Scratching of polymeric coatings: experimental study and mechanical analysis

I. Demirci, C. Gauthier & R. Schirrer
Institut Charles Sadron, CNRS UPR 22, Strasbourg, France

Abstract

Coating with polymers is a common way of improving the scratch resistance of polymeric glasses. It is generally accepted that the critical load generating the first damage in a scratch test is representative of the behaviour of the coating. As the properties of polymers are time and temperature dependent, a single value of the critical load nevertheless cannot describe the overall mechanical response. A new scratch apparatus has been built that allows scratching velocities in the range 1 to \(10^4\) \(\mu\)m/s at temperatures varying from -70 to +120°C. The unique feature of this experimental set-up is a built-in imaging system to record real-time pictures of the in-situ contact during scratching. Damage to the coating can thus be observed during the process. In the case of optical coatings, if damage occurs then cracking appears before flaking, irrespective of the quality of the adhesion between substrate and coating. The flaking mechanism has been found to depend on the quality of the layer adhesion. However, the damage mechanism is not related to the adhesion in a simple way. It has also been observed that cracking of the coating appears within the contact area and King and Sullivan have predicted that this behaviour will be obtained when the ratio of the elastic modulus of the coating to that of the substrate is 2. Scratching of polymeric coatings was studied over wide ranges of tip velocity and temperature to find a set of critical parameters controlling the onset of damage. The ratio of the contact radius to the radius of the tip proved to be a pertinent parameter, which indicates that the mean strain in the contact area at the onset of damage does not depend on the scratch velocity or temperature.

1 Introduction

Most polymeric glasses are sensitive to scratching and coating is a common way of improving the scratch behaviour of these materials. The first solution found to
reduce this scratch sensitivity was to deposit a mineral coating on the surface of the polymer. The large difference between the elastic strain domains of the substrate and coating is one explanation for the low success of this procedure. A second generation of coatings used polysiloxane and acrylic materials. Here the scratch resistance is given by the hardness of the coat and the coatings have elastic strain domains in the same range as the substrate. The last generation of anti-scratch coatings has employed nano-materials, where an organic matrix is filled with nano-sized particles of silica. Most existing models describing the wear behaviour of such coatings use the concept of the critical load. This is the normal load applied to a tip sliding over the surface of the coat which generates the first damage (cracking or flaking). As the mechanical properties of polymers are time and temperature dependent, a single value of the critical load cannot describe the overall mechanical response. Hence we have built an apparatus to investigate the scratch properties of polymers over a temperature range of $-70 \text{ to } +120^\circ\text{C}$ and scratching speeds of $1 \text{ to } 10^4 \mu\text{m/s}$. In the case of transparent polymers, the scratch may be viewed with a microscope during the scratching procedure. When the geometry of the grooves left on the surface was examined as a function of tip speed and temperature, the scratch behaviour proved to be similar to that of indentation [1]. Transitions from viscoplastic scratching to elastic sliding were observed and temperature, strain and strain rate were found to be important parameters controlling the type of scratching on polymers. The importance of the difference between the yield scratch hardness and contact pressure was demonstrated and these parameters were compared to the yield stress. To predict the rear contact area during sliding contact, the elastic plastic depth of a groove was split into its elastic and plastic components. The strain and strain rate during contact had to be taken into account to predict this area and three domains were apparent, corresponding to an elastic, elastic plastic or fully plastic response of the material [2]. The aim of this paper is to present an analysis of the scratch behaviour of ophthalmic organic coatings, after briefly recalling the scratch properties of polymeric materials.

2 Mechanical response of the bulk polymer surface

The majority of existing models describing the scratch properties of materials take into account forces acting at the interface between the material and a grooving tip, but do not consider the stress and strain properties of the material beneath or ahead of the tip. In the case of polymer scratches, most models do not take into account the viscoelastic viscoplastic behaviour of the material. Briscoe and Thomas [3] and Gauthier and Schirrer [1] have shown that an analysis of the viscoplastic response of the surface of a material requires an evaluation of the strain and strain rate during contact. The average value of the strain rate $\dot{\varepsilon}$ may generally be simply estimated as the tip speed divided by the groove width, while the mean strain is proportional to the ratio of the radius of the surface contact area to the radius of the tip. The mechanical properties of polymeric materials are usually stress and temperature activated and follow an Arrhenius process at temperatures below the glass transition. Therefore, the mechanism
may be described by an equation based on concepts similar to those of Eyring, relating the strain rate and temperature to the material properties:

$$\dot{\varepsilon} = A e \left( \frac{-E_a}{kT} \right) e^{\frac{V_\sigma}{kT}}$$

where $A$ is a constant, $E_a$ the activation energy, $T$ the temperature, $V_\sigma$ the activation volume, $k$ the Boltzmann constant and $\sigma$ a material property. Once the activation volume and energy are known, experiments performed at any temperature and strain rate may be plotted on a single master curve at 20°C.

Figure 1 (left). Contact pressure and yield stress versus strain rate, with in-situ photographs showing typical responses. In this experiment, the normal load was 0.5N, the tip was a 120° cone with a tip radius of 200µm, the temperature was 100°C and the sliding speed ranged from $1E^{-4}$ to 15 mm/s.

Figure 2 (right). Contact pressure normalised to the yield stress versus normalised strain.

Temperature, load and radius of the grooving tip may be adjusted to scan a wide range of the ratio of contact radius to tip radius in order to study the scratch behaviour of polymeric materials. To obtain a transition from viscoplastic scratching to viscoelastic sliding, the mean strain is adjusted to a few percent by varying the normal load on the tip and hence the radius of the contact area. Since the material is viscoelastic and viscoplastic and the normal load constant, an increase in tip speed decreases the contact radius and also the mean strain. The same transition may be obtained at a lower temperature by adjusting the strain and strain rate. The geometry of the true contact area, which at high strain and low strain rate is the front half of a disc, is modified as the sliding speed of the tip increases. At intermediate sliding speeds, the matter compressed in front of the tip does not generate a pad and the edges of the groove left on the surface do not lie parallel. The groove relaxes within a time lapse comparable to the contact time of the tip. At higher sliding speeds, the deformation of the surface recovers almost instantaneously and the contact area becomes quasi-symmetric. The contact pressure is the ratio of the normal load to the true contact area, which is the sum of the front and rear areas, while the yield stress can be estimated in the same temperature and velocity range from previous results for a conical tip [1].
Figure 1 shows the contact pressure and yield stress versus the strain rate during a scratching transition, together with three typical photographs. If the yield stress increases linearly with the logarithm of the strain rate as predicted by Eyring’s law, the contact pressure does not increase linearly and is insufficient to describe the response of the material: the nature of the deformation under the sliding tip has changed from plastic to elastic.

The ratio of the contact pressure to the yield stress, the normalised contact pressure, provides information about the nature of the response because when the mean contact strain is normalised to the yield stress, the time and temperature dependencies are masked and this ratio depends only on the strain in the contact area. In elastic static contact, yield occurs when the normalised contact pressure is equal to 1.1 [5]. At the onset of plasticity of the response, the maximum contact pressure is 1.5 times the mean strain, while at full plasticity the contact pressure is by assumption equal to the maximum pressure at the beginning of plasticity:

\[ p_{\text{mean}} = p_o = 1.1 \frac{3}{2} \sigma_{\text{yield}} = 1.65 \sigma_{\text{yield}} \]

Thus plasticity appears when the normalised contact pressure exceeds 1.65. Three domains of stress response can then be identified: elastic, elastic plastic and plastic. In elastic static normal contact, the solution of the normalised contact pressure for a spherical tip is:

\[ \frac{P_m}{\sigma_{\text{yield}}} = \frac{4}{3 \pi (1-\nu^2)} \frac{E}{\sigma_{\text{yield}}} a \frac{1}{R} \]

It is important to note that the ratio \( E/\sigma_{\text{yield}} \) does not depend on time and temperature because the same molecular mechanisms act on these material properties. There exists, between the onset of plasticity and the appearance of full plasticity around the tip or under the contact area, a regime where superposition of the plastic contribution on the elastic plastic response influences the deformation and contact pressure. Johnson [5] has correlated the indentation process with the expansion of a plastic half core in an elastic plastic material by extending the theory of Hill [6]. In the case of an elastic plastic response and a conical tip, the model gives:

\[ \frac{P_{\text{yield}}}{\sigma_y} = \frac{2}{3} \left[ 1 + \ln \left( \frac{E \tan \beta + 4(1-\nu)}{6(1-\nu)} \sigma_{\text{yield}} a \frac{1}{R} \right) \right] \]

while for full plasticity around a spherical tip, it takes the form:

\[ \frac{P_{\text{yield}}}{\sigma_y} = \frac{2}{3} \left[ 1 + \ln \left( \frac{E a}{3 \sigma_{\text{yield}} R} \right) \right] \]

Scratching may be defined as tangential indentation and the radial elastic plastic expansion of a half core transposed to the tangential expansion of a plastic quarter core. During the transition from elastic sliding to plastic scratching, the normalised mean contact pressure increases from 1.1 to 1.65, while at the same
time the geometry of the contact area decreases from a full disc to close to a half disc. A geometrical parameter $\alpha$ can be defined, the ratio of the true contact area to the full disc contact area, which provides an index of the elastic ($\alpha=1$) or plastic ($\alpha=0.5$) response of the surface. We have proposed taking into account this variation of the geometry [7] in order to correct the estimation of the normalised mean strain during sliding contact:

$$\lambda_{\text{sliding}} = \frac{1}{2\alpha} \frac{E^*}{\sigma_{\text{yield}}} \frac{a}{R}$$

The normalised mean strain in static contact remains:

$$\lambda_{\text{static}} = \frac{E^*}{\sigma_{\text{yield}}} \frac{a}{R}$$

One observes good correlation between the normal static laws and tangential experimental data (Figure 2) provided the normalised elastic and plastic mean stresses are expressed respectively as:

$$\frac{P_{\text{mean}}}{\sigma_{\text{yield}}} = \frac{4}{3\pi} \lambda$$

$$\frac{P_{\text{yield}}}{\sigma_{\text{yield}}} = \frac{2}{3} \left[ 1 + \ln \frac{2}{3} \right]$$

Transitions from viscoplastic scratching to elastic sliding have been investigated and temperature, strain and strain rate found to be important parameters to control and predict the type of scratching on viscoelastic viscoplastic materials like polymers. Experimental data for the normalised contact pressure on a viscoelastic viscoplastic material are easily plotted as a function of the normalised mean strain (Figure 2).

### 3 Scratch resistant coatings

#### 3.1 How does an organic coating act?

Since the ratio of the elastic modulus to the yield stress is typically about 30 for amorphous polymers, it is easy to control the mechanical response (elastic, elastic plastic or plastic) of a surface submitted to the action of a sliding rigid tip by adjusting the radius of the tip (or its contact width through the normal load) so as to adjust the ratio $\lambda$.

At a given tip radius, increasing the scratch resistance is equivalent to introducing an elastic contribution into a fully plastic response or to increasing the elastic component in an elastic plastic response. There are three ways to improve the scratch resistance:

-1 by decreasing the ratio $E/\sigma_{\text{yield}}$, although this carries the major risk of decreasing the Young’s modulus with subsequent loss of the macroscopic mechanical properties of the structure. One may note that an elastomeric
material, which has a low $E/\sigma_{yield}$ ratio, is not sensitive to scratching but only to cutting and cracking.

-2 by introducing a strain-hardening effect into the stress/strain relationship of the bulk material, which is a means of increasing the elastic unloading in an elastic plastic strain [8].

-3 by coating the material. In the case of a thin coating (less than 10\(\mu\)m for a contact width of typically 100\(\mu\)m), it will not modify the global mechanical response of the contact. The coating will however hinder the roughness of the micro-scratches created by the tip at the surface of the macro-groove. Since the absence of micro-scratches is a condition for relaxation of the macro-groove, the thickness of the coat must be greater than the roughness of the tip. Figure 3 shows a number of in-situ photographs for an organic coating of variable thickness deposited on ophthalmic glasses. The sliding tip was a ball with a radius of 100\(\mu\)m, a mean square roughness Ra of 0.43\(\mu\)m and a maximum roughness Rt of 2.5\(\mu\)m. The recovery of the groove and the symmetry of the contact area may be estimated in terms of an angle $\omega$ varying from 0 (scratching) to $\pi/2$ (elastic sliding). When the thickness of the coat exceeds the total roughness of the sliding tip (> 2.5\(\mu\)m), there is no micro-scratch along the macro-groove, $\omega$ increases and the groove can relax easily.

![Figure 3: Role of the thickness of the coating. The symmetry of the true contact area (angle $\omega$) increases with the thickness of the coating. When this thickness exceeds the total roughness of the sliding tip, there is no micro-scratch along the macro-groove and the groove can relax.](image)

### 3.2 Analysis of the scratch behaviour of a coating

It is generally accepted that the critical load generating the first damage in a scratch test is representative of the behaviour of a coating. During the test, the
normal load applied to the moving tip, which is sliding at constant speed over the surface of the material, increases step by step or continuously. In the case of a brittle coating, this critical load can give an indication of the quality of its adhesion or toughness, depending on where the first crack starts. As a general rule, however, substrate and coating are not transparent and it is difficult to locate the start of this first crack. Mechanical analyses have been performed, assuming that the interface is submitted to a shear stress, but the adhesion of the coating has never been correlated with the critical load [9]. Moreover, for viscoelastic viscoplastic materials, a single value of the critical load cannot describe the overall mechanical response of a coating. The aim of this work was thus to identify a set of critical parameters controlling the onset of damage, using information obtained by in-situ observation of the true contact area.

3.2.1 Experimental procedure
The material was an amorphous polymer termed CR39 (diethylene glycol bis(allyl carbonate)). CR39 is a thermoset resin cast over a period of 20 hours using a specific temperature cycle (20 to 100°C). The Young’s modulus of this resin is typically 2 GPa at 20°C and 1 Hz. The coating was a spin coating of a nano-composite material, a thermoset matrix filled to about 20% of its volume with sub-micron silica particles (typically 10 nm in diameter). The Young’s modulus of this coating is about 4 GPa at 20°C and 1 Hz. As it is partially filled with mineral particles, it does not have a very marked time or temperature dependency. Coats of different thickness were tested and the present results concern principally the thickness of 5.32 μm. Scratches were made with ball tips having a radius of 30 or 100 μm, using the apparatus described in [1] and [2]. Experiments were performed at various normal loads, sliding speeds and temperatures. After setting the experimental conditions (temperature, sliding speed and geometry of the tip), a first scratch was made to find the critical normal load triggering cracking of the coating. In each test, the moving tip started at 1 μm/s and its speed was increased stepwise.

3.2.2 Mechanical analysis
Cracking disappears at a critical sliding speed and Figure 4 shows this transition. This critical speed depends on the normal load applied to the tip for given values of the temperature and tip radius.

Figure 4: Transition from cracking to smooth grooving at constant normal load.

Values of the apparent friction coefficient (ratio of the tangential and normal loads), elastic modulus, contact pressure and contact radius change during the test and these variations are not independent. The apparent friction coefficient
and normal load are not pertinent to the behaviour of the coating. Figure 5 shows this friction coefficient as a function of the sliding speed for two values of the normal load. Cracking transitions may appear at different normal loads, while the apparent friction coefficient presents no significant variations.

![Friction Coefficient vs. Sliding Speed](image1)

**Figure 5 (left).** Apparent friction coefficient versus sliding speed for different normal loads.

**Figure 6 (right).** Inverse of the distance between two successive cracks versus sliding speed.

Two other parameters may be defined, the length of the cracks and the distance between two consecutive cracks. The distance between successive cracks is very regular and seems to depend on the temperature and the thickness of the coating. Analysis of the inverse of this distance is preferable with 1/d equal to zero if there is no cracking. In a first analysis, cracking appears to depend on the sliding speed (Figure 6). In fact, for a given tip radius, a cracking transition is always observed at the same contact width, whatever the normal load. The distance between two consecutive cracks increases with temperature, whereas the contact width at the cracking transition remains constant. Figure 7 shows the inverse of the distance between successive cracks as a function of the contact radius normalised to the radius of the tip for one thickness of the coating, two tip radii (30 and 100μm) and wide ranges of temperature, tip velocity and normal load. The boundary of the cracking domain is easily discerned: cracking occurs if the normalised contact radius is greater than a critical value, proportional to the contact strain (a). Hence the mechanical behaviour of a coating on a viscoelastic material should not be analysed in terms of the critical load (or contact pressure) but in terms of the form of the strain field given by the ratio a/R, modified by the effect of the true friction between the moving tip and the coat. The present experimental results may be compared with the predictions of O’Sullivan and King [10], who performed a simulation of the sliding contact stress field on a layered elastic body. In cases where the ratio of the Young’s modulus of the coating to that of the substrate was equal to 2, their calculations predicted that the tensile stress in the sliding direction and the Von Mises stress would be highest under the tip in the contact area, near the rear border. Figure 8 shows an in-situ photograph where cracking appears in the rear contact area.
Figure 7: Inverse of the distance between two consecutive cracks versus normalised contact radius. Cracking of the coating appears for a critical value of the normalised contact width.

Figure 8: Crack propagation starts in the rear part of the contact area.
4 Conclusion

The present work shows that a single value of the critical load cannot describe the damage response of a coating on a polymeric material. In the case of a time and temperature dependent material, the strain/stress relationship may be plotted if these parameters are normalised. Whatever the sliding speed, the normal load, the geometry of the tip or the temperature, cracking appears when the ratio $a/R$ exceeds a critical value.

References


