Wear, 158 (1992) 193–211

Friction and wear of PTFE – a review

S. K. Biswas
Department of Mechanical Engineering, Indian Institute of Science, Bangalore (India)
Kalyani Vijayan
Materials Science Division, National Aeronautical Laboratory, Bangalore (India)

Abstract

Polytetrafluoroethylene (PTFE) is an important engineering material. When rubbed or slid against a hard surface, PTFE exhibits a low coefficient of friction but a high rate of wear. These unique properties of the polymer have encouraged many mechanistic and physical examinations of the processes involved in the friction and wear of this polymer. A section of such work carried out over the past 30 years is reviewed here. When rubbed against a hard surface, the PTFE chain undergoes scission, creating active groups which chemically react with the counterface. This results in strong adhesion and a coherent transfer film. Further interaction between the bulk polymer and the transfer film gives rise to anisotropic deformation of the unit cell, which results in closeness of adjacent chains and easy shear between chains. Sliding brings about growth in as well as reorientation of crystallites situated in a very thin subsurface region of the bulk polymer. Such structural rearrangement facilitates the joining of adjacent aligned crystallites to form films and ribbons which emerge as debris.

1. Introduction

Polytetrafluoroethylene (PTFE) is a useful bearing material since it registers a low coefficient of friction when rubbed against metallic engineering surfaces. This coefficient of friction is an order lower than that recorded for other engineering polymers such as high density polyethylene (HDPE), low density polyethylene (LDPE), nylon and polyetheretherketone (PEEK). The wear resistance of PTFE is, however, rather low, which somewhat impairs its usefulness as an engineering material.

Early attention to the complex tribology of PTFE was drawn by Professor David Tabor and his coworkers at the Cavendish Laboratory in the early 1960s. They rubbed PTFE against glass plates and observed that in the steady state the rubbing interaction is confined to the transfer film and a very thin slice of the pin surface. They also noted that this interaction is highly sensitive to sliding speed and inferred that the participation of the amorphous phase in the shear process activates a viscoelastic response which dominates the speed effect.

It is interesting to note that this model remained substantially valid even 20 years after it was proposed and after scores of subsequent research investigations. The latter tended to tackle a number of important questions which arose from the early observations. Some of these questions have been answered and recent work tends to use this model to design new PTFE-based composites for essentially enhancing wear resistance without

sacrificing the low friction performance. The questions which arose out of the early investigations are as follows.

(1) In the rubbing interaction, does the active interface lie at the metal–polymer junction or at the plane where the transfer film meets the PTFE sample surface? This question implies a further question related to the status of the transfer film, *i.e.* is it regenerative or, once formed, does the first film remain adherent and strongly bonded to the metal surface?

(2) If the latter is true, then what is the nature of this chemical bond, since PTFE is generally accepted as a chemically passive material owing to the protection provided by the large fluorine atoms to the inner carbon core?

(3) How does the crystalline structure of PTFE participate in the tribological process? More specifically, how do the crystallites situated close to the surface align themselves to form an oriented, deformed film which shears from the undeformed bulk in the form of oriented fibres or flakes? Is this process thermally activated? Does this imply a structural transition?

Of the large volume of research work which emerged more or less in response to these questions, the work of Professor Kyuchiro Tanaka and his coworkers at Kanazawa University must surely rank as some of the most definitive. Tanaka made microscopic and spectroscopic studies of the transfer film and put forward a realistic model of wear. Of the other workers who have made a significant contribution to this field in this period, Briscoe, Bahadur and Arkcles and their coworkers feature most prominently. Briscoe and coworkers studied the viscoplastic response of PTFE by incorporating structural changes in the material without disturbing its stoichiometry. Perhaps one of the most significant contributions made recently in the field of PTFE–metal adhesion is by the group at Lanzhou Institute of Chemical Physics of the Chinese Academy of Sciences. This field of study, initiated earlier by Donald Buckley of NASA, has been advanced by the Chinese workers to establish the nature of the chemical bonding between the PTFE and the metal surface.

The present review attempts to provide a summary of our knowledge in the field of the tribology of PTFE in the light of the published literature. The review stresses the physical and chemical aspects of the tribological process. The significant body of knowledge gathered in the recent period about lubricated sliding of PTFE and the tribological performance of PTFE composites is not included except where it has some specific bearing on the main theme of this paper.

2. The structure of PTFE

The various mechanisms proposed for the wear behaviour of PTFE are closely associated with its structural characteristics. It is therefore appropriate to include some salient aspects of PTFE's structural characteristics in this section.

PTFE, $(-CF_2-CF_2-)_n$, is known [1–3] to undergo thermally activated structural transformations at 19, 30 and 150 °C. Table 1 lists the structural data relevant to various phases of PTFE. It is well known [1] that the hydrocarbon analogue of PTFE, *i.e.* polyethylene, $(-CH_2-CH_2-)_n$, has a planar, zigzag molecular conformation. PTFE, in contrast, assumes a helical conformation up to about 150 °C. With the fluorine atoms running helically on the surface, the PTFE chain resembles a rigid, cylindrical rod with a smooth surface. As will be described subsequently in this paper, the low friction coefficient and the high wear of PTFE are closely associated with the smooth profile of the rigid-rod-like PTFE molecule.

TABLE 1

Structural details of the thermally activated phases of PTFE

Temperature (°C)	Phase	Molecular conformation	Crystal system and space group	Unit cell constants[a]	Reference
<19	II	13_6 helix	Triclinic, pseudohexagonal	$a=b=5.54$ $c=16.8$ $\gamma=119.5$	[1]
		13_6 helix	Triclinic, pseudohexagonal	$a=b=5.59$ $c=16.88$ $\gamma=119.3$	[2]
		13_6 helix	Triclinic	$a=4.882$ $b=4.875$ $c=5.105$ $\alpha=90$ $\beta=86$–87 $\gamma=86$–87	[30]
		13_6 helix	Monoclinic $P2_1$	$a=5.59$ $b=9.76$ $c=16.88$ $\beta=90$	[31]
		13_6 helix	Monoclinic $P2_1$	–	[32]
		54/25	Monoclinic	$a=9.60$ $b=5.62$ $\gamma'=91.4$	[33]
>19, <30	IV	15_7 helix	Hexagonal $a=b=5.61$ $c=19.50$	[1]	
		15_7 helix	Hexagonal $P3_1$	$a=b=5.66$ $c=19.50$	[2]
		15_7 helix	Hexagonal $P3_1$ 12 or $P3_1$ 21 or $P3_1$	–	[34]
		15_7 helix both left and right handed	Triclinic	$a=11.02$ $b=11.42$ $\gamma=121$	[35]
>30	I	Disordered	–	–	[1]
		15_7 helix	–	–	[2]
		Disordered 15_7 helix	Metrically hexagonal	–	[35]
Around 150		Disordered 15_7 helix	–	–	[3]
<150		Excitation of trans conformation in the 15_7 helix			
>150		Excitation of gauche conformation in the 15_7 helix			

[a] a, b, c in angstroms; α, β, γ in degrees.

Table 1 shows that in all the thermally activated phases the conformation of the PTFE chain is a non-integral helix. Thus the polymer chain as such has no crystallographic symmetry in any of these phases. At temperatures below 19 °C, *i.e.* in phase II which is considered to be the most stable phase, the conformation is a 13_6 helix, *i.e.* 13 $-CF_2-$ units are present in six turns of the chain. Bunn and Howells [1] and Clark and Muus [2] propose the low temperature phase II to be triclinic and nearly hexagonal. They describe the 13_6 helix as a twisted zigzag arrangement, the twist being 180° after every 13 $-CF_2-$ units which form the repeat unit. Also, since the unit cell contains only one molecule, adjacent polymer chains in the unit cell have identical handedness. In the triclinic cell the polymer chains run parallel to the crystallographic c direction. In the basal plane, since $a = b$, each polymer chain has an ideal hexagonal coordination.

At 19 °C PTFE undergoes a first-order crystal-to-crystal transformation to phase IV which prevails up to 30 °C. Phase IV is characterized by a 15_7 helical conformation in a hexagonal unit cell. In Table 2 the parameters characterizing the 13_6 and 15_7 helical structures are listed. Comparison of the values of the residues per turn shows that the 15_7 helix is slightly less densely packed than the 13_6 helix. The major difference between the arrangement of polymer chains in phases II and IV pertains to the interchain distance. Whereas in phase II the chains are separated by 5.59 Å, in phase IV the separation increases to 5.66 Å. The additional room available in phase IV thus permits the helix to untwist slightly or develop rotational disorders.

Above 30 °C in phase I the 15_7 helical conformation is retained but with an increase in the extent of disorder. Unlike in phase IV, the longitudinal displacements in phase I are no longer in units of the zigzag span. Yamamoto and Hara [3] have observed yet another transition at about 150 °C which is also due primarily to the presence of conformational disorder. Conformational disorders of this type are indeed detrimental to the alignment of the smooth molecular profiles.

Another structural feature which is associated with the wear behaviour of PTFE is the crystallite size. A semicrystalline polymer consists of interdispersed crystalline and amorphous regions. The term crystallite size refers to the average size of the crystalline region and it includes many unit cells. As could be expected, the size of crystallites varies with direction. In the case of PTFE, X-ray diffraction profile analysis has shown that the crystallite size along the c direction ranges from 200 to 1000 Å [4]. However, electron micrographs have shown that depending on the details of quenching, the crystallite size ranges from 0.4×50 μm^2 to 1×100 μm^2 [5]. The morphology of PTFE is also related to its wear behaviour. Whereas most melt-grown polymers are spherulitic (*e.g.* polyethylene (PE), nylon, terylene) [6], PTFE is conspicuously non-spherulitic. The lamellar or banded microstructure characterizing PTFE [5] consists of long and narrow bands with striations running along the width of the band. Typical dimensions of the band are 100 μm for the length, 0.2–1 μm for the

TABLE 2

Characteristics of the helical conformations of PTFE

	13_6	15_7
Pitch (Å)	2.813	2.786
Unit twist (°)	166.2	168
Rise per residue (Å)	1.298	1.30
Residues per turn	2.167	2.143

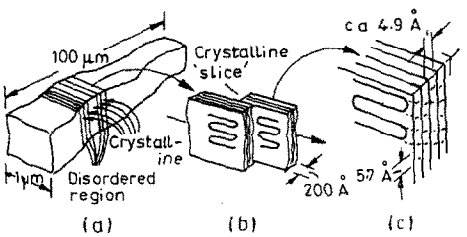


Fig. 1. Structure of PTFE: (a) crystalline block or "band"; (b) crystalline slices of "striae" after sliding; (c) hexagonal array of chains within slices. The structural arrangement shown in (a) and the sliding of crystalline slices is based on published work. However, the arrangement of chains within individual slices as shown in (b) and (c) is deduced from the friction–film structure. There is as yet no direct evidence that the chains are in fact so oriented within the slices. (After Makinson and Tabor [8].)

width and about 300 Å separation between striations. Figure 1 is a schematic representation of the banded structure. The striations represent the crystalline slices with the polymer chains oriented parallel to the striae. Adjacent slices are separated by the less crystalline or the amorphous regions.

3. Friction and wear characteristics

Figure 2 shows the reported variation in coefficient of friction with sliding distance. Beyond 0.01 km sliding distance the coefficient of friction is more or less insensitive to sliding distance. However, within this distance the substrate differentiates the kinetic coefficient of friction (μ_k) from the static coefficient of friction (μ_s).

(1) Smooth glass substrate: $\mu_s \gg \mu_k$.

(2) Rough glass substrate: $\mu_s = \mu_k$.

(3) Smooth steel substrate: $\mu_s < \mu_k$.

The friction behaviour of PTFE is in marked contrast to that of other polymers. The friction coefficients of other semicrystalline (PE, polypropylene (PP), nylon), amorphous (poly(vinyl chloride) (PVC), polymethylmethacrylate (PMMA), polystyrene (PS)) and cross-linked (resin) polymers when rubbed against glass are considerably higher (greater than 0.3) than that of PTFE at all speeds. Further, in rubbing against glass at low speed, unlike in the case of PTFE, the values of μ_s of these other polymers are always more or less equal to μ_k. However, in rubbing against steel, Tanaka [7] shows that the behaviour of HDPE and nylon 6 are similar to that of PTFE: $\mu_k > \mu_s$. Such distinction in the frictional behaviour between PTFE and other polymers has also been reported by Makinson and Tabor [8], Dickens *et al.* [9], Zaitsev and Sysoev [10] and Vaziri *et al.* [11].

In sliding against steel, the sliding distance (0.01 km) which defines the onset of invariant friction coefficient (Fig. 2) was shown by Biswas and Vijayan [12] to mark a jump in the interface temperature (19–20 °C) by a few degrees and a corresponding two to three times jump in the wear rate. Over a range of pressure (0.06–0.42 MPa) the transition temperature decreased by about 1 °C, while over a speed range of 0.1–1.2 m s^{-1} this temperature increases by 1 °C. In this range of speed and pressure the transition was found to be limited to the shaded region shown in Fig. 3. Over the unshaded region to the left, pretransition wear operated over a constant interface

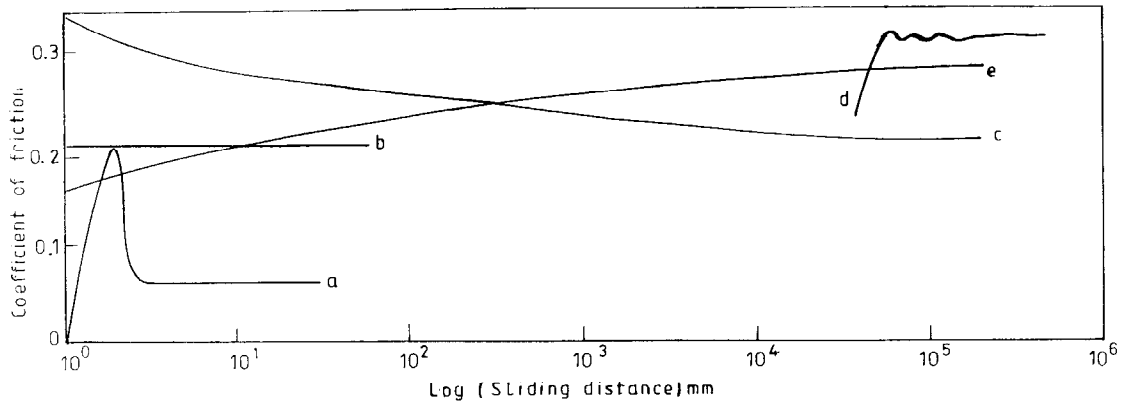


Fig. 2. Friction of PTFE. (a) Sphere on glass: speed, 10^{-6} m s^{-1}; load, 10 N; roughness, less than 0.1 μm c.l.a. (centre-line average); temperature, ambient; pressure, atmospheric [18]. (b) Sphere on glass: speed, 10^{-6} m s^{-1}; load, 10 N; roughness, greater than 0.1 μm c.l.a.; temperature, ambient; pressure, atmospheric [18]. (c) Pin on glass: speed, 3×10^{-1} m s^{-1}; normal pressure, 19.62 MPa; temperature, ambient; pressure, 4×10^{-5} mm Hg [17]. (d) Pin on steel: speed, 3×10^{-1} m s^{-1}; normal pressure, 0.086 MPa; roughness, 0.3 μm c.l.a.; temperature, ambient; pressure, atmospheric [12]. (e) Pin on steel: speed, 1×10^{-1} m s^{-1}; normal pressure, 2.8 MPa; roughness, 0.02 μm c.l.a.; temperature, ambient; pressure, atmospheric [7].

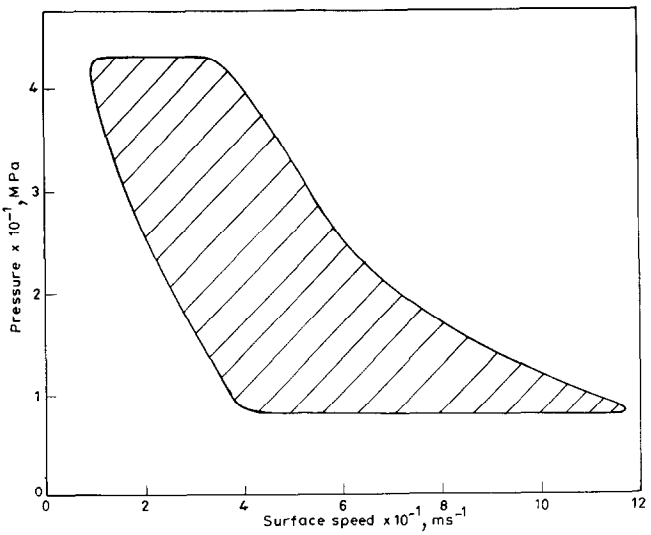


Fig. 3. Pressure–speed map showing (hatched) the regime where transitions were observed: material, PTFE; counterface, En24 steel; roughness, 0.3 μm c.l.a.; temperature, ambient; pressure, atmospheric [12].

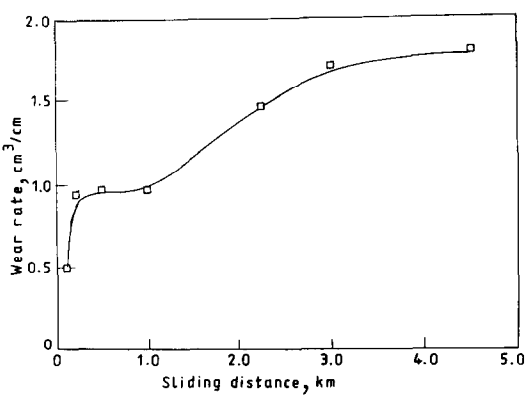


Fig. 4. Wear rate of PTFE slid against En24 steel: normal pressure, 0.24 MPa; surface speed, 0.42 m s^{-1}; roughness, 0.3 μm c.l.a.; temperature, ambient; pressure, atmospheric [27].

temperature up to 10 km sliding distance, while the region to the right of the shaded region showed post-transition wear from the start of the experiment.

Figure 4 shows this wear rate to increase gradually with sliding distance beyond the initial jump and then to stabilize beyond 2–3 km sliding distance. Although the invariance of this substantial wear rate (with respect to sliding distance) in the steady state stage has been observed by a number of authors [7, 9–11], no unanimity exists as to the physical nature of the non-steady-state characteristics at small sliding distances (Fig. 4).

There is, however, very little disagreement between the different authors that the steady state wear rate of PTFE when rubbed against a hard surface is several orders higher than that of most other polymers and that unlike in the case of PTFE the

wear rate of other polymers decreases with increasing sliding distance. Zaitsev and Sysoev [10], in performing their experiments using a crossed cylinder geometry, however, found that at high loads (4.83 MPa, 0.43 m s^{-1}) the wear rate of polymers with reactive groups (*e.g.* PMMA) is substantially higher than that of PTFE.

3.1. Effect of load, speed and temperature

There is agreement in the reported literature [12–14] that the friction coefficient of PTFE decreases with increasing contact pressure. Figure 5 shows the effect of contact pressure on coefficient of friction at different speeds.

McLaren and Tabor [15] drew attention to the viscoelastic origin of the friction of thermoplastic crystalline polymers. Since these flexible chain polymers relax with time their mechanical responses are determined by the speed of load application and temperature. This gives rise to acute speed and temperature sensitivity of the frictional characteristics as shown in Fig. 6 for PTFE. This kind of sensitivity reduces with increasing chain rigidity.

Interesting support for this comes from the study conducted by Briscoe and Ni [16] on the effect of radiation on the friction and wear of PTFE. Figure 7 shows that with increasing radiation dose the kinetic friction of the polymer increases because the chain mobility and therefore the viscoelasticity of the polymer are reduced.

The influence of viscoelasticity, however, appears strongest when one considers the speed, pressure and temperature dependence of the wear resistance of PTFE. Figures 8(a) and 8(b) show constant-pressure and constant-temperature wear rate *vs.* sliding velocity characteristics. It is well known that a time–temperature reduction law holds in expressing the viscoelasticity of polymers and a master curve can be generated by incorporating an Arrhenius shift if the activation energy is known. Tanaka and coworkers [7, 17] shifted constant-pressure and constant-temperature wear rate *vs.*

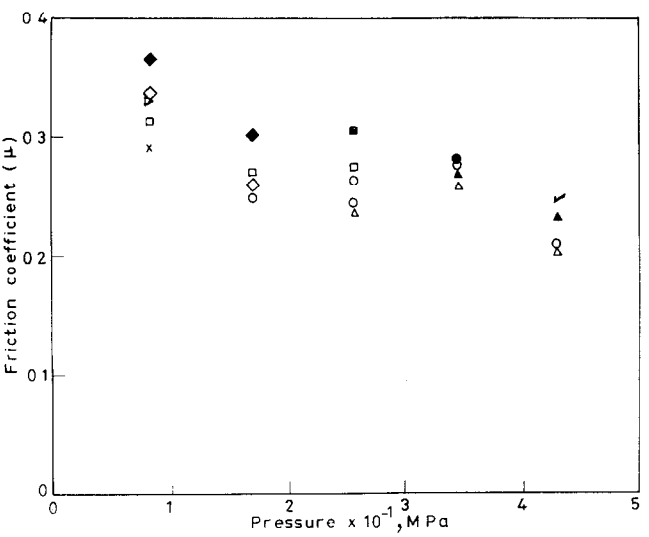


Fig. 5. Friction coefficient of PTFE against normal pressure: roughness, 0.3 μm c.l.a.; counterface, En24 steel; temperature, ambient; pressure, atmospheric; surface speed (◩) 0.14, (△) 0.19, (▲) 0.24, (○) 0.29, (●) 0.34, (□) 0.39, (■) 0.48, (◇) 0.58, (◆) 0.78), (×) 0.97, (▷) 1.17 m s^{-1} [12].

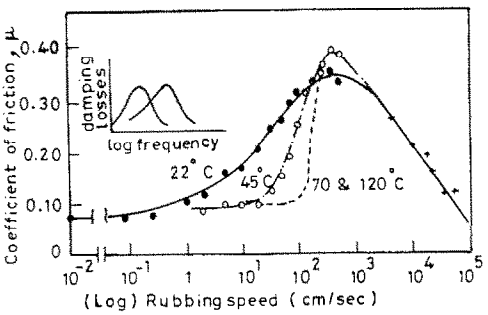


Fig. 6. Friction of PTFE on PTFE (49% crystalline) as a function of sliding speed. The inset shows damping losses as a function of frequency. If the temperature is raised, the peak is shifted to a higher frequency. (After McLaren and Tabor [15].)

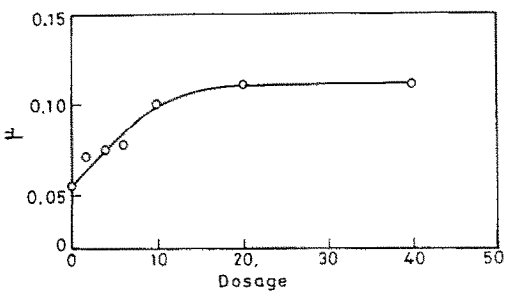


Fig. 7. Coefficient of friction as a function of dose (in Mrad) for linear sliding: counterface, smooth fired glass plate; load, 9.8 N; velocity, 4×10^{-4} m s^{-1}; polymer as a hemispherically ended rod of radius 3.5 mm [16].

sliding velocity characteristics by log a_T to generate a master curve at $T_0=23$ °C. If the linear wear rate is expressed as a function of the sliding speed, $a=K_0(v)$ at temperature T_0 and contact pressure p_0, the linear wear rate at constant pressure p and temperature T is given by

$$\frac{K_0(a_T v)(p/p_0)^n}{b_s}$$

where n is a constant greater than unity and a_T and b_s are shift factors which vary with temperature towards the speed axis and the wear rate axis respectively.

4. Adhesion and transfer

In rubbing PTFE balls on glass slides at a low speed (0.1 m s^{-1}; load 0.5–4 kgf), Makinson and Tabor [8] observed that at the commencement of sliding the coefficient of friction was high (0.1–0.16). On further sliding the friction coefficient drops to a value of less than 0.07. On observing the glass slide after traversal, the authors found the PTFE to be adhering to the glass in the static friction regime in the form of large (several microns) lumps and slabs, while in the low friction regime the transferred material is in the form of thin films of the order of 100–400 Å thickness. Subsequent study by Pooley and Tabor [18] showed that if the direction of sliding on an already

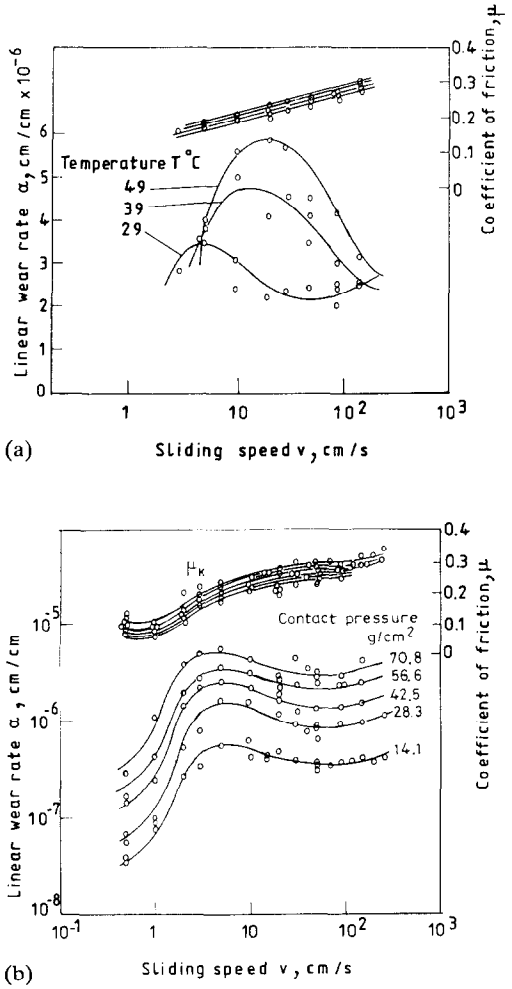


Fig. 8. (a) Relation between linear wear rate of PTFE and temperature at controlled temperatures T: $p = 5.6$ MPa; counterface, chromium-plated brass; surface finish, buffed; pressure, atmospheric [14]. (b) Variation in linear wear rate and coefficient of friction with sliding speed: T 29 °C; counterface, chromium plated brass; surface finish, buffed; pressure, atmospheric [14].

rubbed film is made orthogonal to the original direction of sliding, the initial coefficient of friction climbs back to a high level. Pooley and Tabor also observed that the shear strength associated with the initial high friction is comparable to the bulk strength, while that associated with the kinetic friction is several orders lower than the bulk shear strength. These and detailed microscopic observations of the rubbed counterface led them to the following conclusions.

(1) At the commencement of sliding the adhesion between the counterface and the polymer is high enough to cause fracture in the bulk, leading to lumpy transfer.

(2) With sliding, these lumps and slabs are drawn to make a thin film on the counterface. All further interaction between the slider and the counterface is that between the transferred film and the rider.

(3) The latter interaction causes a thin oriented film to be drawn out from the PTFE rider surface by a shear process. The forces and energy associated with this process are necessarily lower than those associated with the bulk failure as well as those associated with the adhesion between the counterface and the transferred film.

On increasing the sliding speed as well as the specimen temperature, the coefficient of friction increases and then drops beyond a certain speed [14, 15] (see Fig. 5). The increasing coefficient of friction with speed is also accompanied by a reduction in the difference between the levels of static and kinetic coefficients of friction.

Considering that the above mechanism of low friction of PTFE is dependent on the initial adhesion which leads to film formation, the first major question which arises is: how does PTFE, which is chemically an inert substance of low surface energy, form a strong adhesive bond with the counterface. Makinson and Tabor [8] suggested that it is a physical van der Waals type of bonding. If the bond is indeed a physical bond, it is unlikely to be able to anchor the transfer film except under the mildest of conditions. In such a case a fresh film will be created at each traversal. Such a mechanism would lead to high wear, which has of course been observed to be a characteristic feature of PTFE sliding. This line of argument led Briscoe *et al.* [19] to suggest making composites of HDPE (a material very similar to PTFE in its tribological performance) incorporating oxides, which when extruded onto the interface will strengthen the adhesion. Their experimental results show a significant reduction in the wear of HDPE due to the addition of lead oxide and copper oxide as fillers.

While their experimental results have been confirmed by many others, *e.g.* Gong *et al.* [20, 21], their basic reason for using the fillers stands challenged by later experimental results. Tanaka [7] shows that even under sliding speeds and contact pressures which show high friction, the transfer layer thickness builds up to a level of 100–500 nm with sliding time, up to a critical sliding time beyond which the thickness remains stable. Gong *et al.* [20–22], in investigating the effect of metallic and oxide fillers on the wear of PTFE in the sliding speed regime from 0.2 to 1.0 m s^{-1} and the load regime from 120 to 500 N (pin diameter 8 mm), also observed that the peeling of transfer film never occurs at the interface between the first transfer and the counterface.

Brainard and Buckley [23], in studying the adhesion of PTFE to tungsten in a field ion microscope (FIM), found the adhesion to be strong. Their Auger electron spectroscopy (AES) study of the transfer generated by sliding a PTFE pin on a clean tungsten or aluminium disc showed that the strong adhesion observed in the FIM may indeed be due to the formation of carbon–metal bonds. They showed that the bond may be strong enough to pluck out aluminium from the disc surface.

4.1. Chemical bonds

The possibility of chemical bond formation by rubbing interaction between polymers and an apparently inert tungsten carbide (cobalt binder) counterface was shown by IR spectroscopy of the transfer films by Zaitsev and Sysoev [10]. They showed that polymers containing polar and chemically active groups (containing O_2 and carbon) such as polycapramide (PCA), epoxy resin (EDS), PMMA and polytetrafluorochloroethylene (PTFCE) tended to develop much stronger adhesion with the carbide and more conspicuous transfer than polymers such as LDPE, PP, PTFE and PFR (phenol formaldehyde resin) which do not contain such groups.

When PTFE rubs against a metallic counterface, owing to the severe mechanical stresses and thermal vibrations associated with frictional heating, the molecular chain of the PTFE breaks into chain fragments by breaking –C–C– and/or –C–F– bonds. Richardson and Pascoe [24], in studying the catalytic effect of a clean surface of iron film on the decomposition of n-C_5F_{12}, found the compound to rupture into radical chain fragments: CF_3^+, $C_2F_5^+$, $C_3F_7^+$, etc. Further, fluorine ions (F^-) have been identified on a metallic surface rubbed by PTFE by Jintang *et al.* [25]. The active PTFE radicals (chain fragments) and the fluorine ions react and chemically bond with the metallic elements of the counterface. In a later paper Jintang and Hongxin [26] identified NiF_2 (F 1s peak binding energy approximately 684.6 eV) as well as peaks in the O 1s binding energy range. They surmised the latter to be peroxide radicals ($-CF_2-CFOO$) formed via the binding of PTFE fragments with atmospheric oxygen or oxides present on the metallic surface. These oxygen-containing organic fluorides are possibly introduced into the PTFE molecule. Their strong polarities bind the PTFE molecule to the metal surface, thus aiding the process of strong adhesive bonding.

4.2. Transfer film

Formation of coherent and continuous transfer film on the counterface is associated with low friction whereas lumpy and non-coherent transfer is associated with high friction. The latter occurs in the case of thermoplastic polymers of low crystallinity as well as in the case of all polymers at high sliding speeds. Brainard and Buckley [23] found the adhesion force between PTFE and tungsten to increase with time. Assuming that the interfacial adhesive strength per unit area does not change with time, the increase in friction is possibly due to an increase in contact area resulting maybe from the viscoelastic nature of the polymer. Thus in a low speed experiment it is likely that this relaxation process aids in building a coherent and continuous transfer film. With increasing speed this natural spread of the adhesion zone is impeded and the zone of low friction interaction (between transfer film and polymer) decreases, giving rise to an increase in friction. The above argument would suggest that all crystalline thermoplastic polymers with flexible chains which show pronounced viscoelasticity would tend to form coherent and continuous films when rubbed against a counterface at low sliding speeds. Tanaka [7] found that PTFE, nylon 6, HDPE and LDPE, all polymers with pronounced viscoelastic relaxation properties [15], formed more or less coherent films; albeit at different sliding times when rubbed against a glass plate, with the PTFE forming the best film in the shortest sliding time. As the thermoplastic polymer structure becomes more rigid, with the loss of crystallinity its relaxation properties are impaired. This would discourage the formation of a coherent and continuous transfer film on the counterface. In the absence of such a film, as long as strong adhesion between the metal and the polymer is ensured, the wear will take place by bulk fracture, yielding lumpy and large debris.

Strong adhesion of the transfer layer to the counterface and the development of a coherent and continuous transfer film are prerequisites for low friction; the zone of active shear is shifted from the polymer–metal interface to the polymer–polymer interface. However, it is doubtful whether, as long as the above conditions are met, the adhesion itself has any further role to play in determining the levels of kinetic friction and wear of the polymer. Gong *et al.* [20–22] show that while aluminium and steel counterfaces exhibit strong chemical bonding (yielding iron fluoride and aluminium fluoride) with PTFE in sliding interaction but a copper counterface does not, the wear rates corresponding to all three counterfaces are the same. It is likely that in the case of the copper counterface, although instantaneously the polymer–metal adhesion

is greater than the force required to draw out a film, the adhesion is not strong enough to form a permanent transfer film as such. With each traversal a fresh film is deposited and removed. Further, when a surface-treated PTFE pin is slid on an untreated PTFE transfer film or when an untreated PTFE pin is slid on a treated PTFE transfer film (adhesion of the film to the counterface in the two cases being markedly different), the friction and wear levels are found to be characteristic of the pin and bear no relation to the film–metal adhesion [22]. The top surface of the transfer film now slides against the underside of the polymer rider. The tangential force necessary for such sliding must be higher than that required to draw a thin film out of the rider surface by shear. The draw force is the kinetic friction force and the drawn film, once detached, may be deposited as an additional layer of the transfer film [17] or leave the sliding system altogether as debris.

5. Mechanism of wear

The low wear resistance of PTFE has prompted many mechanistic and physical examinations of the wear process. There appears to be a broad consensus that the wear behaviour of PTFE is to a large extent influenced by the specific structural characteristics of the polymer, such as the smooth profile of the PTFE chain, the banded microstructure, crystallite size, the interchain distance in the unit cell, etc.

5.1. The role of the molecular profile

The smooth profile of the PTFE chain described earlier facilitates adjacent polymer chains to slide past each other easily. In a similar manner, adjacent crystallites which are aligned favourably can also slide past each other with ease. The contribution from the smooth molecular profile of PTFE to the frictional properties has been demonstrated by Pooley and Tabor [18], who compared the friction coefficients of PTFE with those of PTFCE and a commercial copolymer Teflon–FEP. In PTFCE, one fluorine atom of PTFE is replaced by a bigger chlorine atom to give rise to the chemical repeat unit $(-CFCl-CF_2-)_n$. In the copolymer (Teflon–FEP), one fluorine atom of PTFE is replaced by a bulkier CH_3 group at specific intervals determined by the composition of the copolymer. In both cases, although the molecular conformation is helical, the smooth profile characterizing the PTFE chain has been destroyed by the incorporation of the respective bulkier substituents. Pooley and Tabor find that the frictional properties of these polymers are significantly different from those of PTFE. Their initial high value of μ_s is attributed to the lack of alignment of crystallites in the regions of contact. On sliding, however, the crystallites reorient and the molecular chains with their smooth profiles become oriented parallel to the direction of sliding. Thus the kinetic friction which corresponds to the aligned state is less than μ_s for PTFE. In the case of PTCFE and Teflon–FEP the major contribution to friction is from the uneven molecular profile, which is common to both the static and kinetic stages, and hence $\mu_s \approx \mu_k$.

5.2. The role of the banded structure

Makinson and Tabor [8] observed that at low sliding speeds crystalline slices of PTFE (Fig. 1) yield plastically into the adjacent amorphous viscous regions and are laid down like a pack of cards spread out on a table. They also mention the possible slippage within the crystalline slices and the molecules themselves becoming extended. In the high friction regime the frictional force increases and may exceed the forces

which hold the crystallites together. Under such circumstances thicker material in the form of ribbons and sheets is pulled out of the sliding surface and transferred to the counterface. The transferred material may include crystallites drawn out of the sliding surface. It may be noted that only the banded structure with alternate crystalline and amorphous regions can favour the process of slippage proposed by Makinson and Tabor. A spherulitic arrangement, on the other hand, is not likely to favour such a slippage.

Tanaka *et al.* [17] have observed long films and fibres generated during the sliding of PTFE on a steel surface. The formation of these has been attributed to the destruction of the banded structure by slippage of crystalline slices. Tanaka *et al.* have estimated the activation energy for the occurrence of slippage between adjacent crystalline slices in the band to be as low as about 7 kcal mol^{-1}. Thus the energy needed for destruction of the banded structure is very low and does not necessitate processes such as melting which are required for the destruction of a spherulitic structure. Tanaka *et al.* have proposed a wear model of PTFE (Fig. 9) according to which a fibre is formed by serial connection of adjacent crystalline slices and the formation of a film is due to lateral connection between adjacent fibres.

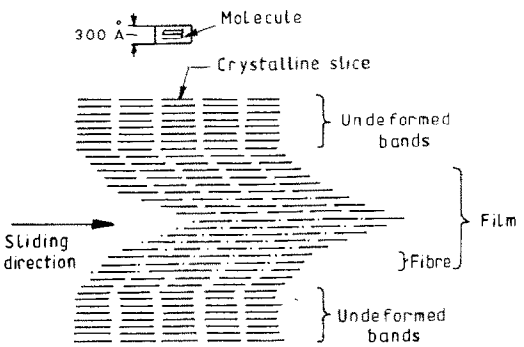


Fig. 9. Mechanism of formation of PTFE film due to change in structures [17].

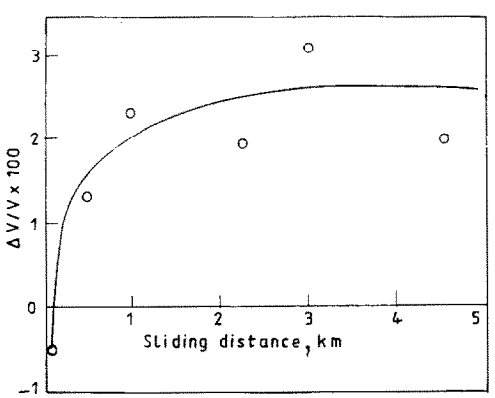


Fig. 10. Change in unit cell volume as a function of sliding distance; the data were obtained by subjecting the worn face of a 3 mm slice to X-rays: material, PTFE; counterface, En24 steel; normal pressure, 0.24 MPa; surface speed, 0.42 m s^{-1}; temperature, ambient; pressure, atmospheric; roughness, 0.3 μm c.l.a. [27].

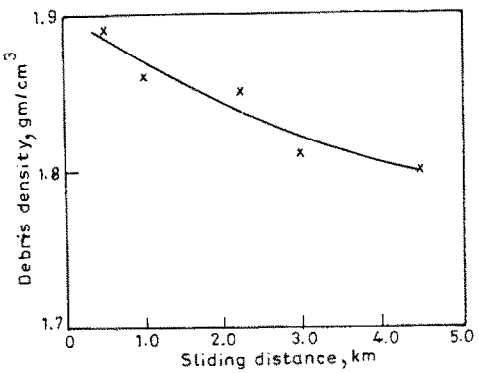


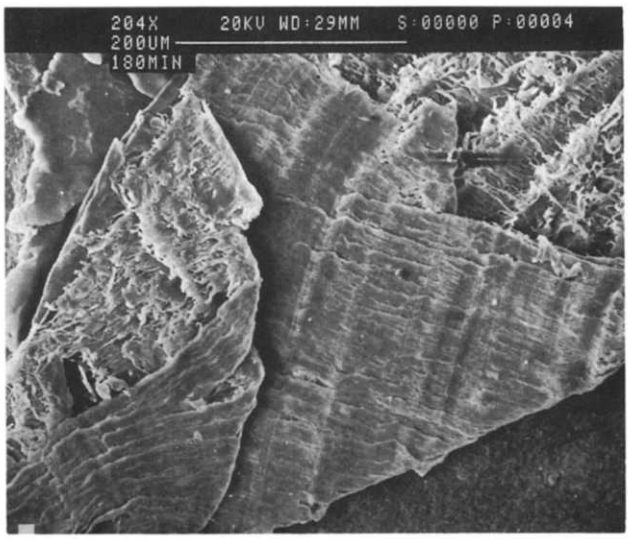
Fig. 11. Change in debris density as a function of sliding distance; the density was measured by flotation in a mixture of bromoform and isopropanal: material, PTFE; counterface, En24 steel; normal pressure, 0.24 MPA; surface speed, 0.42 m s^{-1}; temperature, ambient; pressure, atmospheric; roughness, 0.3 μm c.l.a. [27].

It may be pointed out that the mechanisms proposed by Makinson and Tabor [8] and Tanaka *et al.* [17] deal with gross crystallites and banded structures and are based upon a gross rearrangement of material at the (slid) surface and subsurface level. The crystallites are, however, made up of a large number of unit cells in which the hexagonal array of individual PTFE chains exists. The present authors believe that the key to a structural rearrangement due to tangential traction must lie at the level of the crystal lattice. They sought physical evidence for such deformation by examining thin slices taken from worn PTFE surfaces and wear debris. The following, which is an account of their findings [12, 27], sets out the mechanistic and physical details of the reorientation–rearrangement processes which ultimately yield the wear debris.

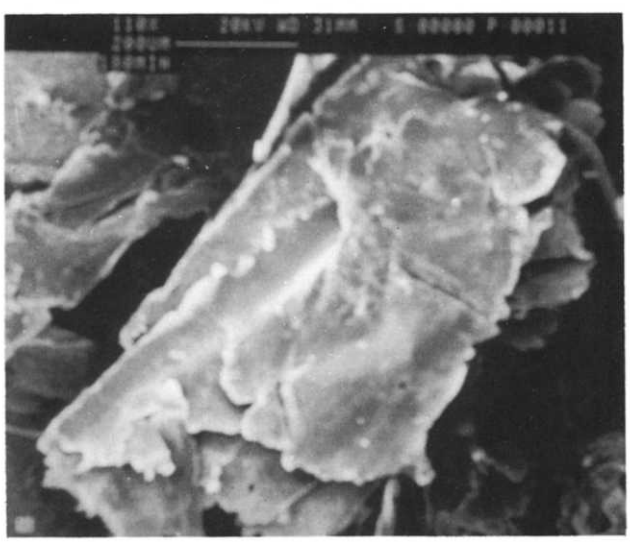
5.3. The deformation of crystallites — a physical examination

Examination of thin slices of slid PTFE pin by X-ray diffraction showed that the slid surface undergoes crystal structural changes due to sliding. Figure 10 shows the changes in unit cell volume due to sliding. Up to sliding distances of the order of 0.04 km the shrinkage is isotropic in nature. With further sliding an anisotropic character is introduced. The reduction in the a-dimension (which is related to the interchain distance) is nearly twice that in the c dimension. Thus (see transition jump in Fig. 4) in the post-transition stage the predominant effect of sliding is to improve the proximity of the chains in the unit cell. In the light of such a strong correlation found between the wear rate and the shrinkage of the unit cell, it can be stated that the wear of PTFE is much influenced by the closeness and improved alignment of the fluorine surfaces in the unit cell brought about by sliding, since this phenomenon will promote subsequent easy sliding of adjacent chains. The realignment appears to be progressive initially and then becomes saturated beyond a finite sliding distance.

Sharpening of the diffraction profiles obtained from the worn surfaces of PTFE provides strong evidence for the wear-induced growth of crystallites. There is, however, no indication of progressive growth of crystallites with sliding. Thus it appears that the transition in wear is accompanied by the growth in crystallites, but once the transition is over, no further growth takes place. In the light of the fact that the wear rate still continues to increase with sliding distance, the contention that the enlargement



(a)



(b)

Fig. 12. Scanning electron micrographs of PTFE wear debris: counterface, En24 steel; normal pressure, 0.24 MPa; surface speed, 0.42 m s^{-1}; temperature, ambient; pressure, atmospheric; roughness, 0.3 μm c.l.a.; (a) crystalline fraction of debris; (b) less crystalline fraction of debris.

of crystallites has a strong influence on the wear rate of PTFE can no longer be accepted as unequivocally valid.

The growth of crystallites may have occurred through reorientation of the randomly oriented crystallites situated near the sliding interface. Tangential forces and frictional heat aid adjacent crystallites (which now contain coplanar crystalline slices) to join

edge-on in giving rise to larger crystallites. Under sliding conditions coplanar slices from such crystallites are pressed together as well as drawn together to form laminates which emerge on detachment as debris. This plastically worked surface layer, until it is detached as debris, is part of the elastically deformed bulk of the PTFE specimen. Thus, when sliding stops, these layers could be expected to develop residual stresses. The presence of residual stresses in these layers was confirmed. A shift was observed in $2\theta_{max}$ of the (00.15) diffraction profile (of the slid surface slice) recorded at $\psi=0°$ and 15°, ψ being the angle between the plane normal and the surface normal. Such a shift is a measure of the residual stress [28].

5.4. Debris

Considering that the thickness of the debris was found in this investigation to be of the order of 1 μm, the above model would imply the pressing together of crystalline sheets up to 20–50 nm thick. Initiation of the phenomena of crystallite growth would also mark the beginning of a high wear regime where these thick and large laminates shear against the bulk to give rise to debris. The rapid diminution in the intensities of the diffraction pattern from the debris indicates lack of long-range order. It may be pointed out that there was no evidence of a similar lack of long-range order in the worn surface. This suggests that the disruption in the long-range order is either confined to a very thin layer of the slid surface which has detached as debris or has occurred during the process of detachment of debris from the slid surface. The reflections from the wear debris are conspicuously broader than those from the worn and the unworn surfaces. The broadening could be due to the reduction in crystallite dimensions and/or the presence of microstrain in the debris.

Values of the measured density of the debris (Fig. 11) provide further evidence for the reduction in crystalline order. The density of the debris collected after 4.54 km of sliding corresponds to about 18% reduction in crystallinity (Fig. 11). The corresponding unit cell volume, however, indicates only about 3% reduction in density (Fig. 10). The discrepancy could be attributed to the presence of both amorphous and crystalline components in the debris. The diffraction maxima from which the unit

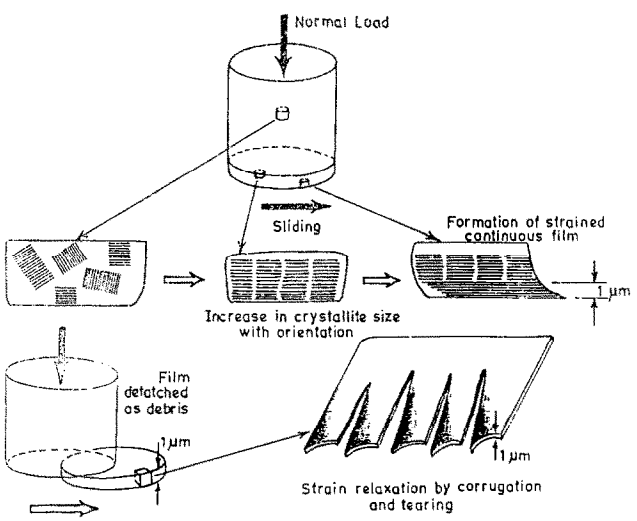


Fig. 13. Schematic model of wear of PTFE [12].

cell parameters are estimated correspond only to the crystalline fraction, whereas the measured density includes the contribution from both crystalline and amorphous fractions. Simultaneous existence of both crystalline and less crystalline fractions in the debris is also supported by the morphological features of the debris shown in Fig. 12. Figure 12(a) represents the debris which shows the characteristics of the banded structure. Within each band the striations which represent the crystallites are running along the width of the band. Figure 12(b) is likely to emanate from the low crystalline region of the material.

A schematic model of the wear of PTFE based on the above observations of Biswas and Vijayan [12] is shown in Fig. 13. While further investigation is required to identify the agency of change in the wear rate during sliding, the change appears to be such as to bring about pronounced mechanical deformation in the thin layers adjacent to the worn surface. Strains are introduced and the orientation of the crystallites changes sufficiently at the transition to increase the crystallite size. These occur at a specific temperature which is sensitive to normal pressure and sliding speed and effect an irreversible change in the wear rate. The mechanical changes remain in the slid layer until such time as the strained layer is detached from the bulk by wear.

It must be added that Lhymn's [29] study of the wear of PTFE suggests a delaminational wear mechanism which is based on the formation of bubbles and the subsequent removal of bulged layers, *i.e.* decohesion of bulged layers. The recent work of Jingtang and Hongxin [26] shows that in addition to the mechanisms which are concerned with slippage and decohesion, wear of PTFE also introduces breakage of covalent bonds.

References

1 C. W. Bunn and E. R. Howells, *Nature, 174* (1954) 549.
2 E. S. Clark and L. T. Muus, *Z. Kristallogr., 117* (1962) 119.
2 T. Yamamoto and T. Hara, *Polymer, 23* (1982) 521.
4 S. M. Wecker, J. B. Cohen and T. Davidson, *J. Appl. Phys., 45* (1974) 4453.
5 C. J. Speerschneider and C. H. Li, *J. Appl. Phys., 33* (1962) 1871.
6 A. Keller, *J. Polym. Sci., 17* (1955) 291.
7 K. Tanaka, *Wear, 75* (1982) 183.
8 K. R. Makinson and D. Tabor, *Proc. R. Soc. Lond. A, 281* (1964) 49.
9 P. M. Dickens, J. L. Sullivan and J. K. Lancaster, *Wear, 108* (1986) 273.
10 A. L. Zaitsev and P. V. Sysoev, *Sov. J. Friction Wear, 8*(2) (1987) 348.
11 M. Vaziri, R. T. Spurr and F. H. Stott, *Wear, 122* (1988) 329.
12 S. K. Biswas and K. Vijayan, *J. Mater. Sci., 23* (1988) 1877.
13 B. J. Briscoe, L. H. Yao and T. A. Stolarski, *Wear, 108* (1986) 357.
14 Y. Uchiyama and K. Tanaka, *Wear, 58* (1980) 223.
15 K. G. McLaren and D. Tabor, *Nature, 197* (1963) 856.
16 B. J. Briscoe and Z. Ni, *Wear, 100* (1984) 221.
17 K. Tanaka, Y. Uchiyama and S. Toyooka, *Wear, 23* (1973) 153.
18 C. M. Pooley and D. Tabor, *Proc. R. Soc. Lond. A, 329* (1972) 251.
19 B. J. Briscoe, A. K. Pogosian and D. Tabor, *Wear, 77* (1974) 19.
20 D. Gong, B. Zhang, Q. Xue and H. Wang, *Wear, 137* (1990) 25.
21 D. Gong, B. Zhang, Q. Xue and H. Wang, *Wear, 137* (1990) 267.
22 D. Gong, Q. Xue and H. Wang, *J. Appl. Polym. Sci., 40* (1990) 1141.
23 W. A. Brainard and D. H. Buckley, *Wear, 26* (1973) 75.
24 M. O. W. Richardson and M. W. Pascoe, in L. H. Lee (ed.), *Advances in Polymer Friction and Wear,* Vol. 5A, Plenum, New York, 1975, p. 123.

25 G. Jintang, Z. Jiazhen and D. Hongxin, *J. Solid. Lub., 1* (1) (1981) 22.
26 G. Jintang and D. Hongxin, *J. Appl. Polym. Sci., 36* (1988) 73.
27 K. Vijayan and S. K. Biswas, *Wear, 150* (1991) 267.
28 B. D. Cullity, *Elements of X-ray Diffraction,* Addison-Wesley, Reading, MA, 1978, p. 447.
29 C. Lhymn, *Wear, 107* (1986) 95.
30 H. G. Kilian, *Kolloid Z. Polym., 185* (1962) 13.
31 F. J. Boerio and J. L. Koenig, *J. Chem. Phys., 54* (1971) 3667.
32 K. W. Johnson and J. F. Rabolt, *J. Chem. Phys., 58* (1973) 4536.
33 B. L. Farmer and R. K. Eby, *Polymer, 22* (1981) 1487.
34 R. G. Brown, *J. Chem. Phys., 40* (1964) 2900.
35 B. L. Farmer and R. K. Eby, *Polymer, 26* (1985) 1944.