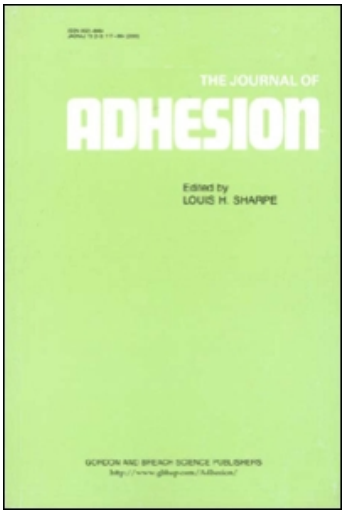


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# On the Character of Failure of Adhesive Joints Between Two Polymers

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NOTE

# On the Character of Failure of Adhesive Joints Between Two Polymers†

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Up to the present there has been discussion of the locus of fracture of adhesive joints, i.e., if it proceeds precisely at the interphase border, or if cohesive fracture in a weak layer of one of the components takes place. There are only a few data available on this point.[1]

It is accepted that the replica method which is used in electron microscopy can not answer the question about the character of fracture because between replica and substrate surface an intermediate layer of adsorbed gas molecules and other admixtures is present. This layer prevents the realization of the true adhesion contact between replica material and substrate.[2, 3] The search for ways to improve the resolution of the replica method has led to the application of the technique of vacuum deposition of various substances, including some modes of obtaining the carbon replica. It was shown[4] that the resolution of replicas in these cases will be limited only by the granularity of their material. This means that high vacuum and controlled heating of the substrate surface, in the course of replication, have eliminated the problem of desorption of adsorbed and occluded gas molecules and have facilitated the realization of adhesion contact. Upon mechanical peeling of such replicas experimenters always observe the presence of a "parasite" ultrathin layer of polymer substrate which is adhered to the replica, its thickness being 5 nm and more. This layer makes the contrast and resolution worse and therefore has to be removed by different methods (destruction, dissolution, thermal decomposition in vacuum) without harming the replica material. The same layer, when the method of wide-angle scattering of

† In memory of J. J. Bikerman, the human being, the scientist, the friend.

rapid electrons is used,[5] may be successfully applied to establish the nature of polymeric substrate, i.e., for the single-valued determination of the locus of fracture of the two adhered polymer bodies.

It is known that in line with improvement of replica resolution power the difficulties of mechanical peeling of replica from polymer surface increase. However, just this circumstance, which by the routine electron microscopy investigation is a hindrance from obtaining the real picture, can be used to determine the character of fracture for adhesive joints. This was the aim of the present study.

To solve the question we have used the fact that, after peeling, an ultrathin surface layer of substrate remains on the replica. On the basis of wide-angle electron diffraction (WAED) the nature of this layer may be established. If we obtain replicas from the surfaces of two polymers separated by peeling, they will have on each of their surfaces an ultrathin layer, these being typical of the locus of failure. If this layer is similar to the main polymer body, the adhesion fracture is believed to proceed; if the layer is similar to the polymer counter body the cohesion fracture takes place.



To check experimentally this suggestion two oriented films of commercial polypropylene (PP) were taken. One of the films after orientation was activated by exposure of its surface to plasma generated in a linear electrodeless high-frequency discharge according to the method described in Ref. 7. Epoxy resin used was a commercial product of condensation of epichlorohydrin and diphenylolpropane and was cured with polyethylenepolyamine (10 parts by weight). The non-hardened resin was applied to the film surface and then cured at 80°C and 80 kg/cm$^2$ for 5 hours. PP is known to be difficult to adhere to and usually needs additional surface activation. In spite of this, we believed we could discover the place of adhesion contact even for non-activated polymer because to obtain samples for investigation elevated temperature (80°C) and pressure (80 kg/cm$^2$) were used.

It was found that the system nonactivated PP-epoxy resin is characterized by spontaneous selfpeeling whereas the peeling of joined activated film and resin needs the application of some force. In the separated state both counterbodies (PP and epoxy resin) differ in their appearance and colour. It is difficult to make a mistake in analyzing the WAED pattern for axially oriented PP. It shows distinctly all changes in molecular orientation, oriented PP being in this way a good test subject. Onto the separated surfaces the vacuum-deposited carbon foil replicas were applied immediately in a vacuum no worse than $10^{-4}$ mmHg using thermal deposition, these replicas having been peeled later. Using the effect of "parasite" adherence of an ultrathin polymer layer to the replica, we have done the structural evaluation of this layer for each peeled counterbody using the WAED technique. To grain the best visualization, the diffraction and morphological pictures were taken

from the same area of the replica. Morphological pictures were obtained using a JEOL-100 C electron microscope.

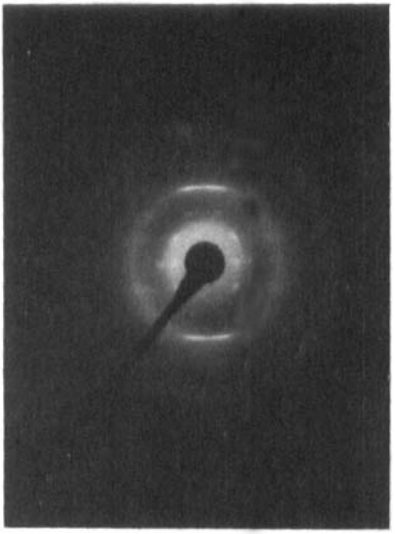
Under the conditions mentioned the foil replicas made of carbon have essential advantages in comparison with other materials used for replication. They have no structure of their own (even according to electron diffraction), are chemically inert, and transparent to electrons up to a thickness of about 0.1 $\mu$m. These replicas reflect the surface relief more precisely and give as a rule a fine adhesion contact with polymer substrate. The latter effect manifests itself in the realization of only cohesive mechanical peeling (for oriented polymers, exclusively in the polymer material). For experimental morphological study the "parasite" layer of polymer may be easily removed, if necessary.

In our experiments we have discovered the presence of reflections characteristic of counterbody on all of the separated pairs of polymers. After peeling, epoxy resin had on its surface an ultrathin layer of PP (Figure 1a) with preservation of the texture peculiarities of the initial PP film. The WAED pattern distinctly shows four orders of layer lines. There were no visible traces of deterioration of texture, i.e., azimuth broadening of reflexes, and the relation of intensities in three main equatorial reflections remains constant second orders of equatorial reflections even being observed. All these data allow the conclusion to be drawn that no diffusion penetration of one component into another takes place, as in the latter case we should have seen the deterioration of the texture up to the full disorientation in the penetrated layer of material. Therefore the WAED pattern obtained favours the concept of cohesional fracture for the case of adhesive joints of two polymers (the fracture proceeds in counterbody of each polymer). On the background of intensive scattering from PP there is seen practically no scattering from the epoxy resin.



On the opposite part of the separated composition, i.e., on the PP film, we have observed the scattering from epoxy resin preferentially with weak profounded fibre texture of PP, namely intensity condensation in the region of meridian reflection on the third layer line (Figure 2a). Weak equatorial reflections may be the result of intense background scattering from epoxy resin superposed on scattering from PP. Such a behaviour is typical for the cohesion failure of adhesion contact of two bodies according to the model developed in 2.

The morphological pictures have very distinguishing features. On the surface of epoxy resin we observe the "forced" fibrillization of PP film with formation of a great deal of rootlike chords (Figure 1b), the same picture having been often observed on fractographical pictures of homopolymers as well. The PP surface has on it great areas covered with small globules of epoxy resin (Figure 2b). We have also found the regions of adhesion contact



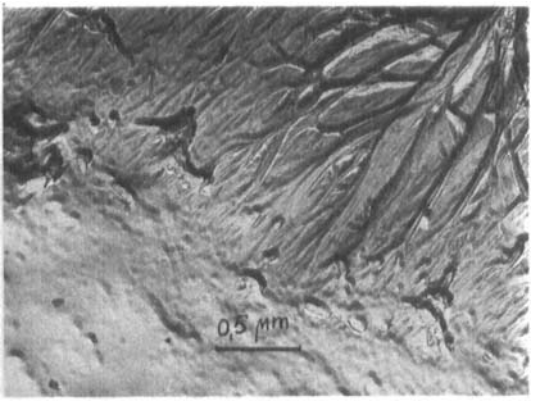



FIGURE 1 Structure and morphology of peeled composition obtained by hardening epoxy resin onto the surface of activated PP: From epoxy resin side: (a) diffractogramme with preferential reflections of oriented PP; (b) electron microscopic picture of root-like chords of fibrillized PP film.

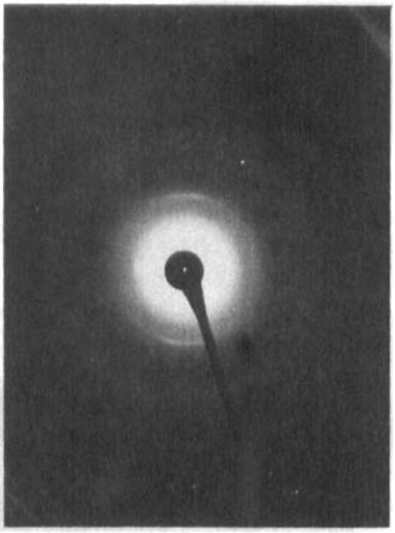
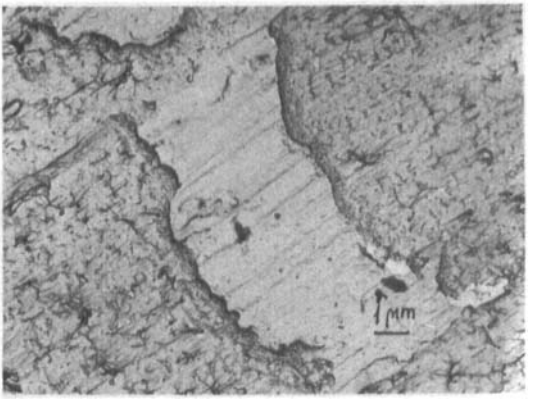


FIGURE 2 The same from the side of PP film: (a) diffractogramme with preferential scattering from epoxy resin; (b) morphology of the surface of PP film with small globules of epoxy resin.




on the surface of nonactivated PP film with surface tension 34 dyne/cm, their scattering intensity being rather weak.

The data obtained show at the same time that the cohesion fracture has a complicated character and does not proceed in the layer of only one polymer. The adhesion joint failure takes place, as we can now conclude, in the interphase border region between two polymers (the region of adhesion contact).

It was earlier shown[6] that for mixtures and blends of incompatible polymers the intermediate or interphase layer arises between the phases of pure components, this layer being formed by the structural elements of both polymers. This means that the phase border has a diffusion character. The experimental evidences given above confirm the existence of such a layer and prove that this interphase layer is the real place of failure of adhesion joints between two polymers. In this layer, its thickness being equal to some $\mu$m, the cohesion fracture of every constituent phase takes place.

Thus we can conclude that in the polymer compositions the fracture processes proceed in the interphase region, involving both phases present in this layer, where they have mainly cohesive character in accordance with concepts so successfully developed for many years by J. J. Bikerman.

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