

Morphological Studies on the Adhesion Mechanism of Pressure-Sensitive Adhesives

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Synopsis

The breaking process of the thin film of pressure-sensitive adhesives which are blends of natural rubber and the pentaerythritol ester of hydrogenated rosin and its surface structure after peeling off have been studied by electron microscopy. The dynamic observation of breaking process of the adhesives during the peeling has also been done by optical microscopy. The fibril structure with diameter of 50–100 Å was observed under the breaking process of the thin film and on the surface after peeling off the adhesive tape consisting of 40–60 wt % of resin. The previously proposed mechanism of adhesion which is based on the dynamic behaviors of fibrils and easy flow regions in the adhesives is confirmed by the electron microscopic observation.

INTRODUCTION

The relationship between the surface and internal structure of resin-rubber pressure-sensitive adhesives by electron microscopy and their physical properties such as temperature dispersion of mechanical loss, tensile modulus, viscosity, stress relaxation modulus, and tackiness has been studied by Toyama et al.^{1,2} and Hino et al.³ It has been found^{1,3} that the adhesives consisting of natural rubber and pentaerythritol ester of hydrogenated rosin have two phases. One is a continuous phase of the homogeneous mixture of rubber and resin and the other is the resin-rich dispersed phase with diameter of 0.5–1 μm, at 40–60 wt % resin concentration at which maximum tack is obtained, and the wettability and the tack are mainly attributable to the continuous phase.

In one of the previous papers,³ the fibril structure with an average diameter of about 50 Å has been observed on the surface of the continuous phase using the single-stage replica method. The role of the continuous phase in the mechanism of adhesion, which is the bonding by wettability and the development of adhesion force under the peeling process, has been proposed in terms of the easy flow region, which was called E–F region in the previous paper,³ and the fibril structure. This is schematically shown in Figures 1(a), (b), and (c). The continuous phase consists of the structure of entangled fibrils having an average diameter of about 50 Å and the surrounding E–F region as shown in Figure 1(a). When the adherend contacts the adhesive, the adhesive easily wets the surface of the adherend with the aid of the mobility of the E–F region, and then some fibrils near the surface of the adhesive stick to the surface of the adherend as shown

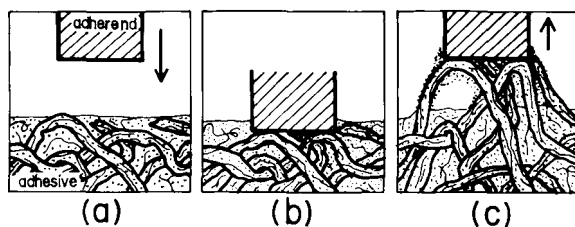


Fig. 1. Schematic illustration of the adhesion process.

in Figure 1(b). In Figure 1(c) showing the separation process, the stuck fibrils resist the separation force because of the disentangling or breaking of the fibrils. The adhesive force is thus mainly caused by stress.

The relationship between the failure mode either interfacial or cohesive failure and the disentanglement of the polyacrylic adhesives has been studied by Kaelble and Reyleck.^{4,5} Dahlquist⁶ has discussed the between the probe tack⁷ and complex tensional modulus of rubber-resin adhesives.

It is rather important to confirm experimentally the mechanism of adhesion suggested in terms of the E-F region and the fibrils described above.

In the present paper, it is shown that the breaking state of the thin film of adhesives has been observed by transmission electron microscope, the surface structure of adhesives after peeling off the adhesive tape has been observed by scanning electron microscope, and the breaking state of adhesives undergoing peel has been studied by optical microscopy. The mechanism of adhesion is also discussed in this paper.

EXPERIMENTAL

The adhesives used were blends of the masticated natural rubber (Mooney viscosity 64) and pentaerythritol ester of hydrogenated rosin (Pentalyn H, Hercules Inc.).

In order to observe the fine structure during the breaking process of the thin film of adhesive with a transmission electron microscope, the sample was prepared as follows. A drop of the solution in *n*-hexane of about 1 wt % of natural rubber and resin in the ratio of 3:2 was placed onto the mesh and dried to remove the solvent which produces the thin film suitable for electron microscopic observation. Strong illumination of electron beam produced sometimes the breaking of the adhesive thin films under electron microscopic observation and the breaking process was observed.

In order to observe the surface structure of the adhesive after peeling with the scanning electron microscope, the sample was prepared as follows. Solution in *n*-hexane of about 10 wt % of natural rubber and resin in the ratio of 3:2 was 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 0.025 ± 0.001 mm. Two pieces of adhesive tape were stuck to each other and peeled at a peeling rate of 3 cm/min, a peeling angle of 90° (T-peeling), and a temperature of 20°C. The surface of the peeled adhesive was coated with a layer of gold approximately 50 Å thick in order to avoid the charge-up of electrons and observed with a scanning electron microscope.

The dynamic behavior of the adhesive undergoing peel was observed with an optical microscope,⁸ since it is too difficult experimentally to observe it with electron microscope.

The adhesive was a blend of natural rubber and resin in the ratio of 3:2. The thickness of the adhesive layer was 0.025 mm. The substrate was a biaxially drawn polypropylene film of 0.06 mm thickness (Torayfan BO No. 60, Toray Industries Inc.). Figure 2 shows the side view of the peeling apparatus. The adhesive tape T is put of the adherend A, which is fixed of the movable support B. The end of the tape is fixed to a point C on the support through the roll R. When the support B moves in a particular direction indicated by arrow which is driven by a motor M at a constant rate, the adhesive tape is peeled at the point P with a constant rate. The optical microscope was focused to the point P, and dark field illumination was used. If the elongation of the tape is ignored, it is then not necessary to move the microscope while observing the peeling process of adhesive, because the peeling angle changes very little and the peeling boundary does not move from place to place. The experiments for this study were carried out at a peeling rate 3 cm/min, a peeling angle 90° and a temperature 20°C. The adherends used were polytetrafluoroethylene (PTFE) and polypropylene (PP), and the surfaces of these adherends were polished with emery paper (no. 1000) before putting the adhesive tape.

RESULTS

Figures 3(a) and (b) are the transmission electron micrographs showing the breaking process of the thin film of adhesive. Figure 3(a) shows the image which was photographed immediately after the break of the thin film of adhesive. The dark particles with diameter of about 0.5 μm are the resin-rich dispersed phase as described in the previous paper.^{1,3} The film breaks into an irregular net like as is seen in Figure 3(a). Fine structure under breaking can be seen in highly magnified image shown in Figure 3(b). By the irradiation of electron beam very many small holes of 100 Å in diameter are formed, and then specimen film becomes into the net like structure, as shown in Figure 3(b). The structure seems to be due to the fibrils in the specimen. Further irradiation produces the breaking of the fibrils. These fibrils with the diameter of about 100 Å have some branches. This behavior suggests the entanglement of the fibrils in continuous phase. In general, the observation with very high magnification requires the high intensity of the illuminating beam which inevitably destroys the specimen

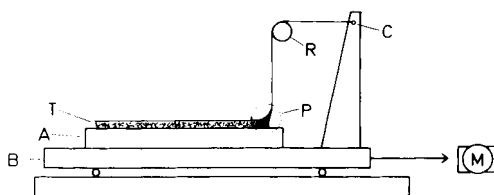


Fig. 2. Side view of the peeling apparatus: (A) adherend; (B) movable support; (T) adhesive tape; (P) the point which the tape is peeled; (R) roll; (C) the point of the support which the end of the tape is fixed; (M) motor.

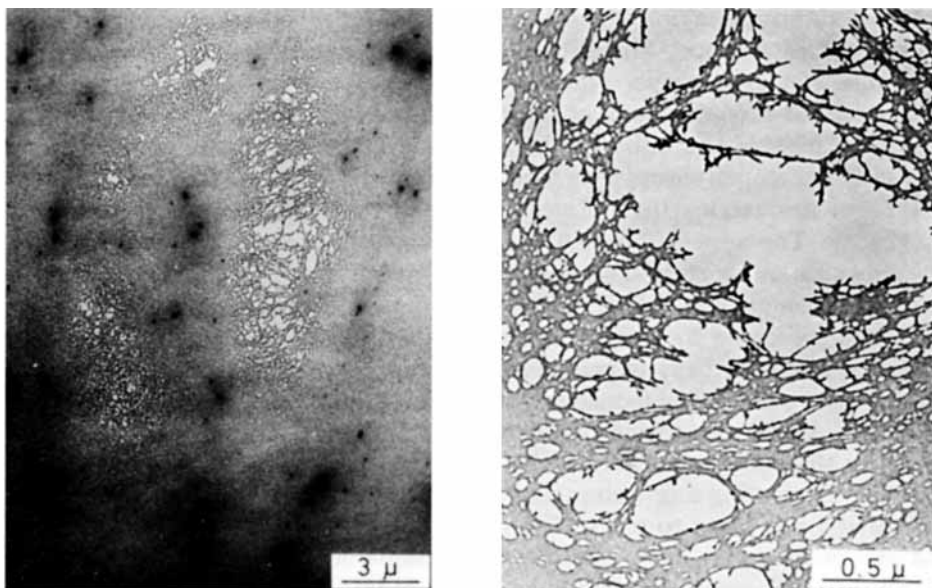


Fig. 3. Transmission electron micrographs of breaking process of thin film of adhesive: (a) image observed immediately after break; (b) highly magnified image.

film completely. Therefore, in this observation, it was very difficult to observe the specimen at very high magnification. Figure 3(b) was taken at a magnification of 10,000 times with 10 s exposure.

Figures 4(a), (b), and (c) show the scanning electron micrographs of the surface of adhesive after T-peeling. Undulationlike structure U with diameters of 20–30 μm , which appeared to grow by rheological flow at peeling, and yarnlike structure Y with diameter of about 0.5 μm suspended between the undulations are observed in Figure 4(a). Droplike materials are also observed on this yarn. This yarn is larger than the fibrils with diameter of about 100 \AA observed in Figure 3(b). However, much finer fibrils seem to have been suspended between undulations in fresh peeled surface, which seems to have been destroyed by the further deformation which has been taking place during the specimen preparing such as coating of gold on the surface of adhesive. Strained adhesives are deformed and relaxed owing to viscoelasticity, which is a fundamental and necessary property of adhesives. Therefore, if observation can be carried out right after peeling, the fibril will be observed as a fine yarnlike structure between the undulations.

In Figure 4(b), which is the scanning electron micrograph with much higher magnification than in Figure 4(a), very fine creaselike structures with diameters of about 1000 \AA which orient to one direction are observed. This means that the adhesive was strained along one direction by the peeling. Figure 4(c), which was observed with higher power magnification compared to Figure 4(b), shows that the fibrils with diameter of about 100 \AA are lying and entangling on the surface of adhesive.

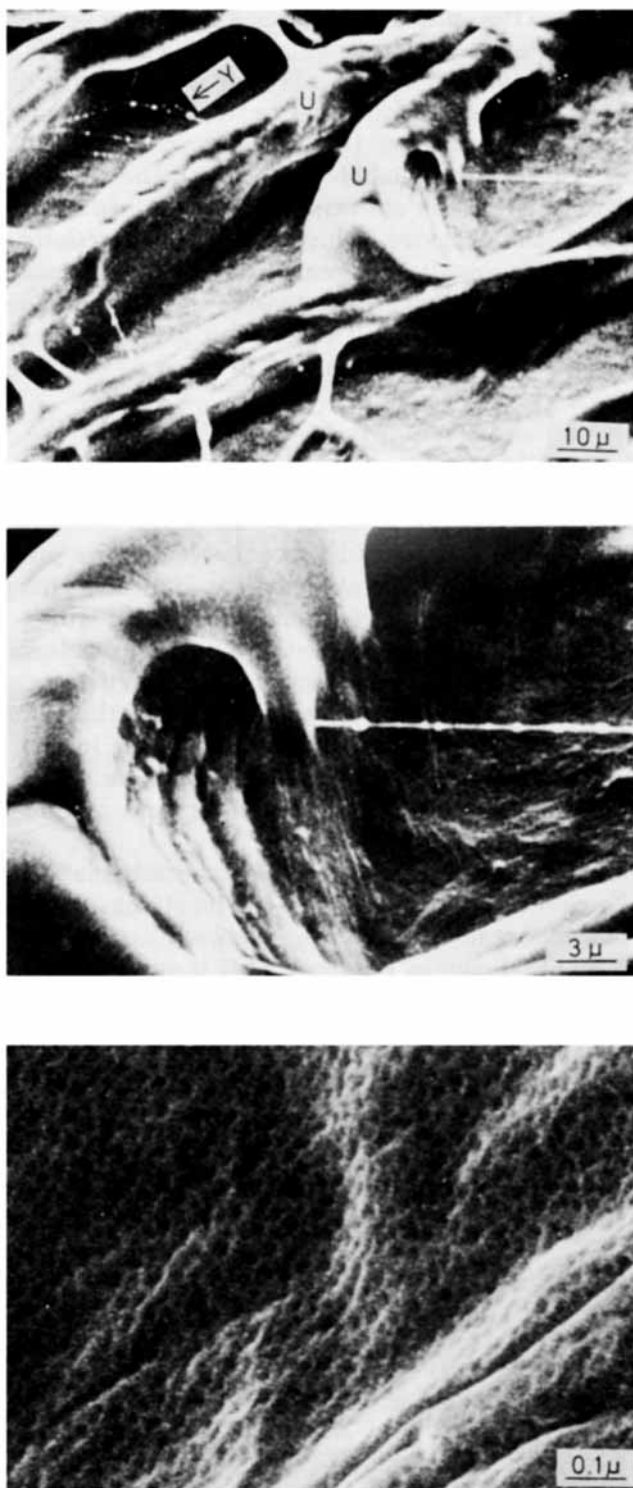


Fig. 4. (a), (b), (c). Scanning electron micrographs of surface of adhesive after T-peeling.

Figures 5 and 6 are the optical micrographs of peeling process which were taken by using the device shown in Figure 2. PTFE and PP were used as adherends, respectively. The stringy state of adhesive are different with the difference of adherends as follows. The thickness of strained strings in case of PP adherend are thinner than the one in PTFE, and observed to be about $1\ \mu\text{m}$. This is nearly same in size with the one observed in the scanning electron micrograph shown in Figure 4(a). In the case of PP as shown in Figure 6, the cohesive failure of adhesive partially occurs since the adhesive materials are slightly remained on the adherend. In the case of PTFE shown in Figure 5, however, such adhesive materials which remain of the adherend are not observed. Therefore, it is clear that the peeling is caused by the apparent interfacial failure in the case of PTFE.

DISCUSSION

The mechanism of adhesion process on the wettability and development of adhesion force, which is discussed in terms of the dynamic behavior of E-F region and fibril structure and was proposed in the previous paper,³ seemed to be reasonable from the observations shown in this paper.

The transmission electron micrographs shown in Figures 3(a) and (b) suggest that the internal structure of continuous phase of adhesive is similar with that which was schematically represented in Figure 1(a). The continuous phase consists of the E-F region and fibrils, and the deformation and the breaking of the continuous phase occurs at first in the E-F region because the E-F region more easily flows and is more deformed than fibrils, and fibrils resist the deformation and breaking, and produce the netlike structure as shown in Figures 3(a) and (b).

The principle of the separation process shown schematically in Figure 1(c) seems to be confirmed by Figures 4-6. The strings of adhesive which was peeled from adherend PP shown in Figure 6 are thinner than those from adherend PTFE shown in Figure 5. This is explained as follows. The stress acting to the fibrils in the peeling process is stronger to the adherend

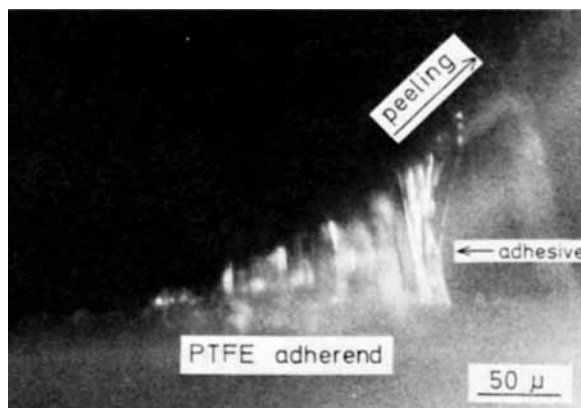


Fig. 5. Optical micrograph of breaking process of adhesive during peeling in the case of PTFE adherend.

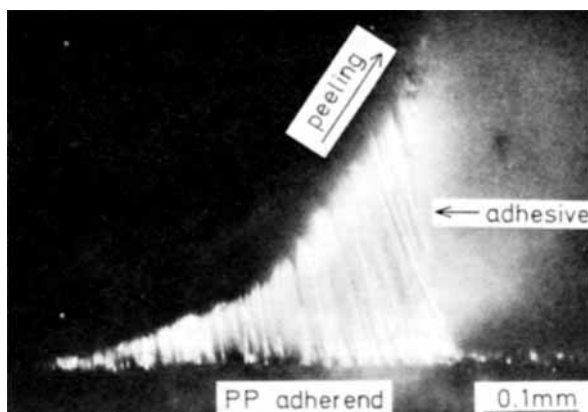


Fig. 6. Optical micrograph of breaking process of adhesive during peeling in the case of PP adherend.

PP compared to adherend PTFE because adhesives more easily wet PP compared to PTFE and therefore are not more easily peeled off from PP.⁹ It has been already discussed^{8,10} that, at the slow peeling rate of 3 cm/min as carried out in this work, the breaking of adhesives is almost responsive to viscous effect than elastic effect. In a brief speaking, the breaking of adhesive mainly occurs with the viscous disentanglement of the fibrils. Therefore, in the case of adherend PP the fibrils are more fully disintegrated and observed to be thinner, and thus disintegrated fibrils are liable to remain on the surface of adherend PP compared to adherend PTFE.

This means that at the higher peeling rate compared to this work, the fibrils do not disentangle easily because the disentanglement slipping rate is higher and stress acting on the fibrils is stronger. This association seems to be supported by the relationship described by Kaelble and Reylek^{4,5} between the failure mode and the entanglement slipping rates of adhesives.

The yarnlike structure with diameter of about 0.5 μm between the undulations observed in Figure 4(a) and the creaselike structures with diameter of about 1000 \AA observed in Figure 4(b) seems to be bundles of fibrils with diameter of 50–100 \AA . Such fibrils are the ones observed in Figure 4(c). Droplike materials on the yarn between the undulations observed in Figure 4(a) seem to consist of disintegrated fibrils and the materials making up the E–F region.

According to the adhesion mechanism suggested by both this study and the previous paper,³ the lower modulus adhesives easily wets the adherends owing to the relative mobility of fibrils with the aid of the surrounding E–F region at the bonding process in which the adhesives deform into very low degree, and at the unbonding process in which the adhesives deform into the very high degree, say more than 500% shown in Figures 5 and 6, the high modulus which induces the high stress acting on the fibrils must obtain the high tack.

The behavior of adhesives in bonding and unbonding process seems to be fully understood by the behavior of the fibrils and the E–F region which were observed in this experiment.

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