

Miscibility and Peel Strength of Acrylic Pressure-Sensitive Adhesives: Acrylic Copolymer-Tackifier Resin Systems

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SYNOPSIS

Influence of miscibility between the components in acrylic pressure-sensitive adhesives upon their peel strength P as a function of temperature has been studied. In case of miscible blend systems, incorporation of tackifier resins into the pressure-sensitive adhesive systems results in the modification of the bulk properties, including T_g , and a plot of P against ΔT gives a smooth master curve, where ΔT is defined as the difference between the temperature of peel test and T_g of the blend. However, in case of immiscible blends where two phases exist in the system, no master curve can be obtained, and P of an acrylic copolymer decreases as the tackifier content increases. In this case, physical properties and adhesive performance will be governed by a matrix phase, and a dispersed phase will act as a filler. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Pressure-sensitive adhesives (PSA) are used for many different applications in the form of tapes, labels, decals, medical products, and others.¹

There are several types of PSA such as natural-rubber-based PSA, block-copolymer-based (SIS, SBS, etc.) PSA, acrylic PSA, etc. The former two types of PSA are blends of rubbery polymers and tackifier resins, and it used to be believed that no tackifier is needed in acrylic PSA because one can easily produce polymers of various properties by combining different kinds of comonomers. However, recently, tackifier resins are often added to the formulations of acrylic PSA to modify the practical performances. Therefore, it can be said that most of the PSA actually used are blends of long-chain molecules and bulky oligomeric materials.

The most important practical performance of PSA are adhesion (peel strength), tack (probe tack, ball tack, and loop tack), and holding power (shear creep resistance), and because they are all closely

related to deformation and failure of the materials, the measured values are dependent not only on temperature but also on rate of deformation.²

It has been pointed out by several researchers that there exist some empirical or semi-empirical correlation between the viscoelastic properties of PSA and their performance.³⁻⁷

Considering the fact that the PSA are blends of elastomeric polymers and tackifier resins, it is very important to investigate the degree of miscibility between the components, because the phase structures are governed by the miscibility, i.e., when the components are miscible with each other, the blends must be in a uniform one-phase structure, but when they are immiscible, phase separation must occur in the materials. And the physical properties and hence the practical performance of the PSA are dependent on the phase structure of the materials.

In a previous study,⁸ we examined the degree of miscibility between the components in some acrylic PSA and analyzed qualitatively the experimentally obtained phase diagrams according to the Flory-Huggins theory based on the mean field approximation.

In this study, the dependence of peel strength of acrylic PSA on the miscibility between the components is investigated.

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EXPERIMENTAL

Materials

Acrylic copolymers used in this study are listed in Table I, where the average molecular weight is also shown. All these samples were kindly supplied by Toyo Ink Manufacturing Co. in the form of ethyl acetate-toluene solution (84.6/15.4 by wt %).

Tackifier resins are hydrated terpene resin (Clearon K-4090), terpene phenolic copolymer (phenol 25%) (YS Polystar T-130), esterified rosin (Superester A-75), and partially polymerized rosin (Polypale), which are kindly supplied by Yasuhara Chemical Co. Ltd., Arakawa Chemical Co. Ltd., and Hercules Co. Ltd., respectively. Their characterizations are listed in Table II. They were dissolved in ethyl acetate (50/50 by vol. %).

Blend Preparation

All the blends of acrylic copolymers and tackifier resins with the blend ratios of 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, and 10/90 by weight are prepared by casting from ethyl acetate-toluene solutions. The solutions were kept at room temperature for 24 days to ensure complete dissolution. Also, the samples for differential scanning calorimetry (DSC) and Rheovibron were prepared by removing the solvent slowly at room temperature for 24 h. All the samples are dried at 80°C for 24 h. And then dried in a vacuum oven at 110°C for 48 h to completely remove residual solvent.

T_g Measurements

The miscibility of the blends is determined according to the criterion that a miscible blend exhibits one T_g whereas an immiscible blend shows the double T_g peaks corresponding to the components. The glass transition temperature (T_g) of various samples

is measured with a Perkin-Elmer DSC-7 differential scanning calorimeter with a heating rate of 40°C/min in helium purge. In all cases T_g is taken as the midpoint of the heat capacity curve change with temperature and obtained from the second scanning. In order to get supplemental information on transition of the blends, the solutions of the blends are impregnated into filter papers, and after removing the solvent, their dynamic mechanical properties are determined as a function of temperature at a fixed frequency of 110 Hz using a Rheovibron Dynamic Mechanical Spectrometer, Model DDV-II, made by Toyo Baldwin Co. Ltd. The T_g is specified in this study as the temperature at which the loss modulus E'' is a maximum.

Phase Diagrams

The solutions of the blends are coated on slide glass in about 40 μm thickness, with a glass rod. Solvent in these films on slide glass were allowed to evaporate slowly at room temperature for 24 h, and all the samples are dried at 80°C for 24 h and then dried in a vacuum oven at 110°C for 48 h to completely remove residual solvent. And after the films on slide glass were maintained at 20°C for 48 h, they are visually observed to see whether they are transparent or opaque at this temperature. Successively, the same procedures are repeated by changing the temperature in a stepwise manner between 50 and 170°C in an air circulation oven.

Measurement of 180° Peel Strength

PSA specimens for peel tests were prepared by coating ethyl acetate solutions of the blends of acrylic copolymers with tackifier resin onto corona-treated polyethylene terephthalate (PET) film of 25 μm average thickness, using our laboratory coating device. Thickness of the PSA tape is adjusted to 20 μm by film thickness gauge. The PSA tape thus obtained

Table I Acrylic Copolymers

Code	Composition of Copolymers (mol %) ^a	M_n	M_w	T_g (°C)
1	Butyl acrylate/acrylic acid (97/3)	112,000	417,600	-42
2	Butyl acrylate/acrylic acid (90/10)	110,800	241,900	-21
3	2-Ethylhexyl acrylate/vinyl acetate/acrylic acid (56/41/3)	80,500	279,100	-37
4	2-Ethylhexyl acrylate/butyl acrylate/vinyl acetate/acrylic acid (39/21/37/3)	80,000	399,000	-40

^a Toyo Ink Manufacturing Co. Ltd.

Table II Tackifier Resins

Tackifier Resins ^a	M_n	M_w	SP ^b	Modification of Resins
Suprester A-75 (R)(1)	900	1100	75	Disproportionation of abietic acid
Polypale (R)(2)	1300	2000	102	Partially polymerized rosin
YS Polystar T-130 (T)(3)	1000	1300	130	Terpene phenolic copolymer (phenol 25%)
Clearon K-4090 (T)(3)	1000	1500	88	Hydrogenated terpene

^a (R), rosin; (T), terpene. (1) Arakawa Chemical Industry Co. Ltd., (2) Hercules Co. Ltd., (3) Yasuhara Chemical Co. Ltd.

^b SP, softening point (°C).

was kept at room temperature in hood for 24 h to remove most of the solvent very slowly and then dried in an oven at 80°C for 12 h and 120°C for 12 h in an air circulation oven. Dried PSA tape is pressed onto release coating paper by a 2-kg rubber roller. And then they were seasoned at 20°C and 65% RH for more than 14 days.

The peel strength is a measure of the force required to remove a PSA film from another substrate. In this study, aluminum was used as a substrate. The aluminum substrate is cleaned with acetone and then trichloroethylene beforehand. PSA tape is pressed on aluminum by a 2-kg rubber roller passing over two times. The 180° peel strength P of acrylic PSA films coated on PET was measured by Tensilon with a crosshead speed of 30 cm/min at 7 different temperatures (20, 30, 40, 50, 70, 90, and 110°C) after keeping the specimen at these temperatures for 24 h.

RESULTS AND DISCUSSION

Peel Strength of Miscible Acrylic PSAs

All the blends of acrylic copolymer 3 with Polypale are transparent. Each of the blends show a single composition-dependent T_g as shown in Figure 1 (lower). The glass transition temperature (T_g) moves gradually to higher temperature with increasing Polypale content, which led us to believe that the blends might be miscible in molecular scale. This is ascertained by the phase diagram shown in Figure 1 (upper). The blends containing 60–70% of Polypale turned cloudy when heated to 125°C, showing that this is a phase diagram of lower critical solution temperature (LCST) type. Therefore, it is concluded that acrylic copolymer 3 is miscible with Polypale within the experimental temperature range where peel strength was measured in this study. Plot of peel strength P against temperature for acrylic copolymer 3 and Polypale system is shown in Figure

2. T_g of the blend systematically increased with the concentration of the tackifier resin, and at the same time the peak of peel strength P shifts toward higher temperature. Plot of peel strength P against ΔT gives a kind of a master curve, where $\Delta T = T - T_g$ is defined as a difference between temperature of experiment and T_g of the blend. The master curve for acrylic copolymer 3 and Polypale system is shown in Figure 3. The master curve of this miscible system is very smooth and almost similar to that of unmodified acrylic copolymer. This means that the PSA performance depends on the dynamic mechanical properties of the bulk phase of the PSA system, which is modified by tackifier resin. The peel strength P of the individual blend has reached its

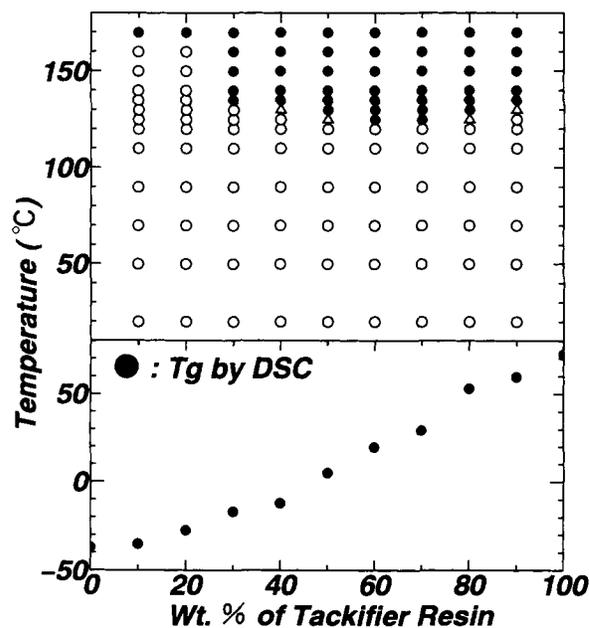


Figure 1 Phase diagram and T_g -composition curve for acrylic copolymer 3 and Polypale system. (O) transparent (miscible), (●) opaque (immiscible) and (Δ) intermediate state.

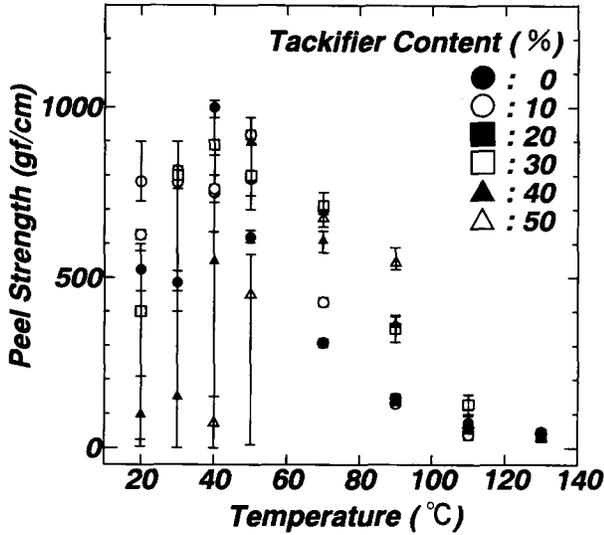


Figure 2 Plot of peel strength against temperature for acrylic copolymer 3 and Polypale system.

maximum at about 60°C above its T_g of the blends. Here, the lower temperature side of the curve corresponds to interfacial failure, and the higher temperature side corresponds mostly to cohesive failure in the adhesive phase.

Also, the blends of acrylic copolymer 1 with Polypale are clear at any blend ratio. Both T_g obtained by Rheovibron and that by DSC systematically increase with tackifier resin. The two kinds of T_g 's are not identical because of the difference of the techniques and also the different heating rates employed,

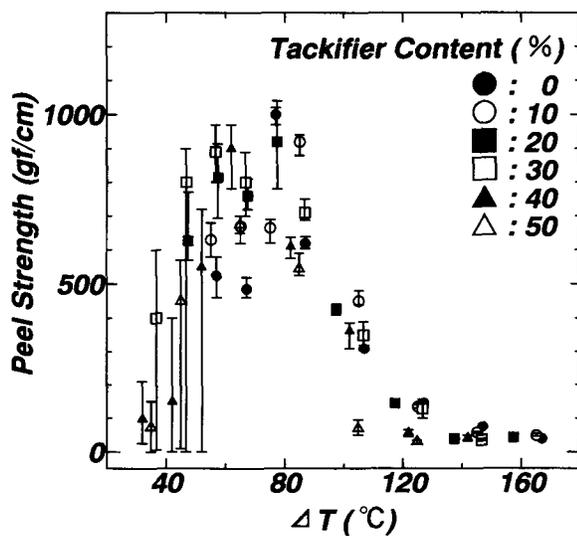


Figure 3 Plot of peel strength against ΔT for acrylic copolymer 3 and Polypale system.

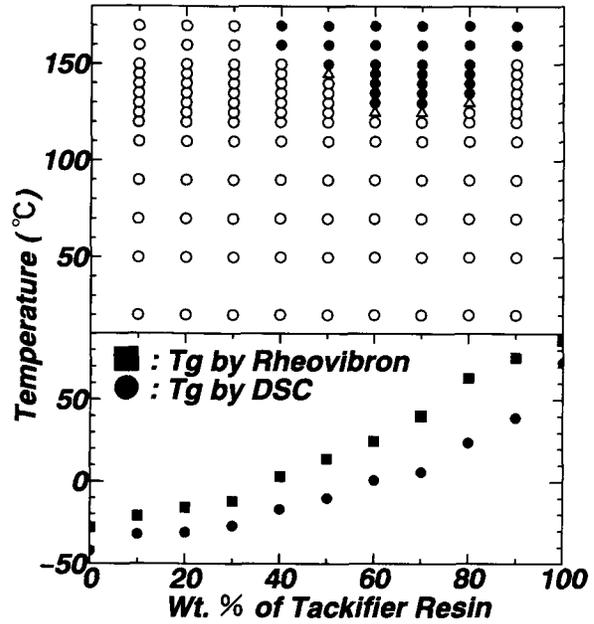


Figure 4 Phase diagram and T_g -composition curve for acrylic copolymer 1 and Polypale system. Symbols as in Figure 1.

but the composition dependence is the same as shown in Figure 4 (lower). Thus, it is evident that these blends have a single composition-dependent T_g . And a phase diagram of the blends is similar to acrylic copolymer 3/Polypale system, which exhibits a phase diagram of LCST type. The plot of peel strength against ΔT for acrylic copolymer 1 and Polypale system is shown in Figure 5. This master

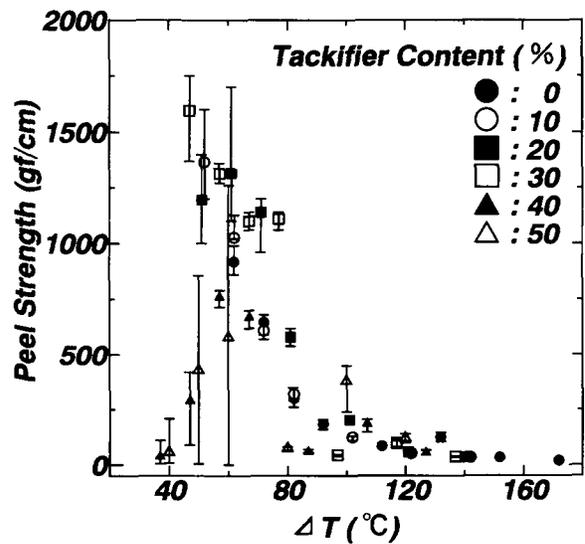


Figure 5 Plot of peel strength against ΔT for acrylic copolymer 1 and Polypale system.

curve is also similar to Figure 3 in shape, but the maximum value of peel strength P of these blends slightly increases with increasing tackifier resin, at a resin concentration of about 30% or lower. The peel strength P of the blends containing more than 40% of tackifier resin is smaller than that of acrylic copolymer without tackifier resin. Thus, the miscible system is systematically modified by incorporation of a tackifier resin.

Figure 6 (lower) shows the T_g -composition curve by DSC for the blends of acrylic copolymer 4 with YS Polystar T-130, which shows only one glass transition temperature at any tackifier resin concentration. These blends are also transparent up to 120°C. The phase diagram of these blends shows LCST behavior, as shown in Figure 6 (upper). The results show that acrylic copolymer 4 is miscible with YS Polystar T-130 throughout the whole composition range at the temperature where peel strength was measured in this work. Figure 7 shows the master curve of peel strength P plotted against ΔT for acrylic copolymer 4 and YS Polystar T-130 system. The master curve is also similar to another miscible blend in shape. This curve has reached its maximum when content of tackifier resin is about 10%. And the peel strength P of the blends containing more than 50% of tackifier resin is smaller than that of polymer without tackifier resin.

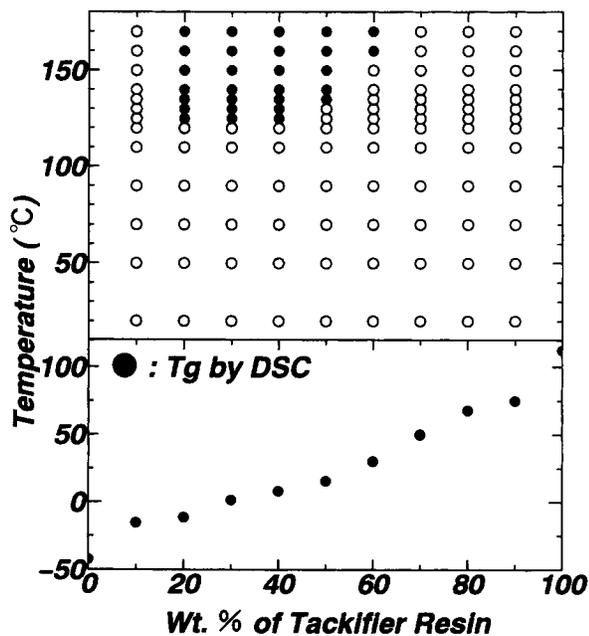


Figure 6 Phase diagram and T_g -composition curve for acrylic copolymer 4 and YS Polystar T-130 system. Symbols as in Figure 1.

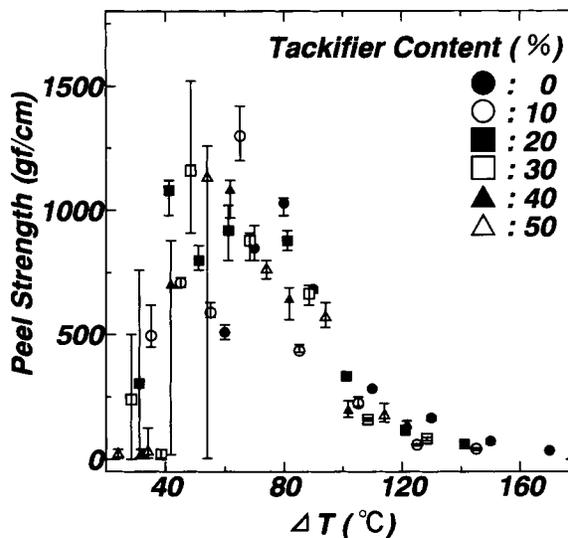


Figure 7 Plot of peel strength against ΔT for acrylic copolymer 4 and YS Polystar T-130 system.

Peel Strength of Immiscible Acrylic PSA

Figure 8 (lower) shows the T_g -composition curve of acrylic copolymer 1 and Clearon K-4090 system, where T_g was measured by DSC and Rheovibron. Two glass transition temperatures (T_g 's) are observed in the whole composition range. The T_g 's are

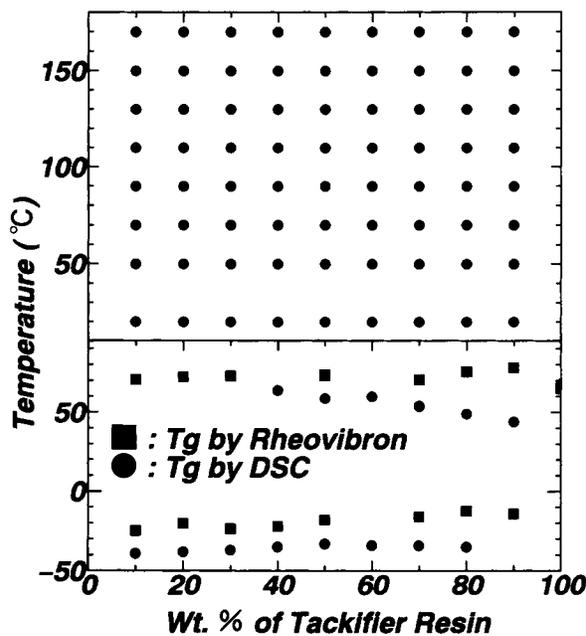


Figure 8 Phase diagram and T_g -composition curve for acrylic copolymer 1 and Clearon K-4090 system. Symbols as in Figure 1.

close to those of acrylic copolymer 1 and the Clearon K-4090 sample. Moreover, all the blends are cloudy. The results show that acrylic copolymer 1 is immiscible with Clearon K-4090 at any blend ratio. The phase diagram of acrylic copolymer 1 and Clearon K-4090 system is shown in Figure 8 (upper). The blend films were cloudy over nearly the entire composition region and experimental temperature region. Figure 9 shows the peel strength at several temperatures for acrylic copolymer 1 and Clearon K-4090 system. Peak of the peel strength is located at about 30°C irrespective of the blend ratio. In this temperature, peel strength of the blend involving less than 40% of tackifier resin is larger than that of unmodified acrylic polymer, while peel strength at another temperature range is almost the same as that of acrylic copolymer without tackifier resin. The master curve of peel strength against ΔT of acrylic copolymer 1/Clearon K-4090 system is shown in Figure 10, where $\Delta T (=T - \text{lower } T_g)$ is defined as a difference between temperature (T) of peel strength measurements and lower T_g , which corresponds to the elastomer phase. It is evident that in case of an immiscible system where two phases exist in the system, a smooth master curve cannot be obtained. The peel strength P depends mostly on the dynamic mechanical properties the matrix phase, and the resin-rich phase acts as a filler, reducing the peel strength P value. Failure modes in the peel tests of immiscible blends are similar to those of miscible blends. The lower temperature side of the curve corresponds to interfacial failure, but the higher tem-

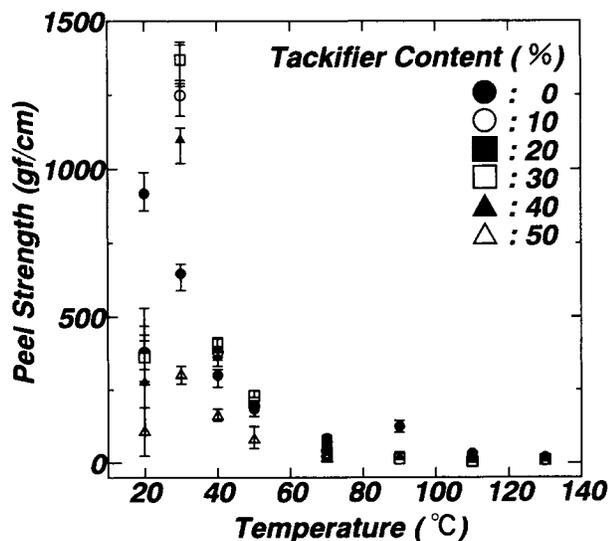


Figure 9 Plot of peel strength against temperature for acrylic copolymer 1 and Clearon K-4090 system.

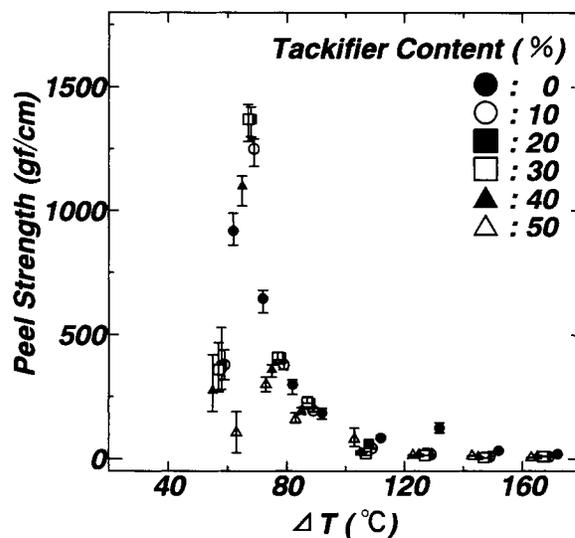


Figure 10 Plot of peel strength against ΔT for acrylic copolymer 1 and Clearon K-4090 system.

perature side ($T > 40^\circ\text{C}$) corresponds mostly to cohesive failure in the adhesive layer.

The T_g -composition curve and phase diagram of acrylic copolymer 2/Clearon K-4090 system are shown in Figure 11 (lower and upper, respectively). On the basis of both the DSC data on glass transition temperatures and film opaqueness, the blends are found to be immiscible over nearly the whole com-

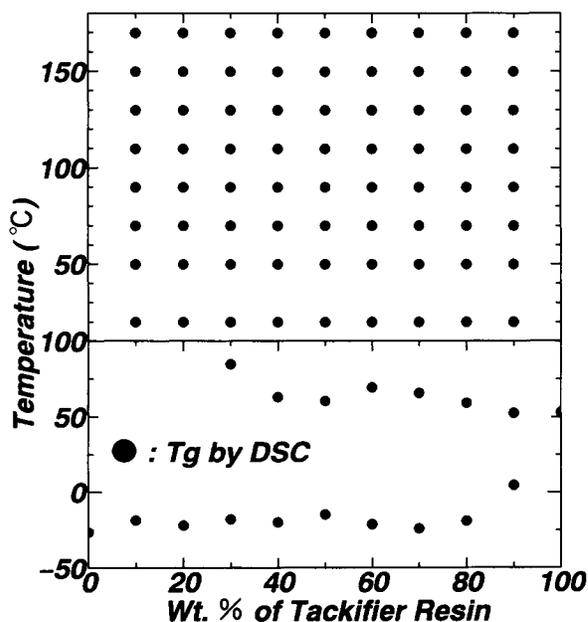


Figure 11 Phase diagram and T_g -composition curve for acrylic copolymer 2 and Clearon K-4090 system. Symbols as in Figure 1.

position region. The lower T_g value is about 5–10°C higher than that of acrylic copolymer 2 and the upper T_g is also about 5–15°C higher than that of the Clearon K-4090. Detailed mechanisms are not known yet, but it might safely be said that there exist two distinct phases in the blends. Figure 12 shows a master curve of peel strength P against ΔT for acrylic copolymer 2 and Clearon K-4090 system. This master curve is also similar to Figure 10 in shape.

The T_g -composition curve and phase diagram of acrylic copolymer 3/Clearon K-4090 system and acrylic copolymer 4/Clearon K-4090 system are shown in Figures 13 and 15, respectively. Here again it is found that these systems are immiscible over the entire composition range judging from double T_g data and opaqueness of the blend films.

The plots of peel strength P against ΔT for acrylic copolymer 3/Clearon K-4090 system and acrylic copolymer 4/Clearon K-4090 system is shown in Figures 14 and 16, respectively. There are many scatter points and smooth master curves cannot be drawn in case of immiscible blends. And it must be pointed out that the peel strength of acrylic copolymer 4 and tackifier system is much smaller than that of acrylic copolymer without tackifier resin.

Peel Strength of Acrylic PSA, the Components of which are Miscible within Some Composition Region

In such a blend system as acrylic copolymer 2/Superester A-75 system, the two components are mis-

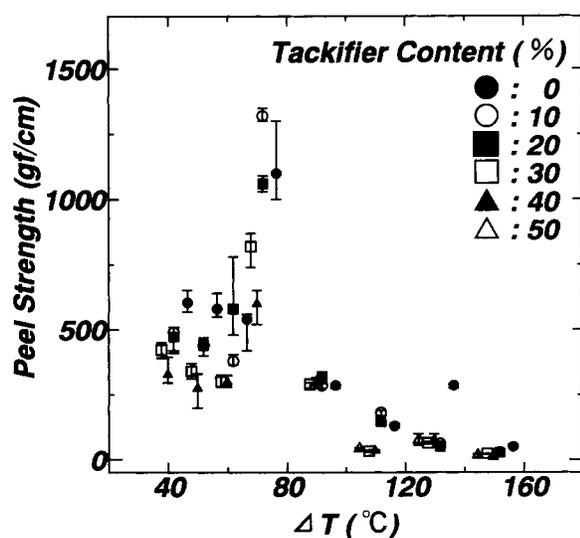


Figure 12 Plot of peel strength against ΔT for acrylic copolymer 2 and Clearon K-4090 system.

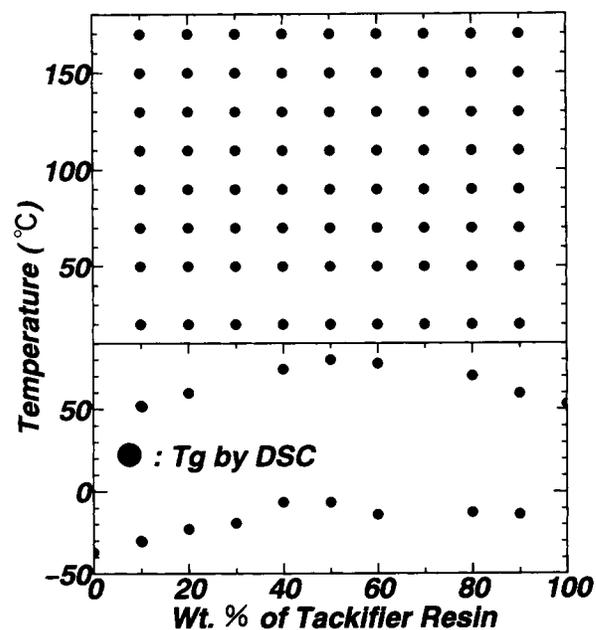


Figure 13 Phase diagram and T_g -composition curve for acrylic copolymer 3 and Clearon K-4090 system. Symbols as in Figure 1.

cible within some composition region and immiscible outside this region, as shown in Figure 17. In the DSC thermograms, a single T_g appears when the tackifier content is between 0 and 30–40%, but two distinctly separate T_g 's appear at higher tackifier content. And this is consistent with the phase diagram of the system given in Figure 17, where it is shown that phase separation occurs at room tem-

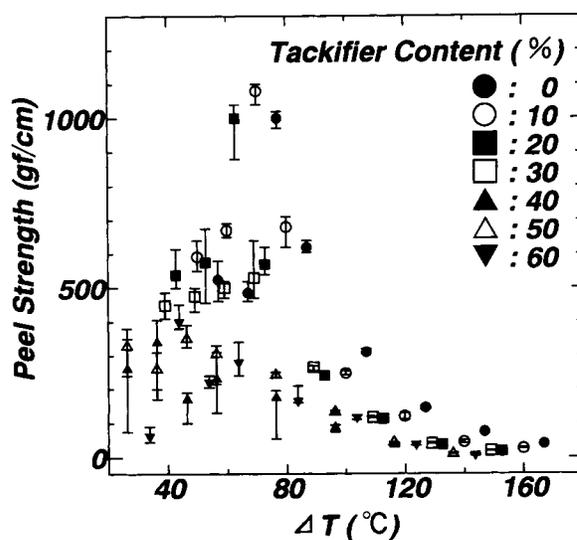


Figure 14 Plot of peel strength against ΔT for acrylic copolymer 3 and Clearon K-4090 system.

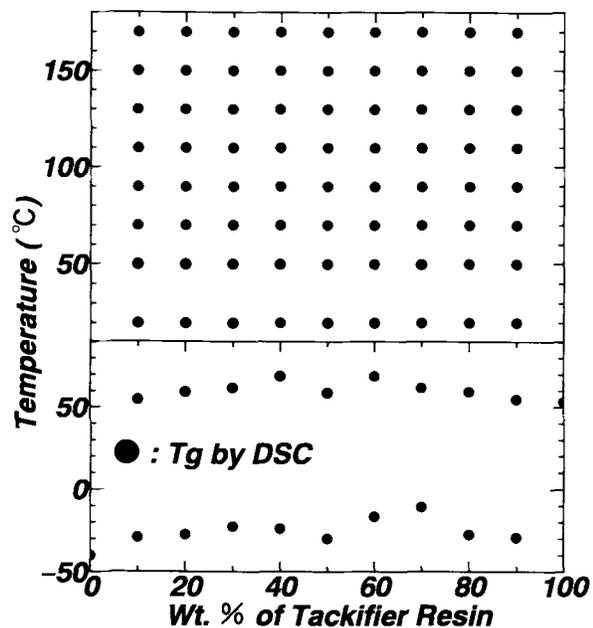


Figure 15 Phase diagram and T_g -composition curve for acrylic copolymer 4 and Clearon K-4090 system. Symbols as in Figure 1.

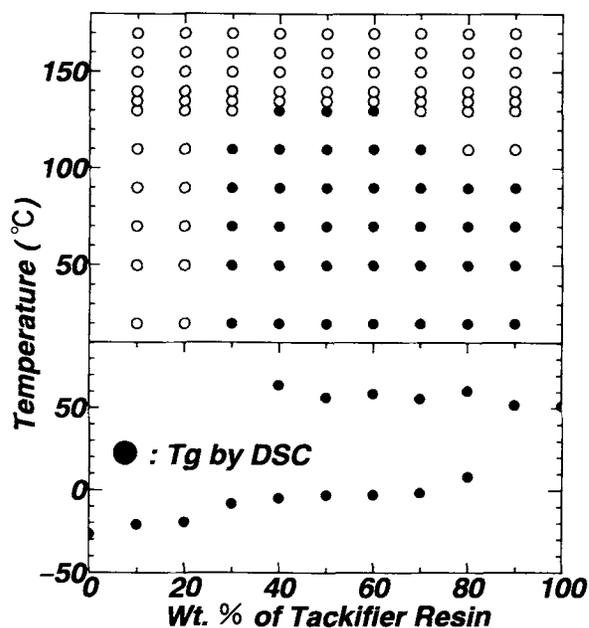


Figure 17 Phase diagram and T_g -composition curve for acrylic copolymer 2 and Superester A-75 system. Symbols as in Figure 1.

perature when tackifier content is more than about 30%. This system exhibits a phase diagram of upper critical solution temperature (UCST) type, i.e., the components are miscible at elevated temperature, but phase separation occurs at low temperature, which is often found in the blends of polymer/oligomer system.⁹

The peel strength P against ΔT for an acrylic copolymer 2 and Superester A-75 system is shown in Figure 18. This master curve may seem to resemble that of immiscible system, but when we look at the plots in detail, we can distinguish the points corresponding to lower tackifier content from those corresponding to higher content, which means that a smooth master curve is obtained only in the region

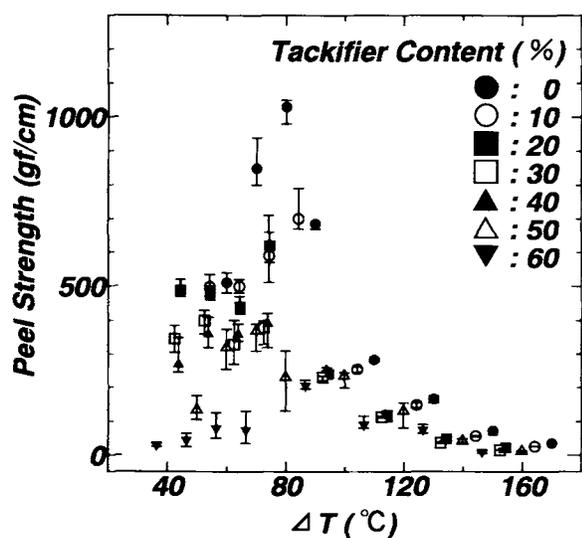


Figure 16 Plot of peel strength against ΔT for acrylic copolymer 4 and Clearon K-4090 system.

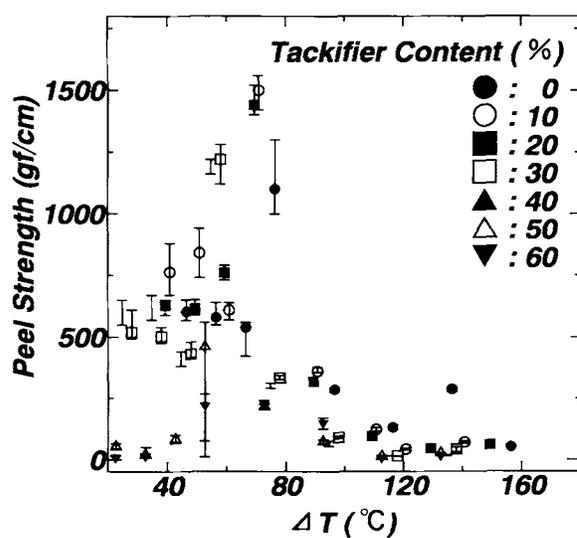


Figure 18 Plot of peel strength against ΔT for acrylic copolymer 2 and Superester A-75 system.

where a uniform phase exists. In the region where phase separation occurs, plots of P against ΔT do not give a master curve. This results in agreement with our earlier findings that some discontinuous drops are found in tack and peel strength around the concentration at which the phase structure changes.¹⁰

The peel strength of the blends in the miscible region is larger than that of unmodified acrylic copolymer, and concentration dependence of peel strength changes remarkably where phase structure changes.

CONCLUSION

Miscibility between components of acrylic pressure-sensitive adhesives, consisting of acrylic copolymer and tackifier resin, has been studied by measurement of T_g 's as well as investigation of phase diagrams, and it is found that the blends are classified into four types: miscible type, LCST type, UCST type, and immiscible type.

Peel strength P of these pressure-sensitive adhesives has been measured as a function of temperature, and relation between peel strength of pressure-sensitive adhesives and miscibility is investigated. Generally peel strength of an acrylic copolymer is low at very low temperature, and it gradually increases, reaches a maximum, and then decreases as temperature is raised. In case of miscible blends, incorporation of tackifier resin results in the modification of the bulk properties of the blends, i.e., the elevation T_g , and accordingly the P vs. T curve shifts along the T axis as the tackifier content changes. Plots of P against ΔT , where ΔT is the difference between the temperature of peeling test and T_g of the blend, can be regarded as a kind

of master curve, and a smooth master curve can be obtained in case of miscible blends. Usually P reaches its maximum when $\Delta T \cong 60^\circ\text{C}$. However, in case of an immiscible blend where two phases exist in the system, a smooth master curve cannot be obtained. The absolute value of peel strength P of an immiscible acrylic PSA decreases as the amount of the dispersed phase increases.

Peel strength P is mostly dependent on the viscoelastic properties of the matrix phase, and the resin-rich phase acts as a filler which reduces the absolute values of peel strength P .

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