

# Miscibility Between Natural Rubber and Tackifiers. II. Phase Diagrams of the Blends of Natural Rubber and Petroleum Resins

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**ABSTRACT:** Natural rubber (NR) was blended in various ratios with 12 kinds of tackifiers that were prepared from petroleum. The blends were heated to various temperatures (20–120°C) 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. NR/aliphatic resin systems and NR/aliphatic–aromatic copolymer systems showed phase diagrams of the lower critical solution temperature type, wherein the blends turned faintly cloudy over the binodal curves. The NR/hydrogenated petroleum resin system also showed a phase diagram of the lower critical solution temperature type. The miscible range of a blend system tends to become smaller as the molecular weight of a tackifier increases. Resins prepared by polymerization of pure aromatic monomers were completely immiscible with NR. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 221–229, 1998

**Key words:** natural rubber; tackifier; miscibility; petroleum resin; phase diagram

## INTRODUCTION

Pressure sensitive adhesives (PSAs) consist mainly of elastomeric polymers and low-molecular weight, high-softening point resins (tackifiers). Blends of natural rubber (NR) and tackifiers have been widely used as PSAs not only in various fields of industry, but also in our daily life for over a century. Because NR alone is not sufficient to provide the required adhesion and tack, tackifier resins (e.g., aliphatic or aromatic hydrocarbons, polyterpenes, and rosin derivatives) have been blended with NR to improve its wettability to the adherend and to achieve rapid and effective bond-

ing. At specific ratios, these rubber/resin blends are PSAs, whereas at other concentrations they are not. The selection of proper tackifiers and their proper concentrations 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 generally accepted that performances of PSAs (peel adhesion, tack, and shear creep resistance) depend strongly on viscoelastic properties of the adhesives. Therefore, it is considered to be 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 Wetzel and Alexander,<sup>1</sup> Sherriff and colleagues,<sup>2</sup> Aubrey and Sherriff,<sup>3</sup> Toyama and associates,<sup>4</sup> Fuku-

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**Table I Characteristics of Tackifiers Made from Petroleum**

Commercial Names of Tackifiers	$M_n^a$	$M_w^a$	$M_z^a$	$T_g$ (°C) <sup>b</sup>	Softening Point (°C) <sup>c</sup>	Phase Diagram	Main Components
ESCOREZ 217 <sup>d</sup>	984	2,063	6,781	50.5		LCST	Petroleum resin, mostly aliphatic <sup>e</sup>
ESCOREZ 355 <sup>d</sup>	1,056	2,093	5,675	63.1		LCST	Aliphatic–aromatic copolymerized resin <sup>e</sup>
ESCOREZ 1102 <sup>d</sup>	1,283	4,104	16,969	50.3	85–115	LCST	Aliphatic resin, polymerized C5 <sup>e</sup>
ESCOREZ 2101 <sup>d</sup>	850	2,071	7,529	46.5		LCST	Mostly aliphatic petroleum resin, including a small quantity of aromatic units <sup>e</sup>
ESCOREZ 5320 <sup>d</sup>	395	723	1,245	75.2	70–140	LCST	Hydrogenated petroleum resin <sup>e</sup>
Quintone A100 <sup>f</sup>	1,396	4,165	14,455	50.9	100	LCST	Aliphatic petroleum resin <sup>c</sup>
Quintone B170 <sup>f</sup>	1,073	2,249	7,687	ND <sup>g</sup>	70	LCST	Aliphatic petroleum resin <sup>c</sup>
Quintone P500 <sup>f</sup>	1,037	2,131	6,325	52.3	95	LCST	Copolymer of aliphatic C5 and styrene <sup>c,e</sup>
Quintone R100 <sup>f</sup>	1,231	2,553	8,152	50.9	96	LCST	Aliphatic petroleum resin, poly(1,3-pentadiene) <sup>c</sup>
Quintone S100 <sup>f</sup>	1,109	2,249	7,626	50.9	92	LCST	Copolymer of aliphatic C5 and styrene <sup>c,e</sup>
Kristalex 1120 <sup>h</sup>	873	3,294	12,038	68.1	80–125	Immiscible	Polymer from pure aromatic monomer <sup>c</sup>
Kristalex 3085 <sup>h</sup>	741	1,119	1,652	47.6	80–125	Immiscible	Polymer from pure aromatic monomer <sup>c</sup>

<sup>a</sup> By GPC measurements.<sup>b</sup> By DSC measurements.<sup>c</sup> Quoted from catalogs.<sup>d</sup> Offered by TONEX Co., Ltd.<sup>e</sup> By measurements of IR spectra.<sup>f</sup> Offered by Nippon Zeon Co., Ltd.<sup>g</sup> ND = not detected.<sup>h</sup> Offered by Hercules Co., Ltd.

zawa,<sup>5</sup> and Class and Chu.<sup>6</sup> However, there have been few studies on phase diagrams of NR/tackifier blends. We investigated miscibilities between NR and tackifiers prepared from rosin and terpenes, and reported that esters of hydrogenated rosin showed complete miscibility with NR and that the miscible range of a NR/tackifier system tended to become smaller with an increase in molecular weight of the tackifier.<sup>7</sup> In this study, miscibilities between NR and various petroleum resins were investigated by visual observation and illustrated as phase diagrams.

## EXPERIMENTAL

NR (Mooney viscosity = 63.4,  $M_n$  = 299,000) was furnished by Uni Industry Co., Ltd. (Shimotsugan, Tochigi, Japan). Tackifiers used in this study were furnished by Tornex Co., Ltd. (Kawasaki, Japan), Hercules Co., Ltd. (Wilmington, DE), and Nippon Zeon Co., Ltd. (Osaka, Japan). Their characteristics 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 : 1–1 : 9). After examining the solutions for uniformity and transparency, we prepared films by coating them all over a surface of 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 drops on 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

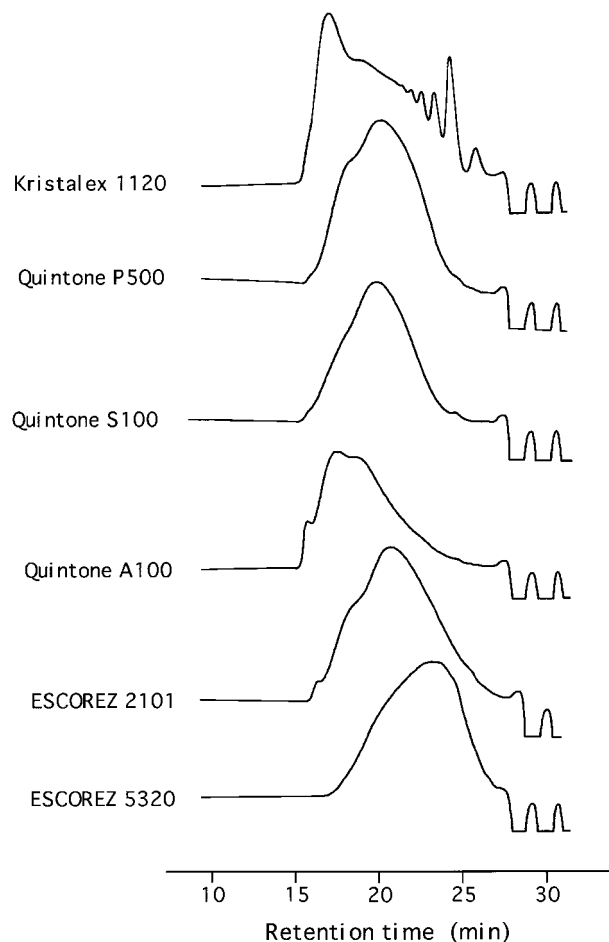
manner by 5°C at 24-h intervals up to 100–120°C in an air circulation oven. Hereafter, this method will be called the “oven method.” At first, miscibilities of all of the blend systems were examined by the hot-plate method, and most of the systems were further examined by the oven method as re-examination. 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 to 150°C, followed by a rapid cooling, then the second scan was run with the same conditions as the first scan. Data from the second scan are reported herein as  $T_g$ s of tackifiers. Infrared radiation (IR) spectra of ESCOREZ resins and some of Quintone resins were measured to examine the main components of the resins.

## RESULTS AND DISCUSSION

Most of the petroleum resins have a broad peak in the molecular weight distribution curves and sometimes with shoulders (as shown in Fig. 1). The polydispersities ( $M_w/M_n$ ) of them were  $>2$ . It is evident that tackifiers are mixtures of molecules with different molecular weights.

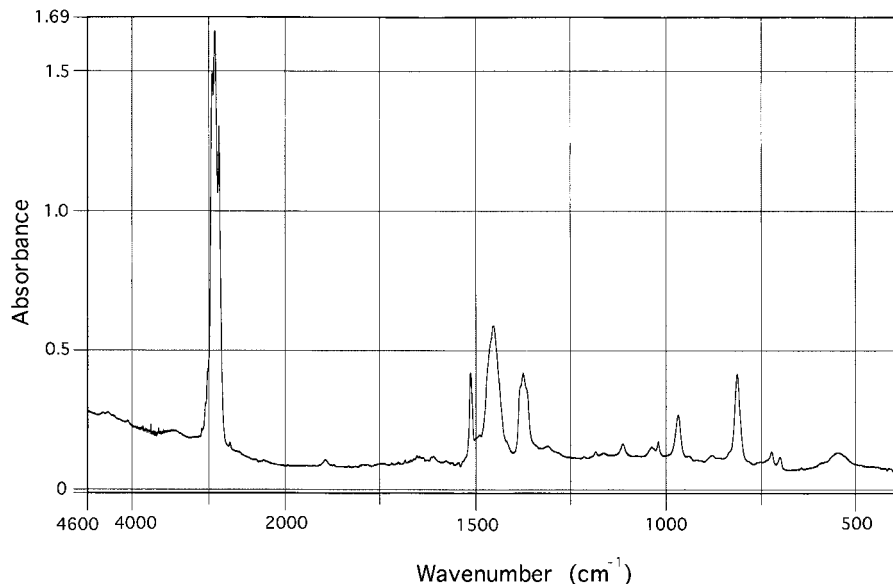
Main components of most of the petroleum resins shown in Table I were quoted from catalogs, but those of ESCOREZ resins were not found in catalogs. IR spectra of ESCOREZ resins were measured to analyze their components. IR spectrum of ESCOREZ 355 is shown in Figure 2 as an example of them. There is a large absorption due to C—H stretching vibrations in the range of 2,800–3,100  $\text{cm}^{-1}$ . There are absorptions at 1450  $\text{cm}^{-1}$  due to C—C stretching vibrations of alkyl



**Figure 1** Gel permeation chromatographs of tackifiers (in descending order: Kristalex 1120, Quintone P500, Quintone S100, Quintone A100, ESCOREZ 2101, and ESCOREZ 5320).

groups, at 1,380  $\text{cm}^{-1}$  due to C—C stretching vibrations of methyl, ethyl, *n*-propyl, or isopropyl groups, and at 970  $\text{cm}^{-1}$  due to C—H bending vibrations of *n*-propyl, isopropyl groups, or cycloalkane, respectively. There are peaks attributable to C=C stretching vibrations of mono- or disubstituted benzene at 1,510  $\text{cm}^{-1}$ , C—H bending vibrations of *para*-di-, or 1,2,4-trisubstituted benzene at 820  $\text{cm}^{-1}$ , and C—H bending vibrations of *para*-disubstituted benzene around 550  $\text{cm}^{-1}$ , respectively. These results indicate that this resin consists of oligomers resulting from copolymerization of aliphatic monomers and a relatively small amount of aromatic monomers.

Phase diagrams of blends of NR/petroleum resins are shown in Figures 3–14. All of the blend systems, except NR/Kristalex resins, show phase diagrams of the lower critical solution tempera-

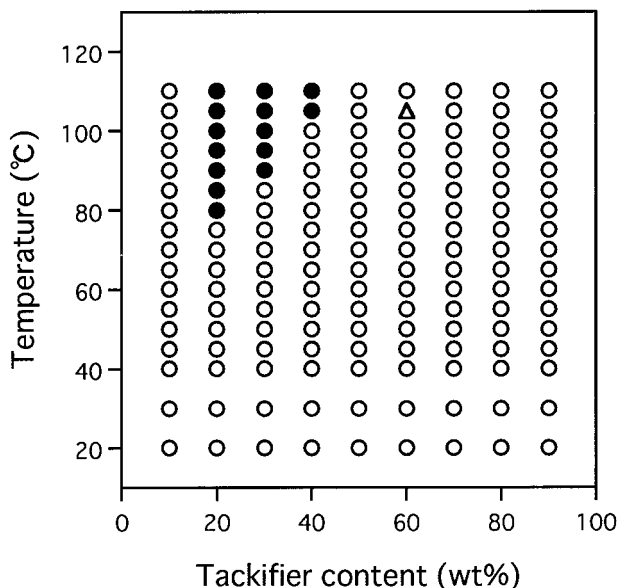


**Figure 2** IR spectrum of ESCOREZ 355.

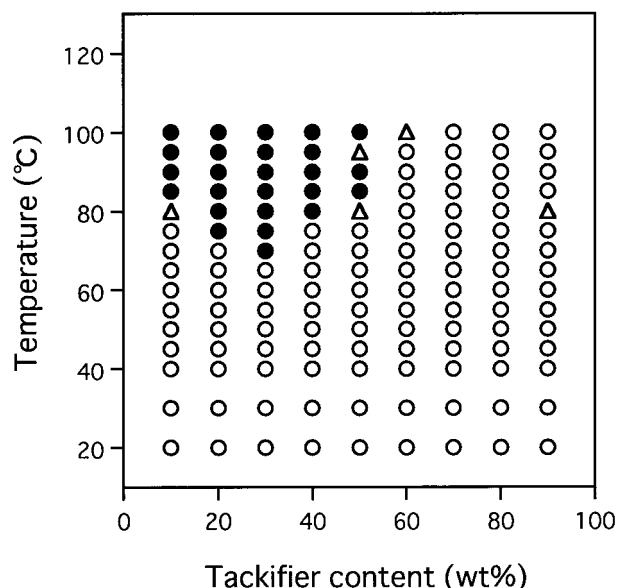
ture (LCST) type in which critical temperatures are in the range of 55–85°C and tackifier contents at critical points are 10–50%. Among the systems having phase diagrams of the LCST type, NR/ESCOREZ 5320 and NR/Quintone P500 blends (Figs. 7 and 10) turned apparently opaque when they separated into two phases, although blends of other systems became faintly cloudy. In addition, the immiscible region of NR/ESCOREZ 5320

system is the largest of all of the systems that have phase diagrams of the LCST type. The main component of ESCOREZ 5320 is hydrogenated petroleum resin. It would indicate that hydrogenated petroleum resins give a little poorer miscibility with NR than aliphatic petroleum resins with double bonds.

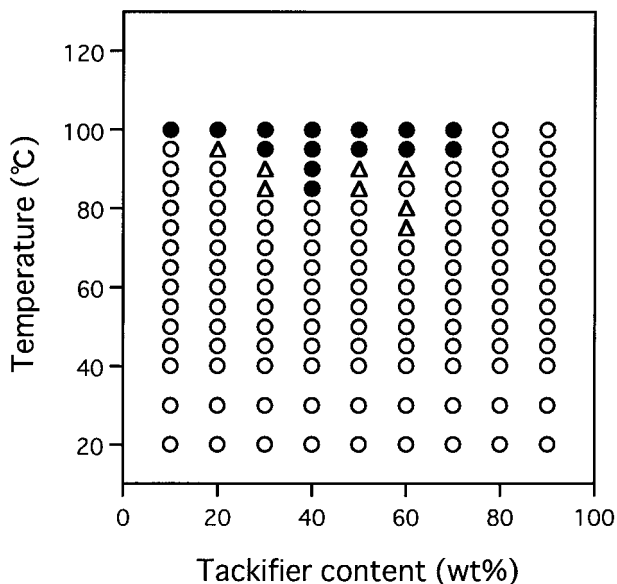
NR/Kristalex 1120 and NR/Kristalex 3085 systems have phase diagrams of the completely



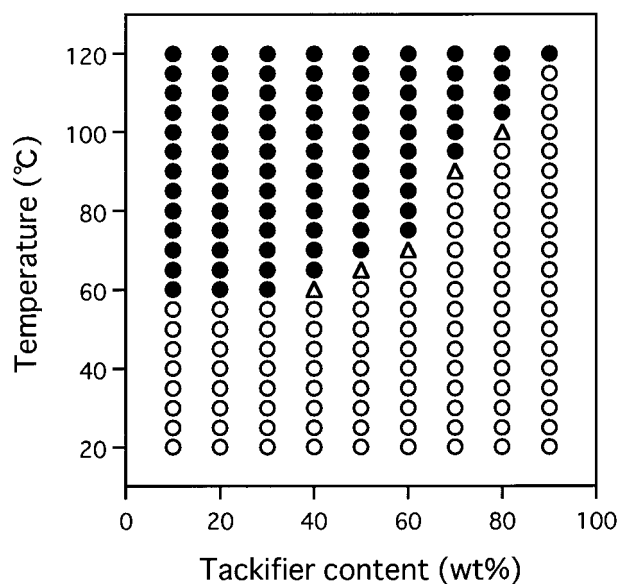
**Figure 3** Phase diagram of the NR/ESCOREZ 217 system (oven method). (○) Transparent; (●) opaque; (△) semitransparent.



**Figure 4** Phase diagram of the NR/ESCOREZ 355 system (oven method). (○) Transparent; (●) opaque; (△) semitransparent.



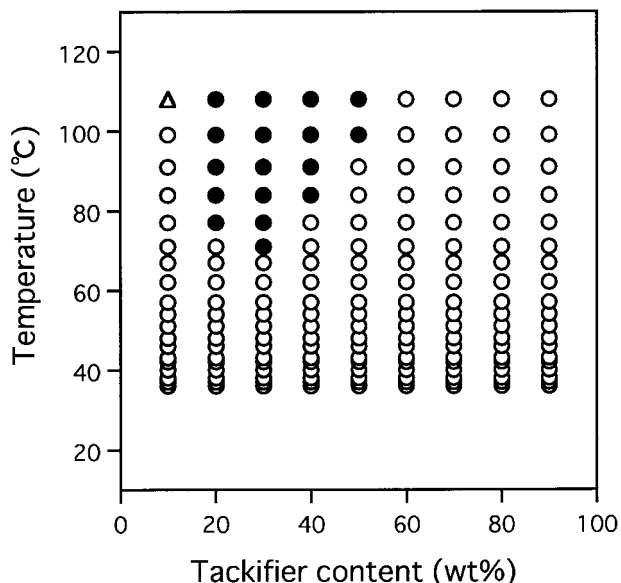
**Figure 5** Phase diagram of the NR/ESCOREZ 1102 system (oven method). (○) Transparent; (●) opaque; (△) semitransparent.



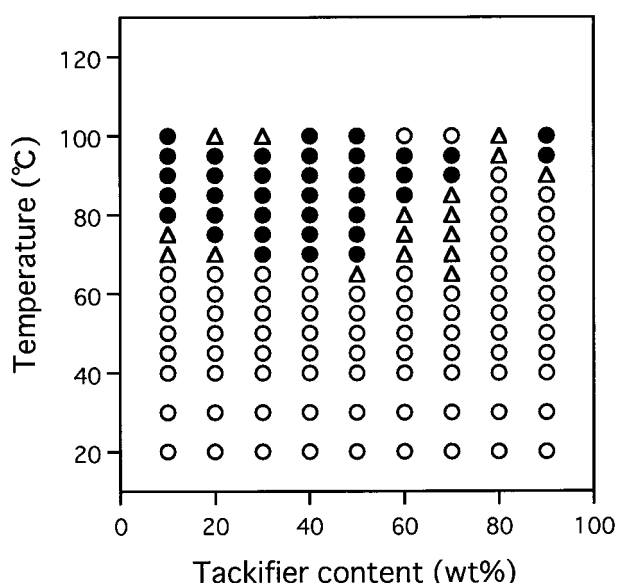
**Figure 7** Phase diagram of the NR/ESCOREZ 5320 system (oven method). (○) Transparent; (●) opaque; (△) semitransparent.

immiscible type (Figs. 13 and 14). The NR/Kristalex 3085 system, however, has a small miscible region in the low temperature and low tackifier content range. The opacity of these blends were visually obvious. These two resins are polymers from pure aromatic monomers.<sup>8</sup>

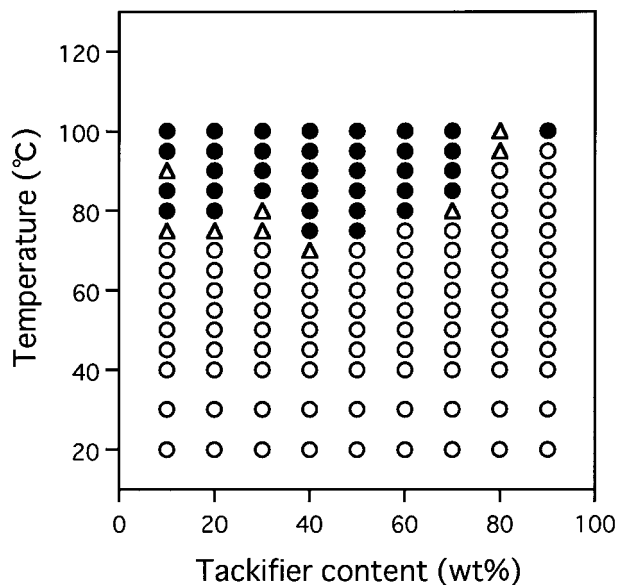
Quintone P500 has the second largest immiscible region among the systems that have phase diagrams of the LCST type. Both Quintone S100 and Quintone P500 consist of copolymers from aliphatic C5 and styrene. Comparing the phase diagrams of the blends of these two tackifiers with



**Figure 6** Phase diagram of the NR/ESCOREZ 2101 system (hot-plate method). (○) Transparent; (●) opaque; (△) semitransparent.

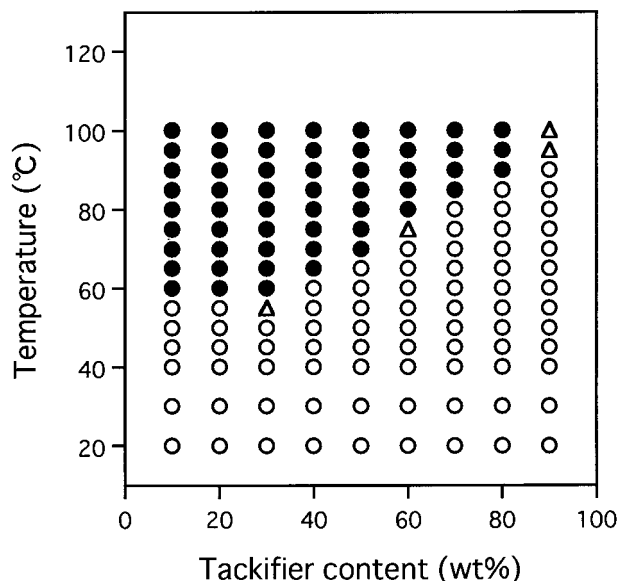


**Figure 8** Phase diagram of the NR/Quintone A100 system (oven method). (○) Transparent; (●) opaque; (△) semitransparent.

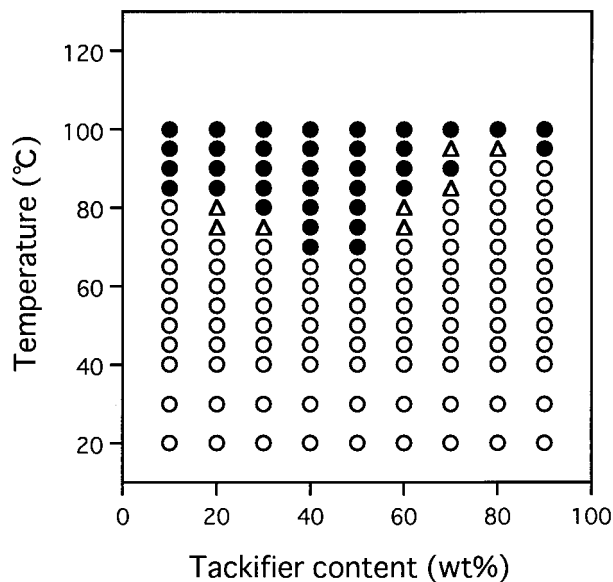


**Figure 9** Phase diagram of the NR/Quintone B170 system (oven method). (○) Transparent; (●) opaque; (Δ) semitransparent.

NR, the NR/Quintone P500 system has a larger immiscible region than the NR/Quintone S100 system and the LCST of NR/Quintone P500 is lower than that of the NR/Quintone S100 system. IR spectra of Quintone P500 and Quintone S100 are shown in Figure 15. There are strong absorp-

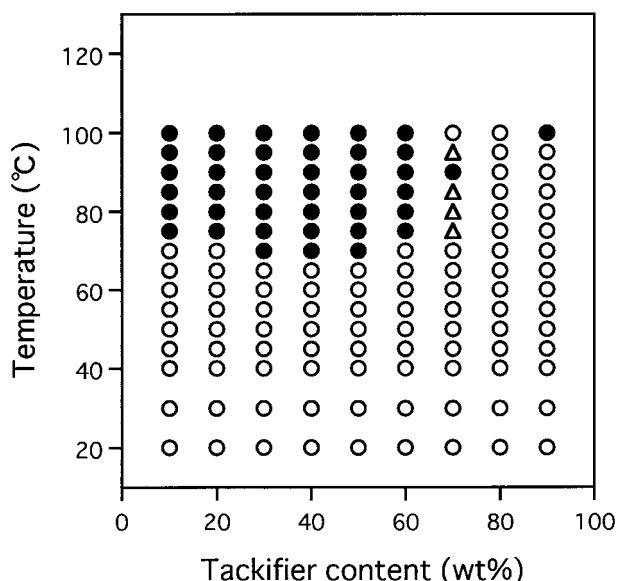


**Figure 10** Phase diagram of NR/Quintone P500 system (oven method). (○) Transparent; (●) opaque; (Δ) semitransparent.

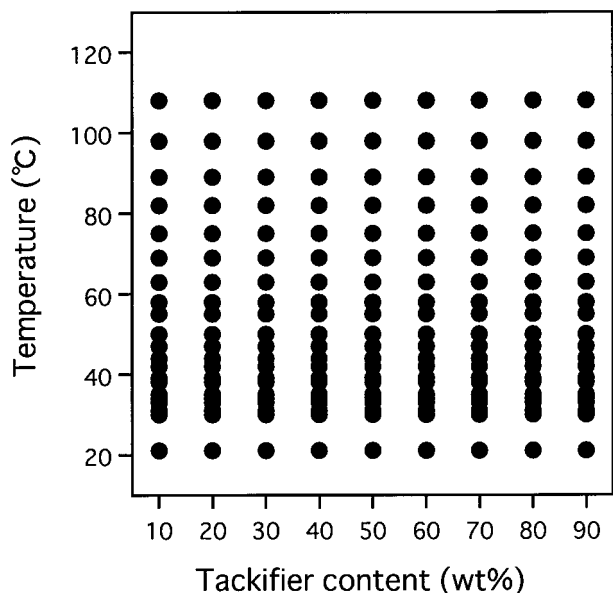


**Figure 11** Phase diagram of the NR/Quintone R100 system (oven method). (○) Transparent; (●) opaque; (Δ) semitransparent.

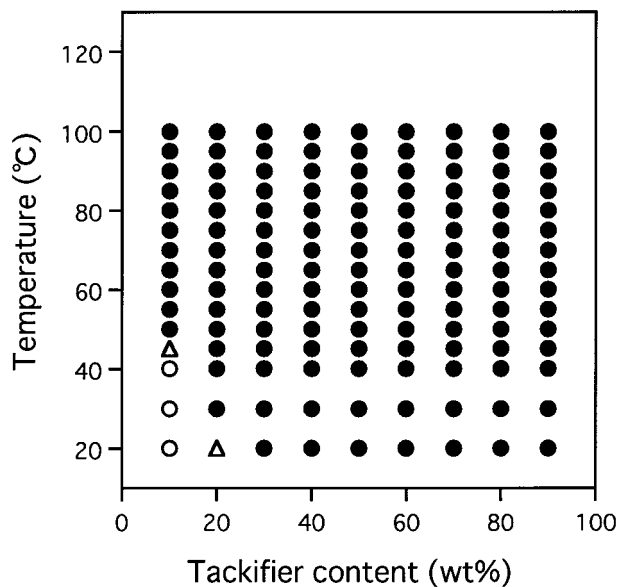
tions at 700 and 755  $\text{cm}^{-1}$  due to C—H bending vibrations of monosubstituted benzene, and there are rather weak absorptions at about 1,495 and 1,600  $\text{cm}^{-1}$ , which are attributable to the C=C stretching vibrations of monosubstituted benzene. There is a large peak at about 2,800–3,000



**Figure 12** Phase diagram of the NR/Quintone S100 system (oven method). (○) Transparent; (●) opaque; (Δ) semitransparent.



**Figure 13** Phase diagram of the NR/Kristalex 1120 system (hot-plate method). (○) Transparent; (●) opaque; (△) semitransparent.



**Figure 14** Phase diagram of the NR/Kristalex 3085 system (oven method). (○) Transparent; (●) opaque; (△) semitransparent.

$\text{cm}^{-1}$  due to C—H stretching vibrations of the saturated aliphatic hydrocarbon. Adjacent to this peak, there exists a small peak at  $3,000\text{--}3,100\text{ cm}^{-1}$  that is attributable to C—H stretching vibrations of aromatic units or unsaturated aliphatic units. Table II summarizes the height ratios of these peaks to the peak at  $2,800\text{--}3,000\text{ cm}^{-1}$ . Obviously, Quintone P500 has larger aromatic peaks than Quintone S100. Namely, Quintone P500 has more styrene units than Quintone S100. From the previous results, it can be concluded that polymers from pure aromatic monomers are immiscible with NR, and that the miscible region decreases as the aromatic content in a tackifier increases. Classand Chu<sup>6</sup> investi-

gated the systems of NR/polystyrene resin and NR/poly(vinyl cyclohexane) resin by viscoelastic measurement and reported that aromatic resins had poor miscibility with NR.

Relationship between number average molecular weights of tackifiers and the LCST of the blends (which show phase diagrams of LCST type) are shown in Figure 16. Data points are scattered, and it is difficult to find out a correlation. But among Quintone resins, the critical temperature is inclined to decrease slowly in a straight line as the  $M_n$  of the resin increases except for one data point. Two data points of ESC-OREZ resins of the aliphatic–aromatic copolymer type are located on the straight line. Although it

**Table II** Relative Absorption Heights of Quintone S100 and P500 in the IR Spectra

Tackifier Names	2,800–3,000 $\text{cm}^{-1}$ <sup>a</sup>	700 $\text{cm}^{-1}$ <sup>b</sup>	755 $\text{cm}^{-1}$ <sup>b</sup>	1,495 $\text{cm}^{-1}$ <sup>c</sup>	1,600 $\text{cm}^{-1}$ <sup>c</sup>	3,000–3,100 $\text{cm}^{-1}$ <sup>d</sup>
Quintone S100	1	0.221	0.0878	0.0777	0.0450	0.122
Quintone P500	1	0.556	0.234	0.202	0.0862	0.196

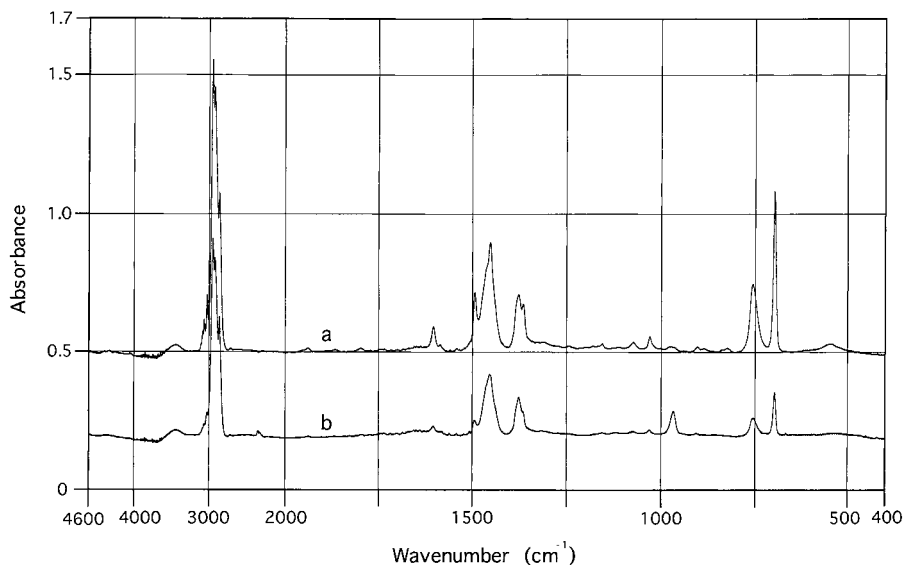
All of the peak heights in this table are relative values when the height of the peak at  $2,800\text{--}3,000\text{ cm}^{-1}$  is assumed to be 1.

<sup>a</sup> Due to C—H stretching vibrations of saturated aliphatic units.

<sup>b</sup> Due to C—H bending vibrations of monosubstituted benzene.

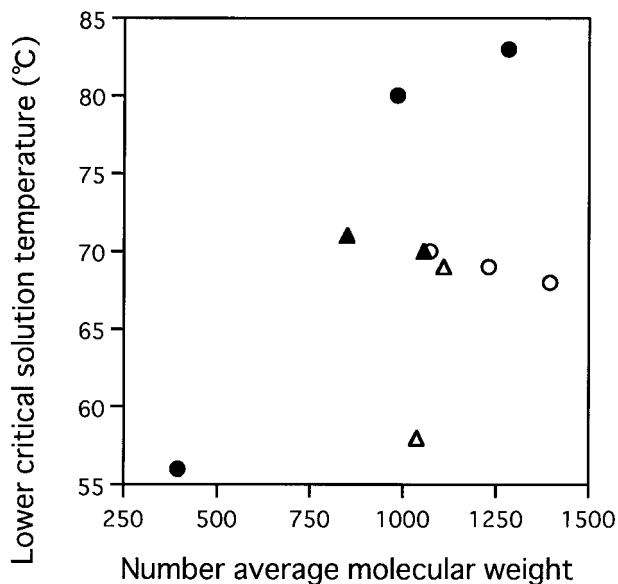
<sup>c</sup> Due to C=C stretching vibrations of monosubstituted benzene.

<sup>d</sup> Due to C—H stretching vibrations of aromatic units or unsaturated aliphatic units.



**Figure 15** IR spectra of Quintone P500 (a) and Quintone S100 (b).

is difficult to assert from Figure 16 that aliphatic–aromatic copolymer resins are less miscible with NR than mostly aliphatic resins, the system of NR/ESCOREZ 1102 (100% aliphatic resin) has the highest critical temperature (83°C) of all of the systems.



**Figure 16** Relationship between critical temperatures of phase diagrams and  $M_n$  of petroleum resins. (●) Aliphatic ESCOREZ resins; (▲) aliphatic–aromatic ESCOREZ resins; (○) aliphatic Quintone resins; (△) aliphatic–aromatic Quintone resins.

The blend containing 80% of Kristalex 3085 was pure white at room temperature before heating. This blend became apparently transparent when it was heated at 90°C for 3 h, although the dispersed phase was observed under an optical microscope. Further heating of this blend made it opaque again after 1 day, and the dispersed phase became gradually larger. The phenomenon of becoming transparent temporarily were seen in other blends of the NR/Kristalex 3085 system, but we cannot explain what causes this. Further study should be done to clarify mechanism of phase separation in each system.

## CONCLUSIONS

1. All of the NR/petroleum resin systems showed phase diagrams of the LCST type, except for blends of NR with polymers from pure aromatic monomers.
2. Polymers made from pure aromatic monomers were completely immiscible with NR.
3. Hydrogenated petroleum resins had poorer miscibility with NR than unsaturated aliphatic petroleum resins.
4. Immiscible region of a NR/petroleum resin system tended to become larger as the molecular weight of the tackifier increases.
5. Immiscible region of a NR/petroleum resin system tended to increase as the



content of aromatic units in the tackifier increases.

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