Measuring the Mechanical Properties of Ground Ophthalmic Polymer Surfaces Using Nanoindentation

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Abstract. This work is motivated by the need to efficiently machine the edges of ophthalmic polymer lenses for mounting in spectacle or instrument frames. The polymer materials used are required to have suitable optical characteristics such high refractive index and Abbe number, combined with low density and high scratch and impact resistance. Edge surface finish is an important aesthetic consideration; its quality is governed by the material removal operation and the physical properties of the material being processed. The wear behaviour of polymer materials is not as straightforward as for other materials due to their molecular and structural complexity, not to mention their time-dependent properties. Four commercial ophthalmic polymers have been studied in this work using nanoindentation techniques which are evaluated as tools for probing surface mechanical properties in order to better understand the grinding response of polymer materials.

Introduction

Bulk and surface properties of materials are of particular interest to tribologists who aim to understand their influence on friction and wear behaviour of sliding contacts under varying environmental, kinematic and loading conditions. The wear of metals and ceramics is dominated by yield strength and fracture toughness. For polymer materials (plastics) wear is further complicated by their unique molecular structure and rheological response. Therefore, the application of conventional models is usually inadequate to describe the behaviour of most polymers.

This raises the question: How can manufacturing techniques traditionally reserved for workpieces made from metals and ceramics be also applied to polymer plastics? The number of studies on polymer response to indentation and scratching has accelerated in recent times to answer such questions [1,2]. Among manufacturing techniques, few are as versatile yet complex as grinding. The small scale and complexity, not to mention the statistical nature of interactions, make separation of variables a challenging task. The ability to study material response by means of highly controlled individual indentations and scratches is proving of great value in untangling the complex web of cause and effect in grinding behaviour.

In this work nanoindentation techniques are used to study the mechanical behaviour of four ophthalmic polymer materials used in the manufacture of eyewear lenses, as summarized in Table 1 (see over). These are: polycarbonate, Trivex (polyurethane-polyurea mix), CR39 (allyl diglycol carbonate based), and MHI (thiourethane based). It is necessary to grind and polish the lens edges to match eyewear frames. The aim is to be able to optimize material removal efficiency and finish quality based on the mechanical properties of the lens material, resulting in faster production, minimal wastage and less reliance on trial and error.

To this end, indentation techniques were used to obtain basic measures of material hardness and visco-elasticity. These results were studied to identify the main differences between the materials tested. Scratch tests were also performed on the materials to further elucidate their response to grinding.

Table 1. Summary of ophthalmic polymers tested.

Type (Abbr.)	Typical constituent	Refractive Index n_d	Abbe value V_d	Density ρ [g/cm^3]	UV cutoff [nm]	Note
CR39 (CR)	Di-allyl diglycol carbonate	1.50	59	1.3	355	Low cost thermoset, highest uncoated scratch resistance, high Abbe value (E=2.3 GPa, ν=0.35) [3]
Trivex (TVX)	Polyurethane-polyurea	1.53	43-45	1.1	380	Ease of drilling and machining, low density, easily tinted, thermoset
Poly-carbonate (PC)	Bisphenol-A polycarbonate	1.59	30	1.2	385	Scratches easily, shatter resistant, thermoplastic (E=2.5 GPa, ν=0.4) [3]
High Index Material (MHI)	Thiourethane	1.60-1.74	32-42	1.3-1.5	380-400	High RI, shatter resistant, thermoset

Theory and Development

Grinding is a dynamic stochastic process. The density, size and shape of the grinding tips are highly variable. The tips can be reasonably approximated, on average, as a hyperbolic body of revolution [4]. The nature of damage is determined by the workpiece material properties and the strain induced by the asperity, which is closely related to its geometry. Zum Gahr [5] classifies wear into four categories: micro-ploughing, micro-cutting, micro-fatigue and micro-cracking. In micro-ploughing, material is plastically deformed either side of the groove without detachment. The other extreme is micro-cutting, which gives rise to limited plastic deformation of the surrounding workpiece material. In ductile materials wear resistance is governed by hardness and their capacity to undergo significant plastic deformation. Fracture toughness tends to dominate over hardness in controlling the material removal rates of brittle materials.

Polymer materials require special consideration, insofar as their wear resistance is governed by ultimate tensile strength and ductility; the latter in particular makes chip formation difficult. Some polymers exhibit high capacity to accommodate elastic strain (high resilience) which makes them scratch resistant; however wear resistance may still be poor if ductility and ultimate strength are sacrificed. Polymer materials also exhibit significant visco-elastic and visco-plastic (creep) behaviour which is linked to their amorphous structure. They also possess low thermal conductivity and low melting temperatures which increase the risk of thermal damage during grinding and polishing; this usually leads to unacceptable surface finish and ultimately, wastage of time and resources. In summary, the benefit of being able to meaningfully characterize the complex behaviour of polymer materials is evident. The possibility of using nanoindentation to achieve this objective is investigated in this work.

Quasi-static hardness and elastic modulus. For the UMIS 2000 instrument used in this work, a typical indentation in bulk material is of the order of 500 nm in diameter. Displacement can be measured from 0-20 µm with resolution the order of 0.003 nm (0.05 nm noise floor) at 2.0 µm full-scale. Force applied can range from 0 to 500 mN with resolution 0.025 µN (0.75 µN noise floor) at 50 mN full-scale.

The measurement of elastic modulus and hardness was achieved by the Oliver and Pharr method [6]; based on Sneddon's equation it relates indenter load P and penetration depth h as follows:

$$P = \frac{2}{\pi} E^* \tan\alpha \, h^2 \tag{1}$$

where α is the half-included angle of the equivalent cone. For the Berkovich indenter the equivalent value α=70.3° [7]. The reduced elastic modulus E^*, defined as follows:

$$1/E^* = (1-\upsilon^2)/E + (1-\upsilon'^2)/E' \tag{2}$$

is a composite of the indenter (υ'=0.07, E'=1050 GPa for diamond) and specimen (υ, E) properties. The Poisson ratio υ of the specimen is required in order to obtain its elastic modulus. Quoted values of υ for thermoplastics and thermosets range from 0.35-0.40. A typical value υ=0.37 was used for all calculations in view of the fact that no values could be found in the literature for TVX and MHI.

The Oliver and Pharr method uses the elastic unloading data to calculate the elastic modulus and hardness of the specimen. It can be shown that the maximum tip penetration h_{max}, is given by:

$$h_{\max} = h_c + \varepsilon \frac{P_{\max}}{dP/dh\big|_{P_{\max}}} \tag{3}$$

from which the contact depth h_c is calculated, allowing the contact area A to be obtained from the indenter geometry. An intercept factor ε=0.75 is used for Berkovich indents. The shape factor β is a correction applied to E^* for non-axisymmetric indenters. For the Berkovich indenter, β=1.034.

The Meyer hardness H can finally be calculated by the relation $H=P/A$, and from Sneddon's equation the reduced elastic modulus E^* can also be calculated:

$$E^* = \frac{1}{2}\frac{dP}{dh}\sqrt{\frac{\pi}{A}} \tag{4}$$

Because of the visco-elastic/plastic nature of polymers the strain rate is very important in determining material properties. In other words, the material response is time dependant. Visco-elastic recovery can cause an increased or even negative slope of the unloading curve giving values of hardness and elasticity that are different from static values. Quasi-static values can be obtained by using very small loading rates. How low depends on the recovery time constant of the material. In this work, the issue was addressed by maintaining the maximum load constant for 30 seconds to allow the material to reach a near state of equilibrium.

Creep Characterization. Creep behaviour is an intrinsic material property that can be measured by observing the change in indenter depth over time for a constant loading force. The response can be modelled according to spring and dashpot models. In this work the Voigt 3-element visco-elastic model was chosen (Fig. 1 over) [7]. The square of the displacement is given by the expression:

$$h^2 = \tfrac{1}{2} P_o \cot\alpha [1/E_1^* + 1/E_2^* (1 - e^{-tE_2^*/\eta})] \tag{5}$$

where P_o is the applied force, E_1^* and E_2^* are the primary and secondary reduced elastic moduli (Pa), η is the viscosity constant (Pa·s), t is time (s) and α is the half angle of the conical indenter. Non-linear regression on the creep data is performed to identify the three material parameters.

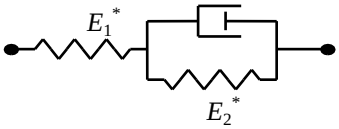


Fig. 1 Voigt 3-element model of visco-elastic material response.

From the model it is evident that energy is dissipated by the viscous component of the model. This is a fundamental property of the material that may affect its grinding response, since strain rates are governed by the kinematic motion and shape of the abrasive asperities. It is with this in mind that the visco-elastic material behaviour is obtained for each sample.

Experimental Details

Equipment. A UMIS 2000 (CSIRO, Australia) nanoindenter was used for the tests. Indentation and creep tests were performed using a diamond Berkovich indenter with area function calibration applied to all measurements to compensate for indenter geometry imperfection. All tests were conducted in an air-conditioned building at temperature of 24.0±0.2°C and relative humidity of 50-60%.

Sample Preparation. Machined ophthalmic lenses were provided by a third party, each circular and about 50 mm in diameter. Two of each type were provided, one highlighting good quality surface finish (suffixed “1”), the other a poor or unacceptable surface finish, as judged visually by the machinist (suffixed “2”). Examples of good and bad surfaces are shown in Fig. 2. A segment was cut off each sample and bonded with cyano-acrylate glue to a steel sample holder. For scratch testing the material was cut and polished with 15, 6, 3 and 1 µm diamond pastes.

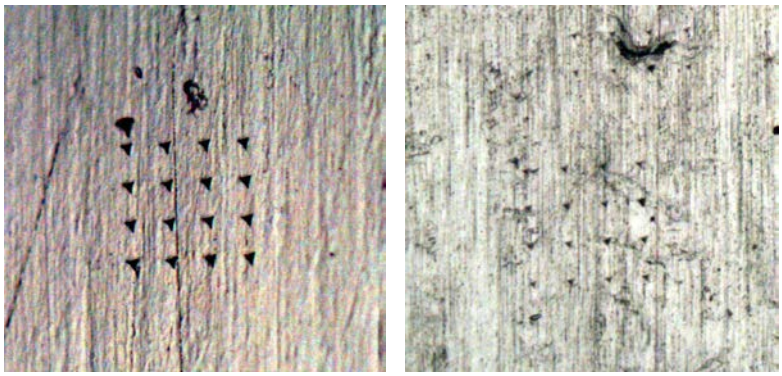

(a) (b)

Fig. 2 Square 100 µm array at 10 mN max load: (a) “good” quality PC1 surface, (b)“poor” quality MHI2 surface.

Indentation and Scratching Procedure. Each sample was indented with a 4 by 4 array for statistical averaging of the calculated properties at loads of 5 mN, 10 mN and 30 mN. The surface detection threshold was set at relatively high 50 nN to account for the difficulty of surface detection of polymers compared to metals and ceramics. The loading rate was approximately 0.5 mN/s for 5 and 10 mN maximum loads and 1.5 mN/s for the 30 mN load case. Once the maximum load was reached, it was kept constant for 30 seconds to log the creep response of the material. Upon completion, unloading followed at the same rate as loading.

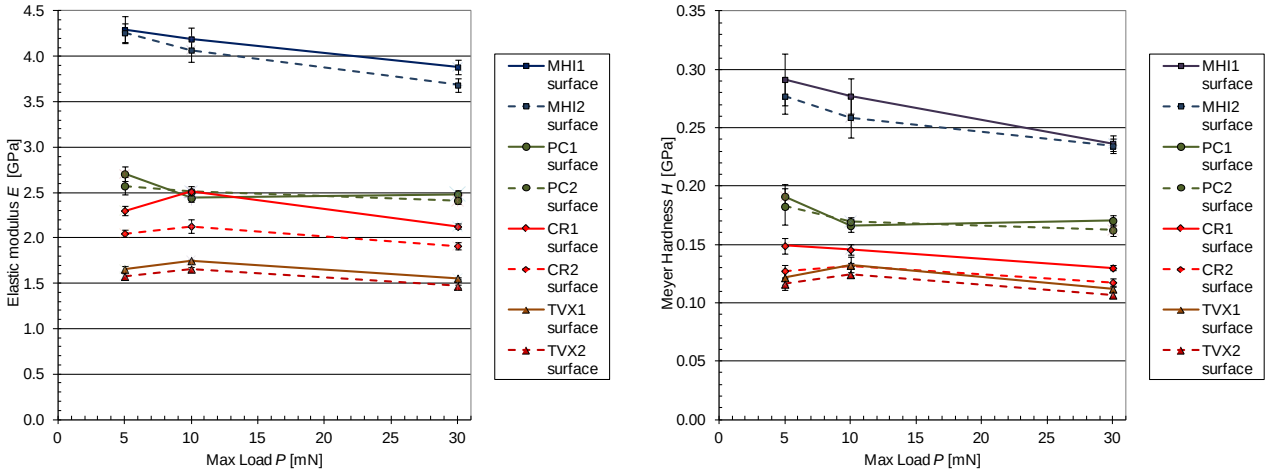
Scratching was performed with increasing load at 0.5 mN/s and sliding speed of 10 µm/s. Three scratches were performed with ramp amplitudes of 10, 20 and 30 mN. This was done to observe the progression of the scratch front with increasing force.

Parameter calculation. IBIS 2 software (Fischer-Cripps Laboratories, Australia) was used for data post-processing to obtain values for elasticity E, hardness H, and creep model parameters E_1^*,

E_2^* and η. Each variable was plotted on a separate chart to compare both good and bad samples at the three applied loads.

Results and Discussion

Quasi-static Properties. The quasi-static properties E and H are shown in Figs. 3(a) and (b) respectively. It is evident that MHI possesses highest values of both E and H, while TVX exhibits the lowest values. PC is higher than CR for both material properties and the values of E agree well with published data [3].



(a) (b)

Fig. 3 Quasi-static material properties: (a) elastic modulus and (b) Meyer hardness of four polymers. (Bars represent 95% confidence interval for the mean of a sample of 16 indentations.)

The purpose of testing two samples of each material was to see if the surface properties were noticeably modified by the quality of the surface finish. This might be expected if thermal damage was a dominant cause of the poor surface finish, particularly with the thermosets. Comparing "good" and "poor" samples, there is a general tendency for reduced E and H values for "poor" samples, particularly with CR (a thermoset) but less so with PC (a thermoplastic). Further tests are required to confirm the significance of this interesting phenomenon.

The effect of increasing maximum load is biased towards a decrease in E and H. At the maximum load of 30 mN, parameter variability is at its least, probably due to the fact that surface roughness has a diminished impact on the deformed volume compared to the smaller loads.

Creep Properties. The creep properties E_1^* and E_2^* and η are shown in Figs. 4(a), (b) and (c) respectively. The ranking of primary modulus E_1^* for the different materials is highly consistent with the quasi-static values for elastic modulus, as expected. When it comes to the visco-elastic properties there is an interesting reversal between MHI and PC, with PC exhibiting both greater secondary stiffness E_2^* and damping η. Little difference exists between CR and TVX.

Polycarbonate shows the highest value of viscosity which may be due to the fact that it is the only thermoplastic in the group. Lack of cross-linking means it can endure large plastic strains without fracture. As a result, it is also the least "scratch" resistant insofar as it is easy to leave a permanent marking on its surface. This should not be confused with wear resistance, which instead is governed by the ductility and ultimate tensile strength of polymer materials, both of which are relatively high for polycarbonate.

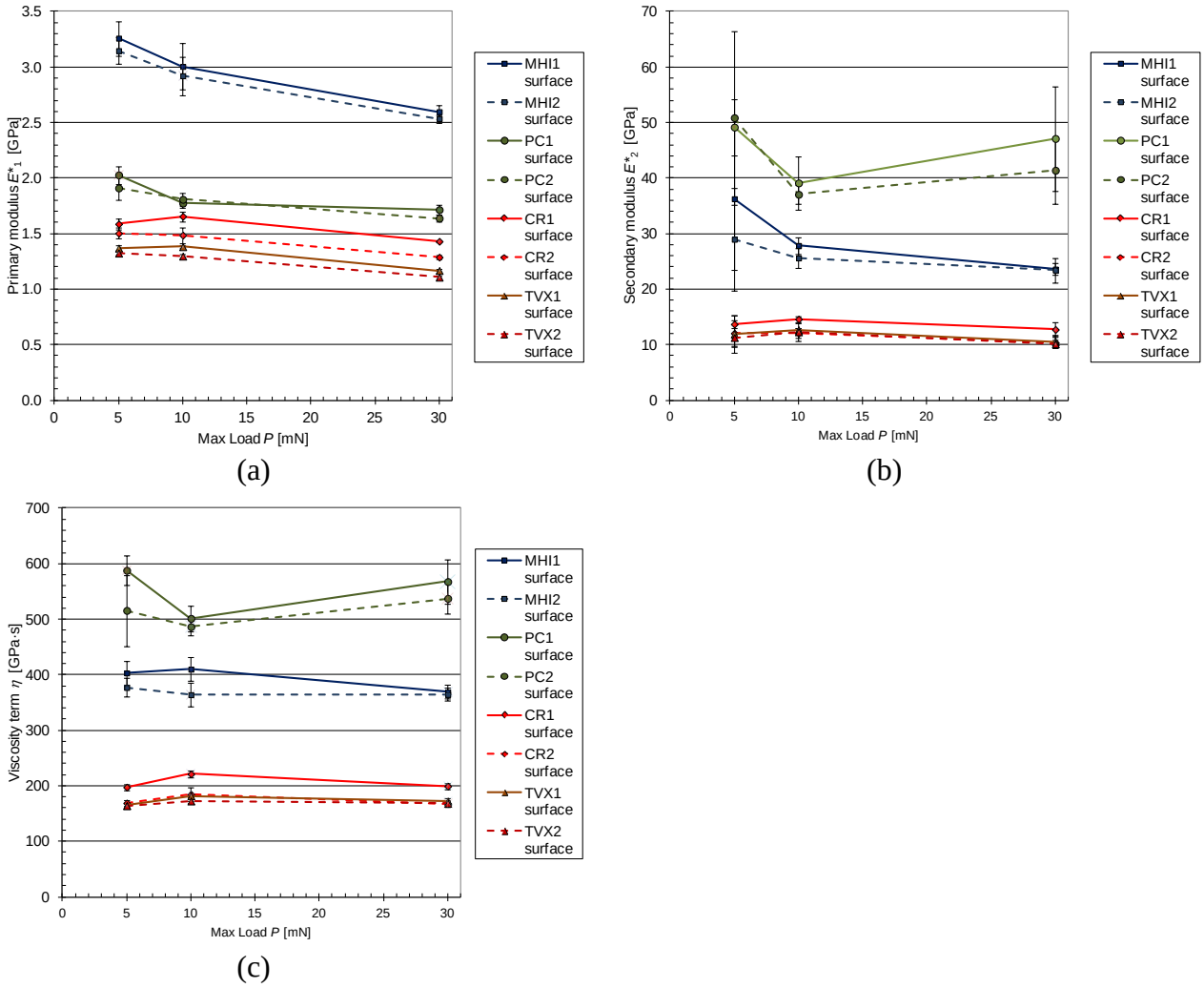
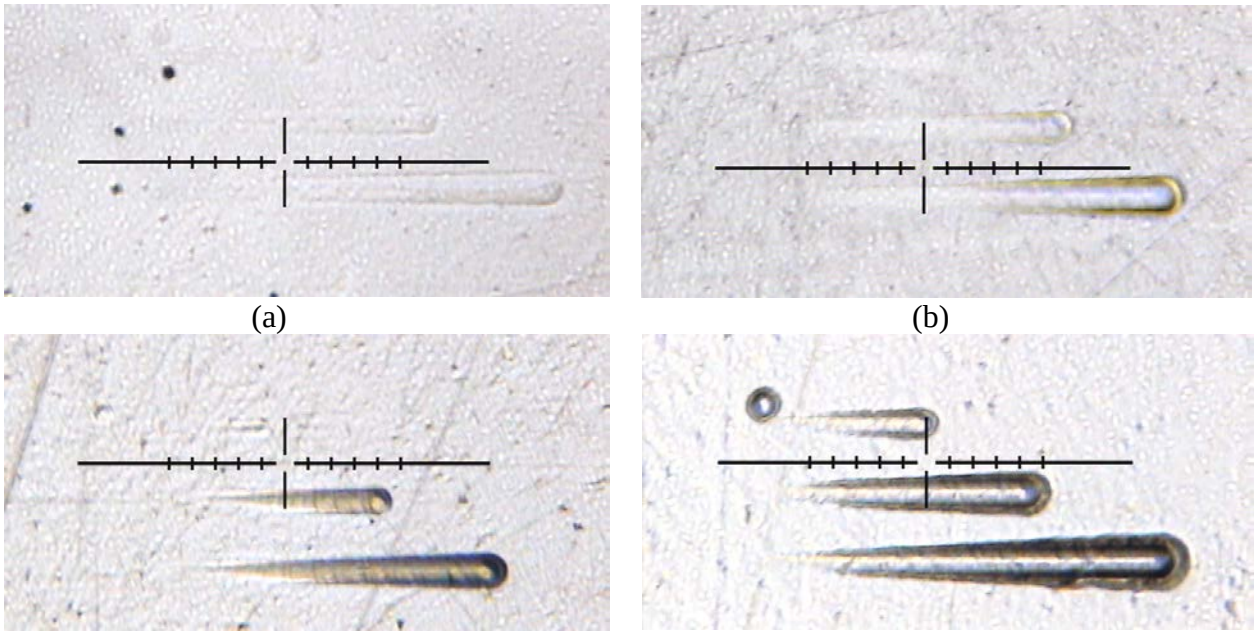


Fig. 4 Creep properties of four polymers: (a) primary modulus, (b) secondary modulus and (c) viscosity term.

The creep data can be used to obtain a creep relaxation time constant $t_c=\eta/E_2^*$ (seconds) for each material. This value ranges between 10 and 16 seconds for all materials; the similarity is rather surprising. Given the very high strain rates in grinding, it is arguable whether the creep properties play a dominant role in the grinding response of these materials.

Making the connection between creep properties obtained from nanoindentation and material behaviour in grinding and scratching remains a challenge. This may be due to the shortcomings of the Voigt 3-element model in separating elastic and plastic contributions to deformation. It is with this in mind that we complement indentation data with scratching experiments to help elucidate the response of polymer materials to scratching.

Scratch Response. The scratch response of polycarbonate (least scratch resistant) and CR39 (most scratch resistant) is illustrated in Fig. 5. Polycarbonate has high ductility and strength which makes it wear resistant, but its low resilience makes it easily scratched. On the other hand, CR39 has a high degree of elastic resilience which makes it scratch resistant, but its low tensile strength makes it easily machined. Trivex possesses similar properties to CR39 however it is slightly less scratch resistant. MHI offers good compromise of properties. It is a thermoset exhibiting high resilience and hardness which both contribute to its scratch and impact resistance.



(a) (b)

(c) (d)

Fig. 5 Scratches with a 10 µm radius tip. Ramped load 10, 20 and 30 mN. (a) CR39, (b) Trivex, (c) MHI, (d) polycarbonate. (Scale: 33 µm vertical separation between centreline of each scratch)

Conclusions

The following conclusions are drawn from the work conducted:

- Lens materials exhibit varying optical and mechanical properties, which must suit the desired application.
- Scratch resistance and wear resistance are different concepts.
- Scratch resistance is characterized by the extent of permanent deformation. In plastics it is governed by the ability to accommodate large elastic strains (resilience) e.g. CR39 and Trivex.
- Wear resistance is governed by ductility and ultimate tensile strength (toughness) e.g. polycarbonate.
- Quasi-static nanoindentation experiments provide limited information about scratch and wear resistance of polymers.
- Creep response provides additional insight into polymer material behaviour.
- High viscosity is a characteristic of the thermoplastic (polycarbonate) which is also the least scratch resistant.
- Low viscosity, hardness and stiffness are characteristics of the most scratch resistant materials (CR39 and Trivex).
- The high hardness and stiffness, but lower viscosity of MHI offers good qualities in terms of scratch and impact resistance.
- Scratch testing of polymers assists in developing a broader understanding of material properties.

Acknowledgments

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