JOURNAL OF MATERIALS SCIENCE 31 (1996) 3955–3963

Scratching behaviour of polymer films using blunt spherical styli

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There are four different kinds of scratch morphologies developed when a blunt spherical stylus is in contact with the surface of a polymer multilayer system in relative motion. Qualitatively, a relationship between scratch morphologies and mechanisms can be established. The main deformation mechanisms are surface shear yielding, surface cracking, subsurface yielding (indentation), and interfacial delamination. Tangential forces during scratching using a blunt spherical stylus are largely due to the friction between materials and the stylus. In that sense, lubricants can improve the material scratch performance by reducing the friction force at a given normal load. Many variables, such as scratching speed, environments, and the sizes of styli, can affect polymer scratching performances to a large degree.

1. Introduction

How to increase scratch and abrasion resistance of materials is of great interest to both academic and industrial communities. Many inorganic and polymeric materials have been developed to be protective coatings for various applications. Scratch and abrasion behaviour of various kinds of materials using spherical styli have been studied [1–5]. It is obvious that there is more than one scratching mechanism associated with spherical indentors. The most recent development [6] in the area of materials tribology indicates that there are three possible operating processes when two contacting surfaces are brought into relative motion with respect to one another. These processes are (1) interfacial slip accompanied with interfacial shear, (2) subsurface shear, (3) interfacial shearing and tensile loading in the vicinity of an asperity, which may initiate crack formation (ploughing effect). The origin of a lateral force during scratching comes from friction and geometrical resistance against tangential motion. In general, scratching problems are complicated mechanical processes. However, scratch and abrasion performance of materials is not solely determined by scratching stress fields. It is not clear how various material properties, such as hardness, yield stress, and toughness, contribute to scratch and abrasion resistance of materials.

The nature and the amount of tangential force during scratching should be important factors affecting scratching mechanisms. Tangential forces contain information in addition to normal force measurements [7–9]. It is well known that surface lubrication may or may not improve scratch behaviour of materials [9]. Therefore, the analysis to tangential forces associated with a particular stylus is needed to understand the origin of tangential forces and their impact on scratching behaviour of materials.

In this paper, we focus on probing scratch and abrasion mechanisms of various polymers using blunt spherical styli. The effect of surface friction coefficient on scratching behaviour using blunt spherical indentors is also described.

2. Experimental procedure

2.1. Materials

Polymers chosen for scratch tests using blunt spherical styli were crystallized polyethylene terephthalate (PET), polypropylene, acetate, polystyrene, and a biopolymer gelatin. As a comparison, glass plates were also included in the study. A detailed description of these materials is given in Table I. Because the mechanical properties of gelatin films are sensitive to moisture, all the experiments of gelatin coatings were done at 50% RH and 70 °F (~21 °C), unless otherwise specified. The surfaces of some of these films were coated with PDMS (about 100 nm thick) to lower their surface friction coefficients.

2.2. Microindentation using a spherical indentor

Microindentation experiments were performed on some of the samples using the Fischerscope H100

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TABLE I Materials

Sample A	Gelatin with 7% PDMS in solution
Sample B	Gelatin with 4% PDMS in solution
Sample C	Gelatin with 1% PDMS in solution
Gelatin	Gelatin
Acetate	Acetate
Acetate/PDMS	PDMS-coated (100 nm) acetate
PET	Kodak PET film
PET/PDMS	PDMS-coated (100 nm) PET
Polypropylene	Exxon
Polystyrene	From Pressure Chemical with M_w of 47.5 K
Glass	VWR micro slides

Hardness Tester. A 75 μm radius spherical indentor was used in order to provide complementary information for the scratch test which uses 75 μm radius styli. A time period of 1.0 s between two load steps was used through out all the measurements. The testing mode included loading, unloading, and creep at a minimum load after unloading. Because all our materials were polymeric, the creep time was set up to 60 s after unloading to eliminate viscoelastic response of polymers and to ensure measurement of the true permanent indentation [10].

Because the average indentation testing time is less than 1 min, the residual indentation after 60 s can be considered as permanent deformation.

2.3. Scratch test

Scratch tests were performed using spherical styli. They are 75 μm radius (sapphire and diamond) and 584 μm radius (diamond). The apparatus was built in-house with a normal load resolution of ± 10 g. The apparent friction coefficients (tangential force, F_f, divided by normal force, F_N) of materials were measured. The standard scratch speed was about 2.7 cm s^{-1}. Scratch tests with various speeds were performed on PET films. In order to ensure permanent deformation, the morphologies of those scratches were studied after 24 h using optical microscopy, atomic force microscopy, and scanning electron microscopy.

3. Results

3.1. Residual indentations

The residual indentations of PET film measured with a 75 μm radius indentor are summarized in Table II. Both residual indentations at $t = 0$ (immediately unloading) and $t = 60$ s (after unloading for 60 s) are listed. It is clear that a creep process after unloading is necessary to obtain true permanent indentation values from polymers, because they have viscoelastic behaviour.

3.2. Morphology of scratches

There are four different scratch morphologies observed in the materials examined using both 75 and 584 μm radius styli. Type I scratch (Fig. 1) shows deformation bands inside a scratch which are convex with respect to the sliding direction. Type II scratch (Fig. 2) shows deformation bands inside a scratch which are concave with respect to the sliding direction. Type III scratch (Fig. 3) shows the removal of the top coating. Type IV scratch (Fig. 4) is a featureless clear track with shoulders on both sides. In general, for a given material, the same morphology was initiated at low normal loads for high surface friction coefficients or initiated at high normal loads for low surface friction coefficients.

TABLE II Residual indentations of PET and acetate

	Load (g)	Res. ind. at $t = 0$ s (μm)	Res. ind. at $t = 60$ s (μm)	S.D.
PET	10	0.02	0.00	0.05
	20	0.06	− 0.01	0.05
	30	0.13	0.04	0.05
	40	0.13	0.03	0.05
	50	0.18	0.04	0.05
	60	0.24	0.06	0.05
	70	0.31	0.10	0.05
	80	0.37	0.12	0.05
Acetate	10	0.14	0.04	0.05
	20	0.20	0.01	0.05
	30	0.35	0.07	0.05
	40	0.44	0.05	0.05
	50	0.61	0.16	0.05
	60	0.90	0.27	0.05

3.3. The tangential force during scratching

The apparent friction coefficients of various materials measured with a 75 μm sapphire stylus are shown in Fig. 5. The apparent friction coefficients are almost independent of normal loads; they do not change much at the onset of scratch initiation. This implies that the spherical styli used did not penetrate the surface under the present experimental conditions. The surface friction characteristics are, therefore, retained even when scratches are produced. On the other hand, it also suggests that tangential forces largely come from surface friction.

For various coatings, the critical tangential forces, F_t, and critical normal forces, F_n, at which types I, II, and IV scratches are initiated (observed under an optical microscope) are listed in Table III. All these forces are measured with a 75 μm radius sapphire stylus, unless otherwise specified.

4. Discussion

As mentioned before, there was no apparent change in friction coefficient when a 75 μm radius spherical stylus began to make scratches on the samples. The slight increase of friction coefficient as the normal load increases was due to the material's resistance to deformation during sliding motion. Because lubrication plays a role, the nature of the tangential force during scratching is due to the friction force between materials and styli. Therefore, there should be a certain correlation between friction force and scratch

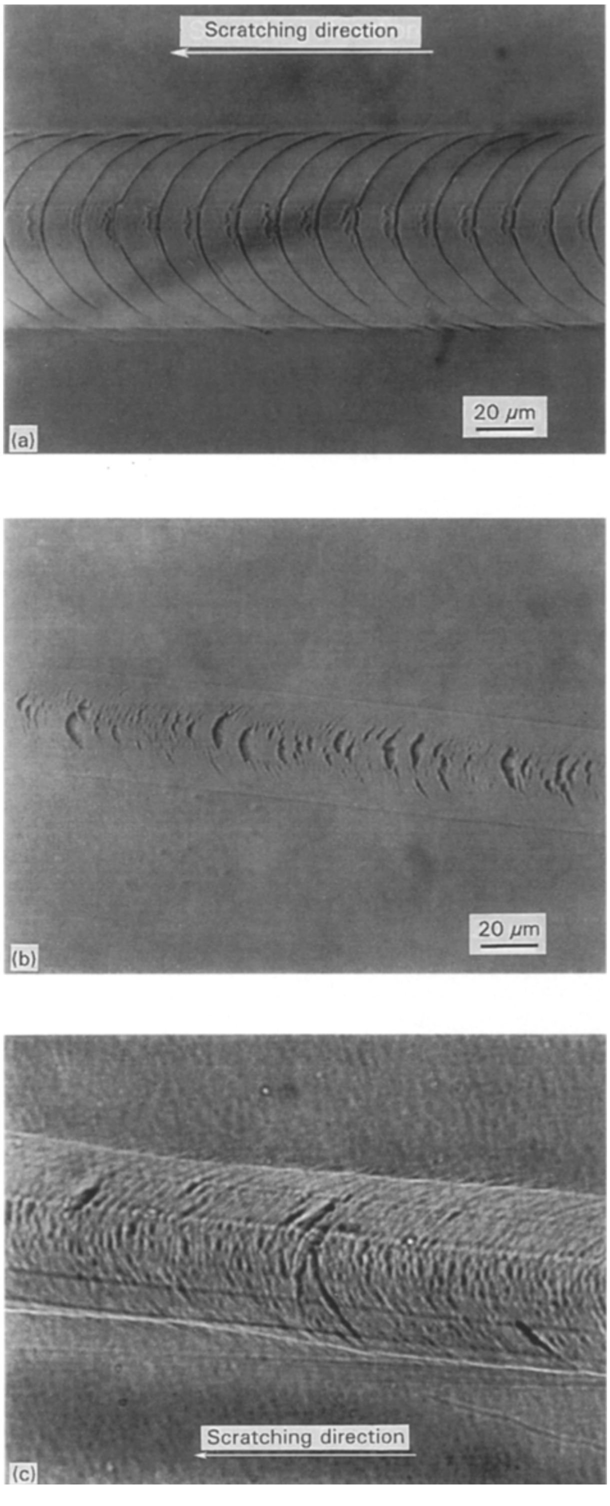


Figure 1 Type I scratches: deformation fringes are convex with respect to the scratching direction (75 μm radius stylus). (a) PET at 120 g normal load; (b) pure gelatin at 50% RH at 30 g normal load; (c) polypropylene at a normal load of 50 g.

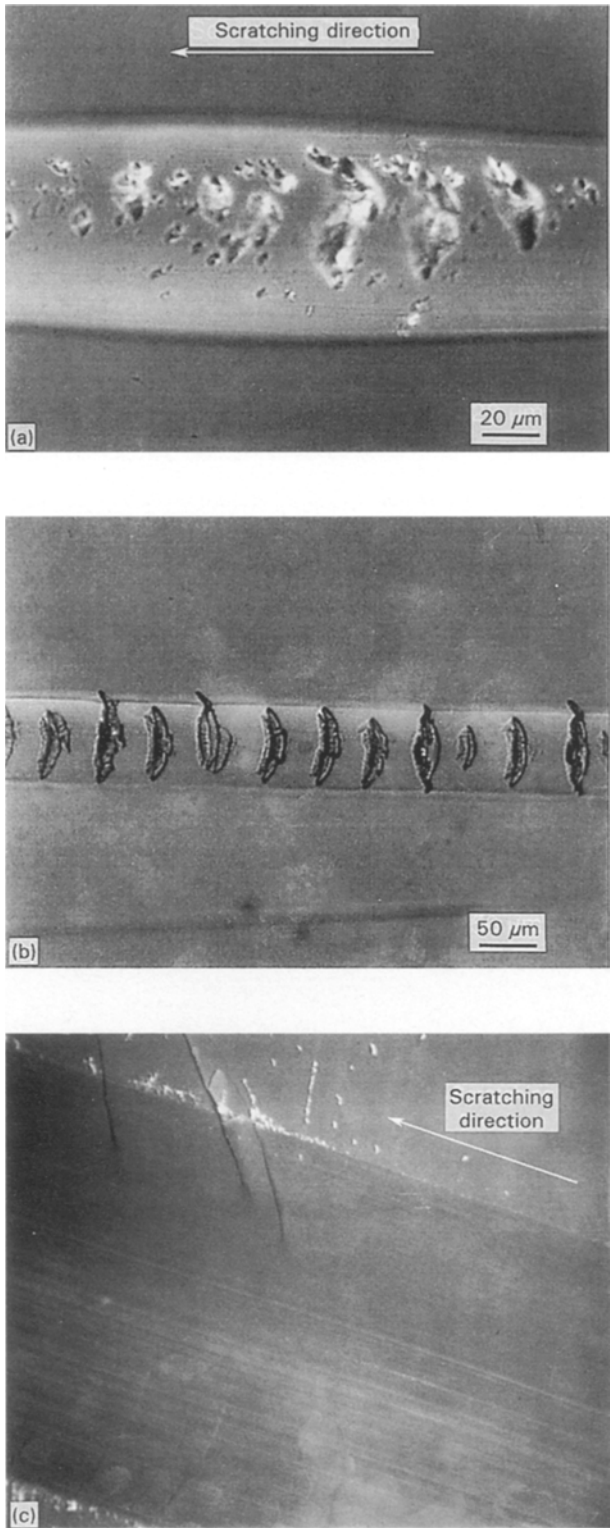


Figure 2 Type II scratches: deformation fringes are concave with respect to the scratching direction (75 μm radius stylus). (a) Acetate at normal load of 100 g; (b) gelatin at 5% RH at normal load of 130 g; (c) glass at a normal load of 1000 g.

morphology. Each scratch morphology is discussed from this point of view.

4.1. Type I scratches
As seen in Fig. 1, type I scratches are deformation bands which are convex with respect to the sliding direction. Similar features were observed in rubber [1, 2] and other inorganic materials [3]. Both AFM and SEM (Fig. 6) micrographs reveal that those deformation bands corresponds to the permanent out-of-surface displacements of material at sufficiently high normal loads. As seen in Fig. 1a, at 120 g normal load, a PET film shows type I scratches while a PDMS-treated PET film shows type IV scratches (Fig. 4a). The difference between these two films under the same normal load is tangential forces. The tangential force for the bare PET film is 30 g, and the

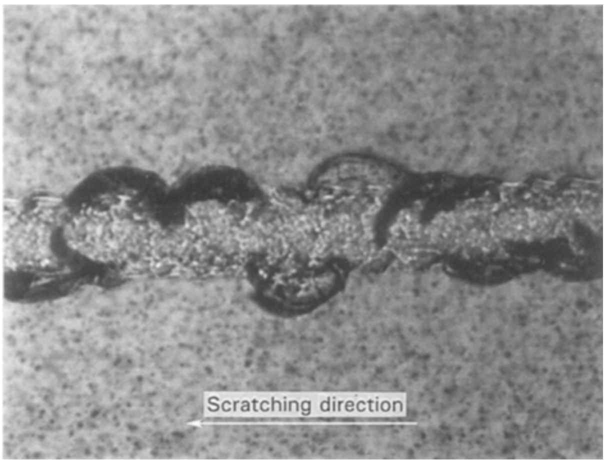


Figure 3 Type III scratches: removal of the overcoat (75 μm radius stylus).

tangential force for the PDMS-treated PET film is 3.6 g. Clearly, the tangential force during scratching is the driving force for type I scratches and the 75 μm spherical stylus is sensitive to the presence of lubricants. Further experiments pointed out that type I scratches do not show fracture and the loss of material, i.e. its deformation, can be recovered upon annealing (Fig. 7).

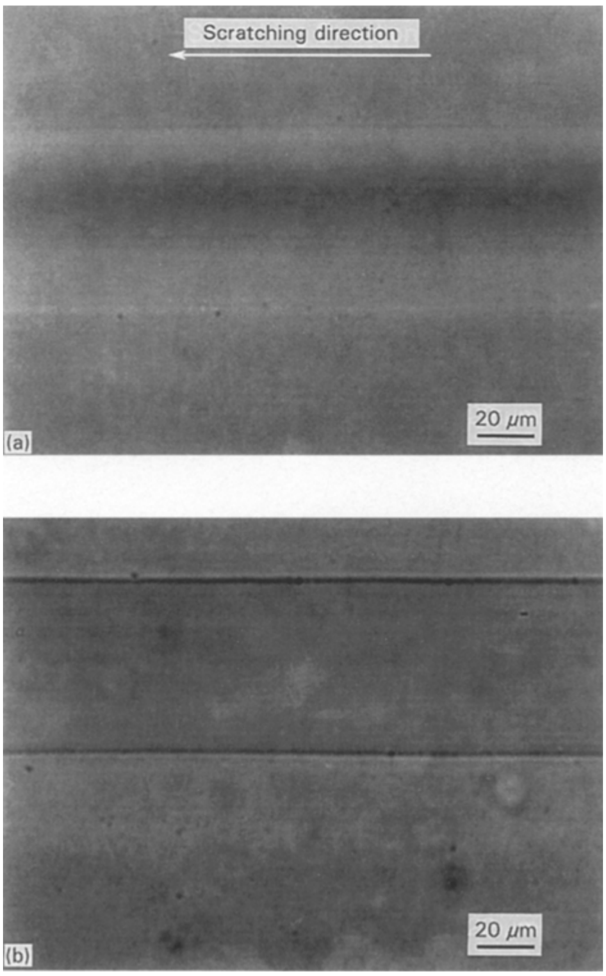


Figure 4 Type IV scratches: clear track (75 μm radius stylus). (a) PET/PDMS at normal load of 120 g; (b) acetate/PDMS at normal load of 100 g; (c) glass at a normal load of 500 g.

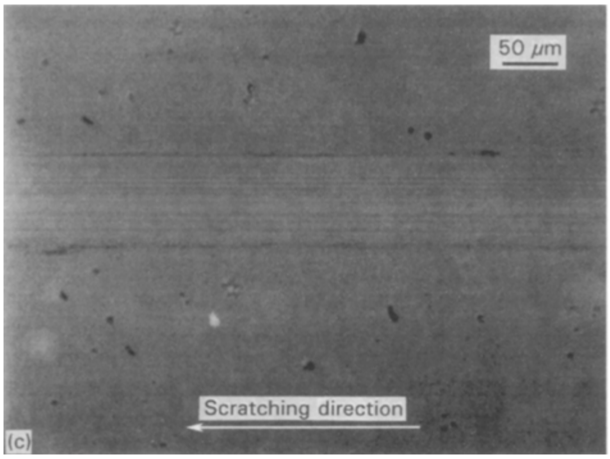


Figure 4 continued

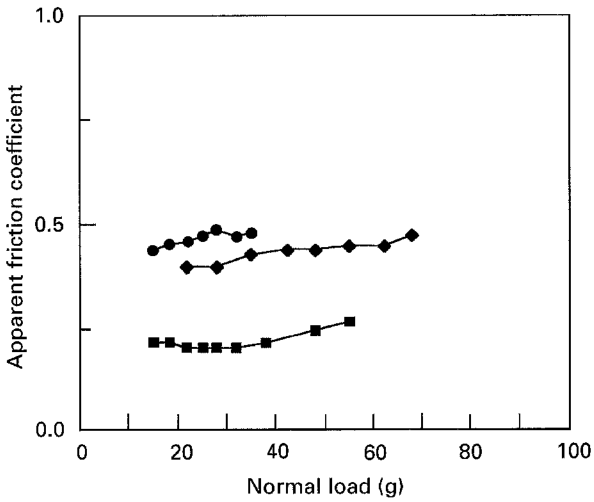


Figure 5 The apparent friction coefficients measured during scratching using a 75 μm radius sapphire stylus: (■) PET, (◆) acetate, (●) gelatin 50% RH.

In our study, type I scratches are observed from various relatively ductile polymers. There must be a deformation process resulting in the universal morphology of type I scratches and the degree of this deformation should relate to tangential forces during scratching. In the presence of friction, the elasticity analysis of a spherical stylus shows that the maximum von Mises stress moves up to the surface [11], and the surface von Mises stress contours are convex with respect to the sliding direction [12]. The shape of the observed deformation fringes suggests that they should correspond to the surface Von Mises shear stress. The deformation process is that the material is squeezed out of the surface in front of a moving stylus by shear stresses. Because all the materials showing type I scratches are relatively ductile and there is no material loss accompanying the deformation, it can be proposed, based on the above arguments, that the deformation of type I scratches corresponds to surface shear yielding developed by the compressive shear stress in front of a moving stylus. Therefore, the surface shear yield stress is the primary material property that governs the initiation of a type I scratch. If the applied surface shear stress exceeds material surface

TABLE III Critical normal and tangential forces

Sample	Scratch type	Critical F_n (g)	Critical F_t (g)	Fric. coeff.
Sample A	I	120	14.4	0.12
Sample B	I	100	13	0.13
Sample C	I	60	10.8	0.18
Gelatin	I	20	9.4	0.47
Gelatin/PDMS	IV	30	0.9	0.03
Gelatin 5% RH	II	80	4.0	0.5
PET	I	70	17.5	0.25
PET/PDMS	IV	60	1.8	0.03
Acetate	II	70	33.6	0.48
Acetate	IV	10	4.8	0.48
Acetate/PDMS	IV	50	1.5	0.03
Polystyrene[a]	I	30	12	0.4
Polystyrene[b]	II	200[c]	80[c]	0.4
PP	I	40	na[d]	na[d]
Glass	IV	500[c]	50[c]	0.1
Glass	II	1000[c]	100[c]	0.1

[a] Tested with a 75 μm radius diamond stylus.
[b] Tested with a 584 μm radius diamond stylus.
[c] Not the critical force.
[d] na = not available.

shear yield stress, the out-of-surface deformation fringes of type I scratches can be initiated. However, the distance between adjacent fringes may be related to the slip–stick process [2] which is governed by adhesion between materials and moving styli. This interface shear yielding mechanism explains why lubricants can improve scratching performance by reducing the tangential force at a given normal load. The type I scratches can be initiated at a lower normal load with a higher surface friction coefficient or, for the same material, they can be initiated at a higher normal load with a lower friction coefficient.

However, the above elastic–plastic material model for scratch initiation is not suitable for polymers in all cases. Polymers have their unique viscoelastic behaviour. Like the time-dependent behaviour of polymers during indentation [10], there are transient type I scratches observed in polymers. As reported by Barquins [2], the deformation fringes of rubber disappear with time. Therefore, elastic–plastic arguments are valid only in the cases in which the loading is high enough to cause irreversible plastic deformations.

4.2. Type II scratches

As seen in Fig. 2, the deformation bands within type II scratches are concave with respect to the sliding direction. Similar patterns were found in other organic and inorganic materials [3–5]. Scanning electron micrographs reveal that the deformation bands are surface cracks (Fig. 8). Again, the driving force for type II scratches is mainly the tangential force. As seen in Fig. 2a, at a normal load of 100 g, an acetate coating shows type II scratches at a tangential force of 43 g, and a PDMS-coated acetate film shows type IV clear track scratches at a tangential force of 3.0 g (Fig. 4b).

The tensile stress in the wake of a moving stylus due to the presence of a friction force is well known. Because all the materials showing type II scratches are relatively brittle, such as acetate, gelatin at 5% RH (gelatin at 5% RH is brittle [13]), and glass, it can be proposed that the deformation of type II scratches corresponds to tensile failure. Therefore, the primary material property governing the deformation is the surface break stress. However, like type I scratches, lubricants can reduce the applied friction force at a given normal load and shift the type II scratch initiation processes to a high normal load to meet the surface break stress of the material.

4.3. Type III scratches

The mechanism of type III scratches is delamination. It may combine with other mechanisms too. Fig. 3 clearly shows that the brittle coating is delaminated under the compressive stress ahead of the stylus and removed under tensile cracking (type II). There are discussions of various factors which influence the critical normal load of delamination. Type III scratches offer opportunities for the study of adhesion between coatings and substrates [14–18]. Obviously, lubricants will delay the initiation of type III scratches using a blunt spherical indentor.

4.4. Type IV scratches

Types I, II, and III scratches are primarily produced by tangential forces during scratching. Often, these three kinds of scratches can be reduced to type IV scratches, which are clear tracks (see Fig. 4) by applying lubricants on surfaces. PET and acetate (Figs 1a, 2a, 4a and b) are good examples of how lubricants can change the morphology of scratches under the same normal loads. Furthermore, as seen in Table III, type IV scratches are initiated at low tangential forces. The evidence suggests that type IV scratches are initiated by normal force rather than tangential force during scratching. However, type IV scratches can be transformed into other kinds if surface friction coefficients between materials and styli are high.

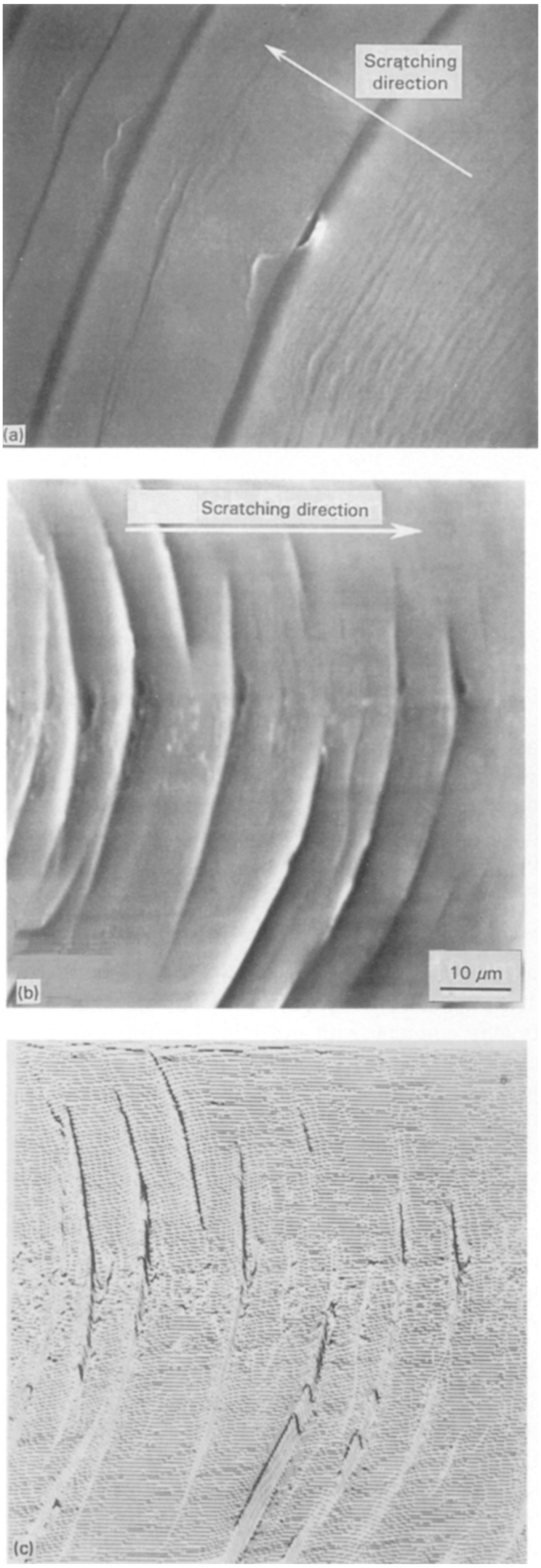


Figure 6 Type I scratches of PET at normal load of 120 g (75 μm radius stylus). (a) Scanning electron micrograph, (b, c) atomic force micrograph.

It can be proposed that type IV scratches are produced through superposition of permanent indented areas under low tangential forces. Obviously, the mechanical property that governs this mechanism is

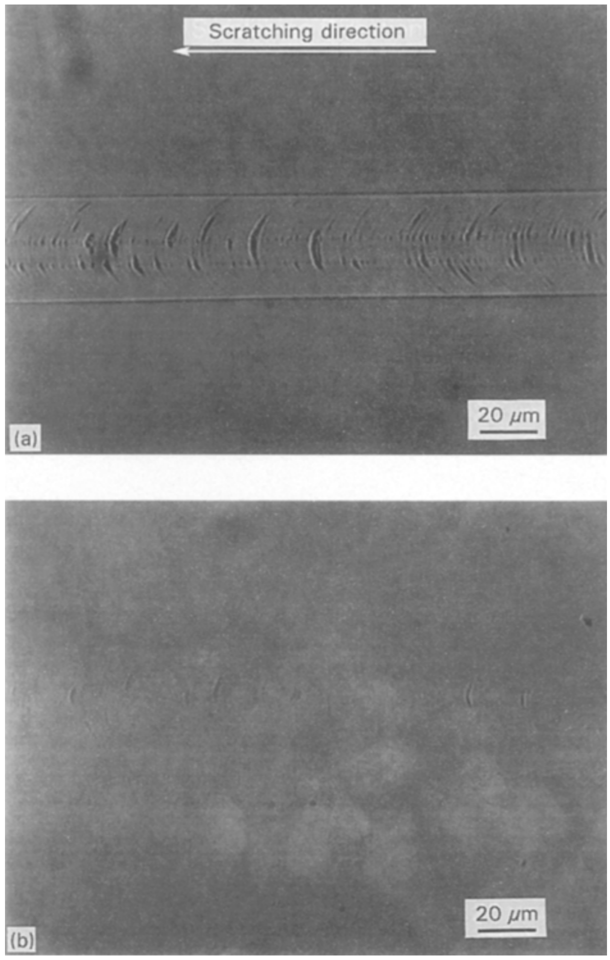


Figure 7 Type I scratches of gelatin (75 μm radius stylus), (a) scratched 50% RH at normal load of 30 g, (b) after annealing at 160 °F/70%RH for 2 h.

the material hardness. Indeed, we found a correlation between permanent indentation and initiation of type IV scratches under the same normal load for PET/PDMS film and acetate/PDMS film using 75 μm radius stylus. A PET film does not show appreciable permanent indentation up to the normal load between 60 and 70 g (see Table II), while the critical normal load for initiation of type IV scratches of PET/PDMS is also 60 g (see Table III). The same statement can be made for the case of acetate/PDMS (see Tables II and III). In general, for a material with high hardness, the critical normal load for initiation of a clear track is higher, such as in the case of a glass slide which does not show clear tracks until the normal load reaches about 500 g. The correlation further confirms that the deformation in type IV scratches is due to indentation. However, the presence of friction force during the sliding process makes a material reach its yielding point sooner than pure indentation. Therefore, material hardness does not directly determine the initiation of clear track scratches in the presence of moderate friction forces. As noted from Table III, acetate ($f = 0.43$) shows clear track at 10 g while acetate/PDMS ($f = 0.03$) shows clear track at 50 g.

It should be pointed out that a thin hard overcoat may not prevent type IV scratches, because the maximum deformation is beneath the surface due to

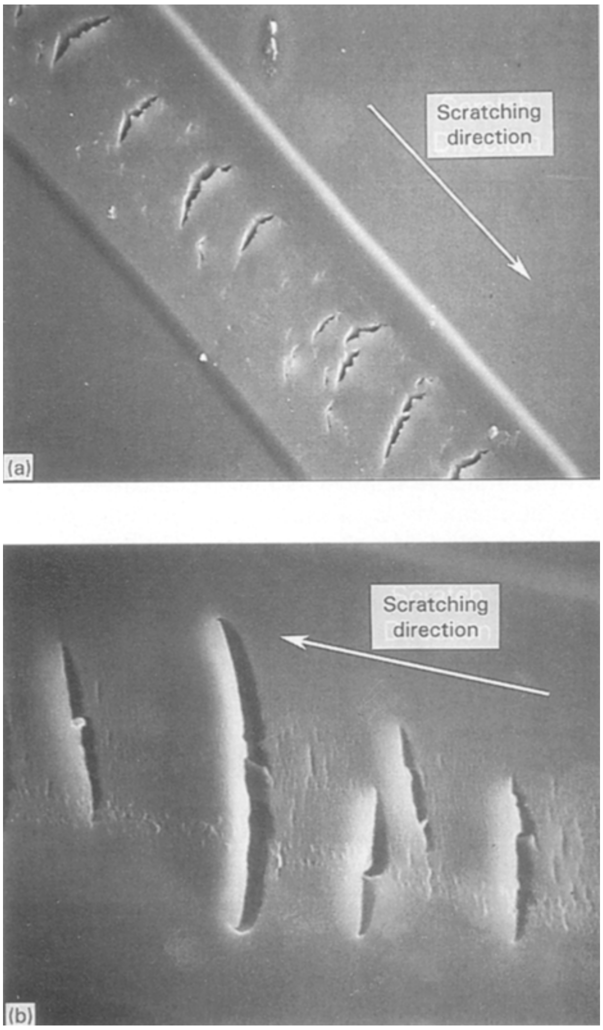


Figure 8 Scanning electron micrographs of type II scratches (75 μm radius stylus). (a) Acetate, (b) gelatin at 5% RH.

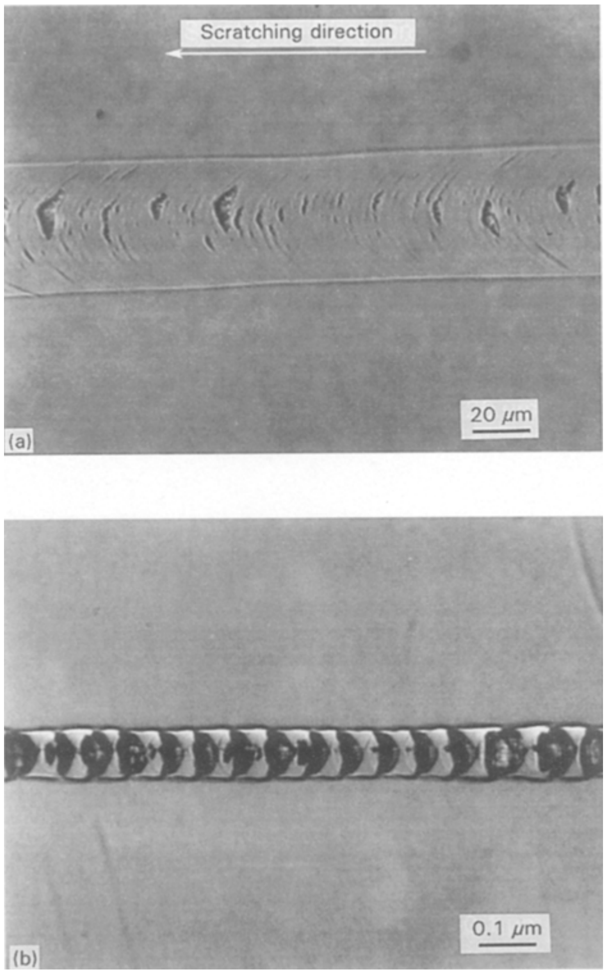


Figure 9 Types I and II scratches of gelatin films (75 μm radius stylus). (a) Type I scratches at a tangential force of 15 g, (b) types I and II scratches at a tangential force of 66 g.

permanent indentation inside the substrate [19]. Therefore, the hardness of a substrate is crucial when a coating is in contact with a blunt spherical asperity.

TABLE IV

Scratching speed ($cm\,s^{-1}$)	Critical tangential force (g)
0.11	12.5
2.7	17.5
4.6	20

4.5. Parameters affecting scratching mechanisms

Since the end use applications of each film are different, it is important to discuss how a particular scratch mechanism transforms into others.

4.5.1. Level of normal and tangential forces

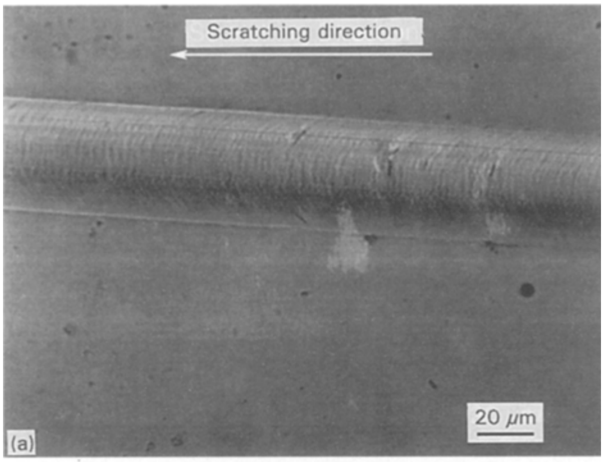
In general, types I, II, and III scratches are driven by tangential forces, and at low tangential forces, type IV scratches are driven by normal loading. Type IV scratches usually coexist with types I, II, and III at high normal loading. Type IV scratches appear alone only if surface friction is low. There is a transition from type I scratches to type I/type II combined scratches as normal load increases. It can be seen in Fig. 1b that a gelatin film (50% RH and 70 °F (~21 °C)) shows type I scratches (shear deformation) at a tangential force of 15 g, while in Fig. 9 it shows both types I and type II (tensile failure) at tangential force of 66 g.

4.5.2. Scratching speed

Because surface shear yielding is the mechanism of type I scratches, it is expected that scratching speed will have an impact on type I scratch initiation by raising or lowering shear yield stress. Indeed, it was found that the critical tangential force for bare PET film increases as scratch speed increases. Table IV shows that the critical tangential forces for initiation of type I scratches of PET film increase as scratching speed increases. Therefore, high scratching speed may cause ductile to brittle transition of a material and ultimately result in transitions from type I to type II scratches.

4.5.3. Environment

Like scratching speed, variables which can change the shear yield stress of a material, such as relative



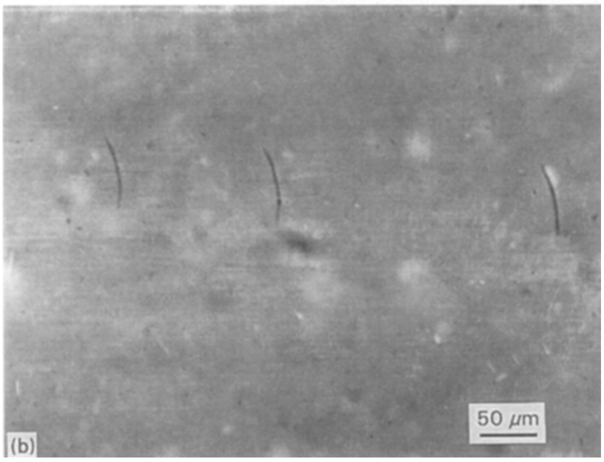


Figure 10 Effect of spherical styli sizes on scratch morphologies. (a) Type I scratch of 47.5×10^3 PS with a 75 μm radius stylus at 30 g normal load, (b) type II scratches of 47.5×10^3 PS with a 584 μm radius stylus at 270 g normal load.

humidity and temperature, may cause transitions between types I and II scratches. For instance, at 50% RH, gelatin shows type I scratches (Fig. 1b) while at 5% RH (Fig. 2b) it shows type II scratches. This is due to the increase of yield stress of gelatin at low relative humidities [20].

4.5.4. Effect of stylus size

When the 75 μm radius spherical stylus was used to scratch a polystyrene film of 47.5×10^3 molecular weight, the film showed ductile behaviour (type I scratches) (see Fig. 10). However, when a 584 μm radius spherical stylus was used to scratch the same polystyrene film, the film showed brittle behaviour (type II scratches) (see Fig. 2b). The effect of stylus size can be understood as the dependence of stress distribution around a stylus on the geometry of the stylus. The difference between maximum tensile stress behind a stylus and the maximum shear stress in front of a stylus is crucial to determine the deformation mechanism during scratching [21]. Therefore, the scratch performance of a material can undergo a ductile to brittle transition depending on the size of a stylus.

In fact, scratch performance has many variables. It should be emphasized that all these mechanisms discussed are only operating in the case of surface contact with a blunt spherical asperity, and the asperity is sensitive to the presence of lubricants. Therefore, it is important to understand that there is no simple way to rank the scratch resistance of a material. Parameters such as speed, amount of lubricants, the level of normal loading, geometry and size of an asperity, and various material properties (hardness, break stress, shear yield stress) all have an influence on the final scratch performance of a material.

5. Conclusion

There are four different kinds of scratch morphology developed when a blunt spherical stylus is in contact with a surface in relative motion. The main deformation mechanisms are surface shear yielding, surface cracking, subsurface yielding (indentation), delamination and combinations of these four. The material properties involved in these mechanisms are basically surface shear yield stress, surface failure stress, and material hardness.

Because the mechanisms associated with blunt spherical styli are controlled by friction, the critical normal load at which a scratch is initiated is not representative to the true material scratch resistance.

Lubricants can improve the material scratch performance by reducing the friction force at a given normal load. Many variables such as scratching speed, environment and stylus size can affect material scratching performance to a large degree.

Acknowledgements

We thank Mr E. Olear and Mr S. Pratt for their excellent AFM and SEM work, Mr J. Carroll, Mr R. Steinmetz, Dr M. Orem, Mr G. Pino and Mr J. Sedita for their assistances in experiments, and Dr J. Pochan, Professor J. C. M. Li, University of Rochester, and Dr L. Shaw-Klein, for stimulating discussions of scratch mechanisms.

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Received 7 September 1995
and accepted 15 January 1996