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Scanning electron microscopy studies on tensile, tear and abrasion failure of thermoplastic elastomers

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The tensile strength, tear resistance and abrasion resistance of four different types of commercial thermoplastic elastomers have been studied and their fracture surfaces examined by scanning electron microscopy. Thermoplastic polyurethane (TPU) showed elastic deformation under tensile fracture, whereas in 1,2 polybutadiene (1,2 PB) the fracture was initiated by craze formation and propagated by tear failure. Styrene–isoprene–styrene block copolymer (K1107) showed ductile type failure whereas in styrene–butadiene–styrene block copolymer containing a higher proportion of styrene and silica filler (K5152), the fracture occurred by shearing action. The tear failure surfaces of the thermoplastic elastomers showed different fracture patterns which could be correlated with the tear strength of the materials. The tear fracture surface of 1,2 PB showed stick–slip tear lines and that of TPU had a broad tear path with vertical striations. The fracture surfaces of K5152 and K1107 had the characteristics of laminar tearing and uninterrupted continuous tearing processes, respectively. The abrasion resistance of the samples was in the order TPU > 1,2 PB > K5152, which was manifested through the type of ridge patterns formed on the abraded surfaces. Abraded surfaces of TPU, 1,2 PB and K5152 showed closely spaced stable ridges, widely spaced ridges bridged by elongated fibrils and highly deformed ridges, respectively.

1. Introduction

Thermoplastic elastomers (TPEs) are a relatively new class of materials which combine the processing advantages of thermoplastics and the physical properties of vulcanized rubbers. These materials may be block copolymers consisting of a hard thermoplastic segment and a soft rubbery segment or blends of a crystalline polyolefin and an elastomer or may be those polymers which have specific stereoregular structure and controlled extent of crystalllinity. Elastomers which contain thermolabile crosslinks are also classified as thermoplastic elastomers. The processing characteristics, physical properties, applications and economic advantages of TPEs have been reviewed by several authors [1–9]. The major fields of application of these materials are in mechanical moulded goods and footwear, wherein factors such as flexing, tear and wear are the main criteria leading to failure of the product. The mechanism of failure of TPEs has received little attention so far. The failure of rubber vulcanizates and that of rubber-based composites have been studied by scanning electron microscopic (SEM) examination of the failure surfaces [10–15]. SEM has also been found to be a valuable tool in studying the mechanism of toughening of plastics and epoxy resins by elastomer particles [16–18]. Recently, SEM has been used in explaining the effect of basic components of the blends on the physical properties of dynamically crosslinked thermoplastic elastomer blends [19–23]. In this paper we report the results of our SEM observations on the nature of tensile, tear and abrasion failure of some

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TABLE I Details of the thermoplastic elastomers used

Code name	Chemical name	Description
1,2 PB	1,2 Polybutadiene	Thermoplastic 1,2 polybutadiene elastomer having 1,2 content greater than 90% and degree of crystallinity 25%. JSR RB 820, manufactured by Japanese Synthetic Rubber Company
K5152	Styrene–butadiene–styrene block copolymer	S–B–S block copolymer having styrene/butadiene ratio 48/52 and containing about 10% by weight amorphous silica. KRATON K5152, manufactured by Shell Chemical Company, USA
K1107	Styrene–isoprene–styrene block copolymer	S–I–S block copolymer having styrene/isoprene ratio 14/86. KRATON D-1107, manufactured by Shell Chemical Company, USA
TPU	Thermoplastic polyurethane	Ester type thermoplastic Polyurethane. Estane 5715 elastomer, manufactured by B. F. Goodrich Company

commercially available thermoplastic elastomers, namely, polyurethane, 1,2 polybutadiene, styrene–butadiene–styrene and styrene–isoprene–styrene block copolymers.

2. Experimental procedure

2.1. Preparation of the test samples

The details of the TPEs used in the present study are given in Table I. The pellet or flake form of the TPE was melted in a Brabender Plasti-corder model PLE 330, for about 4 min, using a cam-type mixer with a rotor speed of 80 rpm and chamber temperature set at 180° C. The molten material was sheeted out through a laboratory mill at 2.5 mm nip setting. The sheeted out stock was compression moulded at 180° 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 x 15 cm x 0.2 cm size and test pieces of dimensions 2 cm square, 1 cm thick were directly moulded for the abrasion test.

2.2. Physical testing of the samples

Tensile testing of the samples was done at 25° C as in ASTM D412-80 test method using dumb-bell shaped test pieces, at a crosshead speed of 500 mm min^{-1} using an Instron Universal Testing Machine (model 1195). The tear strength of the samples was determined as in ASTM D624-81 test method using unnicked 90° angle test pieces. The tear test was carried out at the same conditions of temperature and crosshead speed as described for the tensile test. The abrasion resistance of the samples 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 the normal load was 3.26 kg. The samples were abraded for 10 min after an initial conditioning period of 5 min. The abrasion loss of the samples was calculated and expressed as volume loss in $\text{cm}^3\,\text{h}^{-1}$. The hardness values decreased with time after firm contact between the indentor and the sample, especially for TPU and 1,2 PB. Hence the hardness values were measured after 1 and 5 sec of firm contact, according to ASTM D 2240-81 test method.

2.3. Scanning electron microscopic observation.

The SEM observations of the failure surfaces were made using a Philips 500 model scanning electron microscope. The failure surface of the test samples were carefully cut out from one of the test pieces without touching the surfaces and then sputter coated with gold within 24 h of testing. The specimens were stored in a desiccator before and after gold coating until the SEM observations were made, in order to avoid contamination. The tilt was kept at 0° in all cases. Fig. 1 shows the details of test specimen, failure surface and scan area of the tensile, tear and abrasion test samples.

3. Results and discussion

3.1. Technical properties

Table II gives the technical properties of the TPEs. Since the materials evaluated are manufactured for

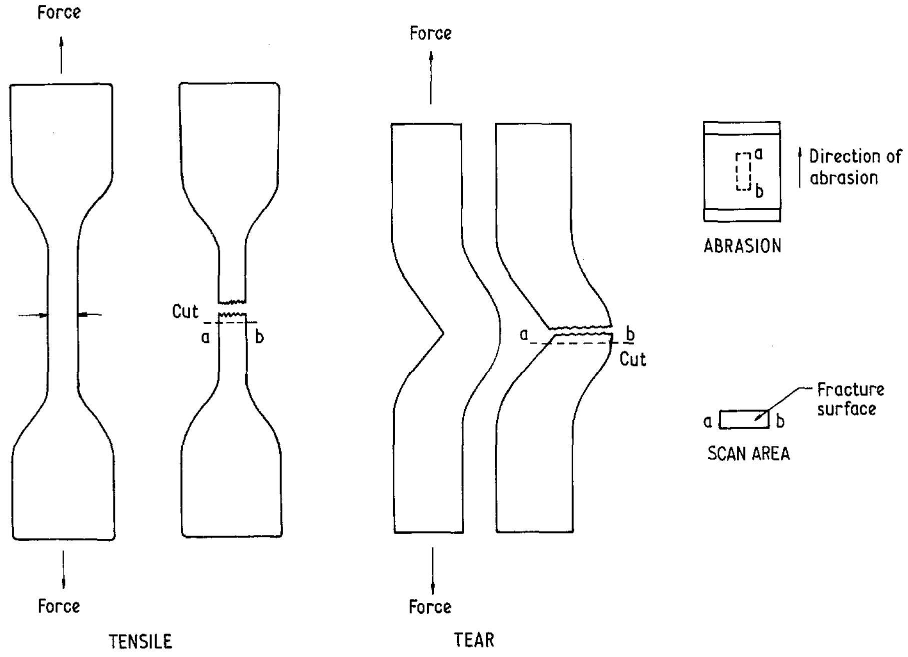

Figure 1 Samples for tensile, tear and abrasion tests, fracture surface and scan area.

specific end uses, direct comparison of the technical properties may not be relevant. But these materials represent each class of thermoplastic elastomer and show certain distinct properties. Thus, TPU is characterized by its high resistance to abrasion, whereas 1,2 PB shows higher tear strength and K1107 provides highest elongation. The abrasion resistance of K1107 could not be tested as the samples chipped out during a 1 min run of the test, probably due to its very poor resistance to cutting and tearing action. The comparative data on physical properties are used for explaining the mechanism of different types of failure of these samples.

The stress–strain curves (Fig. 2) clearly show that the deformation nature of the four TPEs under an applied load in tension, is quite different from one another. At low strains (< 300%), TPU shows a stress–strain curve similar to that of vulcanized elastomers whereas, at higher strains, there is a sharp increase in stress, probably due to the orientation of the hard segments in the direction of the applied stress. This behaviour is typical of ester type thermoplastic polyurethanes [24, 25]. 1,2 PB shows a stress–strain relation that is intermediate between that of plastic and rubber [26]. At lower strains (< 100%), there is a tendency to show yielding, but this is not so prominent as in the case of thermoplastics. At higher elongations, the stress gradually increases with strain and this portion of the curve is similar to that of elastomers. The stress–strain behaviour of K5152 is almost similar to that of gum vulcanizates of noncrystallizable rubbers. K1107 shows very low modulus values at low strains and behaves like elastomers containing a very low extent of crosslinking. But at higher strains (> 800%), there is a sharp increase in modulus

TABLE II Physical properties of the thermoplastic elastomers

Rubber	Hardness (Shore A)		Modulus 300%	Elongation at break	Tensile strength	Tear strength	Abrasion loss
	1s	5s	(MPa)	(%)	(MPa)	(kN m^{-1})	(cm^3 h^{-1})
TPU	86	75	6.0	400	16.1	37.9	0.120
1,2 PB	92	90	6.0	745	9.1	59.1	1.188
K5152	45	45	2.8	520	4.2	17.4	4.786
K1107	35	35	0.34	1450	11.1	10.1	*

*Could not be tested as the sample chipped out after 1 min.

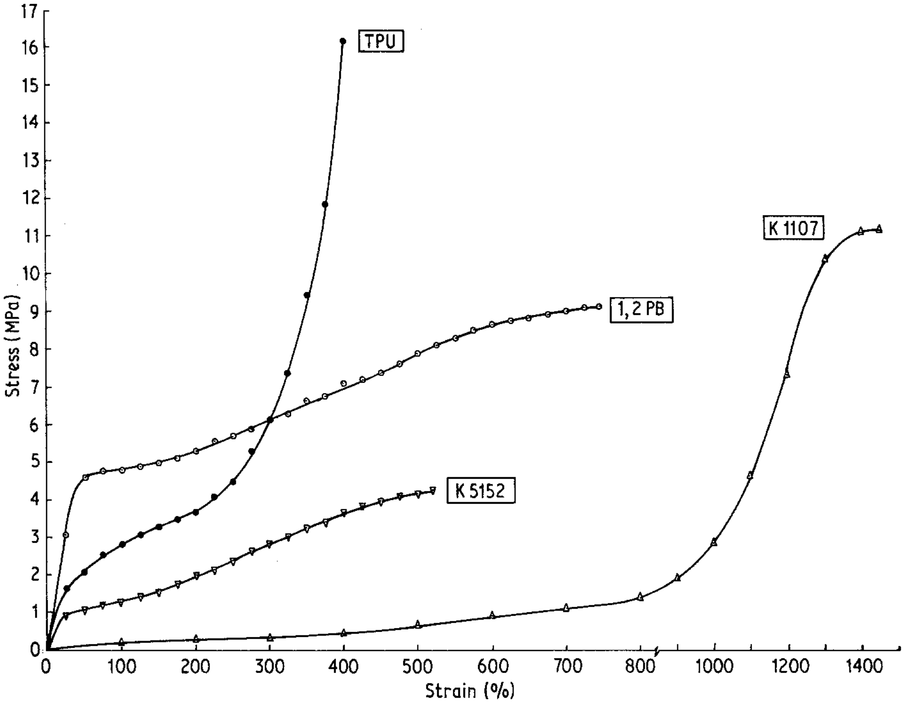

Figure 2 Stress–strain curves of TPEs.

which may be due to the combined effect of orientation of the hard polystyrene segments and strain-induced crystallization of the polyisoprene segments of the block copolymer [27]. Towards the breaking point, the sample yielded and then broke with no definite neck formation.

3.2. Fractographs

3.2.1. Tensile failure

The tensile fracture surfaces of the different types of TPEs shown in Figs. 3 to 9 reveal that these materials vary in their deformation characteristics under an applied load. The tensile fracture surface (Fig. 3) of TPU, which has the highest tensile strength among the four TPEs studied, shows elastic type deformation of the sample under tensile stress, evidence for which is a broad continuous fracture path and less residual deformation, indicated by the absence of peaks or fibrils on the surface. The foldings on the surface adjacent to the fracture path indicate the high extent of elastic deformation undergone by the matrix before failure. The nature of the stress–strain curve of the sample also supports the above views.

The tensile stress in homogenous materials may be relieved by the formation of crazes which have

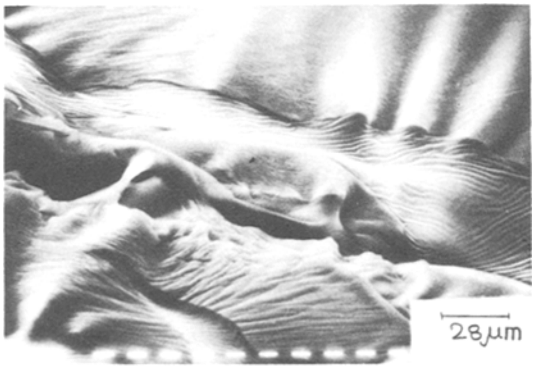

Figure 3 Tensile fracture surface of TPU, broad fracture path.

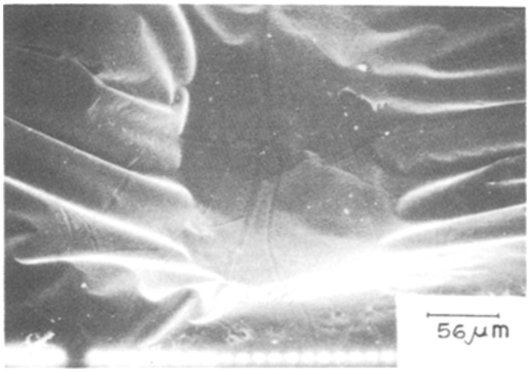

Figure 4 Opened-up craze in tensile failure of 1,2 PB.

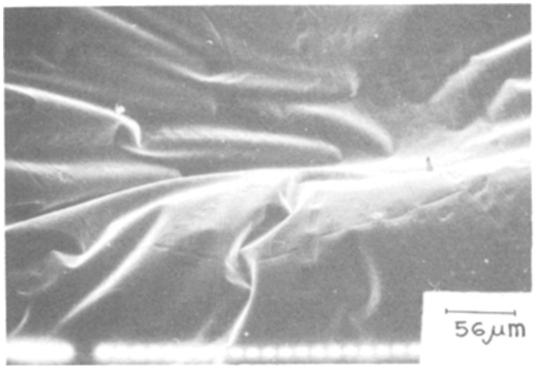

Figure 5 V-shaped foldings in the tear zone of the opened-up craze in tensile failure of 1,2 PB.

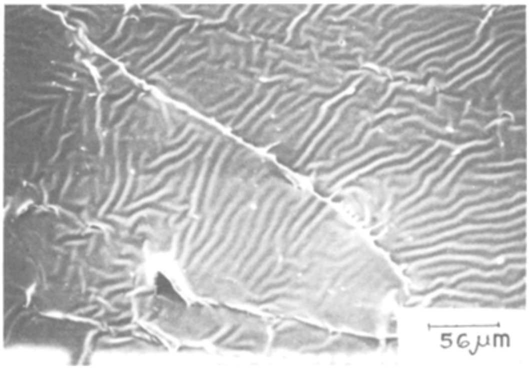

Figure 7 Smooth fracture path with foldings in tensile failure of K1107.

semicircular or circular boundaries. The crazes opened up during tensile failure are characterized by a central normal stress zone with curved boundaries and an adjacnet tear zone [28]. The tensile fracture surface of 1,2 PB shows these features. Fig. 4 shows the central stress zone with circular boundaries. The V-shaped foldings adjacent to the central zone (Fig. 5) indicate the tear zone which further propagated the crack. A network of channels is also observed inside the central stress zone (Fig. 6). Thus in 1,2 PB the fracture is initiated by craze formation and propagated by tear fracture. Craze formation before failure is characteristic of rubber modified thermoplastics [29]. The fractographs and the stress–strain curve indicate that the deformation behaviour of 1,2 PB under an applied load in tension is in between that of rubber and thermoplastics. The fracture surface of K1107 shows a smooth fracture path with peaks due to pulling up of the material before failure (Fig. 7). The foldings, lips and fibrils on the surface (Fig. 8) show a high extent of deformation of the matrix and indicate the ductile nature of the failure. The stress–strain curve of this sample also shows the ductile nature of failure as indicated by yielding with no definite neck formation (Fig. 2). Sample K5152 contains approximately equal proportions of polystyrene and polybutadiene segments in the block copolymer and the polystyrene segments remain as laminar domains in the matrix. It also contains plasticizers and a small quantity of filler. Under the application of tensile stress, shear deformation between the two segments takes place and the fracture proceeds by shearing action. This is clearly indicated by the tensile fractograph of K5152 (Fig. 9) which shows discontinuous fracture paths in different planes.

3.2.2. Tear failure

The resistance to tearing of the elastomers depends on the process by which stress dissipation near the tip of the growing crack takes place. This may be accomplished by several processes

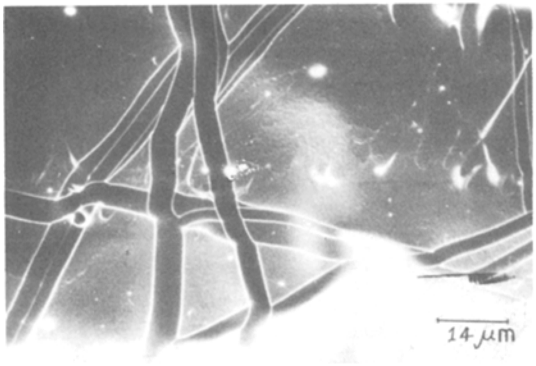

Figure 6 Network of channels inside the central stress zone in tensile failure of 1,2 PB.

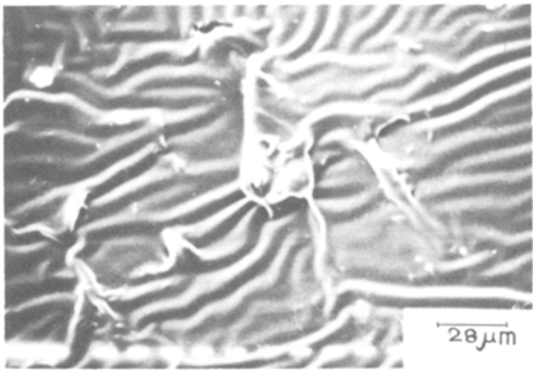

Figure 8 Foldings, lips and fibrils on the tensile failure surface of K1107.

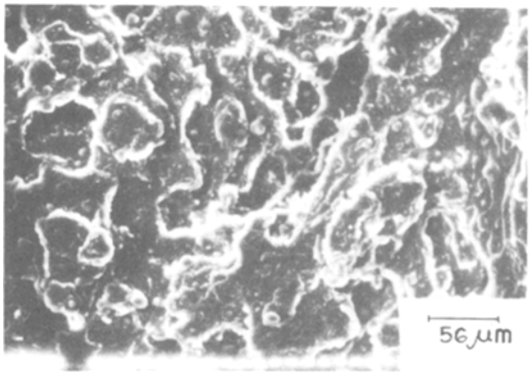

Figure 9 Discontinuous fracture paths in different planes on the tensile failure surface of K5152.

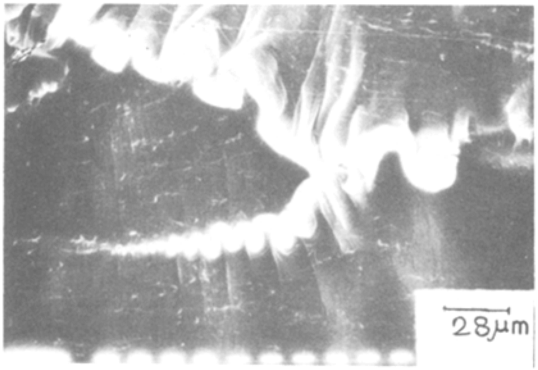

Figure 11 Pulled-up wavy crests on the tear failure surface of 1,2 PB.

such as slippage or breakage of crosslinks or chain entanglements, deviating or arresting of the growing crack by filler particles, etc. [12]. The process of stress dissipation may be understood by careful examination of the tear fracture surfaces. Fig. 10 shows that the tear fracture in 1,2 PB has proceeded through a stick–slip process due to the presence of crystalline regions in the matrix. The presence of a branched tear path, vertical striations on the surface and the stick–slip tear path indicate the high energy expended for the propagation of the tear. The peaks appearing as pulled up wavy crests (Fig. 11) show the high extent of stretching that has taken place before failure. Thus, the high tear strength of 1,2 PB (Table II) compared with that of the other TPEs is due to the higher extent of stress dissipation through the various processes described above. The tear fracture surface of TPU shows a broad tear path and vertical striations (Fig. 12). The tear strength of TPU is less than that of 1,2 PB but greater than that of K5152. The fracture surface of K5152 (Fig. 13) does not contain any continuous tear path, which indicates laminar tearing between the hard and soft segments. Small rounded tear lines seen on the fracture surface may be due to the deflection of the tear path by the silica particles present in the sample. This sample shows a higher tear strength than K1107. K1107 contains about 14% by weight of hard segment which remains as spherical domains in the bulk of the soft segment. The tear fractograph of this sample (Fig. 14) shows a smooth surface and a continuous tear path with irregular foldings. The tear strength of K1107 is poor, which is in line with the continuous tear path observed on the fracture surface. Similar observations have been reported in the tear failure of resin-cured carboxylated nitrile rubber [30].

3.2.3. Abrasion failure

Abrasion resistance of elastomers depends mainly on factors such as strength of the matrix,

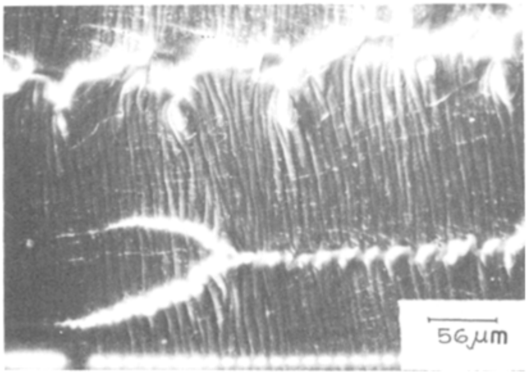

Figure 10 Stick–slip fracture path, branched tear line and vertical striations on the tear failure surface of 1,2 PB.

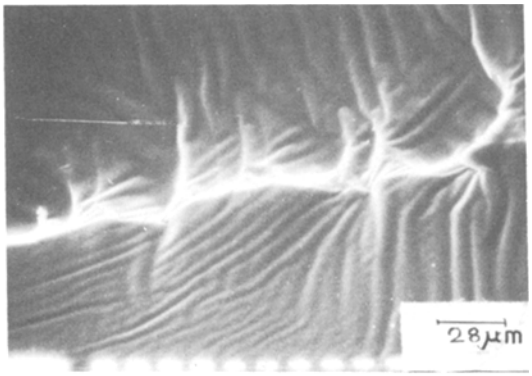

Figure 12 Broad continuous tear line with vertical striations on the tear failure surface of TPU.

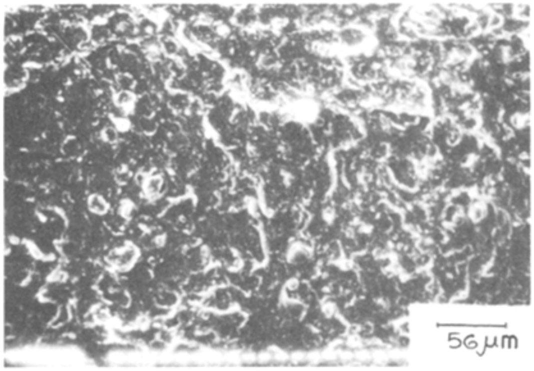

Figure 13 Small number of short rounded tear lines on the tear failure surface of K5152.

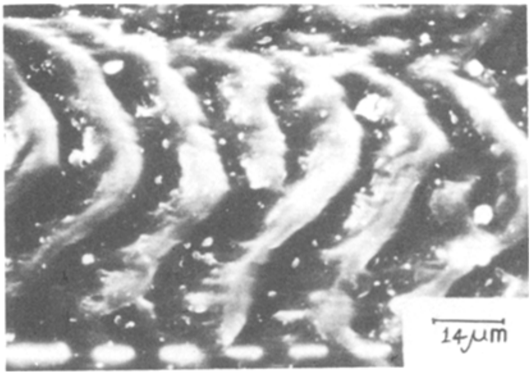

Figure 16 Enlarged picture of the vertical ridges showing abraded particles and stable nature of the ridges of TPU.

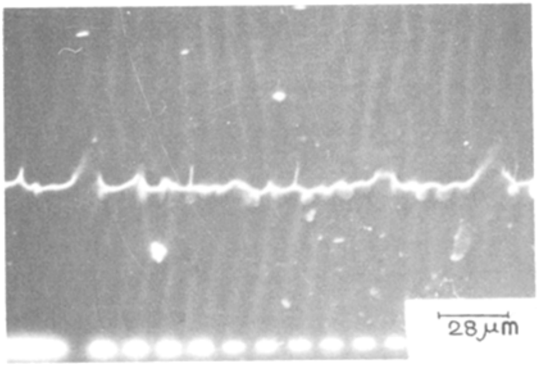

Figure 14 Continuous tear line with irregular foldings on the tear failure surface of K1107.

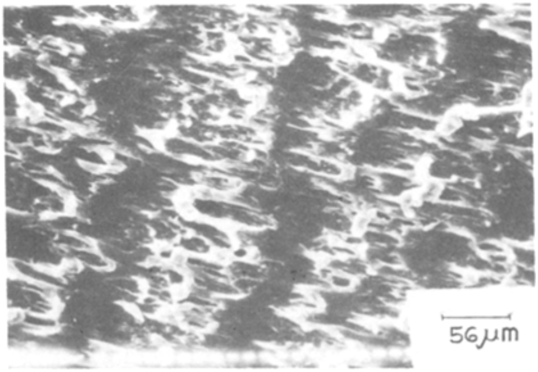

Figure 17 Widely spaced ridges on the abraded surface of 1,2 PB.

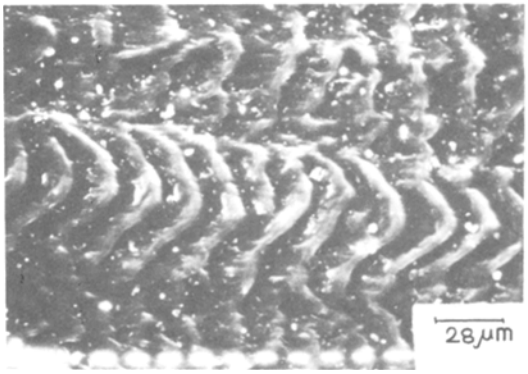

Figure 15 Closely spaced vertical ridges on the abraded surface of TPU.

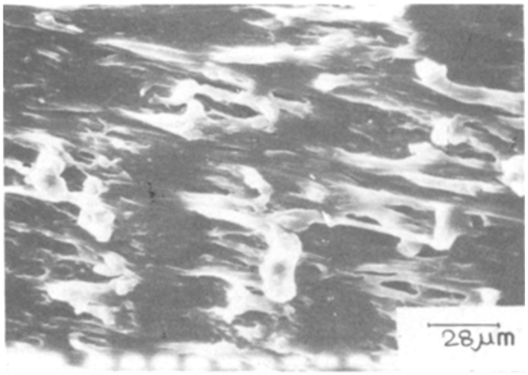

Figure 18 Bridging of the ridges by elongated fibrils on the abraded surface of 1,2 PB.

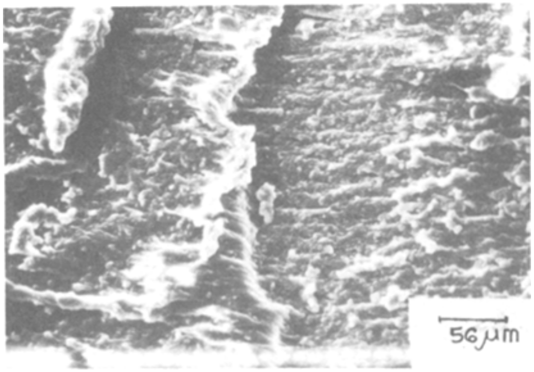

Figure 19 Highly deformed ridges and roll form of the material removed on the abraded surface of K5152.

resistance to thermo-oxidative degradation, crack growth resistance under dynamic conditions etc, apart from other factors such as frictional force and the nature of the abrasive. The nature of definite patterns appearing on the abraded surface has been shown to be indicative of the mechanism of abrasion of elastomers [11, 15]. The abraded surface of TPU shows a well-defined ridge pattern at right angles to the direction of abrasion (Fig. 15). The absence of any lumpy mass and the presence of small particles on the surface indicate that these ridges are highly resistant to deformation (Fig. 16). Low ridge height and close spacing of the ridges are indications of high resistance to abrasion [31]. The formation of the ridges by microtearing and subsequent removal of the material from the surface depend on the tensile strength, tear and cut growth resistance of the matrix [32]. Thus the inherent strength properties of TPU account for its high resistance to abrasion. The abraded surface of 1,2 PB also shows ridge patterns (Fig. 17). But in this case, the ridges are less closely spaced and the channels between the ridges are bridged by elongated fibrils (Fig. 18). 1,2 PB which has a high tear strength and elongation at break (Table II) undergoes high deformation and the torn surfaces are stretched to high elongation before the material is removed from the surface. This sample shows a lower abrasion resistance than TPU but higher than that of K5152. The abraded surface of K5152 shows highly deformed ridges (Fig. 19). The material removal in roll form can also be seen on the surface. This sample is less resistant to the frictional forces of abrasion, due to its very low tensile strength and tear resistance, which account for its lower resistance to abrasion [33].

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