105 system (hot-plate method): (○) transparent; (●) opaque; (△) semitransparent.

phase diagrams of LCST type. In our study, the  $\alpha$ -pinene resin was completely miscible with NR, which was probably due to its small molecular weight. The terpene resins shown in Table I have a tendency to be less miscible with NR as the molecular weight of a resin increases; however, only four terpene resins were examined in this study. We need to examine more blend systems to reach systematic conclusions on miscibility between NR and terpene resins.

## CONCLUSIONS

1. Every blend system of NR with a rosin or terpene resin gave a phase diagram which belonged to one of the following types: completely miscible, LCST, UCST, and completely immiscible.
2. In the same series of tackifiers prepared from rosin, the miscible range of a blend system tends to become smaller with increase in molecular weight of the tackifier.
3. Esters of hydrogenated rosin and of disproportionated rosin showed preferable miscibility with NR, though polymerized rosin and its esters showed poor miscibility with NR.
4. Miscibility between components of PSAs

must be discussed in terms of phase diagrams.

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