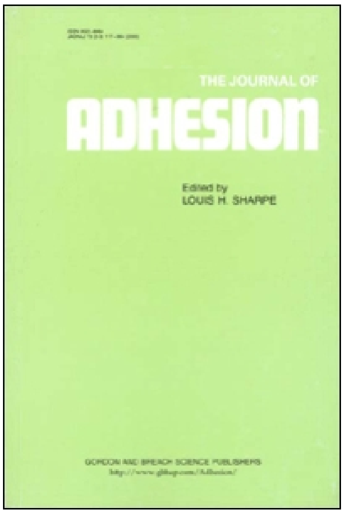

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Miscibility and PSA Performance of Acrylic Copolymer and Tackifier Resin Systems*

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The influence of miscibility of an acrylic PSA and several tackifier resin systems upon PSA performance was investigated. When the acrylic copolymer and the resins were blended in various proportions, three types of mixing state were found: miscible system, partially miscible system and immiscible system. In the case of miscible systems, PSA performance (tack, peel strength and shear resistance) depended upon the viscoelastic properties of the PSA. In the case of completely immiscible systems, the above PSA performance depended primarily upon the viscoelastic properties of a continuous matrix phase, and the separated resin phase acted as a kind of filler. In the case of partially miscible systems, the PSA performance changed discontinuously at the resin concentration where phase separation occurred. It suggests that the phase structure of a PSA greatly influences the PSA's performance.

KEY WORDS acrylic PSA; tackifier; miscibility; tack; peel; shear resistance; phase structure.

INTRODUCTION

Generally it has not been necessary for acrylic pressure sensitive adhesives (PSA) to involve any tackifier for most applications, because a variety of molecular designs are possible in this category of materials. Recently, however, some acrylic pressure sensitive adhesives have been blended with tackifier resins to achieve a modified adhesion property to polyolefins.

It is known that most pairs of high molecular weight polymers, when blended, are immiscible. Even if they are miscible at lower temperature, the pair tends to

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phase separate at elevated temperatures. However, if the molecular weight is low, they are miscible at elevated temperatures and tend to phase separate at lower temperatures.[1] This behavior is often observed in a mixture of oligomers. Because the molecular weights of acrylic polymers or those of copolymers for PSA are usually high and those of commercially-available tackifiers are relatively low, a PSA having phase-separated structures at working temperatures should be dependent on the combination of acrylic polymer and tackifier.

Although it is well known that PSA performance is highly dependent on the structures and the dynamic mechanical properties of the PSA, only a few studies have clarified the relationship between the phase structures and PSA performance.[2,3] In this study, miscibility of acrylic copolymer/tackifier resin systems are studied, and correlations among phase structures, dynamic mechanical properties and their performance are clarified.

EXPERIMENTAL

Materials

The polymer used was a copolymer composed of 97 mol % of butyl acrylate and 3 mol % of acrylic acid. The ethyl acetate solution of the polymer of which solid content was 38% and viscosity was 2,100 CPS, was kindly supplied by Toyo Ink Manufacturing Co. Ltd. and used as received.

Tackifiers employed were commercially available rosins and terpene resins, which are listed in Table I. These tackifiers were kindly supplied by Arakawa Chemical Industry Co. Ltd., Hercules Co. Ltd. and Yasuhara Chemical Co. Ltd. They were dissolved in ethyl acetate and blended with the acrylic copolymer in various proportions.

The blends were cast and dried at 100°C in vacuo. The state of mixing in the films cast on glass plates was observed by means of a microscope at 20°C.

Measurement of Glass Transition Temperatures and Dynamic Mechanical Properties

The glass transition temperatures (T_g's) were measured by a Perkin Elmer DSC7 differential scanning calorimeter in helium atmosphere. A heating rate of 40°C/min was employed.

Filter papers were impregnated with solutions of the blends and their dynamic mechanical properties were measured by a Toyo Baldwin Rheovibron DDV-II at 110 Hz in order to obtain supplemental information on transitions of the blends.

Dynamic mechanical properties of some of the blend films were measured by a Rheometrics RDS-II at a frequency of 62.8 rad/sec.

Measurement of PSA Performance

The blends were coated on PET film and dried. Thicknesses of the PET and PSA layer were approximately 25 μm and 40 μm, respectively. Tack of the PSA tape

TABLE I
Microscopic observation (a) and T_g measurement (b) of acrylic copolymer/tackifier resin systems

Tackifier Resins \ Content (wt.%)	10	20	30	40	50	60	70	80	90
Super ester A-75 (R)	O −36	O −29	O −25	O −21	O −10	O −3	O 5	O 10	O 32
Super ester A-100 (R)	O −34	O −27	O −24	O	O −8	X 1	X 7	X 23	O 53
Super ester A-125 (R)	O −38	O −36	X −28	X −24 109	X −20 105	X −20	X −17 93	X −13 89	X 82
Pencel CS (R)	O −37	O −34	X −26	X −28	X −20	X −12	X −8	X −6	X 66
POLYPALE (R)	O −32	O −31	O −27	O −17	O −10	O 1	O 6	O 24	O 39
Pentalyn CJ (R)	O −38	O −33	O −24	X −21	X −15	X −17	X −12 89	X −9 84	X −11 67
YS Polystar T-130 (T)	O −32	O −27	O −18	O −5	O 16	O 32	O 40	O 52	O 47
Clearon K4090 (T)	X −39	X −38	X −37	X −35 64	X −33 59	X −34 60	X −34 54	X −35 49	X 44

(R): rosin (T): terpene
(a): Microscopy (O: Single Phase, X: Two Phases)
(b): T_g (°C) by DSC

thus prepared was measured in terms of rolling friction coefficient, f, by a pulling cylinder method, with a pulling speed of 10 cm/sec at 20°C.[4]

The PSA tapes were adhered to polypropylene by rolled pressure and the 180° peel strength (P) was measured by a Tensilon with a cross-head speed of 0.5 cm/sec at 20°C. For some selected blend systems, P was measured as a function of cross-head speed in the range from 10^{-4} to 10^{2} cm/sec at 20°C.

In order to obtain information on the holding power (the shear creep resistance) of the PSA tapes, three series of typical samples were adhered on aluminum plates and the time to rupture (t_b) was measured at 50°C as a function of shear stress.

RESULTS AND DISCUSSION

Preparation of the Blends

Acrylic copolymer and tackifier resin were blended in various proportions in ethyl acetate. The solutions were optically clear at a concentration of about 45 wt % at 20°C. When they were cast, it was found by microscopic observation that there were three types of mixing states of these polymer/tackifier resin systems at 20°C.

Super ester A–75, Polypale and YS Polystar T–130 were miscible with the acrylic copolymer over the whole range of resin concentration.

Super ester A–100, Super ester A–125, Pencel CS and Pentalyn CJ were partially miscible with the acrylic copolymer in the sense that they were miscible within some range of resin concentration, but phase separation occurred outside this range.

Clearon K4090 was not miscible with the polymer at any resin concentration.

Glass Transition Temperatures of the Blends

The results of microscopic observations are consistent with the results of differential scanning calorimetry (DSC) and also with the dynamic mechanical properties. Figure 1 shows the variation of T_g measured by DSC with the resin concentration for three miscible blend systems. A single T_g was found at all resin concentrations in each system. The data are almost fitted to the Fox equation,[5] which suggests that they are miscible systems. Figure 2 shows similar data for a partially-miscible

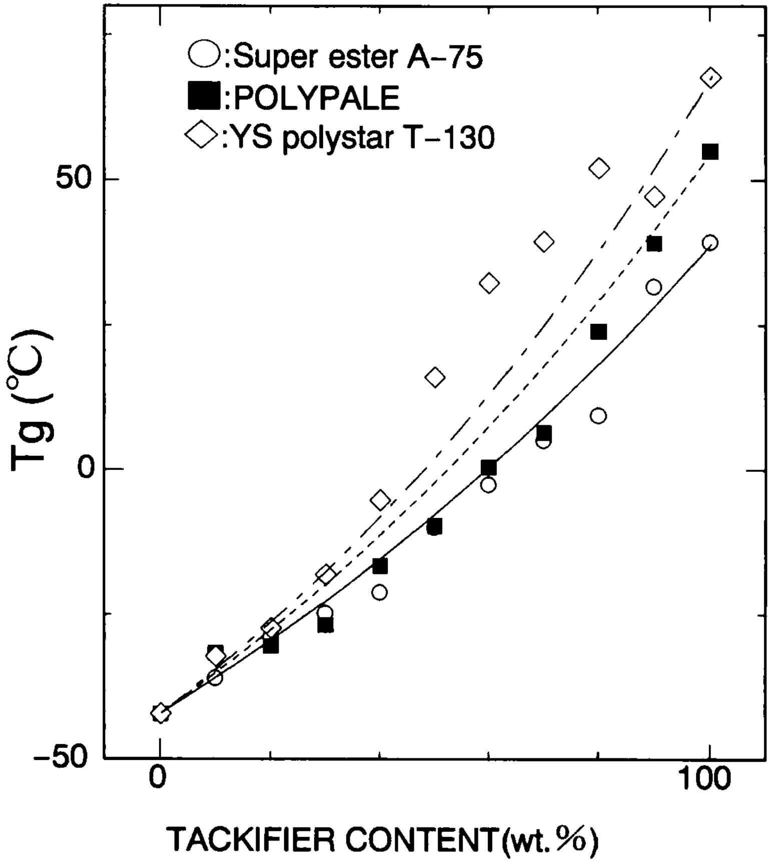

FIGURE 1 Plot of T_g *vs.* tackifier content for miscible systems measured by DSC. Lines correspond to the Fox equation.

system. A single T_g appeared in the lower resin concentration region, but double T_g's appeared at higher resin concentration. Figure 3 shows the case where polymer and resin are not miscible with each other. The T_g's of both polymer and resin were found separately at all resin concentrations. These data are summarized in Table I.

Measurement of PSA Performance

Tack (f) and peel strength (P) of the miscible blend systems are shown in Figure 4. Both f and P become maximum when the T_g of the PSA is about −35 to −25°C. When a curve of T_g *vs.* resin concentration is steeper, the maxima of f and P appear at lower resin concentration, which is consistent with our previous observations.[6–9] Figure 5 shows similar data for a partially-miscible blend system. Some discontinuous drops are found in both f and P around the concentration at which the phase structure changes. This might reflect that the dependence of mechanical properties of the PSA changes at the specified resin concentration on the phase diagram.

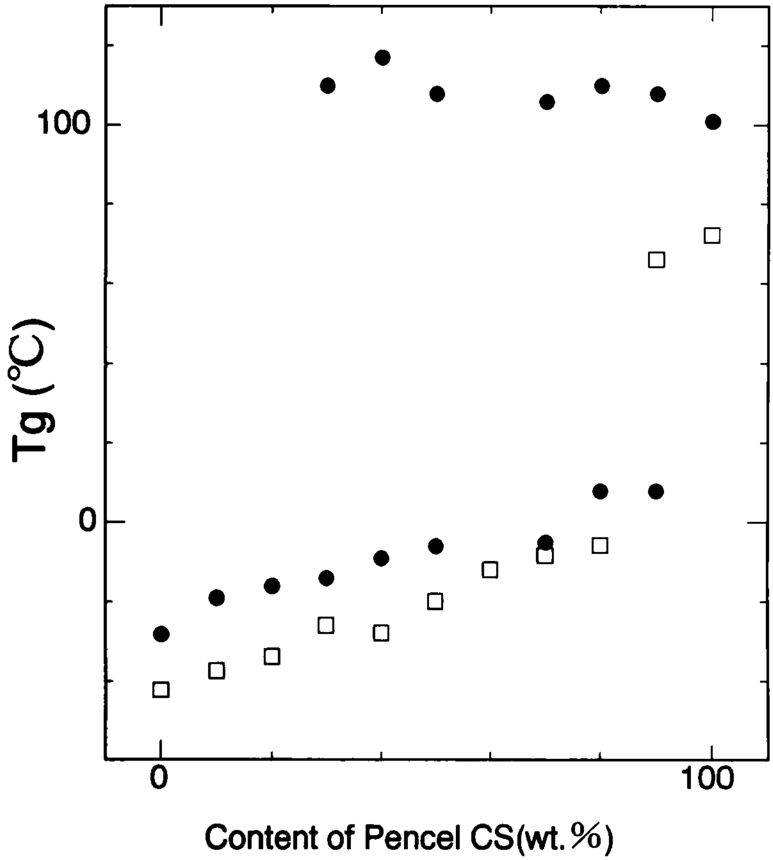

FIGURE 2 Plot of T_g *vs.* tackifier content for a partially-miscible system: ●:measured by Rheovibron, □:measured by DSC.

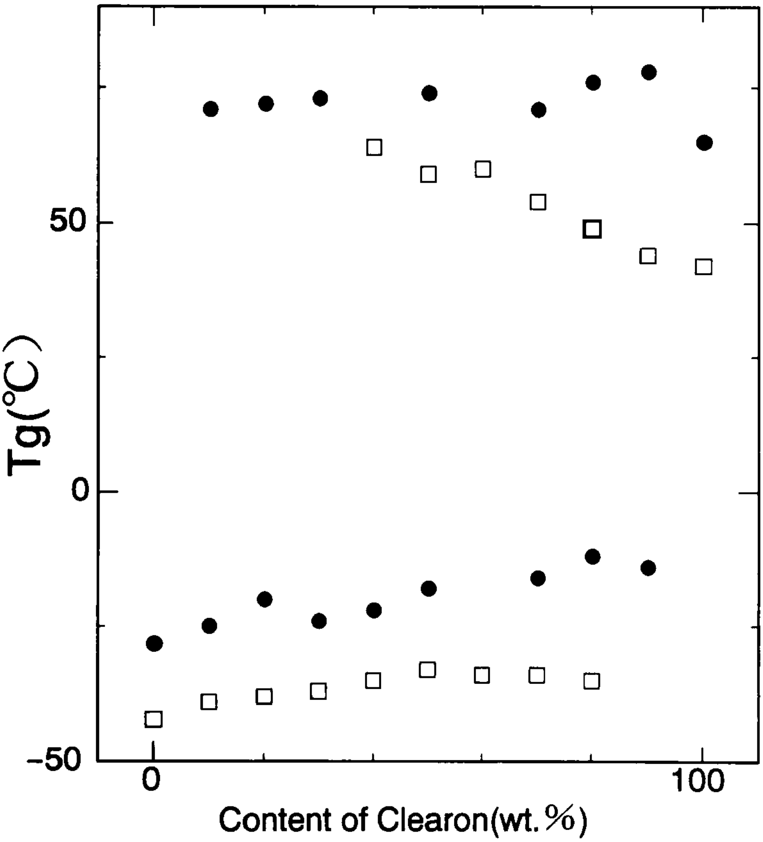

FIGURE 3 Plot of T_g *vs.* tackifier content for an immiscible system: ●:measured by Rheovibron, □:measured by DSC.

Figure 6 shows a case of an immiscible blend system, where no significant dependence of f and P upon resin concentration is found.

In order to obtain further information on the influence of miscibility between PSA components upon peel strength, three typical blend systems were selected and peel strength was measured as a function of velocity. Figure 7 shows that for a series of completely miscible systems, a plot of P *vs.* log v gives a curve having a peak at some velocity and that as the concentration of the resin becomes higher (or, as T_g of the blend becomes higher), the peak shifts toward lower velocity. This is in good agreement with our previous observations,[6,7,9] and also with our theoretical predictions.[4,10] Figure 8 shows similar data for a series of blends where the polymer is miscible with the resin within some limited low resin concentration region and phase separation occurs outside this region. Obviously, similar trends are seen within the region where the blend forms a uniform phase. However, the shape of the curve of P *vs.* log v becomes quite different when phase separation occurs. In the case where resin concentration is 30 wt %, P decreases monotonously without

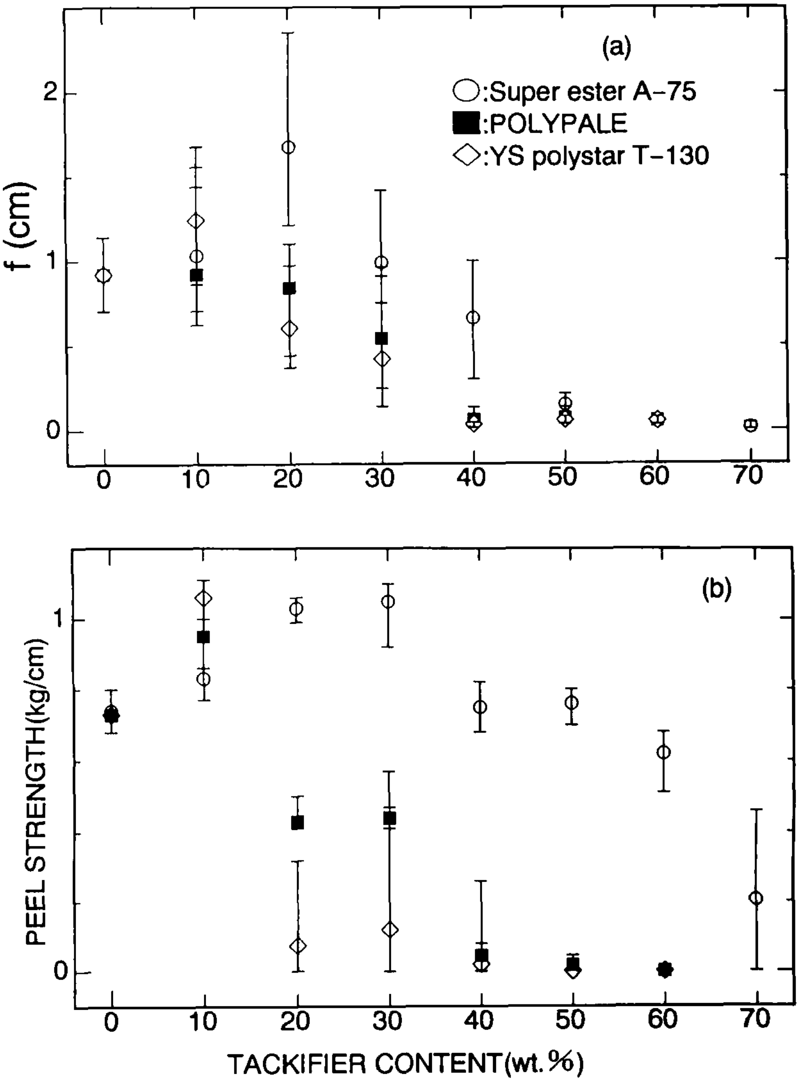

FIGURE 4 Plot of f (a) and P (b) *vs.* tackifier content for miscible systems.

any peak as shown in Figure 8. As the dispersed phase increases the absolute value of P decreases. It is suggested that peel strength is dependent primarily upon the viscoelastic properties of the matrix phase in the PSA and the dispersed phase acts as a filler, reducing the absolute value of the peel strength. Figure 9 shows P *vs.* log v curves for the completely-immiscible system where the acrylic copolymer forms a continuous phase and the resin (Clearon) is dispersed in the matrix. The shapes of the P *vs.* log v curves for all the PSAs of this system are similar to that of the copolymer without resin, the curves having maxima at around 1 cm/sec, and

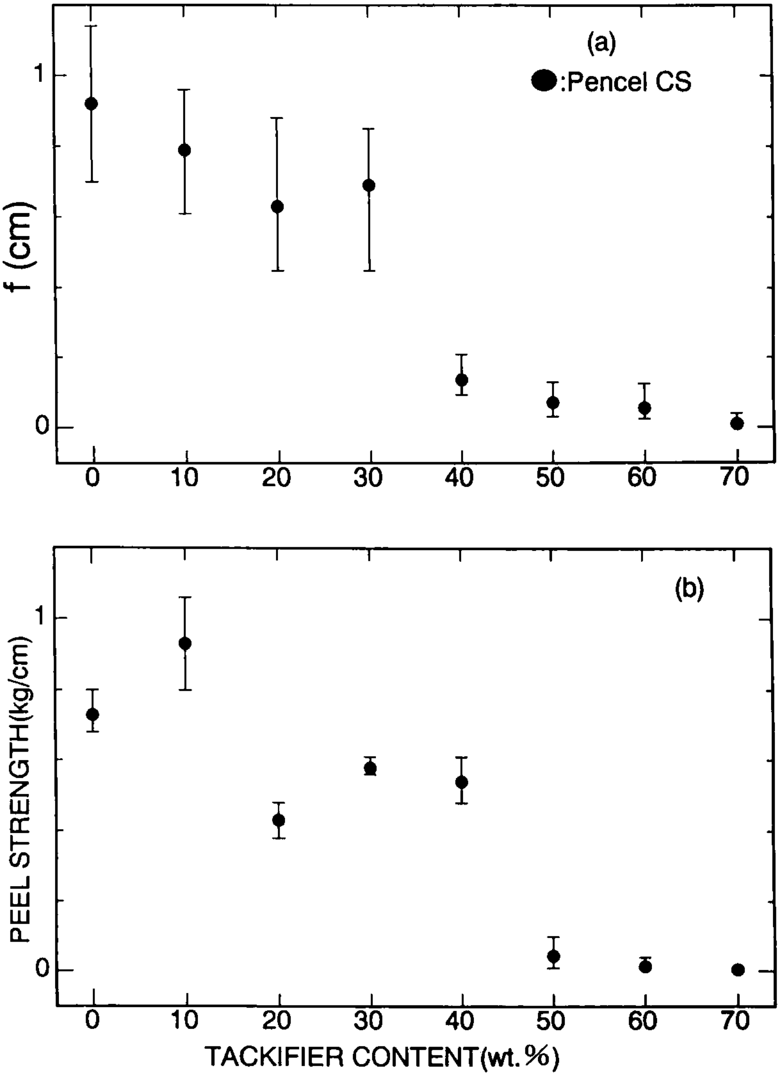

FIGURE 5 Plot of f (a) and P (b) *vs.* tackifier content for a partially-miscible system.

the absolute value of P decreases as the amount of the dispersed phase increases. Peel strength is mostly dependent upon the viscoelastic properties of the matrix phase, and the immiscible resin acts as a filler which reduces the absolute value of P.

Shear creep resistance of PSA tape is also influenced by miscibility between the components of the PSA. Figure 10 shows a plot of shear stress (σ) *vs.* log t_b (lifetime) for a completely miscible system. The curves of σ *vs.* log t_b are not altered greatly by the incorporation of the resin but, on the average, the shear creep life-

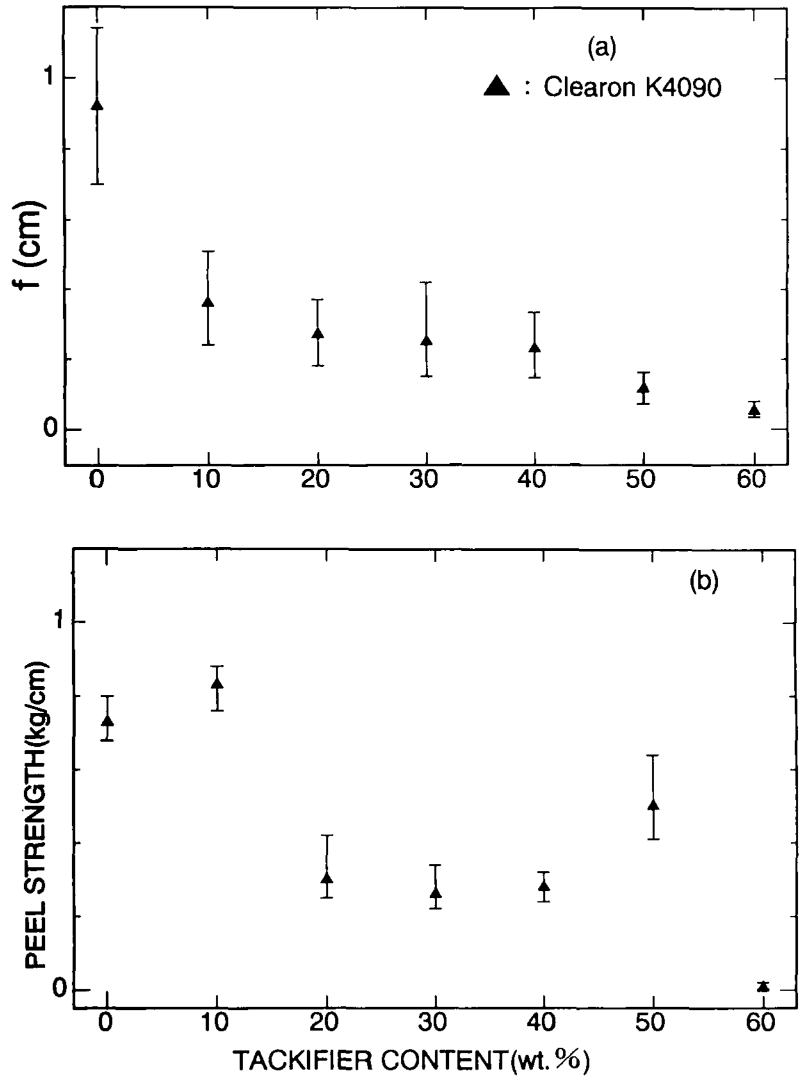

FIGURE 6 Plot of f (a) and P (b) *vs.* tackifier content for an immiscible system.

time, t_b, increases slightly with increase in T_g of the PSA. This is consistent with our previous observations.[11] Figure 11 shows similar data for a series of PSA where the components are miscible within some restricted concentration region. In this case, t_b is slightly increased by the incorporation of the resin in the low resin concentration region where the blend forms a uniform phase. The above trend is similar to that in Figure 10. However, once the second phase appears in the matrix, t_b increases discontinuously to a great extent. Figure 12 shows the σ *vs.* log t_b curves for the completely immiscible system. Clearon would form the dispersed phases in the

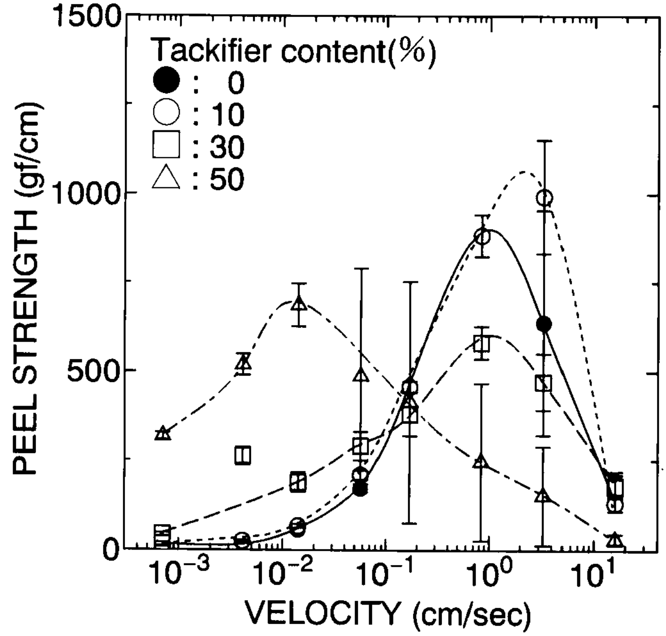

FIGURE 7 Dependence of P upon v for a miscible system at 20°C.

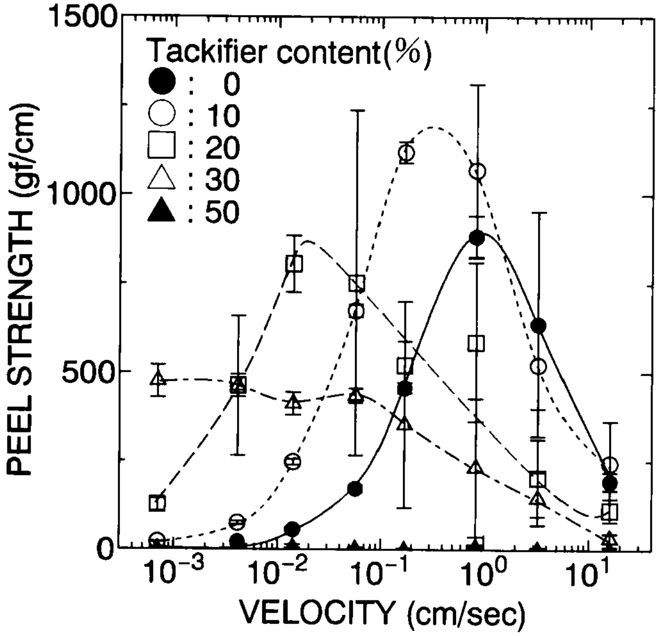

FIGURE 8 Dependence of P upon v for a partially-miscible system at 20°C.

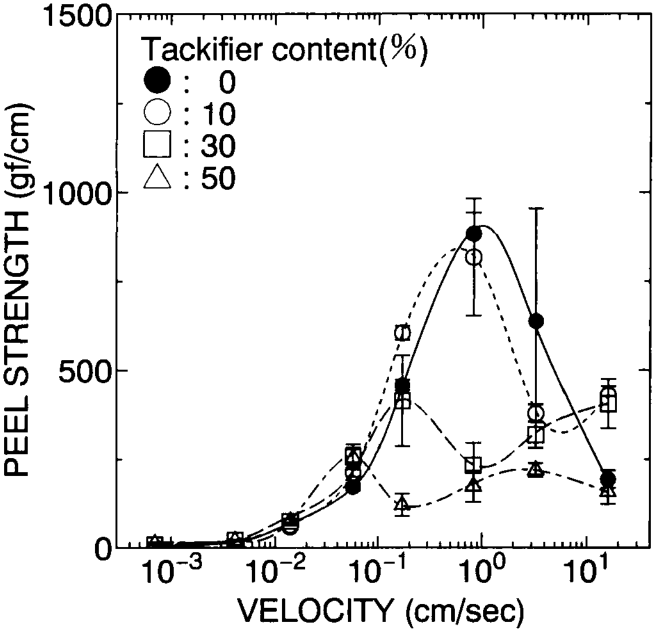

FIGURE 9 Dependence of P upon v for an immiscible system at 20°C.

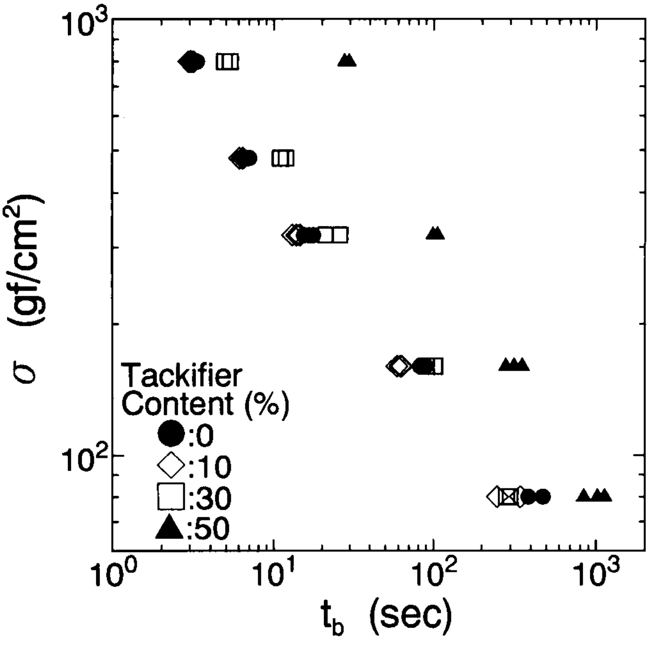

FIGURE 10 Plot of σ *vs.* log t_b for a miscible system of acrylic copolymer/Super ester A-75 at 50°C.

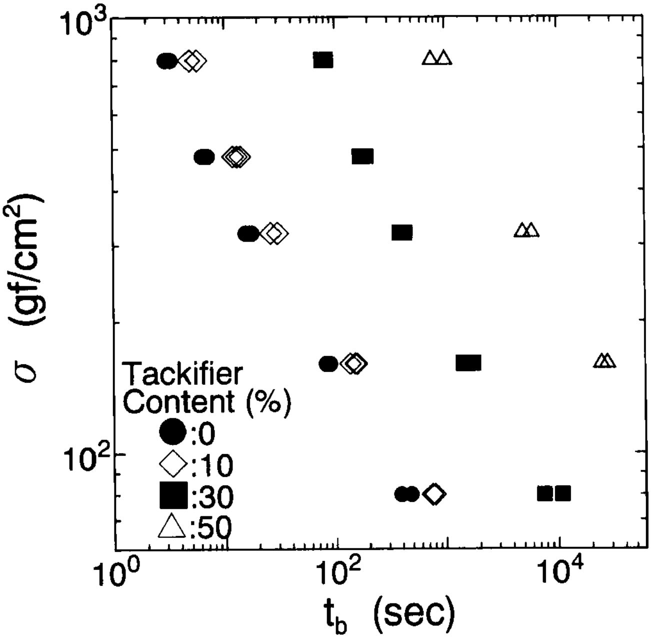

FIGURE 11 Plot of σ *vs.* log t_b for a partially-miscible system of acrylic copolymer/Pencel CS at 50°C.

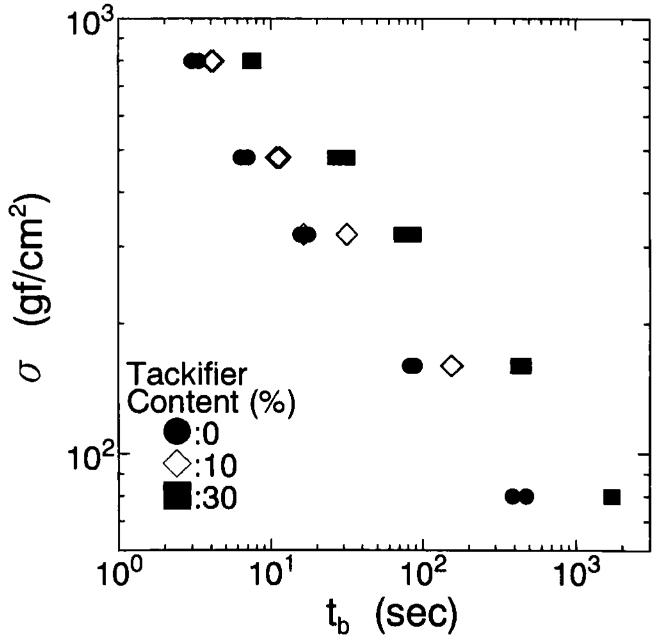

FIGURE 12 Plot of σ *vs.* log t_b for an immiscible system of acrylic copolymer/Clearon K4090 at 50°C.

matrix of the acrylic copolymer at any blend ratio, and the t_b increases greatly as the amount of the dispersed phase increases.

The detailed mechanisms of these phenomena are not understood yet, but it is clearly shown that the PSA performance such as tack, peel and shear resistance are influenced to a great extent, each in a somewhat different manner, by the miscibility between the components of the PSA and its phase structure.

CONCLUSIONS

1. Three kinds of acrylic copolymer/tackifier systems were found: miscible systems, partially miscible systems and immiscible systems.
2. In the case of miscible systems, both f and P became maximum when the T_g of the blend was about -35 to -25°C.
3. In the case of a partially-miscible system, values of f and P changed abruptly at a concentration where the phase structure was changed.
4. In the case of an immiscible system, no significant correlation between PSA performance (f and P) and resin concentration was found.
5. The shear resistance (t_b) of PSA was also dependent upon the miscibility of the components. In the case where the system formed a single phase, t_b increased as T_g of the PSA increased. On the other hand, when phase separation occurred, t_b increased remarkably as the amount of the dispersed phase increased.
6. PSA performance depended primarily upon the viscoelastic properties of a continuous matrix phase and the dispersed resin phases acted as a kind of filler.

Acknowledgement

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