

STUDIES ON THE BLEND OF POLYACRYLATE EMULSIONS AND TACKIFIER RESIN EMULSIONS

HU Shuwen (胡树文) and YANG Yukun (杨玉昆)

(*Institute of Chemistry, Academia Sinica, Beijing 100080*)

ABSTRACT

A series of polyacrylate emulsions were blended with tackifier resin emulsions such as modified rosin emulsion, C5 resin and C9 resin emulsion. The miscibility of the polyacrylates and tackifier resins was investigated by means of SEM and visual observation. The phase diagrams of the miscibility change systematically with the polarity of polyacrylates and tackifier resins. The influence of the content of the tackifier resins on the adhesion properties of the polyacrylate emulsions were also studied. The results show that the 180°C peel strength is improved as the amount of the tackifier resin increases and comes to a maximum at a specific content. The ball tack property decreases slightly and the hold strength changes complicatedly as the tackifier resin increases.

INTRODUCTION

Pressure-sensitive adhesives (PSAs) have widely been manufactured by blending rubbery polymers such as natural rubber, various synthetic rubbers and block copolymer elastomers, with tackifier resins such as rosin and modified rosins, terpene resins and synthetic resins (C5 resin, C9 resin, etc.)^[1]. When these components are blended with each other, the modulus and bulky viscosities of the blends decrease extensively, and they become very sticky. The miscibility of based polymers and tackifier resins in the natural-rubber-based PSAs has been thoroughly studied^[2]. But in acrylic PSAs, which have exceeded over rubber-based PSAs both in the performance of products and in the scale of production, tackifier resins are usually not used in their formulations because the adhesion properties can be produced by adjusting the ratio of the "soft" and "hard" monomers. However in some recent patents tackifier resins have been added to the formulations of acrylic PSAs to modify the practical performances and reduce the cost of products^[3].

Some studies about the miscibility of polyacrylates with tackifier resins and the influence of tackifier resins on the adhesion property of solvent-based acrylic PSAs

have been published^[4]. However, the analogous studies in the water-based (emulsion) acrylic PSAs, which have been widely used and on a large scale both in China and abroad, are scarcely reported^[5].

In this paper the miscibility between the polyacrylates and tackifier resins in some acrylic emulsion PSAs was investigated by means of scanning electron microscope (SEM) and phase diagram, and the influence of the tackifier resins on the adhesion properties of these acrylic emulsion PSAs was also studied.

EXPERIMENTAL

Materials

The polyacrylate emulsions used in this study to produce water-based PSAs are listed in Table 1. All these emulsions were prepared according to the following polymerization procedure:

Table 1 Polyacrylate emulsions

Code No.	Monomer ratio (wt%)	Content of solid (%)	pH	T_g of polyacrylate ($^{\circ}\text{C}$)
AP-1	AA:EA=15:85	40	5.0	-19
AP-2	EA=100	35	6.0	-24
AP-3	EA:BA:2-EHA=65:20:15	45	5.5	-39
AP-4	EA:BA:2-EHA=40:40:20	35	5.5	-47
AP-5	EA:BA:2-EHA=20:40:40	35	6.0	-5.6
AP-6	BA:2-EHA=34:66	40	6.0	-60
AP-7	BA:2-EHA:AA=64:32:4	50	5.5	-57

Table 2 Tackifier resin emulsions

Code No.	Emulsions	Main component	Content of solid (%)	pH
1	103#	rosin modified by maleic anhydride	51	5.5
2	C5	C5 petroleum resin	25	6.5
3	C9	C9 petroleum resin	25	6.5

A monomer's pre-emulsion was prepared by adding the mixture of butyl acrylate (BA), 2-ethylhexyl acrylate (2-EHA), ethyl acrylate (EA) and acrylic acid (AA) to the solution of emulsifiers in distilled water. Then a portion of pre-emulsions were added into the reactor. The blends were allowed to warm to 82°C in nitrogen atmosphere surrounding. Whereupon the persulfate initiator and pre-emulsion were

fed at a rate of 5ml/min and 0.5ml/min respectively. Then the reaction mixture was maintained at 83°C for 3h to obtain the polyacrylate emulsions.

The tackifier resin emulsions employed are 103# rosin emulsion, C9 resin emulsion and C5 resin emulsion (see Table 2), which are all purchased without further purification.

Preparation of blend emulsions

All of the blend emulsions were prepared by mixing the polyacrylate emulsions and the tackifier resin emulsions with the ratios of 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90, 0/100 by weight and stirring at room temperature for one hour, then standing for 48h before measurement.

SEM measurement

The blend emulsions were coated in 100 μ m dry thickness on a slide glass and then kept at room temperature for 24h. The samples were immersed in the liquid-nitrogen for 30 min and tore into two parts. The cross sections were kept in fresh for SEM measurement. The measurement was carried out in S-530 SEM (made in Japan).

Phase diagrams of miscibility

The blend emulsions were coated in about 30 μ m dry thickness on the slide glass. After keeping at room temperature for 24h, all of the samples were dried at 80°C for 24h and then in vacuum oven at 100°C for 12h. They were visually observed at various temperature between 20°C and 150°C to see if they are clear (miscible) or opaque (immiscible). The phase diagrams of miscibility were drawn with the weight percentage of the tackifier resins in the blends as abscissa and the observed temperature as coordinate.

Adhesion properties

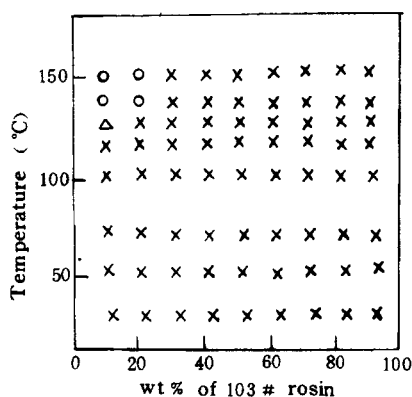
PSAs tapes were manufactured by coating the blend emulsions of polyacrylates and tackifier resins in 30 μ m dry thickness onto polyethylene terephthalate (PET) film of 25 μ m thickness, drying in air oven at 110°C for 10 min, and cutting into some tapes with 25 mm width. The samples for measurement of 180° peel strength, ball (J. Dow) tack property and hold strength were prepared and measured at 15–20°C according to the National Standard Measurement Methods GB-2792-81, GB-4852-84 and GB-4851-84 respectively^[6].

RESULT AND DISCUSSIONS

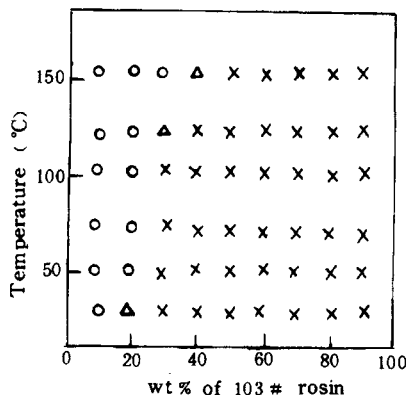
About the miscibility of components in the blends

All of the polyacrylate emulsions listed in Table 1 are miscible at room temperature with any tackifier emulsion listed in Table 2 at any ratio, and all of the blend

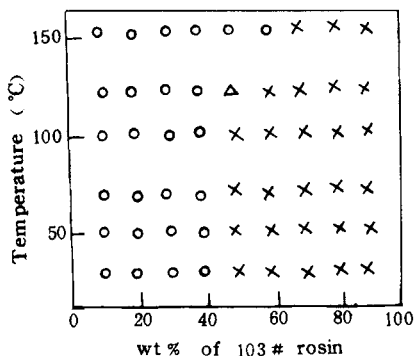
emulsions obtained in this study are still stable after storing at room temperature for more than 6 months. The excellent miscibility between the polyacrylate emulsions and the tackifier resin emulsions and the good storing stability of the blend emulsions are important and necessary to prepare a water-based PSAs useful in industry.



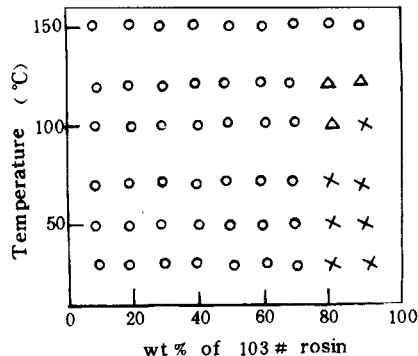
1-A. The blend of AP-1/103# rosin



1-B. The blend of AP-2/103# rosin



1-C. The blend of AP-3/103# rosin



1-D. The blend of AP-5/103# rosin

Fig. 1 Phase diagrams of polyacrylate/103# blend systems. tiny $\bigcirc$: transparent (miscible); $\times$: opaque (immiscible) and $\triangle$: intermediate

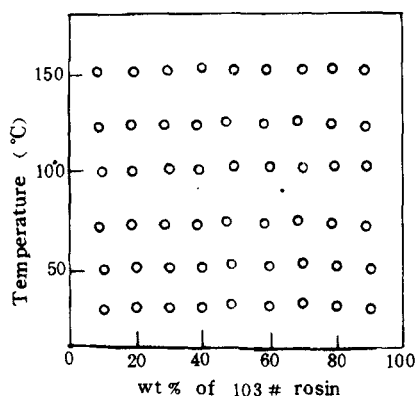
However, it is more important to examine if the components in the blends after dried completely are miscible with each other, because the miscibility has a great influence on the phase structure, physical property, and practical performance of the PSAs. After the evaporable liquids in the blend emulsions were evaporated completely, the miscibility of the polyacrylates and the tackifier resins was investigated in detail by visual observation, which has been proved to be a reasonable method^[4], and SEM measurement.

The results were shown in the phase diagrams of miscibility (in Fig. 1 and 2).

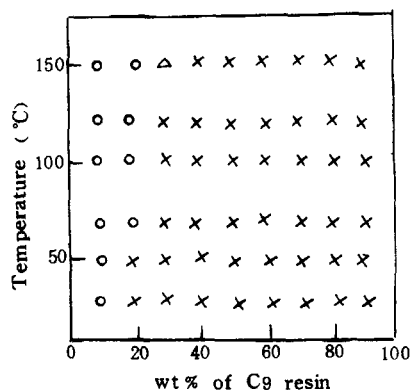
From Fig. 1 we know that all of the four blend systems are upper critical solution temperature (UCST) type, in which the miscibilities of components at high temperature are better than those at low temperature, and in any blend system the miscibility of the polyacrylate and 103# modified rosin decrease as the percentage of the rosin increases. It is also clear from Fig. 1 that the polarity of the acrylic macromolecules has a great influence on the miscibility with 103# modified rosin: the lower the polarity of polyacrylate is, the better the miscibility with 103# rosin will be. The copolymer AP-1, made of ethyl acrylate (EA, 85%) and acrylic acid (AA, 15%) has the largest polarity and the highest T_g among these polyacrylates. It is almost immiscible with 103# rosin at any ratio (see Fig. 1-A). The homopolymer AP-2, whose molecules are less polar than that of the AP-1, can be miscible with 103# rosin when the latter's content in the blend is less than 20% (see Fig. 1-B). The copolymer AP-3, which was made of low polar butyl acrylate (BA) and 2-ethylhexyl acrylate (2-EHA), except ethyl acrylate (EA), has better miscibility than the polymer AP-2 (see Fig. 1-C). And the much lower polarity of AP-5 macromolecules, which consist of much more BA and 2-EHA units and therefore have much lower T_g . Thus it makes the copolymer AP-5 having much better miscibility than the copolymer AP-3: except when the 103# rosins content is more than 70% and at lower temperature, the two components of the blends are miscible with each other completely (see Fig. 1-D). The copolymer AP-6, which is made of 34% of BA and 66% of 2-EHA and therefore has the lowest polarity and the lowest T_g among these polyacrylates, can be miscible with 103# rosin at any ratio and at any temperature (see Fig. 2-A).

Fig. 2 is the phase diagrams of the miscibility of acrylic copolymer AP-6 with various tackifier resins. Here the molecular polarity of tackifier resins plays a very important role in the miscibility. The main component of rosin is abietic acid which has an appreciable polarity in its molecules. C5 resin was prepared by polymerizing the petroleum component which mainly consists of C5 olefins (pentane, cyclopentane, etc.), and therefore its molecules are almost non-polar. C9 resin was produced by polymerizing the petroleum component which consists of C9 aromatic olefins (α -methyl styrene, vinyl tolylene, etc.), and its molecular polarity is between the 103# rosin's and the C5 resin's. It is clear from Fig. 2 that 103# rosin is completely miscible at any ratio and at any temperature with copolymer AP-6 which has an appreciable polarity in its molecules even though it is the lowest polar in the series of polyacrylate, and C-5 resin is completely immiscible with AP-6 at any ratio and at any temperature (see Fig. 2-C). The miscibility of C-9 resin with AP-6

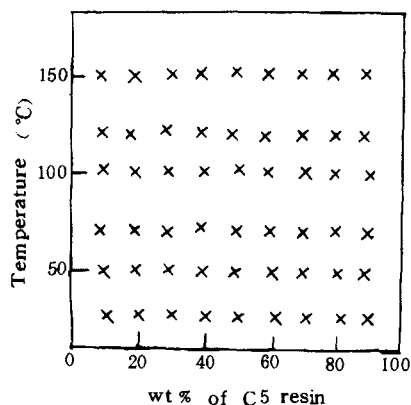
is also lying between the C-5 resin's and 103# resin's (see Fig. 2-B).



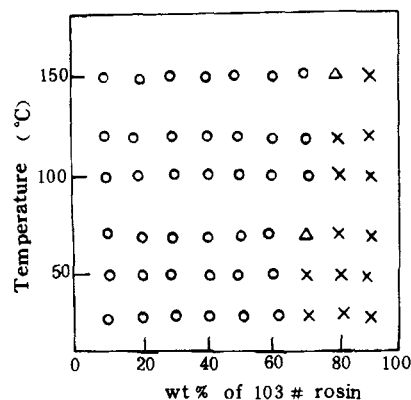
2-A. The blend of AP-6/103# resin



2-B. The blend of AP-6/C9 resin



2-C. The blend of AP-6/C5 resin



2-D. The blend of AP-7/103# resin

Fig. 2 Phase diagrams of polyacrylate/tackifier. The symbols are the same as in Fig. 1

About the microphase structure of the blends

The micro-phase structure of the blends of the polyacrylate AP-2 and 103# modified rosin at different ratios were observed by means of SEM, as shown in Fig. 3. Three different microphase structures in these pictures can be clearly seen.

In the miscible region where the rosin's content in the blend is less than 10%, the rosin has almost completely dissolved in the continued phase of the acrylic polymer and there is a homogeneous and clear microphase structure (see Fig. 3-A and 3-B).

In typical immiscible region, for example, the rosin's content is 50%, a lot of rosins have crystallized out and formed a new opaque continued phase except a transparent polyacrylate continued phase in which some rosins have dissolved. (see

Fig. 3-D).

In the intermediate region where the rosin's content is about 20%, the 'sea-island' type of microphase structure is formed. The crystallized rosin particles have been well dispersed as 'island' in the polyacrylate continued phase in which some rosin have dissolved (see Fig. 3-C).

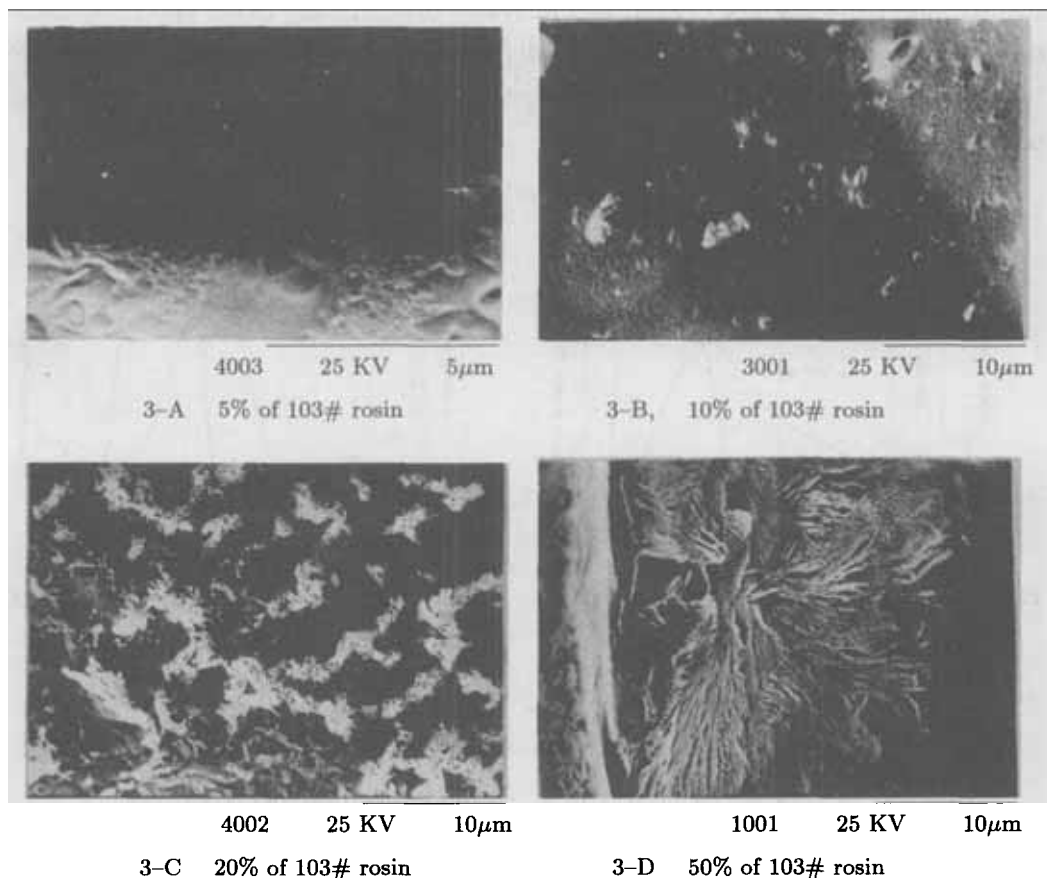


Fig. 3 The SEM photographs of AP-2/103# blend system ($\times 1000$)

About the adhesion properties of the blends

After the PSA tapes were prepared by coating the blend emulsions on PET film and drying at 110°C for 10min, their three main adhesion properties (180° peel strength, ball tack and hold strength) were measured at room temperature according to the National Standard Measurement Method. The plots of the measured results against the content of tackifier resins are shown in Figs. 4—7.

From these figures the following rules of change can be clearly found. In all of the four blend systems, the 180° peel strength is improved as the amount of tackifier resins increase and come to a maximum at some specific contents of resins. The

specific contents are different for various blend systems: 50—60% for AP-3/103# rosin, 55—65% for AP-4/103# rosin, about 30% for AP-7/103# rosin and 10—20% for AP-7/C-9 resin. As the tackifier resins contents increase, the ball (J. Dow) tack properties change slightly below the specific contents of resins and decrease dramatically above the contents. With the increase of tackifier resins, the hold strength improves slightly at first, and increases dramatically in the specific content, then reaches a maximum value and finally decrease smoothly to zero, except AP-7/103#rosin system in which the hold strength decreases continually as 103# rosin increases.

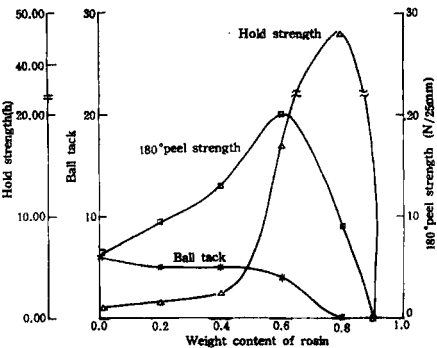


Fig. 4 The adhesion properties of AP-3/103# blend system

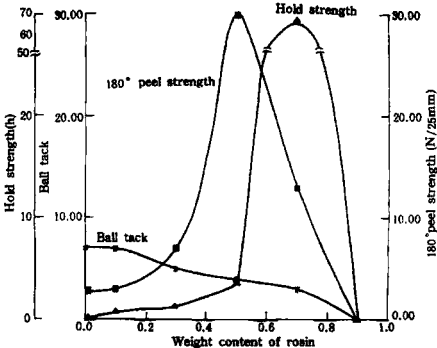


Fig. 5 The adhesion properties of AP-4/103# blend system

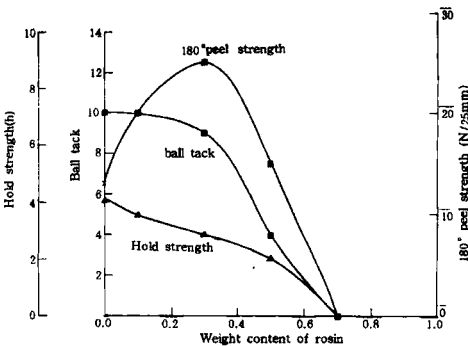


Fig. 6 The adhesion properties of AP-7/103# blends system

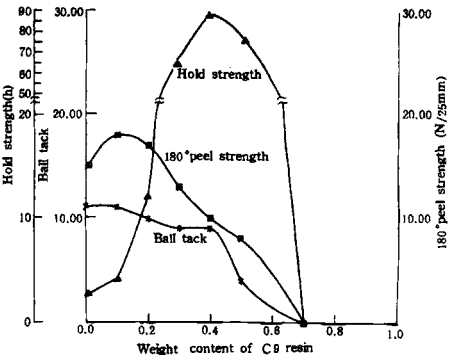


Fig. 7 The adhesion properties of AP-7/C9 blend system

Furthermore, it can be found from these figures that the specific contents of the tackifier resins are just lying between miscible and immiscible regions in phase diagrams of miscibility except AP-7/103# rosin system (see Fig. 2-D). And in

the special intermediate regions there are typical 'sea-island' type of microphase structure existed (see Fig. 3). This may be the main reason for the best adhesion properties appearing at these special contents of the tackifier resins. The relationship between the contents of components, the micro-phase structure and the adhesion properties in acrylic emulsion PSAs are being studied further in detail.

CONCLUSION

In the water-based PSAs consisting of the blends of polyacrylate emulsions and tackifier resin emulsions, the miscibility of polyacrylates and tackifier resins is improved as the polarity and T_g of the polyacrylates decrease (from AP-1 to AP-7) and deteriorate as the polarity of the tackifier resins decrease (from 103 rosin, C9-resin to C5-resin). As the contents of the tackifier resins in the blend emulsions increase, the adhesion properties (180° peel strength, ball tack and hold strength) of the blend emulsion PSAs change systematically and the best adhesion properties are obtained at some special contents of tackifier resins.

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