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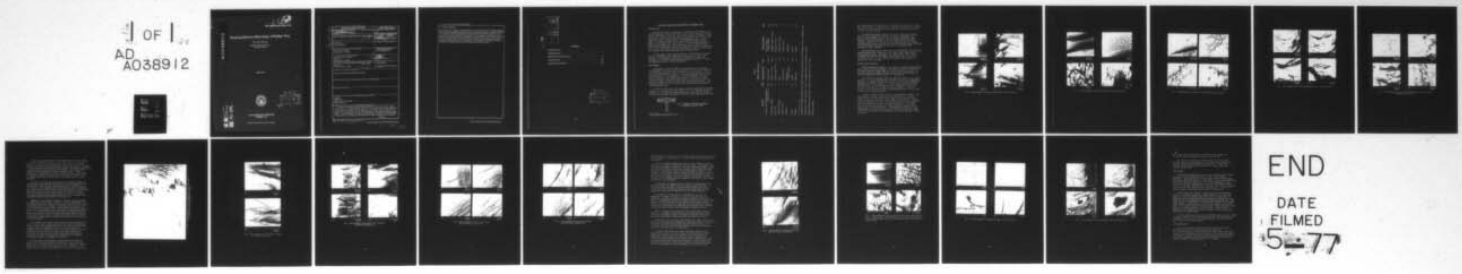

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NRL Memorandum Report 3478

Scanning Electron Microscopy of Rubber Tear

WILLARD D. BASCOM

Polymeric Materials Branch
Chemistry Division

April 1977

NAVAL RESEARCH LABORATORY
Washington, D.C.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A simple technique was devised for SEM observation into tears or cuts in rubber or other flexible polymers. A rectangular specimen (about 2 × 1 × 0.5 cm) was held in a bent configuration in a SEM holder and a shallow razor cut made at the top of the bend. Tensile stresses cause the rubber to tear and advance the cut depth. Observing along the tearing direction the highly stressed rubber at the tear tip (damage zone) could be observed in detail. A number of commercial rubbers including natural, nitrile, neoprene, polybutadiene and fluorocarbon compositions were examined → next page

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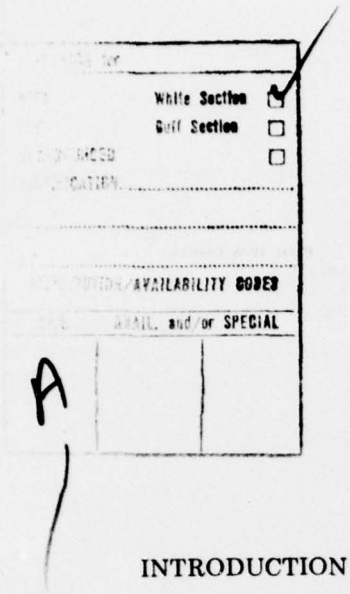
20. Abstract (Continued)

using this technique. Initially, the stressed rubber at the tear tip was more or less continuous although some structure and occasionally cavitation were observed at high magnifications (> 5000X). Removal of the specimens from the microscope and exposure to laboratory air resulted in gradual (2-20 hr) development of an open network of fibers and nodules, due to oxygen/ozone attack on the stressed rubber. The process resembled the slow relaxation of a stretched film of a highly viscous liquid under the action of surface forces. The rate of the network formation was generally proportional to the oxidation resistance of the rubber. The significance of these observations is discussed in reference to the practice of cyclizing rubber surfaces as a pretreatment for adhesive bonding.



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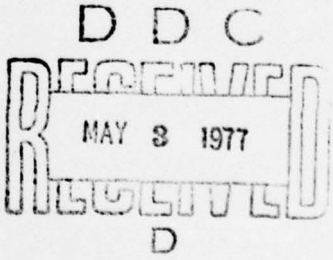

SCANNING ELECTRON MICROSCOPY OF RUBBER TEAR

INTRODUCTION

The tear or fracture resistance of elastomers and polymers is largely determined by the events that occur in the damage or "plastic" zone of the tear or crack tip. The energy required to advance a tear is directly related to the deformational processes that occur in the damage zone due to applied stress, environmental attack or both. There are numerous theories that relate the macroscopic yielding behavior of polymers with their tear or fracture energy and some of these relationships have useful predictive value. None the less, most of these theories are based on supposition about the deformations that occur in the damage zone simply because so little is known about the yielding and failure processes that actually occur.

In this paper a very simple technique is described for scanning electron microscope (SEM) observation into a tear or crack under tension. The technique is used here to examine the crack tip deformation of various commercial rubbers and to follow the effects of oxygen/ozone attack on the damage zone.

EXPERIMENTAL

Rectangular pieces of rubber or polymer were held in a bent configuration in an SEM holder as shown in Figure 1. The holder had a 1.3 cm square base with two end plates 1.5 cm in height. It was constructed by bending a single 0.2 cm thick aluminum strip and then press fitting a 0.5 cm diameter, 1.3 cm long aluminum rod into a hole in the base. The samples were about 1.8 cm long, 1 cm wide and had variable thickness and were bent into place with a drop of conductive cement at each end where they contacted the holder. The cement provided electrical contact and also prevented the specimen from springing loose.

A razor cut was made in the upper surface of the mounted specimen (Figure 1) to a depth of no more than 0.25 of the specimen thickness. Usually, the cut advanced spontaneously due to the tensile stress in the bent elastomer specimens so that the damage zone being observed

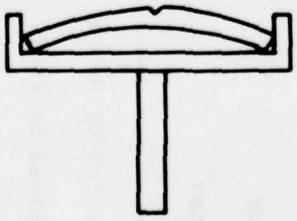

Fig. 1 — Schematic of SEM holder for observing into surface cuts or tears in rubber

Note: Manuscript submitted March 10, 1977.

Table I

RUBBER FORMULATIONS

Nitrile[a]	PBW[d]	Polybutadiene[b,c]	PBW	Natural Rubber[a]	PBW
Paracril CLT (polybutadiene-acrylonitrile)	100	Diene 35 NFA	100.0	Natural Rubber (Smoked Sheet)	100
Philblack A (N550)	50	Vulcan 3 (N330)	50.0	Thermax (carbon black)	15
Fyrol CEF	5	Philoich HA5 (oil)	5.0	Neothax A (oil)	15
Protox 166 (ZnO_2)	5	ZnO_2	3.5	Protox 166 (ZnO_2)	5
stearic acid	1	stearic acid	2.5	stearic acid	1
Octamine	1	phenyl-β-naphthylamine	1.0	Neozone A	2
sulfur	1.5	sulfur	2.0	sulfur	3
Thionex	0.5	Santocure	5.0	Captax	0.5

[a] Prepared by Rubber Branch, David Taylor Naval Ship Research and Development Center, Annapolis, MD.

[b] Supplied by Prof. Alan Gent, Inst. of Polymer Science, University of Akron.

[c] Sample without carbon black (Vulcon 3) supplied by Prof. Gent.

[d] Parts by weight.

was characteristic of rubber tear. Occasionally, the tensile forces were insufficient to cause the cut to advance spontaneously, in which case the cut was made before mounting and the specimen was manually flexed to produce tearing.

The mounted specimens were given a thin (~200A) gold coating using a vacuum evaporator ("Hummer", Technics, Alexandria, VA). This coating lessened surface charging in the SEM which, unless reduced, caused photographs of the SEM image to have very poor contrast. However, the coating process tended to heat the rubber slightly and in order to be certain that the heating was not affecting the observations, each specimen was given a preliminary SEM examination before coating.

The microscope used in this study was an AMR model 1000 (American Metals Research Corp.) having a X-ray energy spectrometer (XES) attachment (Kevex-Ray, Burlingame, CA, model 5100). The nitrile, polybutadiene, and natural rubber formulations used in this study are given in Table I. The formulations of the other materials studied were not available.

RESULTS AND DISCUSSION

The photographs in Figure 2 are views of increasing magnification into a tear in a nitrile rubber. The razor cut surface is seen as the smooth areas to either side of the tear area in Figure 2A. In the tear region the rubber had undergone a process that appears to involve stretching and then rupture of the material.

The specimen in Figure 2 had been examined within 0.5 hr. after cutting. If the cut was made and allowed to stand in the laboratory atmosphere for about 24 hrs., the tear tip had a totally different appearance as shown in Figure 3. A fibrous and nodular structure had developed. If allowed to stand for a few weeks in air this structure coalesced into clumps as shown in Figure 4. Note in Figure 4 that fibers and nodules had developed further into the tear tip beyond the clumped material.

Similar observations were made of a polybutadiene rubber. The photographs in Figure 5 show the tear formed within 15-30 mins. after cutting. As with the nitrile rubber, the yielding process appears to involve stretching and rupture of the material. Holding the cut specimen for 24 hrs. in the laboratory air also produced a fibrous and nodular structure as shown in Figure 6. Note that the wall of the tear (Figure 6D) which initially had been smooth has developed a nodular texture. A polybutadiene having the same composition as the material of Figures 5 and 6, but without carbon filler, had the same tear tip appearance initially and after 24 hrs. air aging.

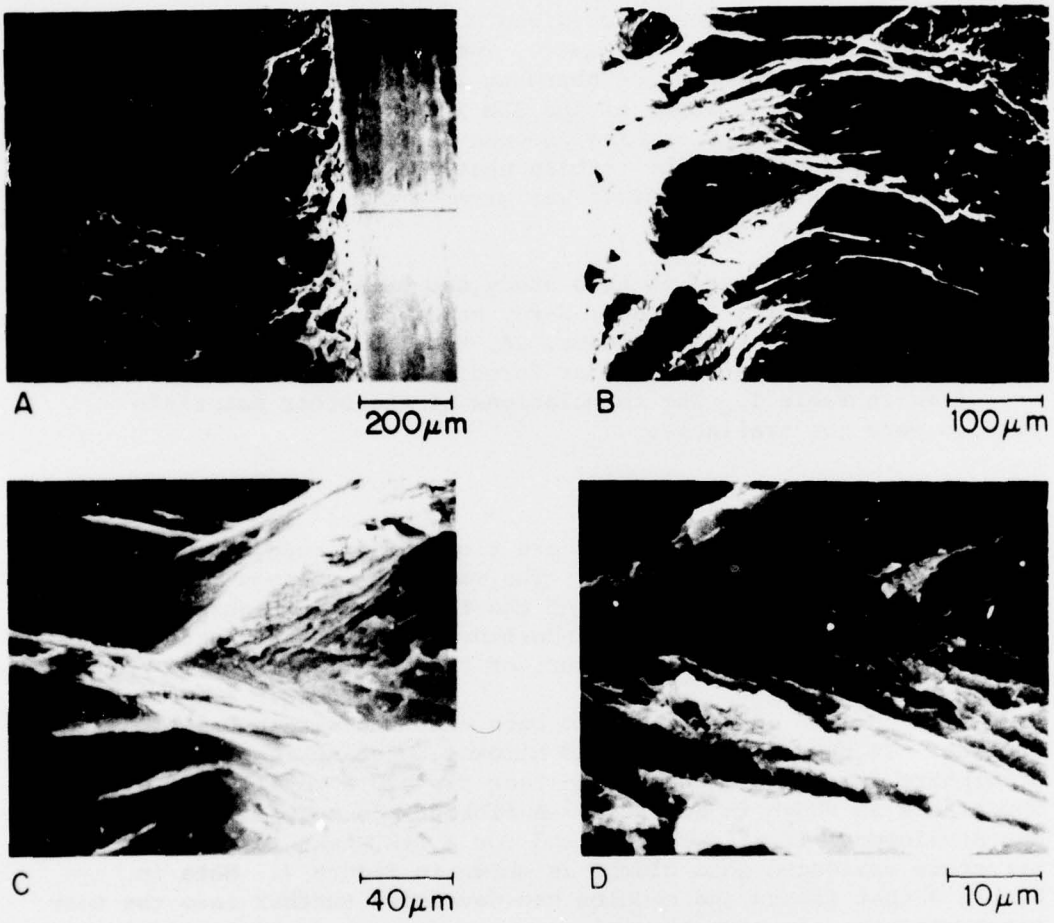

Fig. 2 — SEM photographs of a tear tip in a nitrile rubber < 0.5 hr after cutting

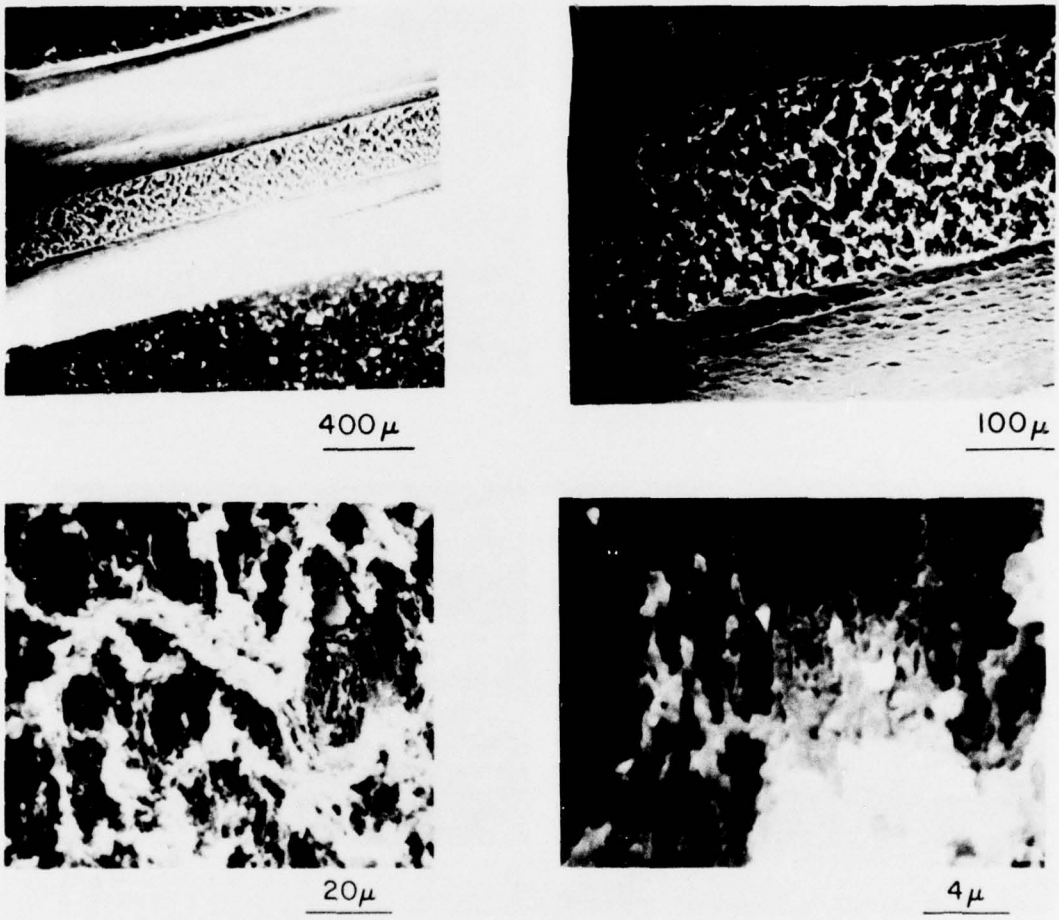

Fig. 3 — SEM photographs of a tear tip in a nitrile rubber 24 hours after cutting

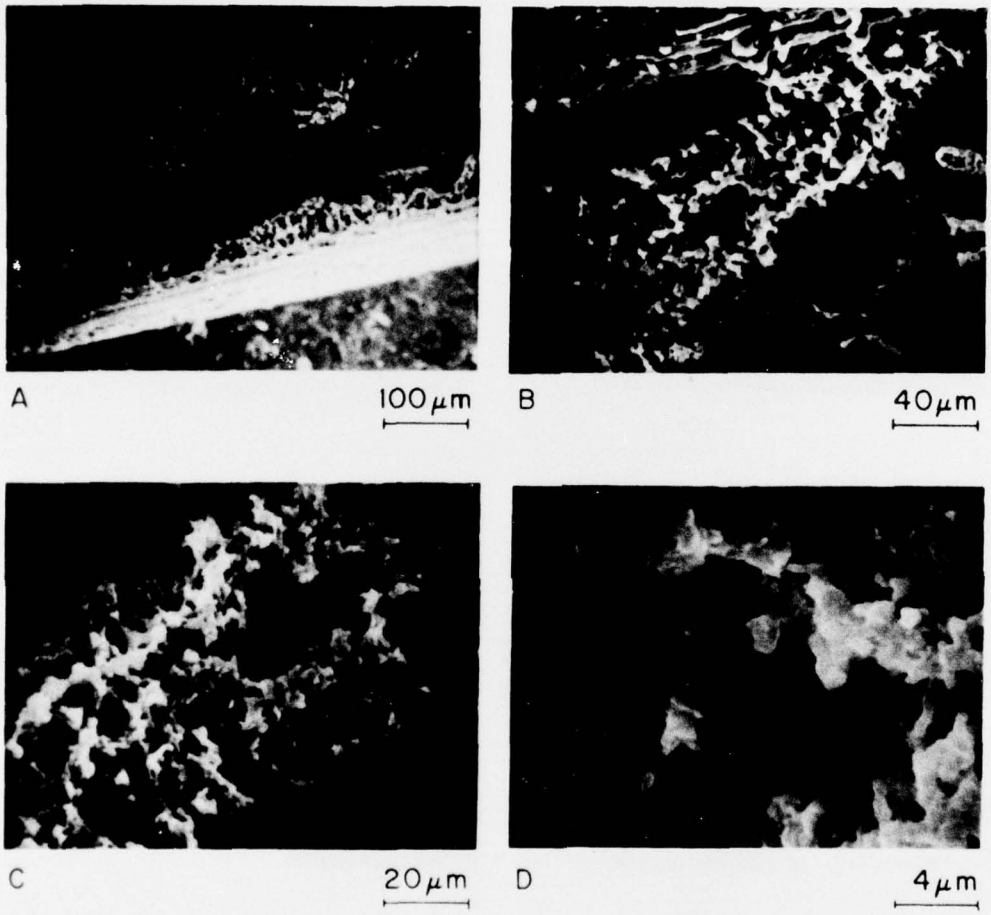

Fig. 4 — SEM photographs of a tear tip in a nitrile rubber 2-3 weeks after cutting

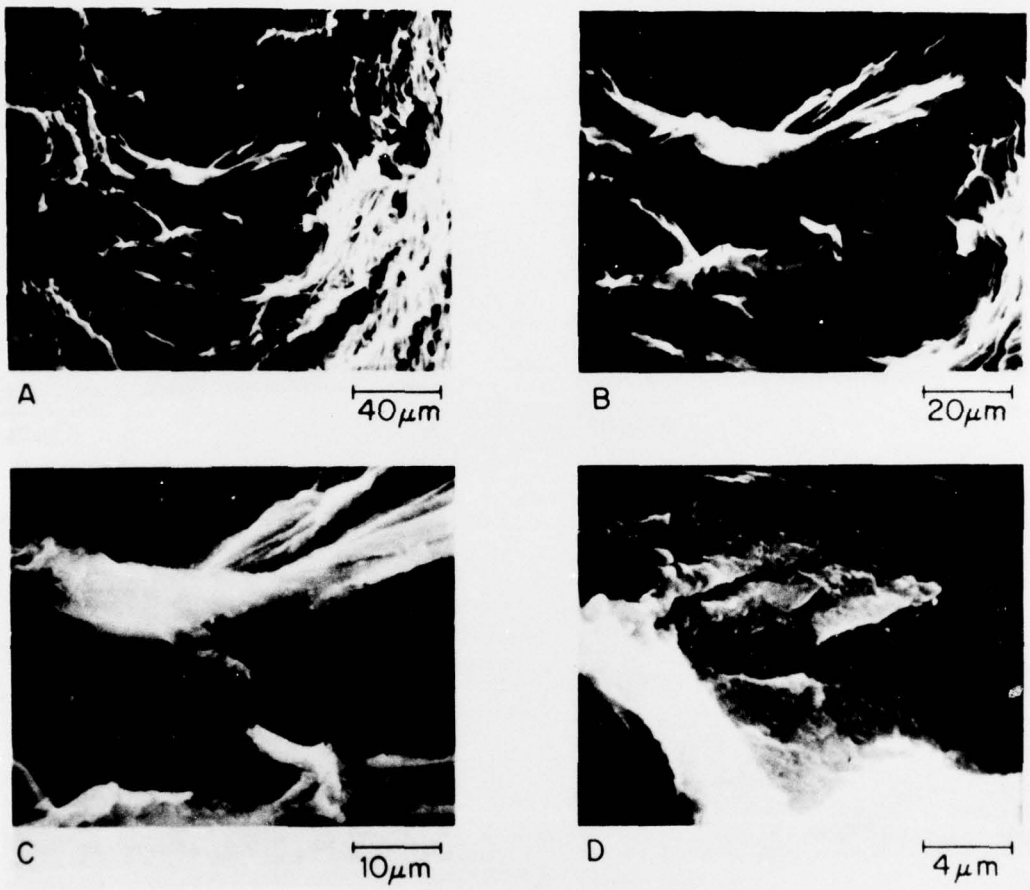

Fig. 5 — SEM photographs of a tear tip in a polybutadiene rubber < 0.5 hr after cutting

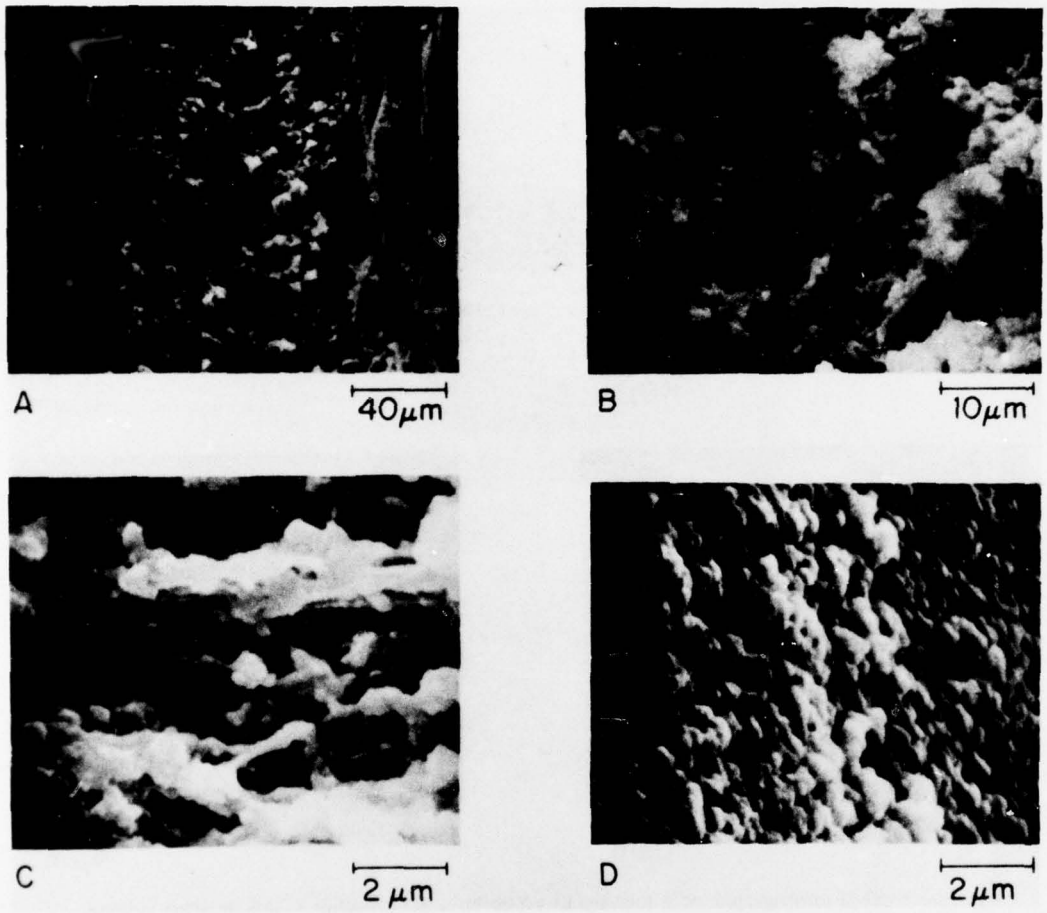

Fig. 6 — SEM photographs of a tear tip in a polybutadiene rubber 24 hrs after cutting. Photograph D is of the tear wall.

A specimen of natural rubber was examined and the initial tear (~15 mins) is shown in Figure 7. The bright strip in the center of the tear is an area that is charging in the electron beam because yielding had occurred after application of the gold coating. As with the other rubbers, the yielding process appears to involve a stretching of the material followed by localized rupture. The failed rubber appears to have relaxed into folds on the tear wall. Higher magnification photographs of the tear region of Figure 7 are shown in Figure 8. Some of the material is in the form of tendrils and presumably under tension while other of the material has a lacy appearance.

So long as the specimen was held in the evacuated chamber of the SEM there was no change in the extent or the appearance of the tearing zone. However, when removed and placed in laboratory air for 5 hours, holes developed as shown in Figure 9 and the rubber in these holes had a fibrous, nodular structure similar to the structure developed by 24 hrs. aging of the nitrile and butadiene rubbers. Note that the area of the holes is bright in Figure 9, and since the specimen had not been recoated after the 5 hrs. of aging, this brightness denotes new yielding of the material.

Removal of the specimen of Figure 9 from the SEM and exposure to laboratory air for 24 hrs. resulted in further development of the fibrous and nodular areas, but not across the entire tear width. On the other hand, if a specimen of this same rubber was cut, held out of the SEM for 24 hrs. before coating and then examined, the entire tear area developed fibers and modules as shown in Figures 10 and 11. It is suspected that the gold coating evaporated onto the initial cut (Figure 7) had some protective action against environmental attack on the rubber. Similar experiments with the nitrile and butadiene rubbers also indicated that the gold coating slowed the aging process.

The formation of the fibers and nodules is unquestionably the result of ozone and/or oxygen attack on the rubbers. The process did not occur if the specimen was held in the evacuated microscope chamber. Also, the protective action of the gold coating is consistent with an oxidative attack. Since the composition of the laboratory air was not known it cannot be judged whether the attack was by ozone alone. However, the presence of ozone was noticed by its odor on a number of occasions and was probably produced by electrical equipment in the room.

The fact that the atmospheric attack causes the rubber to gather into fibers and nodules is suggestive of surface tension forces acting to minimize surface area by the formation of columns and spheres. Evidently, the oxidative attack, "liquifies", the rubber by chain scission thus allowing it to relax by viscous flow.

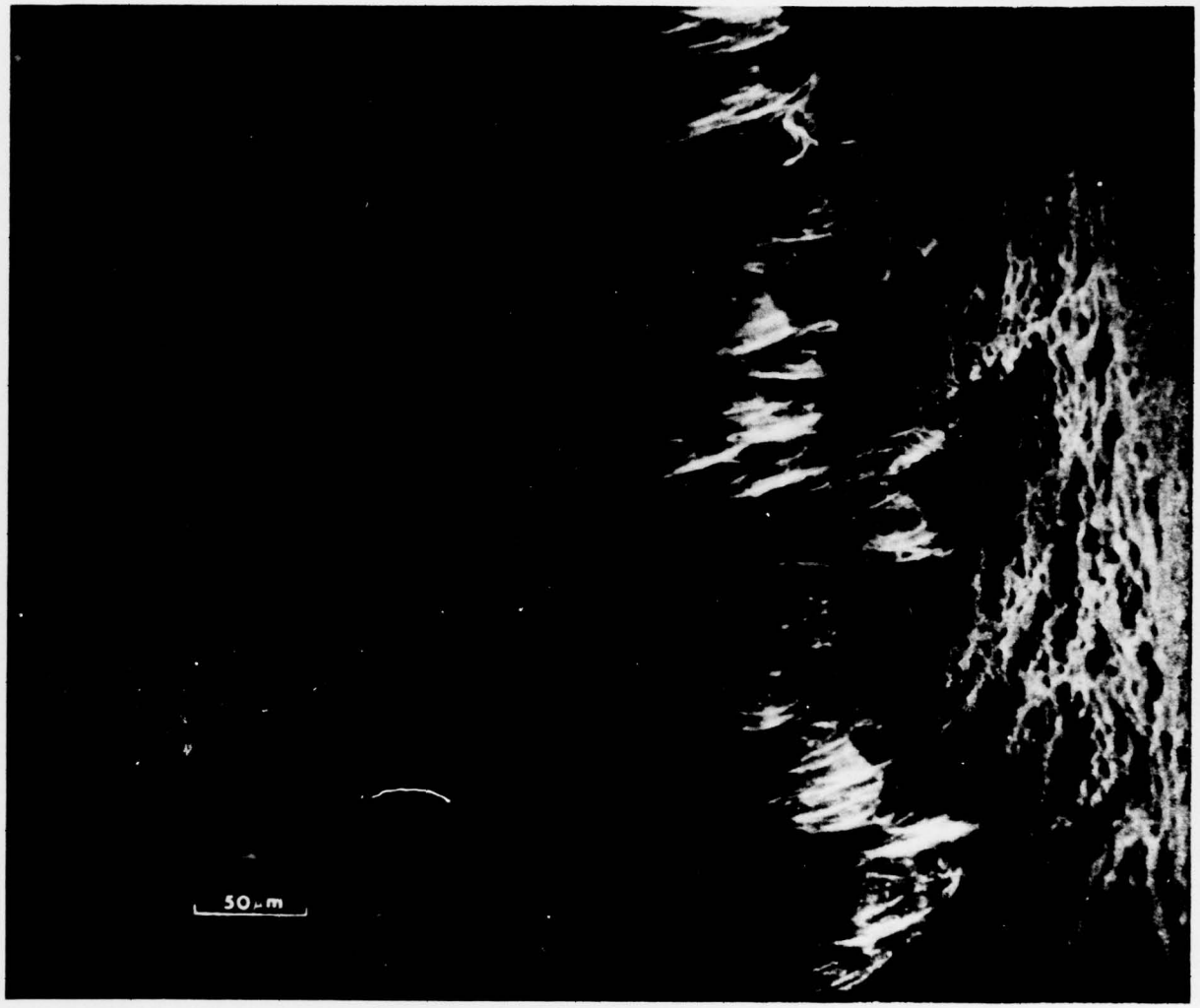

Fig. 7 — SEM photograph of a tear tip in natural rubber < 0.5 hr after cutting.
The light strip represents yielding after Au coating.

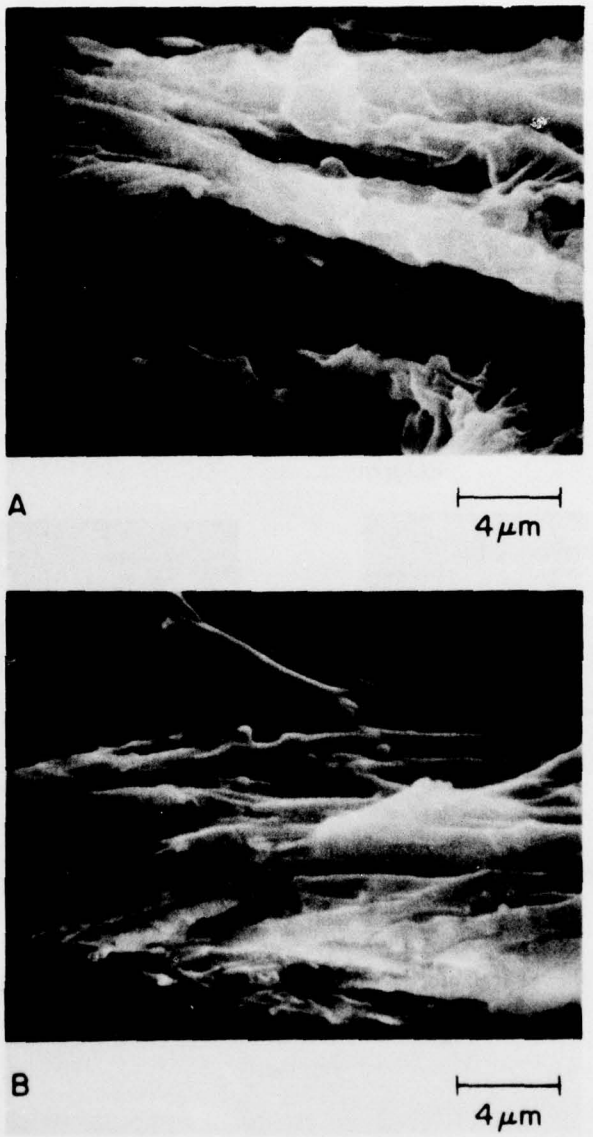

Fig. 8 — High magnification views of the tear tip in natural rubber 0.5 hr after cutting

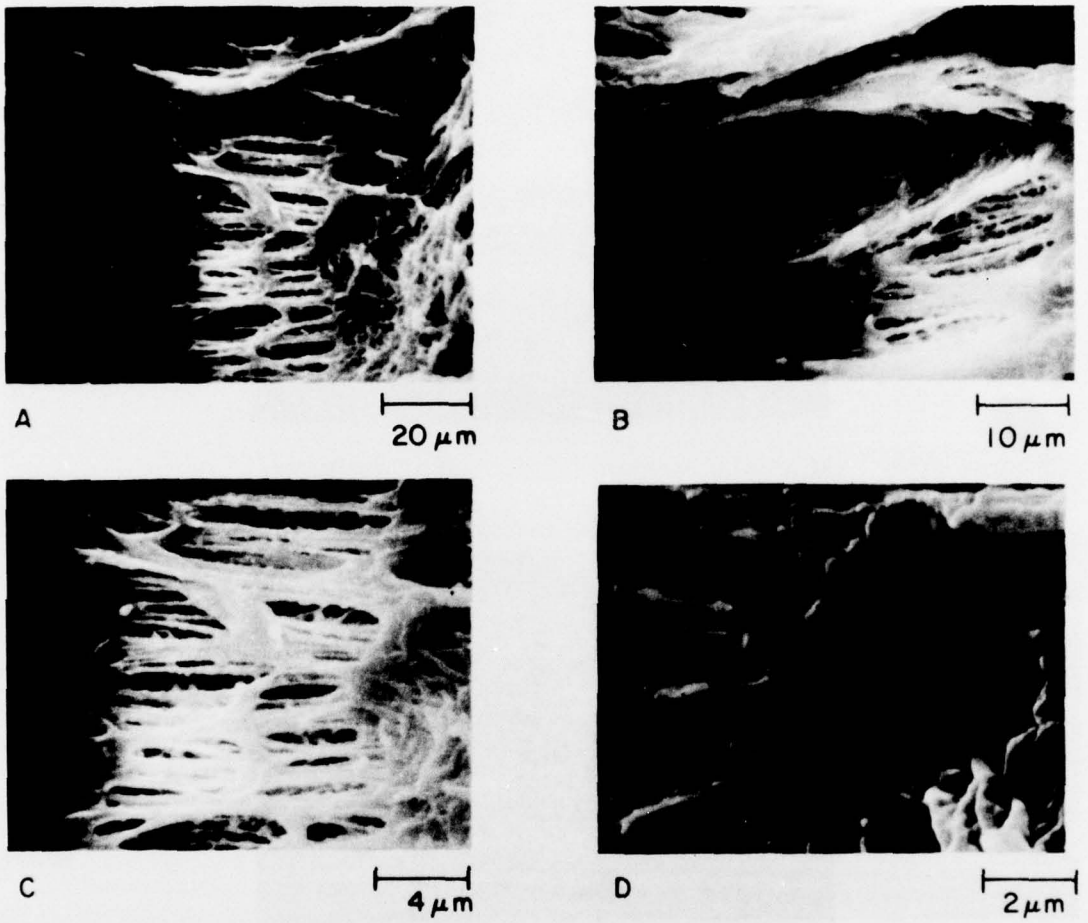

Fig. 9 — SEM photographs of the specimen of Figs. 7 and 8 after 5 hrs exposure to laboratory air

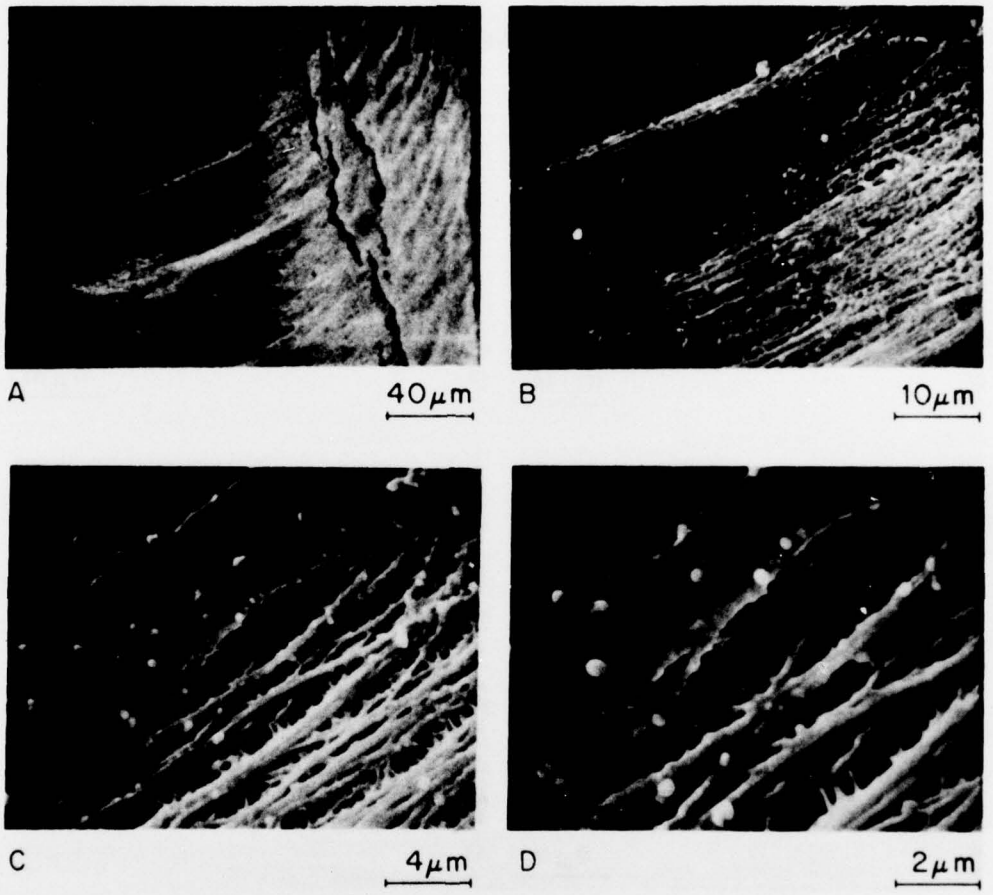

Fig. 10 — SEM photographs of a tear tip in natural rubber after 24 hrs exposure to laboratory air

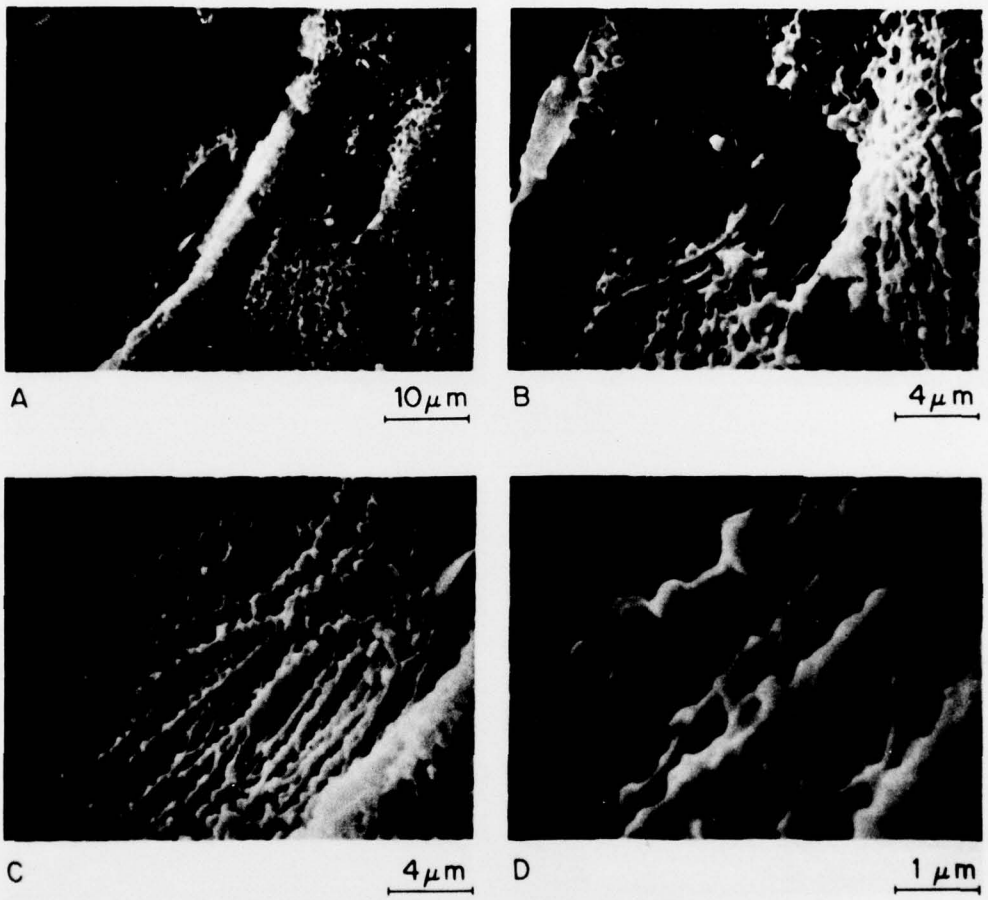

Fig. 11 — SEM photographs of a tear tip in natural rubber after 24 hrs exposure to laboratory air

The photographs in Figure 12 for a natural rubber tear aged for 24 hrs. look very much like the rupture of a soap film caught by high speed photography.

This microscopy technique was used to study surface cracks in sulfuric acid treated, "cyclized", nitrile rubber. Photographs from the study are shown in Figure 13. The acid treatment produces a thin (40 μm) brittle layer on the rubber surface which cracks when bent. The brittle layer can be seen in the photographs of Figure 12 and beneath it the fibrous, nodular structure formed by oxidative attack. The flower-like features on the cracked wall of the brittle layer gave strong XES signals for Zn and S and are believed to form by the escape of a zinc sulfate solution trapped in the brittle layer during the sulfuric acid treatment.

Cyclization of rubber surfaces is done as a pretreatment for adhesive bonding the rubber to rigid (usually metal) surfaces. It is possible that the open, fibrous structure within the surface cracks aids bond strength by allowing deep penetration and thus mechanical locking of the adhesive into the rubber adherend.

A specimen of Viton rubber was examined and the tear tip appearance is shown in Figure 14. Note that the material is failing by a process of viscous flow and cavitation, unlike the nitrile, polybutadiene and natural rubbers tested in this study which appear to yield by stretching, followed by semi-brittle rupture. However, in the presence of oxygen and ozone the failure process of these other rubbers give the appearance of cavitation when examined a few hours after cutting (see for example, Figures 9 and 12).

There is clearly a particulate filler in the Viton rubber of Figure 14. Analysis of the particles using XES gave only silicon (elements with atomic numbers less than 10 could not be detected with this spectrometer) suggesting that the filler is silica.

Examination of a Viton specimen held 24 hrs. after cutting and before gold coating, had an appearance identical to that of Figure 14. Evidently, there had not been any oxidative attack and this is consistent with the high oxidation resistance of the fluorocarbon elastomer from which Viton is formulated.

A sample of Neoprene, cut from a laboratory stopper, also showed the presence of a filler (Figure 15) but unlike the Viton rubber the filler was not well bonded to the Neoprene matrix. Examination of these particles using XES gave no evidence of elements of atomic number greater than 10 which suggests the filler is an organic material rather than a mineral. Note in Figure 14 that the sockets around the filler particle are essentially smooth with little evidence of having conformed to the particle shape.

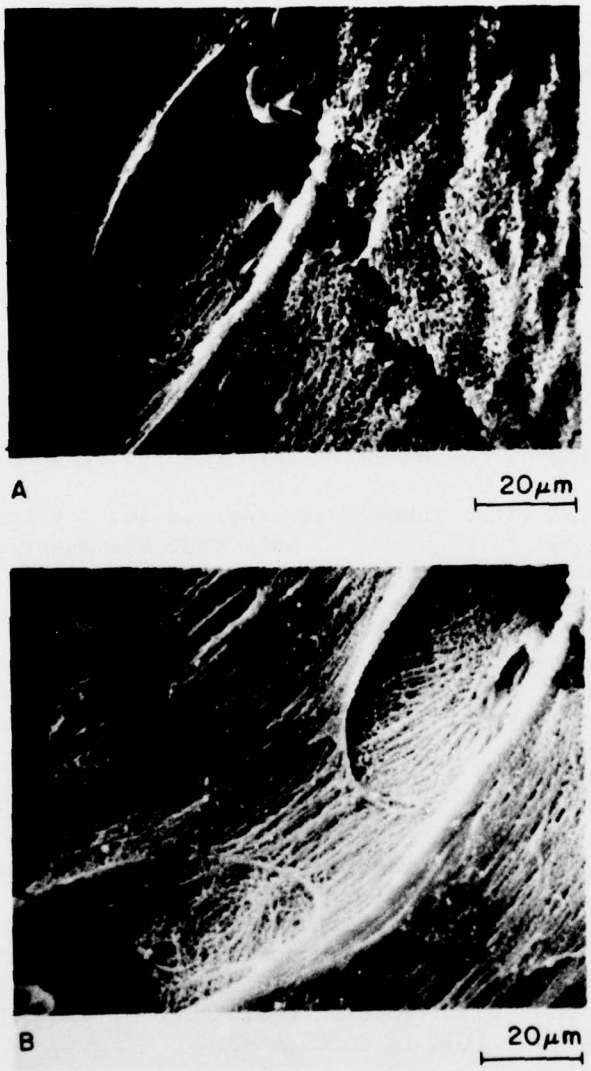

Fig. 12 — SEM photographs of a tear tip in natural rubber after 24 hrs exposure to laboratory air

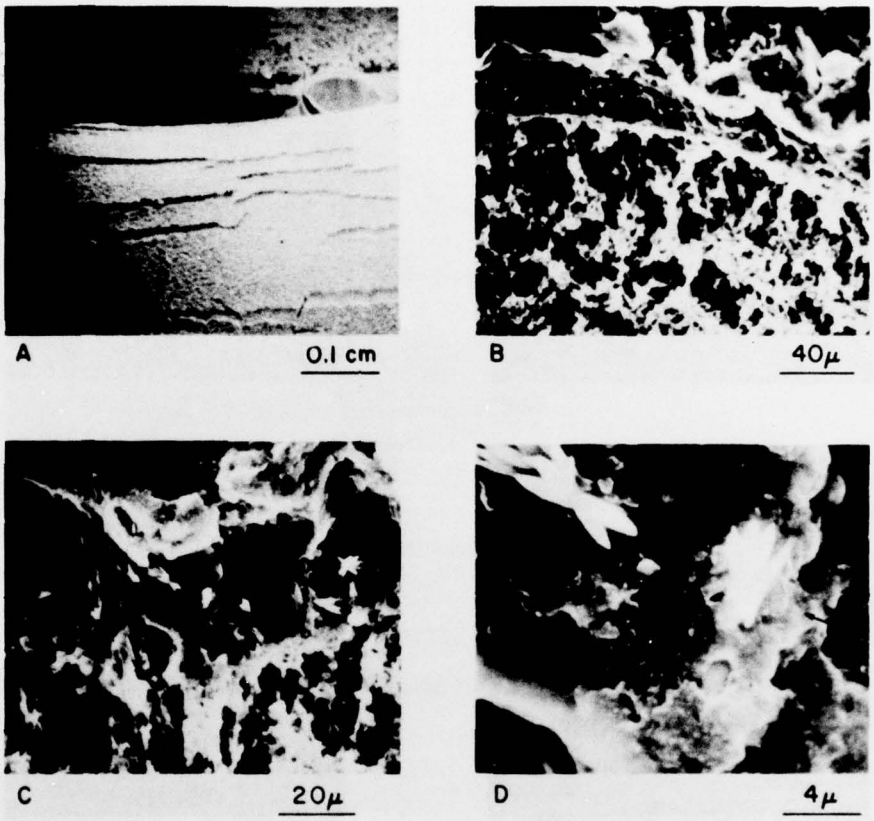

Fig. 13 — SEM photographs of nitrile rubber after cyclization treatment with sulfuric acid. Note in A the microcracks in the brittle surface layer. Fibrous and nodular structure can be seen beneath the surface layer (B and C). The flower-like features in C are believed to be $ZnSO_4 \times H_2O$.

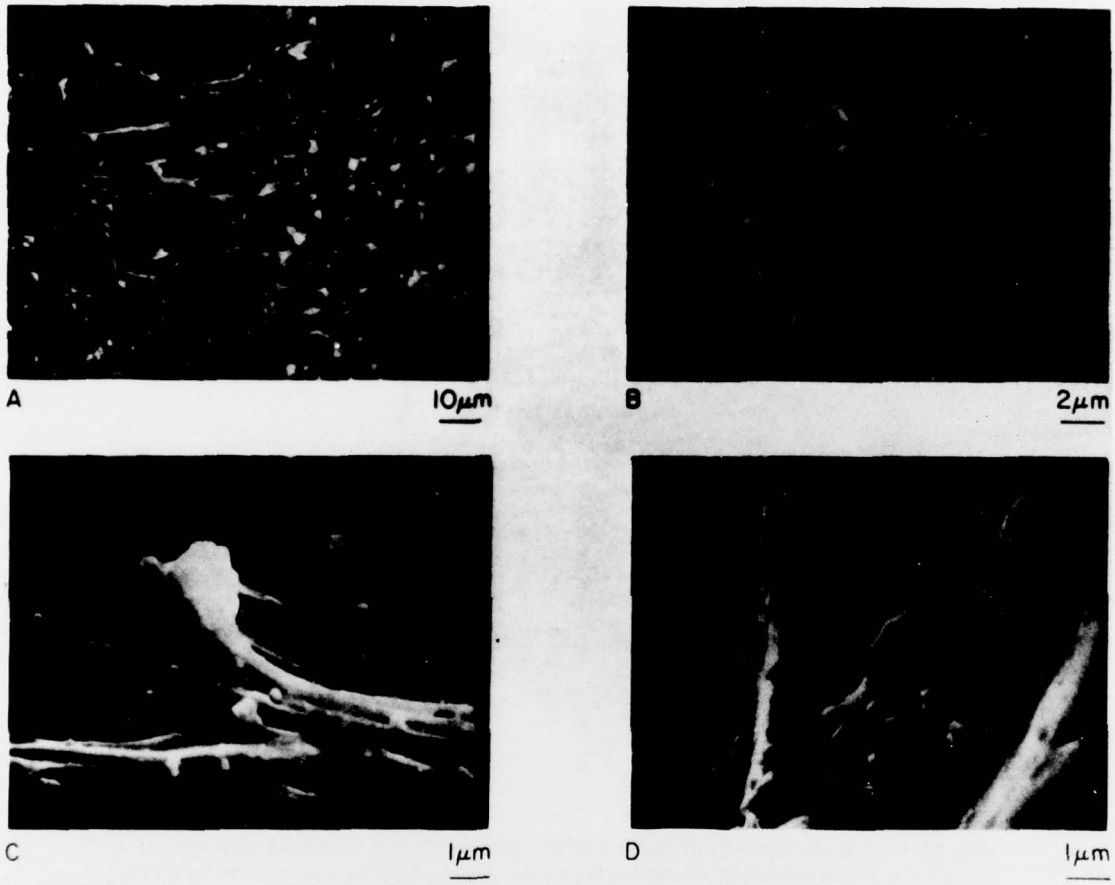

Fig. 14 — SEM photographs of a tear tip in Viton rubber < 0.5 hr after cutting

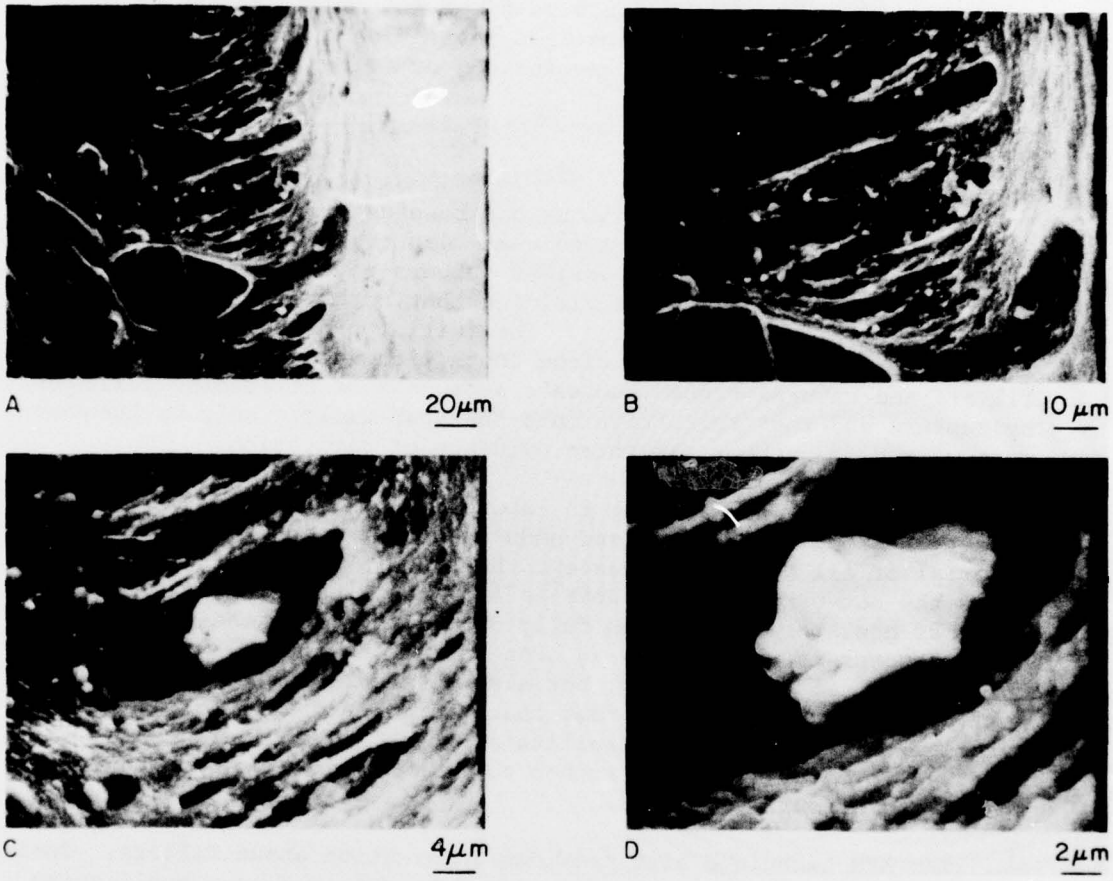

Fig. 15 — SEM photographs of a tear tip in Neoprene rubber 24 hrs after cutting

Apparently, there had not been initimate contact between the filler and matrix presumably because of poor wetting.

The specimen of Figure 14 had been aged for 24 hrs. after cutting. There is some evidence of fiber and nodule formation of the tear tip material and associated cavitation. Some of the cavities appear to have been "nucleated" by filler particles (Figure 14C and 14D).

CONCLUSIONS

A relatively simple technique has been described which allows observation of the deformation zone at tear tips in rubber specimens. Investigation of various rubbers revealed qualitative information about the type of yielding that occurs in the deformation zone under different conditions. The initial appearance of the tear tip in nitrile, polybutadiene (both with and without carbon filler) and natural rubber suggests a process of stretching followed by rupture and then relaxation onto the tear walls. Only in the case of a Viton rubber was there evidence of cavitation.

On the other hand, aging in laboratory air had the dramatic effect of producing fibrous and nodular networks in the tear tip material of all the rubbers except the Viton. In the first few hours the network structure developed as cavities (Figure 14) but after 24 hrs. the network was fully developed across the tear. The aging process is very likely an ozone attack not only on the rubber under stress at the tear tip, but also on the rubber on the tear wall. It is quite possible that there were residual stresses in the material on the wall which facilitate attack. Chain scission appeared to be allowing the rubber to relax by viscous flow under the action of surface forces.

The SEM technique also provides information about fillers. Their elemental composition can be determined by XES, and some qualitative information can be gained about their adhesion to the matrix and their effect on tear tip yielding.

ACKNOWLEDGEMENTS

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