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Scanning electron microscopy studies on tensile, tear and abrasion failure of plasticized poly (vinyl chloride) and copolyester thermoplastic elastomers

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Scanning electron microscopic observations on the tensile, tear and abrasion failure of plasticized poly (vinyl chloride) (PVC) and copolyester (Hytrel 40D) thermoplastic elastomers showed that the patterns developed on the fracture surfaces could be correlated with the strength and type of failure of these materials. Hytrel was found to undergo ductile failure whereas PVC showed shear fracture under tensile stress. The higher tear and abrasion resistances of Hytrel than those of PVC were also manifested by the difference in fracture patterns on the failure surfaces of these samples.

1. Introduction

Thermoplastic elastomers are materials which have properties of vulcanized rubbers but can be processed like thermoplastics. Such materials can be blends comprising rubber–plastic combinations or block copolymers consisting of hard thermoplastic segments and soft rubbery segments or those polymers which have a specified stereoregular structure and controlled extent of crystallinity. The thermoplastic rubbery character of PVC, according to Lundberg [1], is due to the presence of the amorphous PVC chains as continuous phase and the semicrystalline chains as hard block. In the case of Hytrel, which exhibits a two phase domain structure, the crystalline phase serves as thermally reversible chemical crosslinks while the amorphous phase contributes to the elastomeric character [2]. The commercial importance of thermoplastic elastomers is due to their superior processing characteristics over conventional rubbers. The processing characteristics, physical properties, applications and economic advantages of thermoplastic elastomers have been reviewed by several authors [3–8]. Since thermoplastic elastomers are used for a variety of applicaitons, a thorough understanding of their failure mode is vital to predict the service life of the products. Until recently the failure characteristics of thermoplastic elastomers have not been studied extensively. Recently De and co-workers [9–14] have used scanning electron microscopic studies in exploring the failure mechanism of natural rubber and different synthetic rubbers including thermoplastic elastomers. In this paper we report our observations on the mode of fracture of Hytrel 40D and PVC under tensile, tear and abrasion failure.

2. Experimental details

2.1. Preparation of test samples

The details of the materials used in the present study are shown in Table I. The pellet form of the thermoplastic material is melted in the Brabender Plasticorder PLE 330 (Brabender OHG, West Germany) for 7 min using a cam-type mixer with a rotor speed of 80 rpm and chamber temperature set at 180° C. This is then sheeted out in a 15 cm × 30 cm two roll laboratory open mill at 2.5 mm nip setting. The sheeted-out stock was compression moulded at 200° C for 3 min in specially designed moulds so that the mould with the sample inside could be cooled immediately after moulding, keeping the sample still under compression. Samples for tensile and tear tests were punched out along the mill grain direction from the moulded sheets of 15 cm × 15 cm × 0.2 cm size. The test pieces of 2 cm × 2 cm × 1 cm size were directly moulded for abrasion testing.

TABLE I Details of the thermoplastic elastomers used

Code name	Chemical name	Description
PVC(ST-60)	Plasticized poly (vinyl chloride)	Poly (vinyl chloride) containing 60 phr of dioctyl phthalate by weight and small amounts of lubricants and stabilizers. The *K* value of the polymer is in the range of 65–70. The material is manufactured by Nocil, India.
Hytrel 40D	Thermoplastic copolyester	Random block copolymer of tetramethylene terephthalate (4GT units) hard segments and polyalkylene ether terephthalate (PTMEG/T) soft segments. Hytrel 40D is manufactured by E. I. du Pont de Nemours Company, USA.

0022–2461/86 $03.00 + .12

2.2. Physical testing of the samples

Tensile testing of the samples was done at 25° C following the ASTM D412-80 test method using dumbbell shaped test pieces at a crosshead speed of 500 mm min^{-1} using an Instron Universal Testing Machine (model 1195). Tear strength of the samples was determined according to the ASTM D624-81 test method using unnotched 90° test pieces. The tear test was carried out at the same conditions of temperature and crosshead speed as in the case of tensile testing. The abrasion resistance of the sample was tested in a Du Pont abrader using silicon carbide abrasive paper of grain size 320. The speed of rotation of the abrasive disc was 40 rpm and normal load was 3.26 kg. For each material, samples were abraded for 10 and 20 min after an initial abrasion period of 5 min. The abrasion loss of the samples was calculated and expressed as volume loss, in cm^3 h^{-1}. The hardness of the samples was measured and expressed in Shore A units (according to ASTM 2240-80). The tensile set of the samples at 100% elongation and that after failure were also determined according to ASTM D412-80.

2.3. Scanning electron microscopic (SEM) studies

The failed test specimens were stored in a desiccator to avoid contamination from dust particles. Fracture surfaces were sputter coated with gold within 24 h of testing. SEM observations were made using a Philips 500 model scanning electron microscope and the photomicrographs were taken along the direction of fracture propagation adjusting the tilt to zero degree in all cases. Fig. 1 shows the details of the test specimen, failure surface and scan area of the tensile, tear and abrasion test samples.

3. Results and discussion

3.1. Mechanical properties

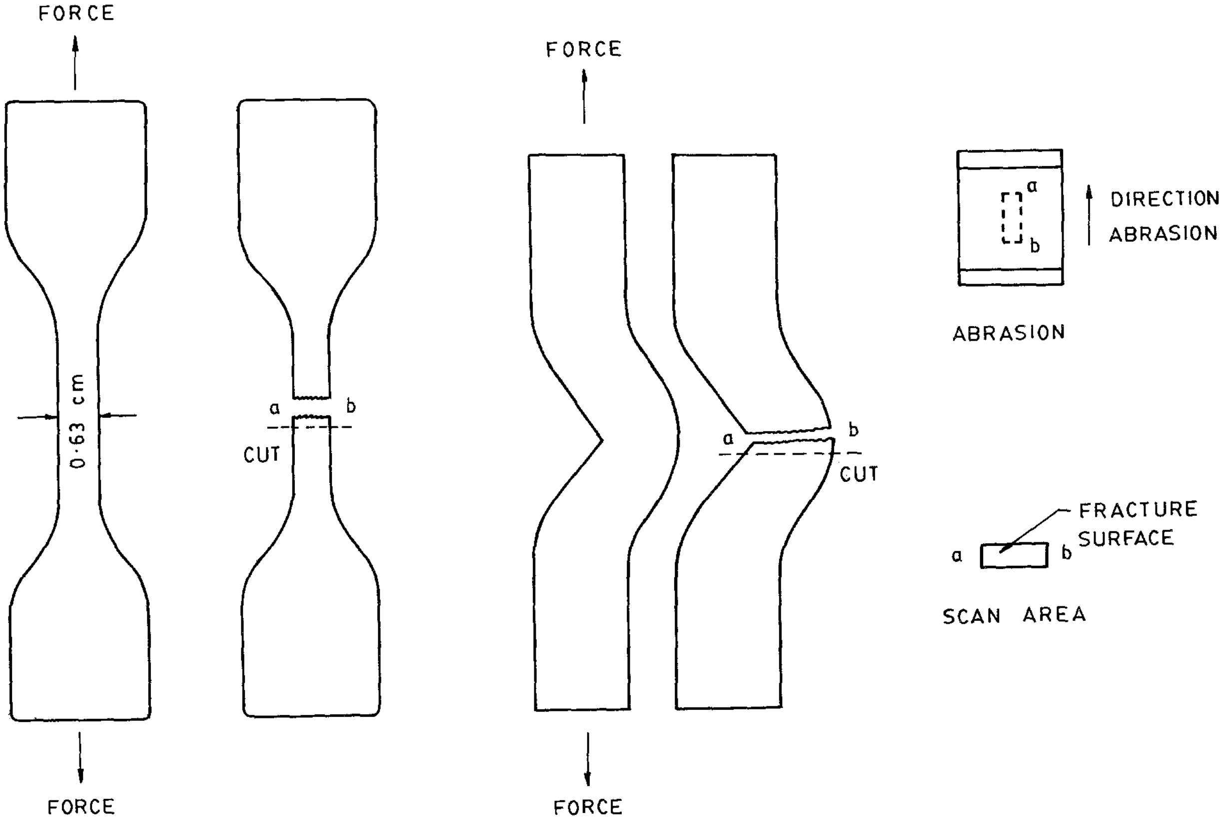
The mechanical properties of the materials are given in Table II. Hytrel exhibits higher tensile strength, tear strength, elongation, tensile set and abrasion resistance compared to that of plasticized PVC. As will be seen later, the comparative data on physical properties correlate with the fracture mechanism of the samples.

The differences in deformation characteristics of both thermoplastic elastomers are clearly evident from their stress–strain curves (Fig. 2). The stress–strain curve of Hytrel shows very high initial modulus with a broad yield point at lower strains, which is a characteristic feature of plastics. The gradual increase in stress at higher strains is attributed to the orientation of the crystalline hard segments in the direction of applied stress. This portion of the curve is similar to that of elastomers which undergo strain induced crystallization during stretching. The stress–strain curve of PVC is similar to that of vulcanized rubbers. In this case, the stress increases steadily with strain without yield until it fails.

3.2. Fractographs

3.2.1. Tensile failure

The tensile fracture surfaces of the materials are shown in Figs. 3 and 4. The fractographs clearly indicate that the materials have different deformation characteristics under an applied load. The fracture surface of Hytrel which has a higher tensile strength



TENSILE TEAR

Figure 1 Samples for tensile, tear and abrasion tests showing fracture surface and scan area.

TABLE II Mechanical properties of the thermoplastic elastomers

Material	hardness (Shore A)	Modulus at 100% elongation (MPa)	Elongation at break (%)	Tensile strength (MPa)	Tear strength (kN m^{-1})	Abrasion loss (cm^3 h^{-1})	Tensile set at 100% elongation (%)	Tensile set after break (%)
PVC	63	5.10	450	12.40	43.38	0.300	15	70
Hytrel 40D	92	7.30	950	18.00	102.77	0.182	25	360

than PVC shows ductile-type failure with high plastic deformation as evidenced by the presence of long continuous fibrils on the fracture surface (Fig. 3). It has been reported that fibril formation is a characteristic feature of ductile failure with high plastic deformation [15]. Moreover, these fibrils indicate the extreme stretching of the material before failure. The nature of the stress–strain curve as well as the tensile set values support the above observations.

The tensile fracture surface of PVC sample (Fig. 4) reveals that the failure is mainly due to shear fracture. Plasticized PVC consists of continuous blocks of amorphous and semicrystalline chains. Under the application of tensile stress, shear deformation takes place between the two segments and the fracture proceeds by a shearing action. This is evident from the discontinuous fracture paths in different layers observed on its failed surface. Similar observations were reported in the case of styrene–butadiene–styrene thermoplastic elastomers, SBS [14].

3.2.2. *Tear failure*

The tear resistance of elastomers is mainly dependent on the processes by which stress dissipiation near the tip of the growing crack takes place. Several processes such as slippage or breakage of crosslinks or chain entanglements or arresting of the growing crack by filler particles take place during the tear failure of elastomers [10]. The process of stress dissipiation can be explored by careful examination of the tear fracture surfaces. The fracture surface of Hytrel shows closely packed well defined vertical striations (Fig. 5) with a large number of fracture paths which contain frequent sinusoidal foldings (Fig. 6). The above observations clearly indicate the high energy expended during the propagation of tear. Similar observations have been reported in the case of thermoplastic 1, 2-polybutadiene [14].

The fracture surface of PVC (Fig. 7) shows continuous branched tear lines with less frequent sinusoidal foldings. The vertical striations, as observed in the

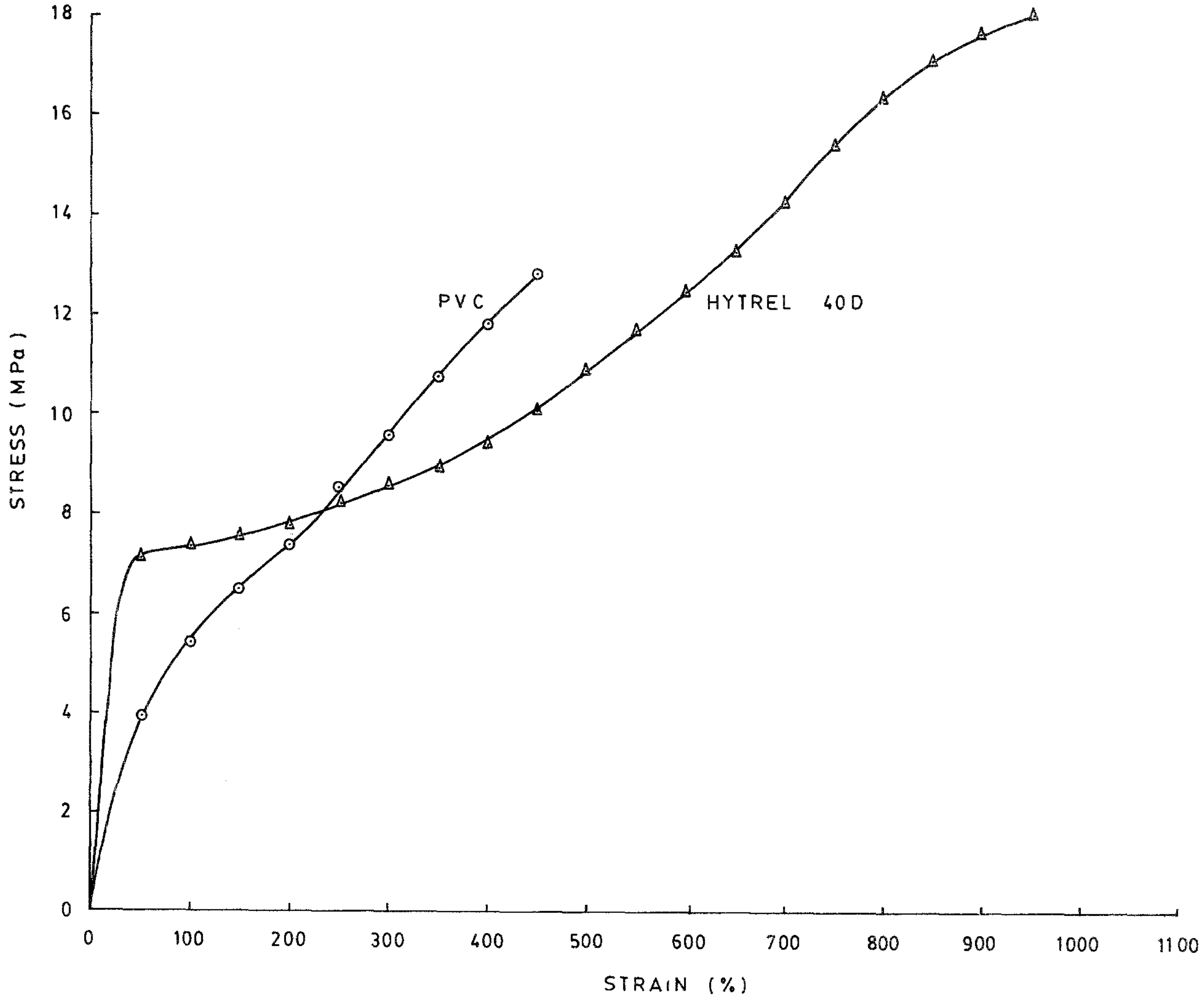


Figure 2 Stress–strain curves of the thermoplastic elastomers.

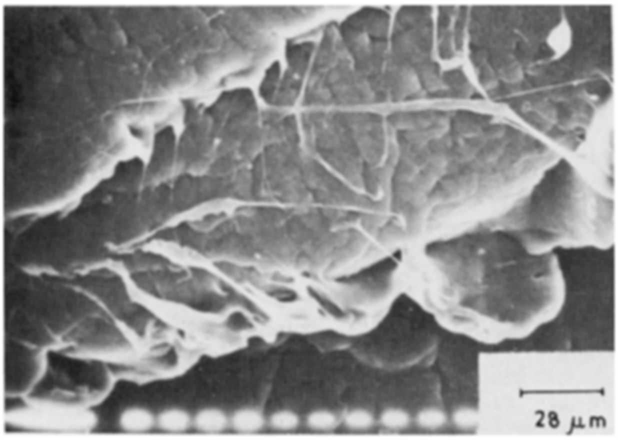


Figure 3 Tensile fracture surface of Hytrel, showing ductile type failure and long continuous fibrils.

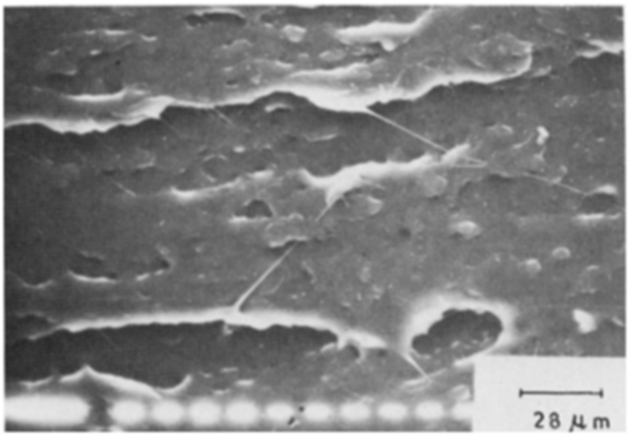


Figure 4 Discontinuous fracture path in different layers in the tensile fracture of PVC.

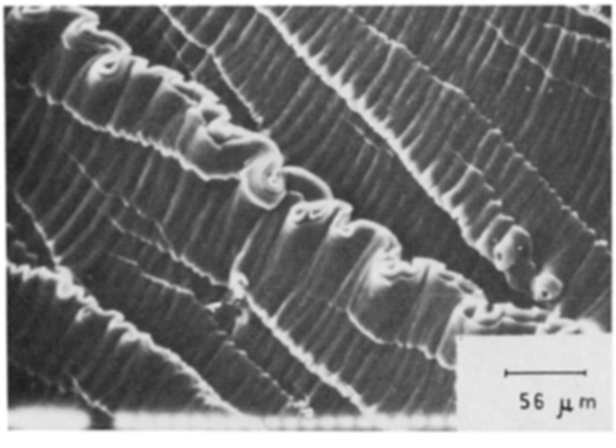


Figure 5 Closely packed well defined vertical striations on the tear failure surface of Hytrel.

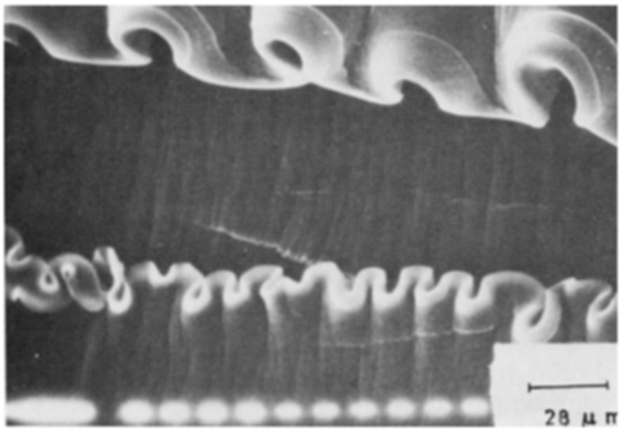


Figure 6 Enlarged picture of the sinusoidal foldings and vertical striations on the tear failure surface of Hytrel.

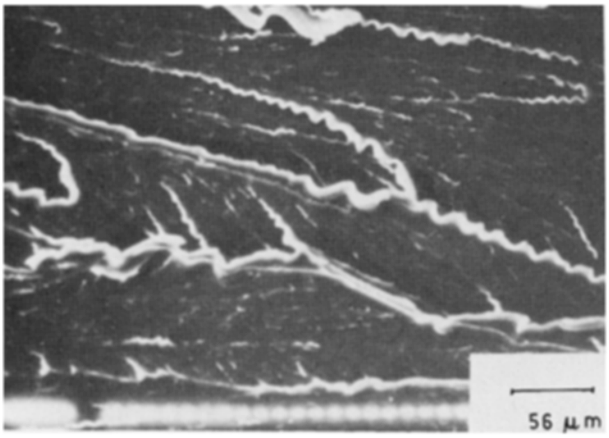


Figure 7 Continuous branched tear lines with foldings on the tear failure surface of PVC.

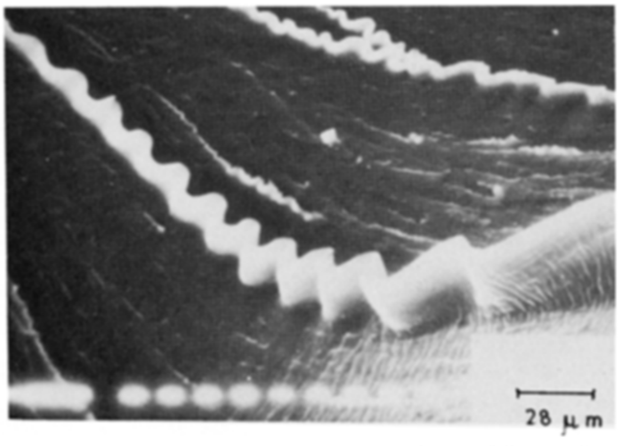


Figure 8 Enlarged picture of the foldings on the tear failure surface of PVC.

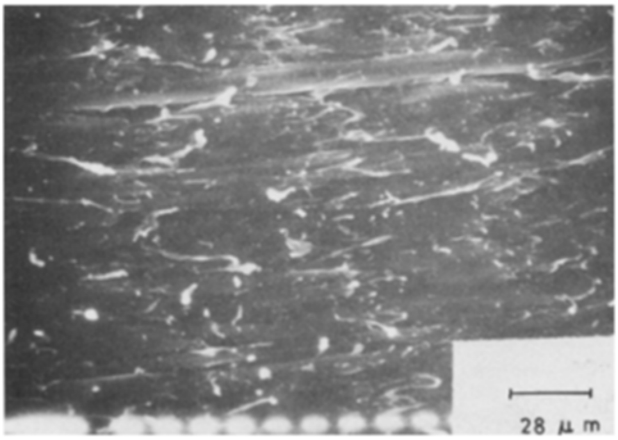


Figure 9 Primary ridges on the abraded surface of Hytrel after an abrasion period of 10 min.

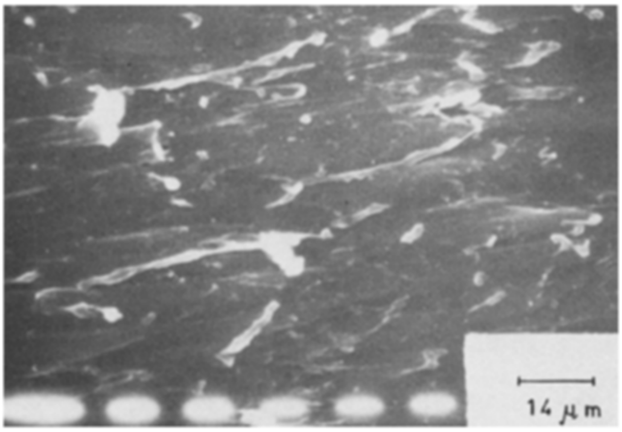


Figure 10 Enlarged picture of the primary ridges showing abraded particles connected by elongated fibrils on the abraded surface of Hytrel.

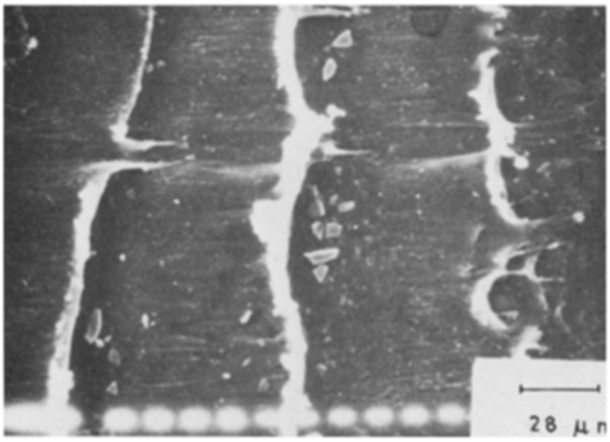


Figure 11 Fully developed secondary ridges on the abraded surface of Hytrel.

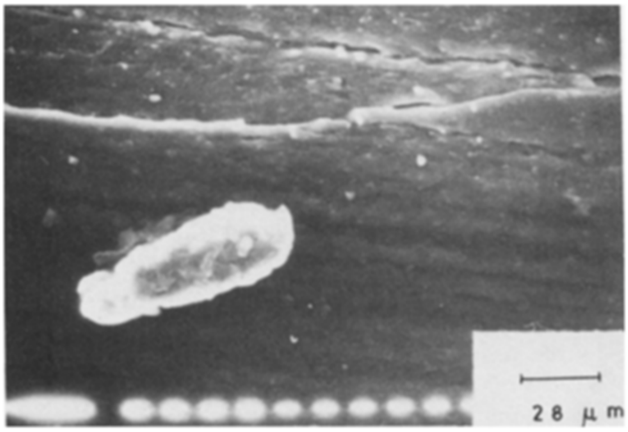


Figure 12 Abraded surface of PVC after a period of 10 min abrasion showing development of parallel grooves.

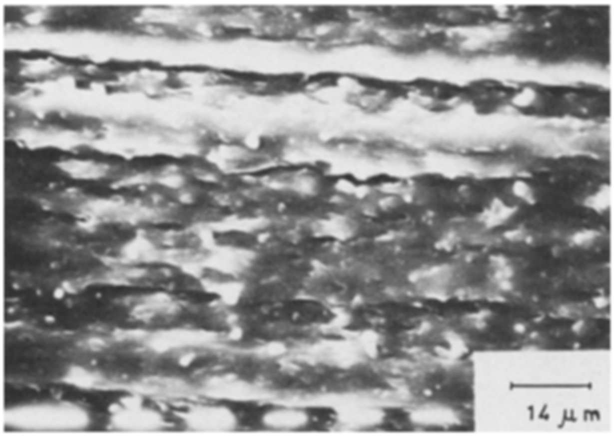


Figure 13 Enlarged picture of parallel grooves on the surface of PVC after an abrasion period of 10 min.

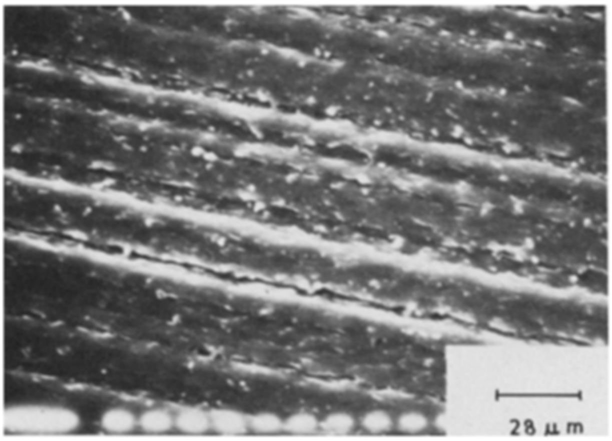


Figure 14 Fully developed shallow parallel grooves on the PVC surface after an abrasion period of 20 min.

case of Hytrel, are completely absent in the case of PVC (Fig. 8). The tear strength of PVC, as manifested from physical measurements, is also lower than that of Hytrel.

3.2.3. Abrasion failure

Abrasion of elastomers is a complex phenomenon. In general, it involves a combination of processes which may be mechanical, mechano-chemical and thermochemical [16]. Hence the abrasion resistance of elastomers is dependent on factors such as strength of the matrix, resistance to thermo-oxidative ageing, resistance to crack growth etc. It has been reported that the nature of abrasion pattern is indicative of the mechanism of abrasion [11]. In order to understand the development of abrasion patterns with time of abrasion, samples were abraded for 10 and 20 min. The surface of Hytrel after an abrasion period of 10 min (unsteady state wear) shows the presence of small abraded particles connected by elongated fibrils (Fig. 9). Moreoever, careful examination of the surface reveals the development of microridges spreading over the whole worn surface (Figs. 9 and 10). It has been reported that the process of ridge formation consists of two stages [17]. At first many microridges are formed in tight uneven rows which are termed primary ridges. The surface after an abrasion period of 20 min (steady state wear) shows uniformly distributed fully developed ridges held by elongated fibrils perpendicular to the direction of abrasion (Fig. 11). These fully developed macroridges in the steady state wear are termed secondary ridges. The formation of ridges by microtearing and subsequent removal of material from the surface depend on the tensile strength, tear and cut growth resistance of the matrix [18]. Thus the inherent strength properties of Hytrel account for its high resistance to abrasion.

The surface of PVC after an abrasion period of 10 min shows the development of parallel grooves (Figs. 12 and 13). Fully developed shallow parallel grooves are observed after an abrasion period of 20 min (Fig. 14). The formation of shallow parallel grooves on the PVC surface is attributed to its relatively low matrix strength and soft surface (Table II) compared to that of Hytrel. The physical measurements of abrasion resistance also support the above views.

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