

Miscibility Between Components of Acrylic Pressure-Sensitive Adhesives: Phase Diagrams of Poly(butyl acrylate-co-acrylic acid) and Esterified Rosins

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SYNOPSIS

A series of acrylic copolymers, poly(butyl acrylate-co-acrylic acid), were blended with tackifiers and dehydroabietic acid esters, and the miscibility between the components was investigated. The phase diagram of the blends changed from an LCST type to a UCST type as acrylic acid content increased, and the miscibility region in the phase diagrams decreased as the tackifier became bulkier. It was found that some of the trends can be accounted for on the basis of mean field approximation. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Pressure-sensitive adhesives have been manufactured by blending gums with resins. Gums are polymers of very low glass transition temperature (T_g) such as natural rubber, synthetic rubber, or block copolymer (SIS, SBS, SEBS, etc), and resins are oligomeric materials such as rosins, terpene resins, or some kinds of synthetic resins [C-5, C-9, and (C-5)₂ resins].¹ When these components are blended with each other, the modulus and viscosity of the blends decrease extensively, and then they become very sticky. In acrylic pressure-sensitive adhesives, tackifier resins are not used in the formulations because one can produce a variety of polymers by combining different comonomers. But recently there were many cases where acrylic copolymers were blended with tackifier resins to modify their adhesion properties. When dealing with the blended materials, it is necessary to examine to what extent the components are miscible with each other, because the miscibility has a great influence on the phase structure, physical properties, and practical performance of the materials. Miscibility in the natural-rubber-based pressure-sensitive adhesives has been extensively studied.²⁻⁷ Hot-melt pressure-sensitive

adhesives or block copolymer/tackifier resin systems have also been studied.^{8,9} However, there have been few studies where the miscibility in the acrylic pressure-sensitive adhesives or acrylic copolymer/tackifier resins were systematically examined.

In this study the miscibility between a series of poly(butyl acrylate-co-acrylic acid) and tackifier resins of the modified rosin type were investigated by means of calorimetry, dynamic mechanical measurements, and visual observations, and phase diagrams could be drawn. And we have tried to analyze qualitatively the phase diagrams according to the Flory-Huggins theory on the basis of mean-field approximation.

EXPERIMENTAL

Materials

The polymers used are a homopolymer of butyl acrylate (BA) and a series of copolymers consisting of BA and acrylic acid (AA) with varying composition: BA/AA = 97/3, 95/5, 93/7, 90/10, and 85/15 by mole percent. These monomers were polymerized in ethyl acetate (Toyo Ink Manufacturing Co. Ltd.). Their characterization data are listed in Table I.

Tackifier resins employed are chemically modified rosins (Arakawa Chemical Industry Co.

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Table I Acrylic Copolymers

Code No.	Composition (mol %)	M_n	M_w	T_g^a
1	BA/AA (100/0)	79,300	291,600	-36
2	BA/AA (97/3)	112,300	417,600	-42
3	BA/AA (95/5)	187,600	362,100	-29
4	BA/AA (93/7)	154,000	302,500	-23
5	BA/AA (90/10)	110,800	241,900	-21
6	BA/AA (85/15)	9,600	15,900	-17

BA, butylacrylate; AA, acrylic acid.

^a Determined by DSC (°C).

Ltd.). The main component of rosin is abietic acid, and the Superester A series are dehydroabietic acid esterified by diethyleneglycol and glycerol (A-75), glycerol (A-100), pentaerythritol (A-115), or pentaerythritol with fumaric acid (A-125), as shown in Table II.

Molecular weight of acrylic polymers and tackifier resins was measured by gel permeation chromatography (GPC) using a Shodex KF-802, -803, -804, -805 column with tetrahydrofuran (THF) at 40°C.

Preparation of Blends

Acrylic polymers and tackifier resins were blended in ethyl acetate solution in various blend ratios: 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, and 10/90. After ensuring that the solutions were uniform and transparent for more than 24 h, filmy samples were prepared by casting them on glass plates. The samples were kept at 80°C for 24 h and then evacuated at 110°C for 48 h to remove the solvent from the samples.

Measurement of T_g by Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Properties

T_g of the blends was measured by a Perkin-Elmer DSC-7 equipped with a thermal analysis data station

with a helium purge. Samples of 9–18 mg were encapsulated in standard aluminum pans. The samples were first cooled to -100°C, then heated to 150°C at a rate of 40°C/min (first scan). They were immediately quench cooled to -100°C at a cooling rate of 200°C/min and kept at this temperature for 5 min. The samples were then reheated to 150°C at a heating rate of 40°C/min (second scan). The T_g reported in this study was obtained from the second scan to assure reproducible thermograms free from thermal history effects. In all cases T_g was taken as the intersection of the extrapolated low temperature baseline with the tangent to the heat capacity rise endotherm.

To get supplemental information on transition of the blends, the solutions of the blends were impregnated into filter papers, and, after removing the solvent, dynamic mechanical properties of the composites were determined as a function of temperature at a fixed frequency of 110 Hz using a Rheovibron Dynamic Mechanical Spectrometer, Model DDV-II (Toyo Baldwin Co. Ltd.). Blends of higher tackifier resin content with acrylic copolymer were too brittle to be tested in unsupported form. This method is effective for the determination of transition temperatures, but does not permit quantitative measurement of the complex dynamic modulus of the matrix polymer. The T_g is specified in this study as the temperature at which the loss modulus E'' is a maximum.

Table II Tackifier Resins

Superester	M_n	M_w	SP	T_g^a	Modification of Dehydroabietic Acid
A-75	900	1,100	75	51	Esterified by glycerol, diethyleneglycol
A-100	1,000	1,200	100	71	Esterified by glycerol
A-115	1,000	1,200	115		Esterified by pentaerythritol
A-125	1,400	2,500	125	102	Esterified by pentaerythritol (involving some fumaric acid)

SP, softening point (°C).

^a Determined by DSC (°C).

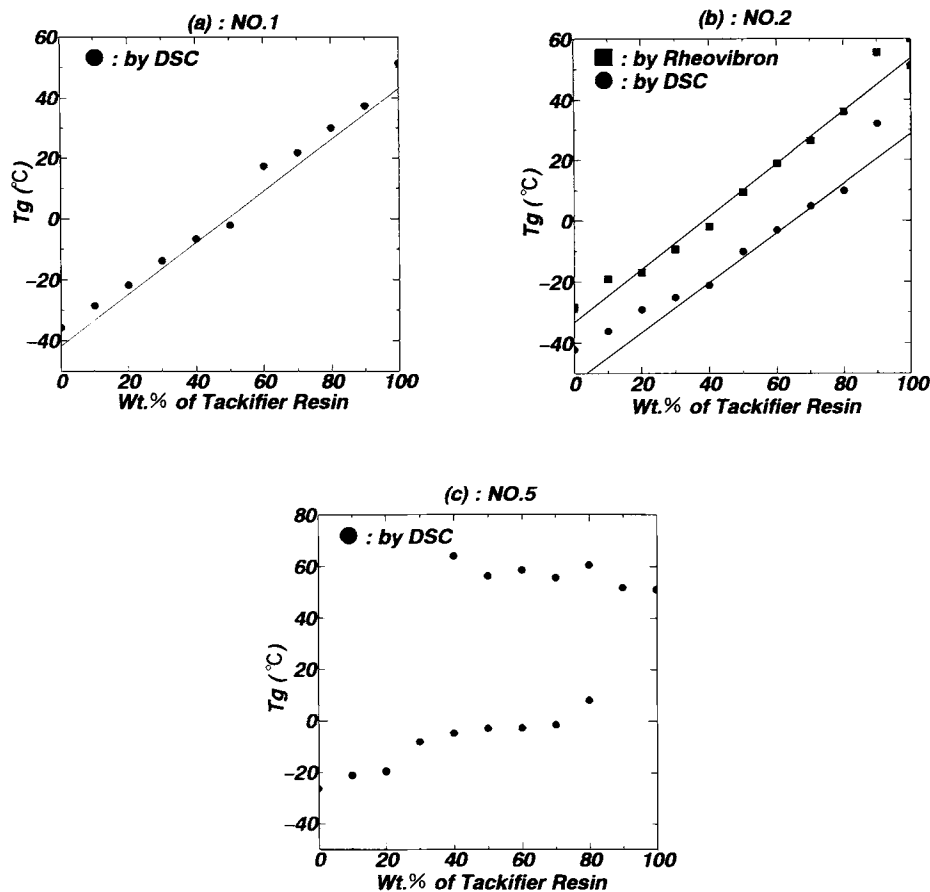


Figure 1 T_g composition curves of acrylic copolymer/Superester A-75. The solid curve represents the Gordon-Taylor equation.

Phase Diagrams

The solutions of the blends were coated on a glass slide at about 40- μm thickness with a glass rod. After drying in a vacuum oven at 110°C for 48 h, the films were maintained at 20°C for 48 h to attain phase equilibrium, and then visually observed to see whether they were transparent or opaque at this temperature. The same procedures were repeated by changing the temperature in a stepwise manner up to 170°C in an air circulation oven. In most cases phase diagrams could not be drawn above 180°C due to discoloration of tackifier resin.

RESULTS AND DISCUSSION

T_g of Blends

DSC has become a classical method in the determination of miscibility. The phase structure of a blend is assessed by the number of T_g s observed in the thermograms; two transitions are a clear indication of phase separation. A single glass transition

located at a temperature intermediate between those of the pure components indicates miscibility.

All of the solution cast films of the acrylic homopolymer No. 1/Superester A-75 systems were optically transparent. The T_g -composition curve of the blends is shown in Figure 1(a). Only one well-defined glass transition lying between the glass transition of the pure components was detected for each blend and it changed monotonously with composition. The optical clarity of the blends and the existence of one composition-dependent T_g are evidence that acrylic homopolymer No. 1 is miscible with Superester A-75 below T_g . Figure 1(b) gives a summary of the experimental T_g s measured by DSC and a Rheovibron for the acrylic copolymer No. 2/Superester A-75 system. The blends were also transparent and showed only one T_g . Once again, the optical clarity and existence of a single composition-dependent T_g demonstrate that acrylic copolymer No. 2 is miscible with Superester A-75. The difference of T_g between DSC and the Rheovibron is attributed to the different nature of the two techniques and to different heating rates; 2°C/min for

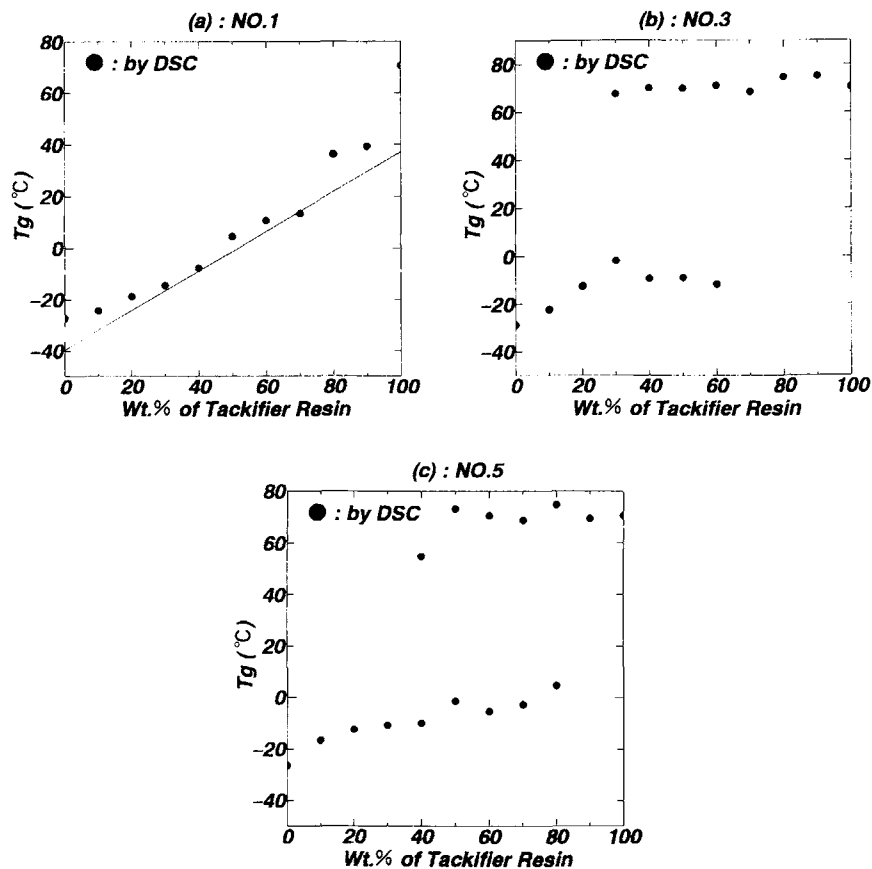


Figure 2 T_g composition curves of acrylic copolymer/Superester A-100. The solid curve represents the Gordon-Taylor equation.

the Rheovibron and 40°C/min for DSC. The T_g -composition curve of the blends for acrylic copolymer No. 5/Superester A-75 is shown in Figure 1(c). The blends are transparent and a single T_g is observed at lower tackifier resin concentration (i.e., between 0 and 40% tackifier resin content), but the blends became cloudy and double T_g s appeared at higher tackifier resin concentration.

All of the solution cast films of the blends of acrylic homopolymer No. 1/Superester A-100 were transparent. Each of the blends shows a single composition dependent T_g [Fig. 2(a)]. It is concluded that acrylic homopolymer No. 1 is miscible with Superester A-100. Figure 2(b,c) gives T_g -composition curves of acrylic copolymer No. 3/Superester A-100 and No. 5/Superester A-100 systems, respectively. These blends are transparent and a single T_g was observed at lower tackifier resin concentration, but the blends became cloudy and double T_g was observed at higher tackifier resin content.

The T_g -composition relationship for the blends can often be represented by the Gordon-Taylor equation¹⁰:

$$T_g = \frac{w_1 T_{g1} + \kappa w_2 T_{g2}}{w_1 + \kappa w_2} \tag{1}$$

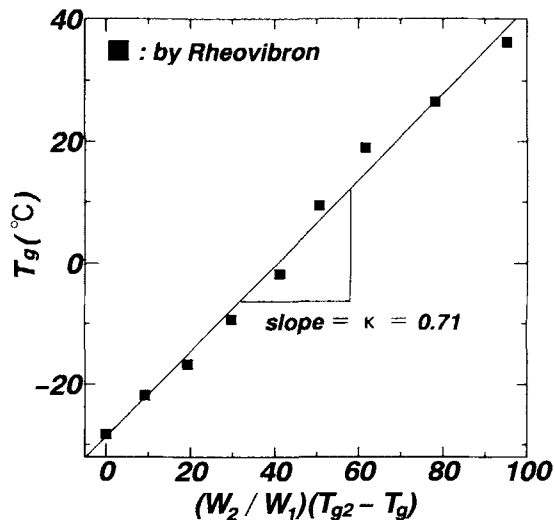


Figure 3 T_g of acrylic polymer No. 2/Superester A-75 plotted according to the Gordon-Taylor equation.

where: T_g , T_{g1} , and T_{g2} are the glass transition temperatures of the blend, acrylic polymer 1, and tackifier resin 2, respectively; w_1 and w_2 are the weight fractions of the components; and κ is the adjusting parameter related to the degree of curvature of the T_g -composition diagram. This curvature is generally believed to be large in polymer/polymer blends in cases where a strong interaction exists between different segments.^{11,12} To compare a series of blends used in this study, values of κ were calculated according to eq. (2):

$$T_g = T_{g1} + \kappa(w_2/w_1)(T_{g2} - T_{g1}). \quad (2)$$

For the acrylic copolymer No. 2/Superester A-75 system, T_g is given in Figure 3 as a function of $(w_2/w_1)(T_{g2} - T_{g1})$. The data were fitted by a least-squares regression technique, and the slope (κ) of the straight line was found to be 0.71. Values of κ obtained by this method for some blends are listed in Table III. Belorgey and Pru'dhomme¹³ suggested that the value of κ gives a qualitative measure of the degree of interaction between components in the blend: the higher the value of κ , the higher the degree of interaction, but no fundamental basis for this connection has been presented. By comparing the κ values in Table III with the corresponding phase diagrams which will appear later, it becomes evident that the above-mentioned empirical rule does not necessarily hold true in every case. For example, polymer No. 2/Superester A-75 is completely soluble in the temperature range from 20 to 170°C, and polymer No. 1/Superester A-75 is a blend of lower critical solution temperature (LCST) type, which means that solubility of the former system is better than the latter. However, the κ value is in the reverse order.

Phase Diagrams

Phase diagrams of acrylic copolymer/Superester A-75 are shown in Figure 4. The phase diagrams systematically change as AA content in the copolymer increases. The blends of acrylic homopolymer No. 1 with Superester A-75 gives a phase diagram of typical LCST type. And when the content of AA is 3%, the blends are miscible at any temperature between 20 and 170°C, irrespective of the tackifier content. It is interesting to note that at above 3% AA content, the phase diagram abruptly changes into an upper critical solution temperature (UCST) type. The range of miscibility of the acrylic copolymer and Superester A-75 system decreases as AA content increases. And when content of AA is 15%,

Table III κ Values of Acrylic Polymer and Tackifier Resin Systems

Blends	κ
Homopolymer No. 1/ Superester A-75	0.6 (by DSC)
Copolymer No. 2/ Superester A-75	0.4 (by DSC)
Copolymer No. 2/ Superester A-75	0.7 (by Rheovibron)
Homopolymer No. 1/ Superester A-100	0.3 (by DSC)

the range of miscibility of the blends almost disappears.

Phase diagrams of acrylic copolymer/Superester A-100 are shown in Figure 5. These phase diagrams also systematically change as AA content in the polymer increases. The acrylic homopolymer No. 1 and Superester A-100 system gives a phase diagram of LCST type. At 3% AA content, the type of phase diagram converted from LCST to UCST type. As AA concentration increases the range of miscibility of the blends decreases. The phase diagram of acrylic copolymer No. 5/Superester A-100 is similar to an hourglass or UCST type. In addition, when content of AA reaches 15%, the range of miscibility of the blends almost disappeared. The phase diagram of acrylic polymer No. 1/Superester A-100 is similar to that of acrylic polymer No. 1/Superester A-75, but the LCST of acrylic polymer No. 1/Superester A-75 is over 15°C higher than the cloud temperature of acrylic polymer No. 1/Superester A-100 and the UCSTs of acrylic copolymer/Superester A-75 is lower than those of acrylic copolymer/Superester A-100, namely the range of miscibility of blends of acrylic polymers with Superester A-75 is greater than those with Superester A-100 in the concentration and given temperature.

Phase diagrams of acrylic copolymer/Superester A-115 are shown in Figure 6, which is similar to Figure 5 in type. But blends of acrylic homopolymer No. 1 and Superester A-115 do not give a phase diagram of LCST type. The blends became cloudy at higher tackifier resin concentration. As AA concentration increases the range of the miscibility of the blends markedly decreases.

Phase diagrams of acrylic copolymer/Superester A-125 are shown in Figure 7. Components of these systems are immiscible, irrespective of AA content.

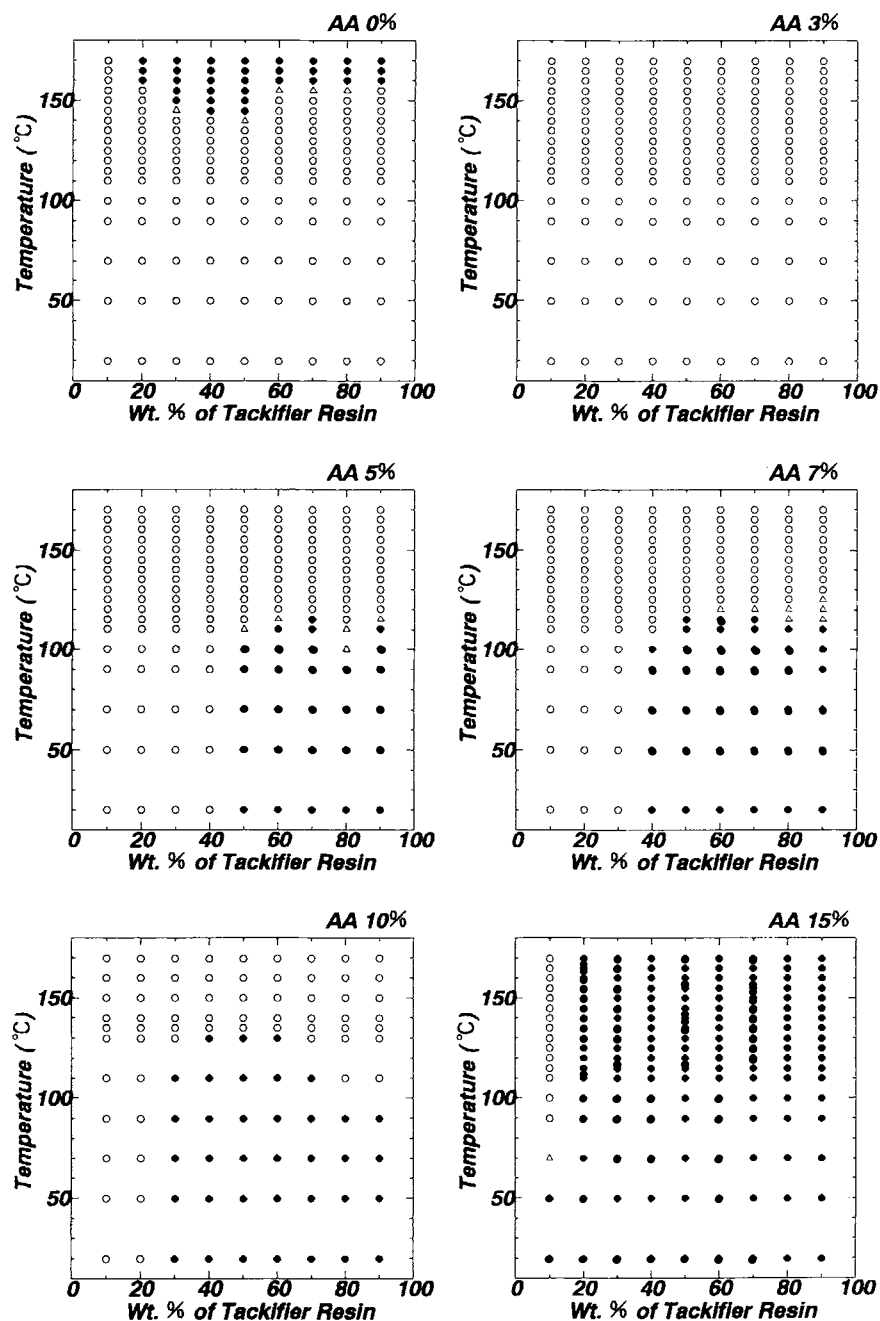


Figure 4 Phase diagrams of acrylic copolymer/Superester A-75. O: transparent (miscible), ●: opaque (immiscible), and Δ: intermediate.

Systematic changes in the phase diagrams of acrylic copolymer/dehydroabiestic esters may be explained in terms of not only the specific interaction between the polymer segment and the tackifier resin, but also the bulkiness of the resin.

In this study we have tried to analyze the phase diagrams in a formal way according to the Flory-Huggins theory.¹⁴

Binodal curve can be expressed by the following equations¹⁵:

$$\chi_{\text{blend}} = A_{\text{blend}} + B_{\text{blend}}/RT \quad (3)$$

$$1/T_{\text{bn}} = 1/T_c^\infty \{1 - 1/[2A(\phi_2' - \phi_2'')]\} \\ \times \{1/m_2[\ln(\phi_2'/\phi_2'')] - 1/m_1[\ln(\phi_1'/\phi_1'')]\} \quad (4)$$

$$2(1/m_1 - 1/m_2)(\phi_2' - \phi_2'') + [2 - (\phi_2' + \phi_2'')/m_1] \\ \times \ln(\phi_1'/\phi_1'') + [(\phi_2' + \phi_2'')/m_2]\ln(\phi_2'/\phi_2'') = 0 \quad (5)$$

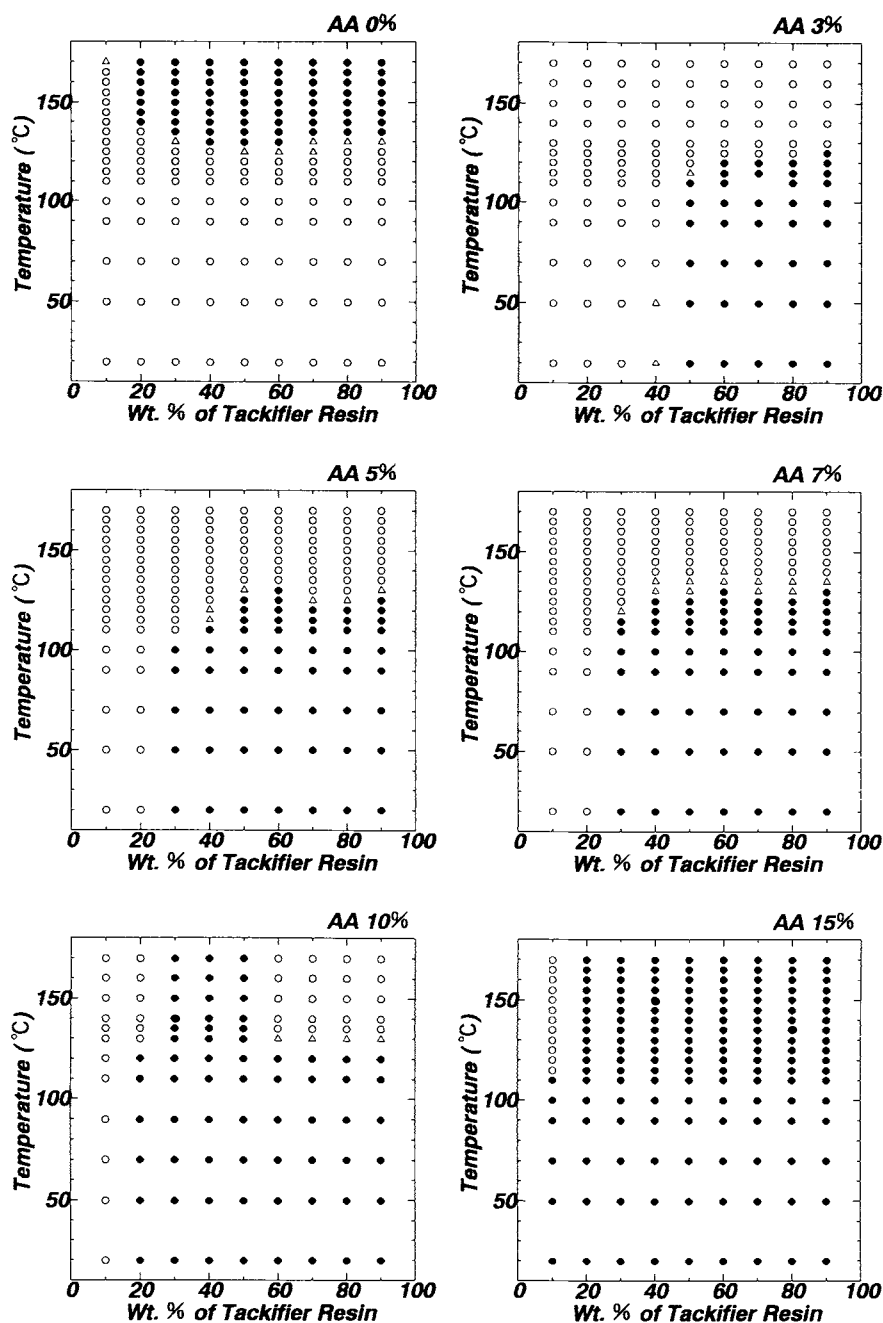


Figure 5 Phase diagrams of acrylic copolymers/Superester A-100. The symbols are the same as in Figure 4.

where χ_{blend} is the overall segmental interaction parameter for a pair of copolymer and tackifier resin, A_{blend} and B_{blend} are constants, R is the gas constant, T_{bn} is the binodal temperature, T_c^∞ is the critical temperature where number of segments in the copolymer is infinity, $1/T_c^\infty = A_{\text{blend}}R/B_{\text{blend}}$, (ϕ_1', ϕ_2') , (ϕ_1'', ϕ_2'') are volume fractions of the two components in the two phases. m_1 and m_2 are number of segments in tackifier resin and copolymer, respectively. Here, $m_1 = 1$ and m_2 is the ratio of number-average mo-

lecular weight of the copolymer to that of the tackifier resin.

In principle, the curve fitting can be done for the experimentally observed phase diagrams, but in this study it was rather difficult to determine the strict values of the parameters. The approximate χ_{blend} values obtained are summarized in Table IV.

Figure 8 is the schematic illustration of the temperature dependence of χ_{blend} for the acrylic

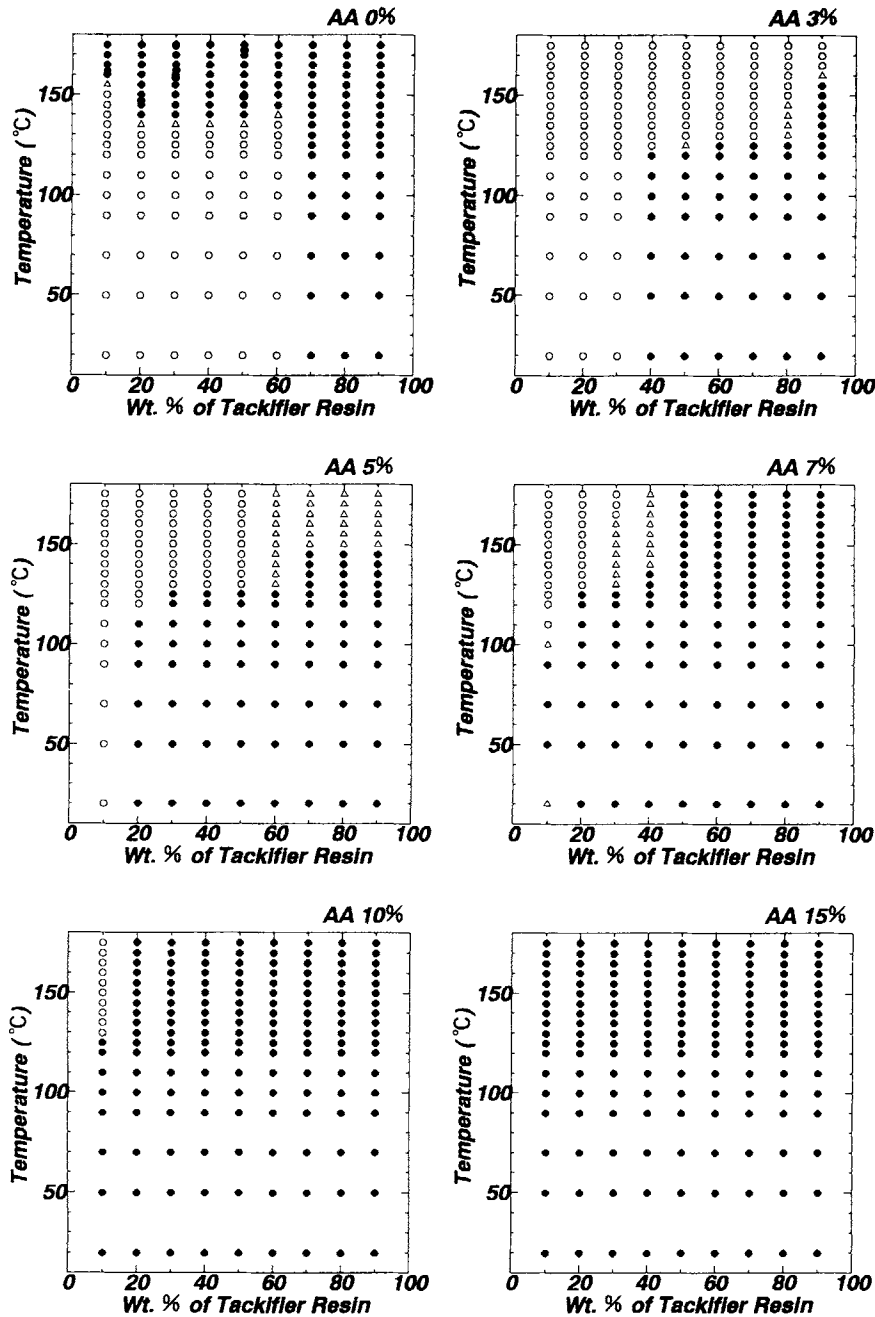


Figure 6 Phase diagrams of acrylic copolymer/Superester A-115. The symbols are the same as in Figure 4.

copolymer/Superester A-75 system. When AA content (mole fraction, y) is zero (homopolymer of BA), the phase diagram is of LCST type, which means that χ_{blend} is larger at higher temperature. When $y = 0.03$, the two components are miscible with each other and χ_{blend} is lower than the critical value within the temperature range of these experiments. And when y is larger than 0.03, the phase diagram of UCST type appears instead of LCST. In this case, χ_{blend} is lower at higher tem-

perature. Or, in other words, if χ_{blend} is expressed by eq. (3), A_{blend} must be a decreasing function and B_{blend} must be an increasing function of y , which is qualitatively consistent with the data shown in Table IV. Similar trends can be seen in the other blend systems in Table IV.

It can be pointed out that the extent of miscibility decreases as the tackifier resin becomes bulkier, and Superester A-125, which is the bulkiest because the main component is pentaer-

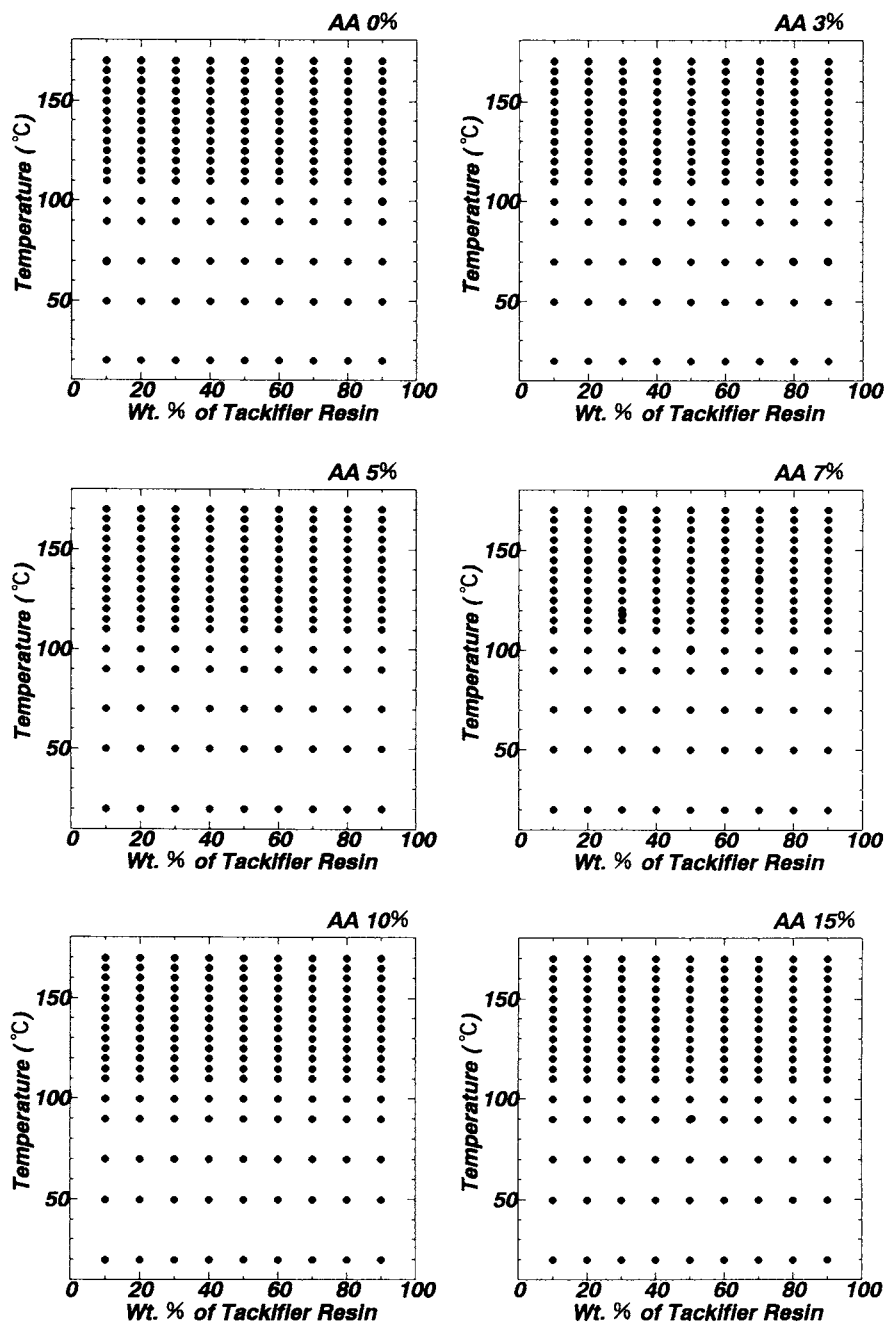


Figure 7 Phase diagrams of acrylic copolymer/Superester A-125. The symbols are the same as in Figure 4.

thritol ester of dehydroabiatic acid, does not dissolve in the acrylic copolymer under study at all.

Part of these characteristics can be qualitatively accounted for on the basis of mean-field approximation. The overall segmental interaction parameter χ_{blend} for a blend of a $(A_y B_{1-y})_{m2}/T_{m1}$ system, where A, B, and T refer to AA, BA, and tackifier, respectively, can be expressed by the following equation¹⁸:

$$\begin{aligned}\chi_{\text{blend}} &= y\chi_{\text{AT}} + (1 - y)\chi_{\text{BT}} - y(1 - y)\chi_{\text{AB}} \\ &= y^2\chi_{\text{AB}} + y(\chi_{\text{AT}} - \chi_{\text{BT}} - \chi_{\text{AB}}) + \chi_{\text{BT}}\end{aligned}\quad (6)$$

where χ_{ij} is the interaction parameter of each combination of segment or molecule. And if χ_{ij} is expressed by

$$\chi_{ij} = A_{ij} + B_{ij}/RT\quad (7)$$

Table IV χ_{blend} of Acrylic Copolymer and Tackifier Resin Systems

Polymer	Superester	χ_{blend} of Blends
BA/AA (100/0)	A-75	$20 - 7660/T$
BA/AA (97/3)	A-75	$4.4 - 1905/T^a$
BA/AA (95/5)	A-75	$-3.1 + 1404/T$
BA/AA (93/7)	A-75	$-3.7 + 1676/T$
BA/AA (90/10)	A-75	$-5.3 + 2400/T$
BA/AA (100/0)	A-100	$28 - 10724/T$
BA/AA (97/3)	A-100	$-3.9 + 1766/T$
BA/AA (95/5)	A-100	$-4.6 + 2083/T$
BA/AA (93/7)	A-100	$-5.3 + 4031/T$

BA, butyl acrylate; AA, acrylic acid.

^a Calculated from eqs. (3), (10), and (11).

then the overall A_{blend} and B_{blend} should also be expressed by the quadratic equation:

$$A_{\text{blend}} = yA_{\text{AT}} + (1 - y)A_{\text{BT}} - y(1 - y)A_{\text{AB}} \quad (8)$$

$$B_{\text{blend}} = yB_{\text{AT}} + (1 - y)B_{\text{BT}} - y(1 - y)B_{\text{AB}} \quad (9)$$

Data of acrylic copolymer/Superester A-75 listed in Table IV are approximately reproduced by the following equation:

$$A_{\text{blend}} = 2900y^2 - 600y + 20 \quad (10)$$

$$B_{\text{blend}} = -4.38 \times 10^6 y^2 + 1.7 \times 10^6 y - 6.3 \times 10^4 \quad (11)$$

Then we can calculate the value of χ_{blend} at any AA content, and we can also calculate the binodal curve of the phase diagram, using eqs. (4) and (5).

Figure 9 shows the calculated phase diagrams of acrylic copolymer/Superester A-75 for $y = 0, 0.03, 0.05,$ and 0.07 . The calculated phase diagrams do not agree quantitatively with the experimentally observed ones, but the general trends are qualitatively the same. Because tackifier resins used in this study are large and bulky molecules, and acrylic copolymers are long linear molecules, values of the parameters obtained according to a simple lattice model have little physical significance. If we want further insight into the segmental interaction between linear polymers and bulky oligomers in a strict sense, we may have to analyze the phase diagrams according to the new Flory theory^{17,18} or Sanchez-Lacombe theory^{19,20} where equations of state of the component materials are needed.

CONCLUSION

A series of poly(butyl acrylate-co-acrylic acid)s, which are used as acrylic pressure-sensitive adhe-

sives, were blended with tackifier resins made of chemically modified rosin, the main component of which is dehydroabietic acid ester. The miscibility between various combinations of the materials was investigated by means of DSC, dynamic mechanical measurements, and visual observations. The phase diagrams changed systematically with the change of chemical structure of the component molecules. It was often found in this study that phase diagram changed from LCST type to UCST type as the AA content in the acrylic copolymer increased. And it can also be pointed out that the miscibility decreased as the tackifier resin became bulkier. Some of these findings can be qualitatively accounted for on the basis of mean-field approximation, but if more detailed information on the segmental interaction between linear polymers and bulky oligomers is needed, the phase diagrams of the materials according to the advanced theory of polymer blend will have to be analyzed.¹⁷⁻²⁰

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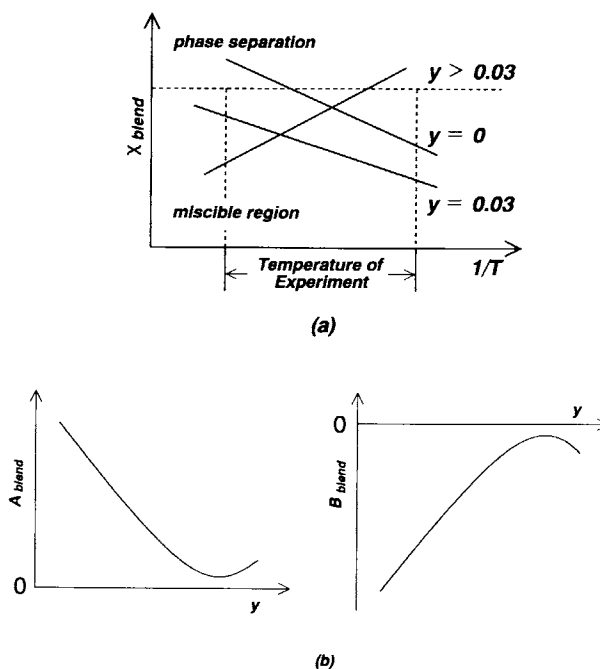


Figure 8 Schematic illustration of temperature dependence of the χ_{blend} parameter of acrylic copolymer and Superester A-75. (a) Temperature dependence of χ_{blend} , (b) composition, (y) dependence of A_{blend} and B_{blend} .

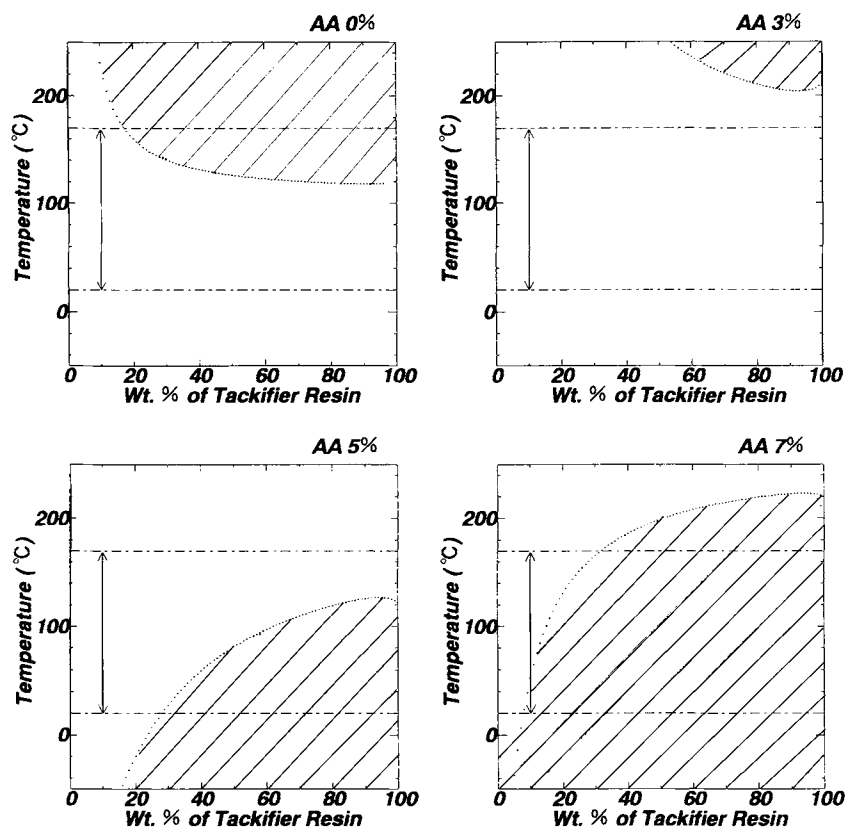


Figure 9 Binodal curve of acrylic copolymer and Superester A-75 calculated according to eqs. (3), (4), (5), and (11). The arrow line represents the range of experimental temperature and the hatchings represent immiscible region.

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