

Morphological Studies on Wettability and Tackiness of Pressure-Sensitive Adhesives

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Synopsis

The surface structure of pressure-sensitive adhesives consisting of natural rubber and pentaerythritol ester of hydrogenated rosin has been studied using the single-stage replica method. The fibril structure with average diameter of about 50 Å was observed on the surface of an adhesive consisting of 40 to 60 wt-% resin at which maximum tack is obtained. The role of fibrils in adhesion is discussed.

INTRODUCTION

A number of studies have been reported¹⁻⁴ concerning whether resin-rubber pressure-sensitive adhesives have a single phase or two phases. In the previous paper,¹ we have already discussed the relationship between the internal structure of resin-rubber adhesives observed by electron micrographs and their physical properties such as temperature dispersion of mechanical loss, tensile modulus, viscosity, stress relaxation modulus, and tackiness. It has been found that the small amount of resin-rich phase (deposited phase saturated with resin) is dispersed in the continuous phase (homogeneous mixture of rubber and resin), and the glass transition temperature, modulus, and viscosity of the homogeneous phase are lower compared to the dispersed phase. Since the tack is correlated with rheological flow of adhesive at the surface of adherend,^{1,5-7} the tack is more responsive to the homogeneous phase than to the dispersed phase. Therefore, it is of interest to observe the surface structure of the homogeneous phase of adhesives.

Because of the experimental difficulties in applying electron microscopy, however, hardly any morphological studies on adhesive surface have been reported except Hock² and Fukuzawa,⁸ who observed the surface structure of adhesives using a two-stage replica method. However, the resolving power of the two-stage replica is rather poor and about 150 Å at the most.

In the present paper, we observed the fine surface structure of the homogeneous phase using the single-stage replica method. Although the resolving power of the single-stage replica method is excellent and attained about 12 Å, a skillful technique is required because the carbon film is easily broken when the adhesive film is separated from the replica film. From the results obtained from the surface observation as described above, we discussed the role

of the fine-surface structure to the development of tackiness of resin-rubber adhesives.

EXPERIMENTAL

The adhesives used were mixtures of milled pale crepe (Mooney viscosity 64) and pentaerythritol ester of hydrogenated rosin (Pentalyn H, Hercules Inc.). The ratios of rubber to resin were 100 (pure rubber), 80/20, 60/40, 40/60, and 20/80 by weight, respectively. The samples of adhesive films were prepared as follows: Solutions in *n*-hexane of about 10 wt-% of these adhesives were coated on a biaxially drawn poly(ethylene terephthalate) film 0.025 mm thick (Lumirror No. 25, Toray Industries Inc.) and dried to remove the solvent. The thickness of the adhesive layer was 0.03 ± 0.001 mm.

The replica films of the surface of adhesives were prepared by the chromium-carbon single-stage replica method; the surface of the adhesive film was shadowed with chromium and then the replica film was reinforced with carbon. The specimens were then immersed in cyclohexane for 24 hr to separate the replica films from the adhesive films. To completely remove the adhesives, the replica films were treated several times as above with fresh cyclohexane. In order to check whether the single-stage replica films replicate exactly the surface structure of adhesives or not, the replica films of the cloven surface of KCl crystals, whose surface is known to be quite smooth, were prepared at the same time that the replica films of the adhesives were prepared. Water was used to remove KCl from the replica films.

The observation of the internal structure of adhesives was carried out in the same manner as described in the previous paper¹; solutions in *n*-hexane of about 1 wt-% of adhesives were taken up on the mesh and dried to remove the solvent.

The electron microscope used was a JEM 6A (made by Japan Electron Optics Lab. Co. Ltd.). Transmission electron micrographs of replica films of adhesive surfaces and thin films of adhesives were taken.

RESULTS

The electron micrographs of pure natural rubber are shown in Figures 1a, b, and c, respectively. Figure 1a shows a transmitted image of a thin film of rubber. The internal structure of rubber film is observed to be homogeneous as reported in the previous paper.¹ Figure 1b shows a transmitted image of replica film of rubber surface. The surface appears to be smooth except for the dark spots, which are approximately 0.3μ in size and probably represent the undissolved rubber. In order to observe the fine structure of the surface, Figure 1b was magnified and is shown in Figure 1c. Some fine structure is observed; however, the size is smaller than about 20 \AA .

Figures 2a, b, and c show the electron micrographs of adhesive consisting of 20 wt-% resin and 80 wt-% rubber. Figure 2a shows the internal structure of thin film of adhesive; it gives every indication of being homogeneous. Figure 2b shows a surface replica image of adhesive film; the surface structure is somewhat different from that for pure rubber. Some fibril-like fine structure is visible; however, the sizes of the fibrils are small. The dark spots in Figure

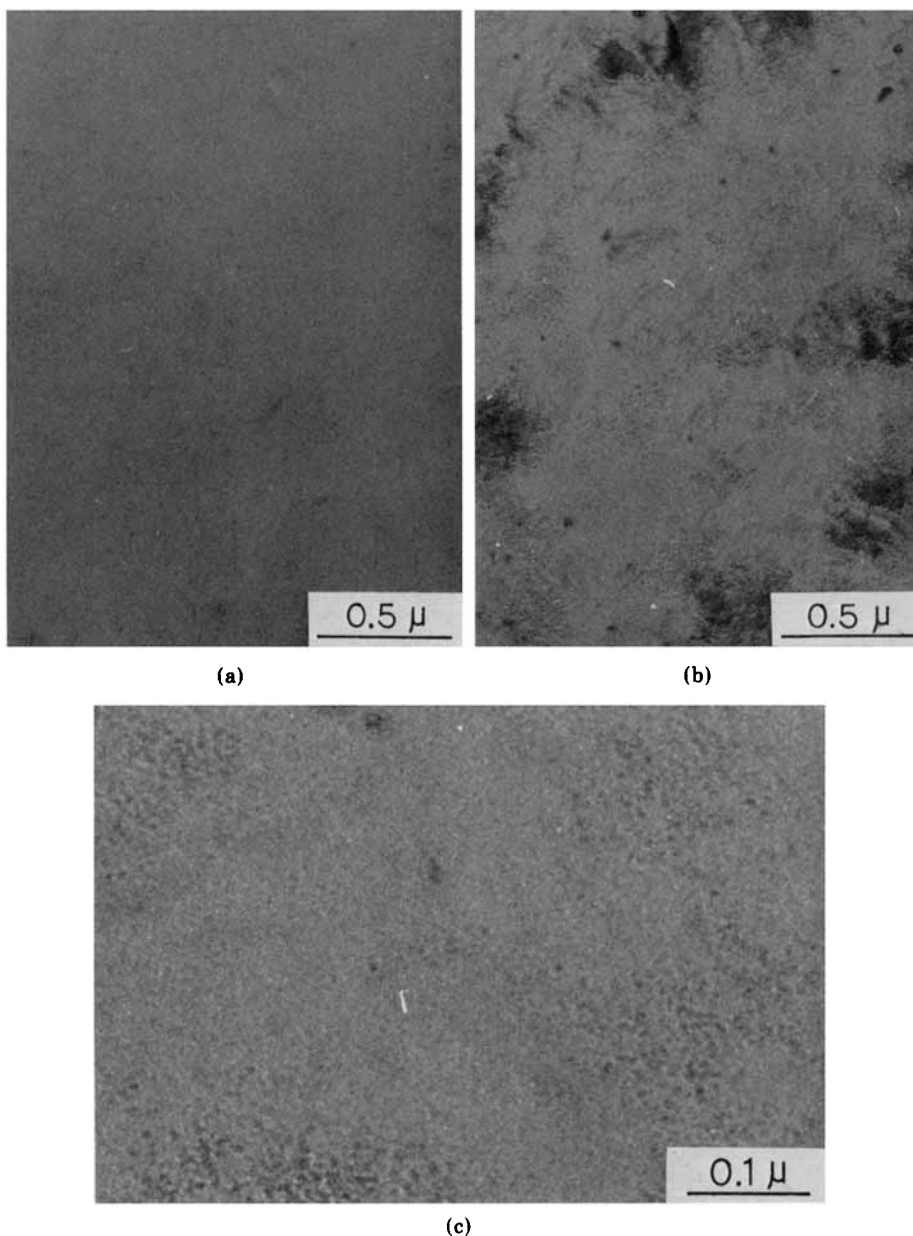


Fig. 1. Transmission electron micrographs of natural rubber: (a) internal structure; (b) surface structure; (c) magnified image of surface structure of rubber.

2b are also due to the undissolved adhesive. A magnified micrograph of replica image is shown in Figure 2c; the fibril-like structure is observed widely on the surface; the fibrils have an average diameter of approximately 30 Å.

Figures 3a, b, and c are the electron micrographs of adhesive consisting of 40 wt-% resin and 60 wt-% rubber. Figure 3a shows the internal structure of thin film of adhesive; the second dispersed phase can be slightly seen as semi-dark spots with diameters less than 0.1 μ in the homogeneous phase. This second phase is probably attributable to the resin-rich phase as described in

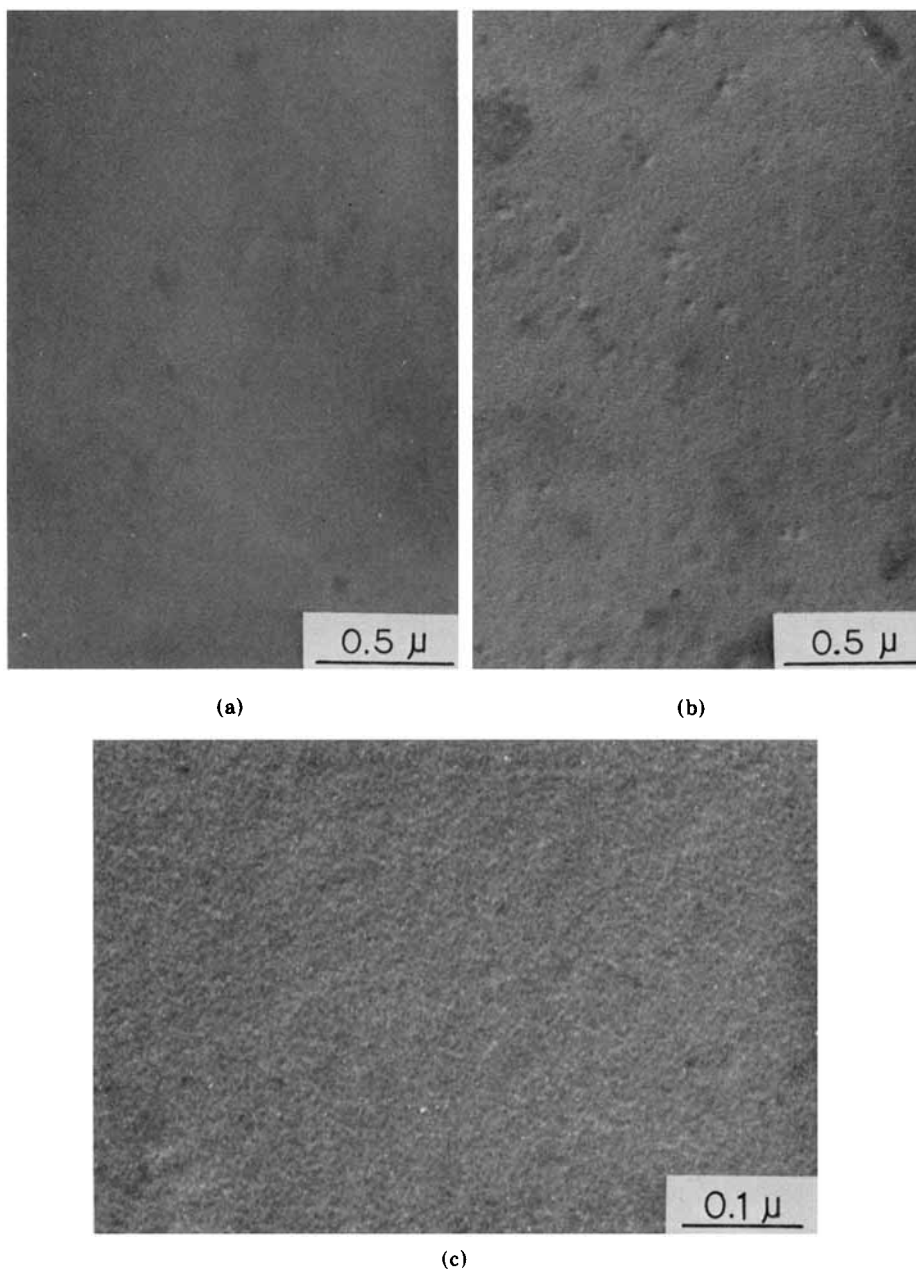


Fig. 2. Transmission electron micrographs of 20 wt-% resin concentration: (a) internal structure; (b) surface structure; (c) magnified image of surface structure of 20 wt-% resin concentration.

the previous paper.¹ Figure 3b shows a surface replica image of adhesive; dark spots with diameters ranging from 0.1 to 0.2 μ, fibril-like structures, and some protuberances can be observed. The dark spots represent the undissolved adhesive as described above; however, the protuberances are not due to the undissolved adhesive but probably replicate the surface structure of adhesive because they have been shadowed by chromium. However, they

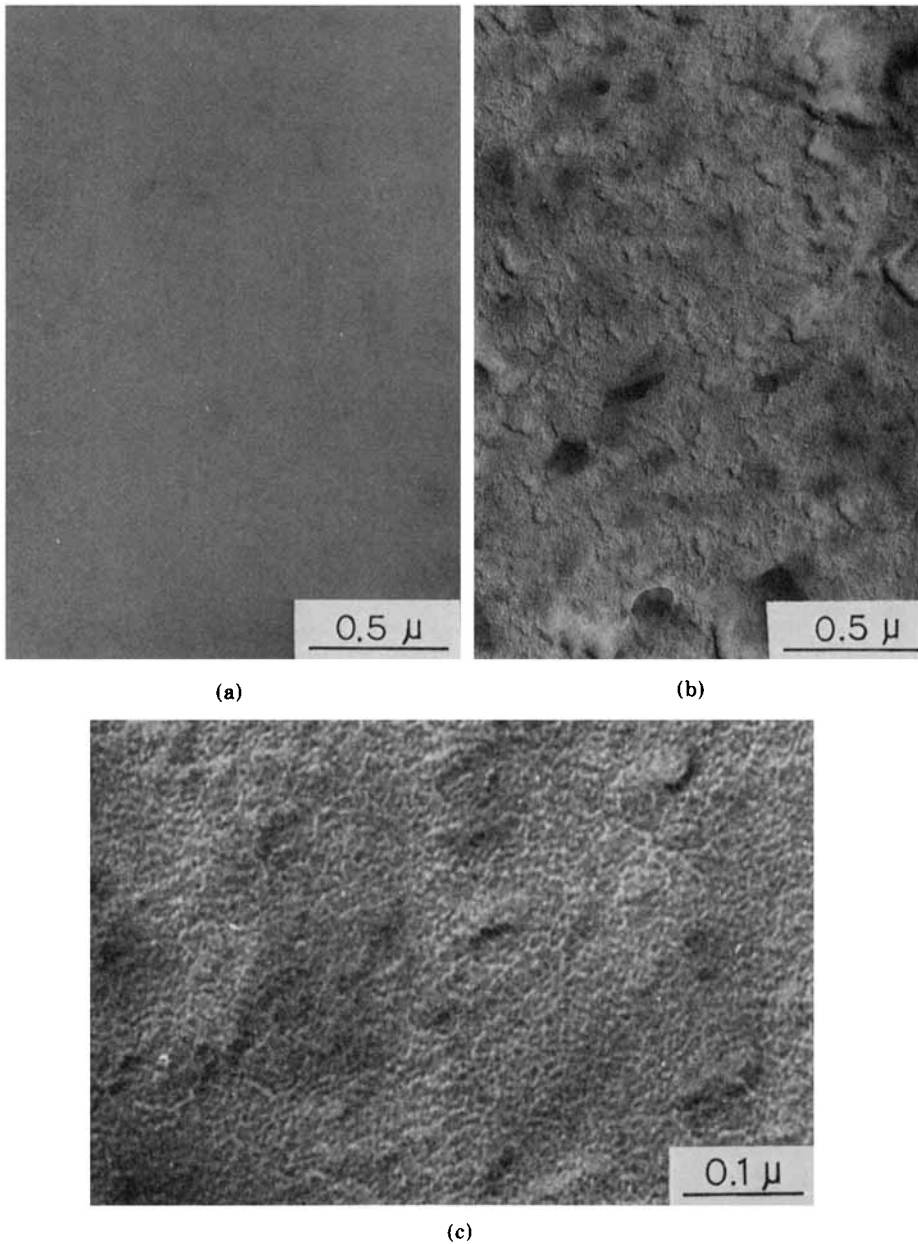


Fig. 3. Transmission electron micrographs of 40 wt-% resin concentration: (a) internal structure, (b) surface structure; (c) magnified image of surface structure of 40 wt-% resin concentration.

were not observed at every surface replica film of the adhesive consisting of 40 wt-% resin. In order to observe the fine structure, Figure 3b was magnified and is shown in Figure 3c; the fibril structure with a diameter of about 50 Å is clearly observed.

The electron micrographs for adhesive consisting of 60 wt-% resin and 40 wt-% rubber are shown in Figures 4a, b, and c, respectively. The second dis-

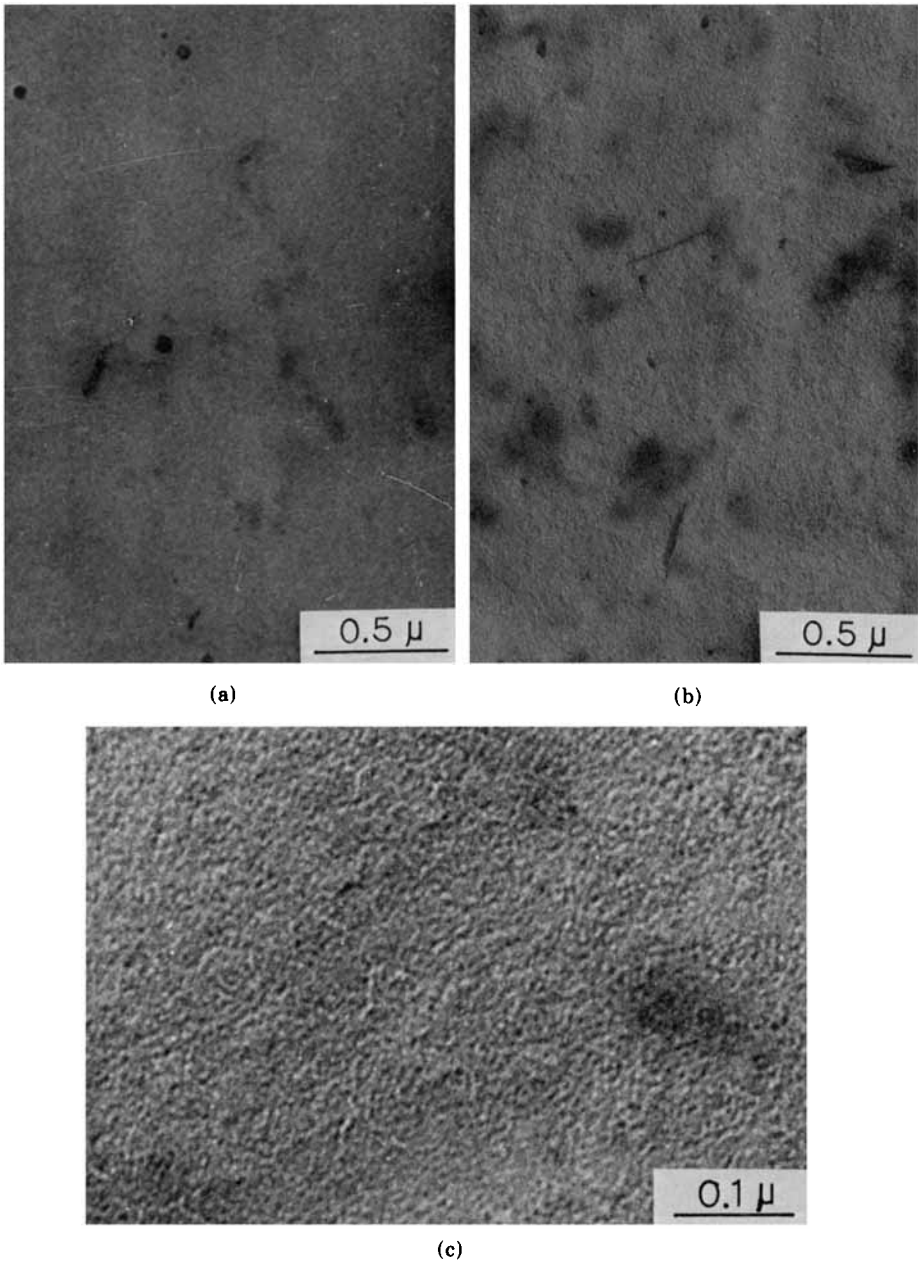


Fig. 4. Transmission electron micrographs of 60 wt-% resin concentration: (a) internal structure; (b) surface structure; (c) magnified image of surface structure of 60 wt-% resin concentration.

persed phase is now clearly seen as dark particles as shown in Figure 4a, which indicates the internal structure of the adhesive. In the replica image of the surface structure shown in Figure 4b, fibril-like fine structure is clearly observed; the dark spots are due to the undissolved adhesive. A magnified micrograph of replica image is shown in Figure 4c; a fibril structure with an average diameter of about 50 Å is distinctly observed. In general, the adhe-

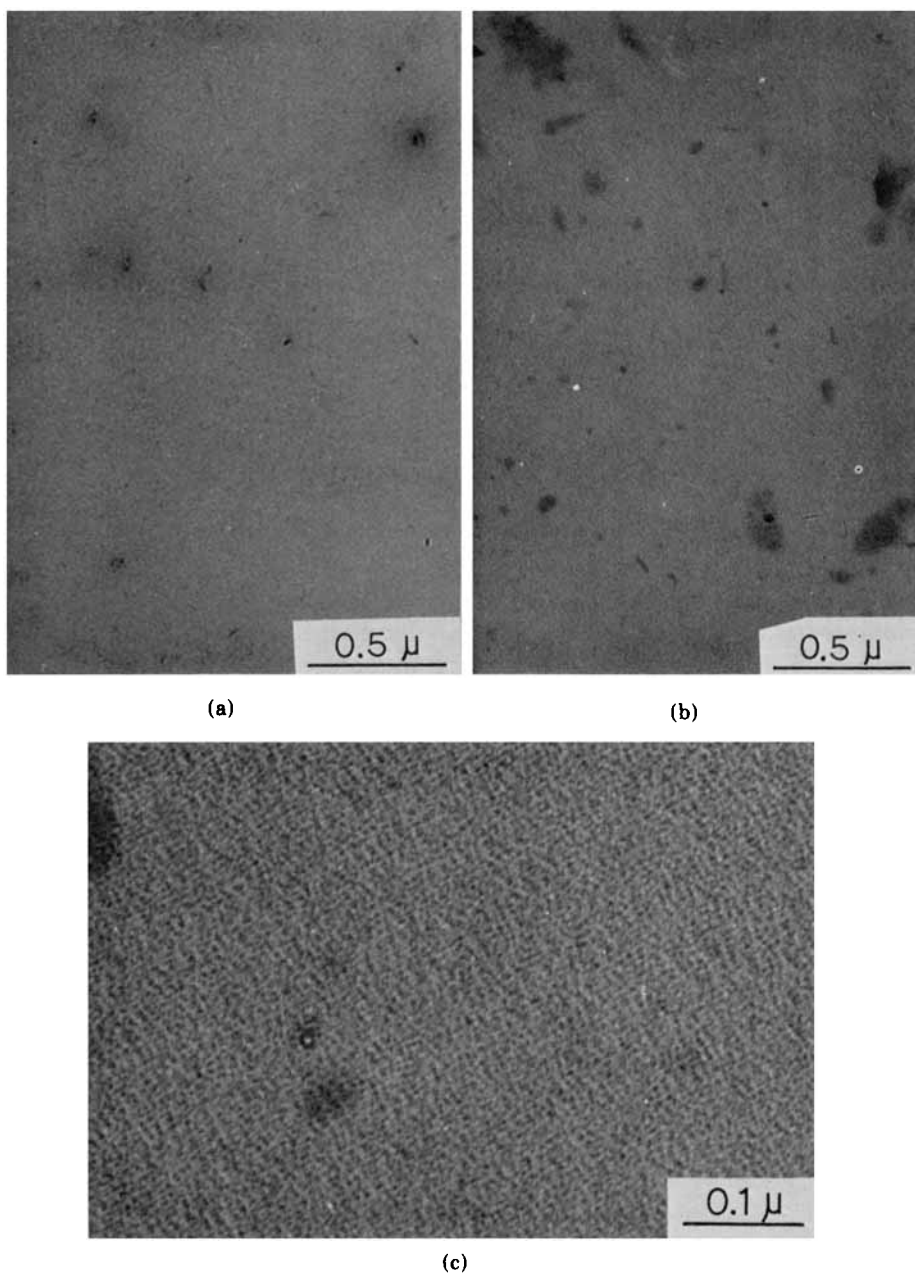


Fig. 5. Transmission electron micrographs of 80 wt-% resin concentration: (a) internal structure; (b) surface structure; (c) magnified image of surface structure of 80 wt-% resin concentration.

sive consisting of about 60 wt-% resin shows high tackiness.^{1,5}

Figures 5a, b, and c show the electron micrographs of the adhesive consisting of 80 wt-% resin and 20 wt-% rubber, at which tack value is extinguished. In the internal structure shown in Figure 5a, the dispersed phase is clearly observed at the whole surface of the micrograph; however, the particles are smaller in size. Figure 5b shows the surface replica image of the adhesive;

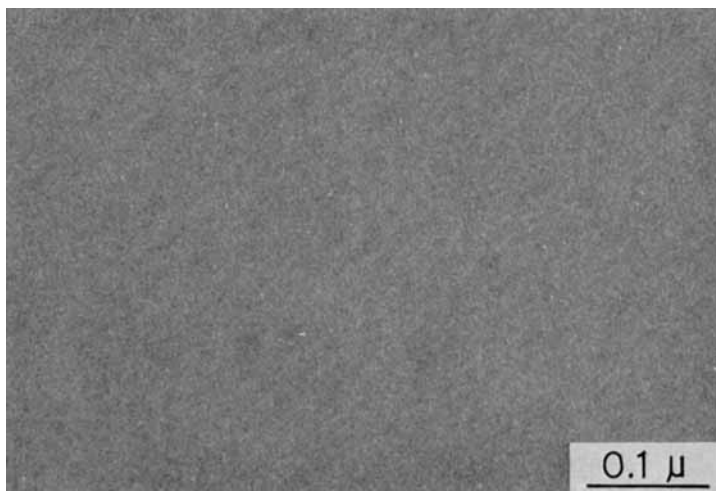


Fig. 6. Replica image of cloven surface of KCl crystal.

the fibril-like fine structure is visible; however, the surface appears smooth as compared with Figures 3b and 4b, and the diameter of the fibrils has decreased. The semidark regions in Figure 5b represent also undissolved adhesive. Figure 5c shows a magnified micrograph of replica image; the fibrils are packed closely, and the average diameter of the fibrils has decreased to about 30 Å.

In order to confirm whether the replica film replicates the actual surface structure of the adhesive film or not, the replica film of the cloven surface of KCl crystals was prepared at the same time that the replica film of the adhesive was prepared. Figure 6 shows an example of the replica image of the cloven surface of KCl crystals, which was prepared at the same time that the surface of adhesive consisting of 60 wt-% resin was replicated. The surface appeared to be smooth, and hardly any particular structure can be observed. By comparing Figure 4c with Figure 6, it is confirmed that the fibril-like surface structure with a diameter of about 50 Å is not due to the artifacts which are accidentally produced in replication but is due to the surface structure of the adhesive.

DISCUSSION

As shown in transmitted micrographs of thin films of adhesive, the internal structure of the adhesive is almost homogeneous up to 40 wt-% resin content, and a small amount of dispersed phase is deposited in the matrix of homogeneous phase when the resin concentration increases further. As described in the previous paper,¹ the resin-rich dispersed phase has a higher glass transition temperature than the homogeneous phase. Therefore, tack presumably is more responsive to the homogeneous phase than dispersed phase. The viscosity and elasticity of the homogeneous phase decrease with increasing resin concentration up to 60 wt-% resin in rubber. The fibril structure with average diameter of about 50 Å is clearly observed on the surfaces of adhesives consisting of 40 wt-% and 60 wt-% resin. In general, a maximum tack is ob-

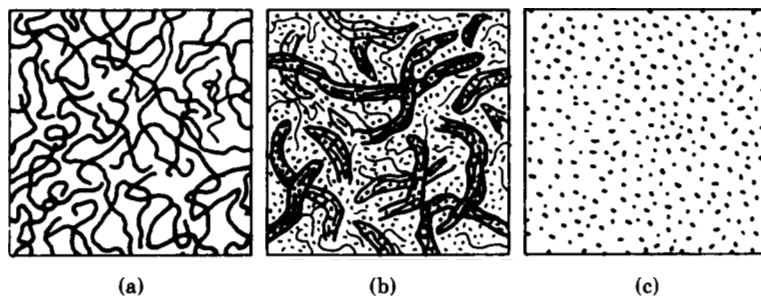


Fig. 7. Schematic representation of structures of (a) rubber, (b) adhesives; (c) resin.

tained at 40 to 60 wt-% resin in rubber.⁵ Therefore, it will be possible to correlate the tackiness of adhesive with the fibril structure of homogeneous phase. The decrease of viscosity will allow easy movement of molecules and contribute to the formation of the fibril structure.

In order to consider the role of fibril structures in the adhesion process, the following structural changes in the homogeneous phase are schematically presented: Figures 7a, b, and c indicate the internal structures for pure rubber, resin-rubber adhesive, and pure resin, respectively. In the case of rubber, the movement of molecular chains is restricted because of entanglement as shown in Figure 7a; therefore, no tack is obtained. Figure 7c shows the glassy state of resin; and no tack is observed.

Figure 7b shows the internal structure of the homogeneous phase of adhesives consisting of 40 to 60 wt-% resin; the entanglement of large molecules of rubber is loosened by including small molecules of resin, and then fibrils and surrounding easy flow regions are formed. (Hereafter, this region is called E-F region for convenience). In Figure 7b, molecules of resin may be included not only in the surrounding E-F region but also in fibril structures. In the adhesives consisting of 40 to 60 wt-% resin, relative movement of fibril structure will be increased by the presence of the E-F region. This will result in an increase of wetting the surface of adherends, and, consequently, tackiness increases.

We propose mechanism of adhesion as follows: In Figures 8a, b, and c are shown schematic sketches of bonding and unbonding processes. When the adherend contacts the surface of the adhesive, some fibrils near the surface of the adhesive stick to the surface of the adherend with the aid of the motion of

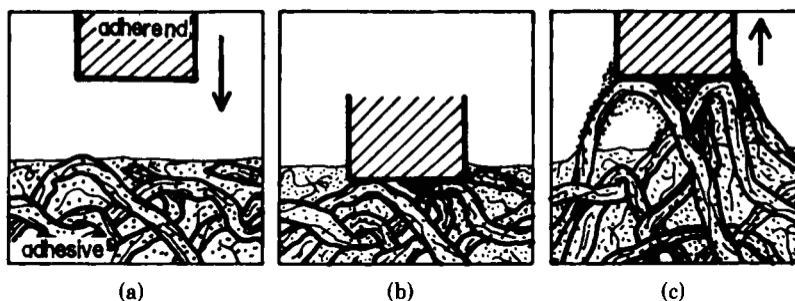


Fig. 8. Schematic process of adhesion.

the E-F region as shown in Figures 8a and b; this will indicate the wetting or bonding process. When the adherend is pull up as shown in Figure 8c, the stuck fibrils resist the separation force; this will indicate the separation process. This process suggests that the wettability of adhesives is mainly attributable to the easiness of mobility of the E-F region, while adhesive force is mainly caused by the stress that is produced by the untangling or breaking of the fibrils.

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