 Ann Ophthalmol 1985;17:708–713

Lubrication and Surface Chemical Properties of Ophthalmic Solutions

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Surface chemical and lubrication parameters such as contact angle, surface tension, and coefficient of friction, together with viscosity, were measured for commercial ophthalmic solutions. A sensitive friction-testing instrument was employed to measure the coefficient of friction between low-energy polymeric surfaces, e.g., polymethylmethacrylate (PMMA). The viscosity of ten commercial tear substitutes employed in the present study ranged from 2 to 25 cp. The results showed that there is no correlation between the coefficient of friction and viscosity, surface tension, or contact angle of these tear substitutes. The coefficient of friction of tear substitutes appears to depend upon the structure, conformation, and adsorption characteristics of polymer as well as surface characteristics of sliding surfaces.

A systematic study was undertaken to evaluate the effect of speed and load on the coefficient of friction between different sliding surfaces, namely PMMA/nylon and PMMA/PMMA. The analysis of data established that our system was operating in the region of "boundary lubrication." In general, a PMMA/PMMA system exhibited a lower coefficient of friction as compared with the PMMA/nylon system.

Surface phenomena such as the spreading of meibomian oil at the air/tear interface, the kinetics of thinning of the tear film, the rate of evaporation of water from the tear film, and the lubrication of corneal surface and eyelid are pertinent to the normal blinking process. Most of these processes occur every time we blink.[1] It is generally believed that the dry-eye syndrome is related to an unstable tear film. The thickness of the tear film decreases to a very low value, resulting in the rupture of the film. This process results in the formation of dry spots on the surface of the cornea. It is likely that under these conditions, considerable friction develops between corneal and eyelid surfaces during the blinking process, resulting in discomfort or damage to the corneal surface (i.e., corneal abrasion), or both. Artificial tear substitutes containing polymers that would mimic the action of conjunctival mucin have been employed to stabilize the thick layer of water on the cornea.[2] Such ophthalmic solutions are also available for the purposes of wetting and cushioning of contact lenses in addition to their application to the mucin-deficient and aqueous-deficient states of the eye. Most ophthalmic solutions have been designed to have a strong affinity for the ocular surface, prolonged retention time, and low viscosity, since high viscosity fluids would result in blurring of the vision or a tendency to pull off epithelial filaments.

The critical role of viscosity in protection of the endothelium by intraocular agents, such as sodium hyaluronate (SH), methyl cellulose (MC), and chondroitin sulfate (CDS), was well described by Burch and associates.[3] According to these authors, low-viscosity (0.7 cp) preparations permit the lens to contact the endothelium, while high-viscosity (30,000 cp) ocular solutions exert excessive drag forces to the endothelium. Intermediate viscosity (10, 30, 100, 300 cp) preparations, employed as thin-layer coatings, provide optimal endothelial protection. It has been reported from the studies[4] of the flow dynamics and the thickness of tear film (employing a slit-lamp fluorophotometer) that the tear-film thickness decreases between blinks, presumably because of drainage or thinning process of the tear film. The thickness of the precorneal tear film (PTF), however, increases in the presence of surface-active polymers.[4] The observed increase in the thickness of PTF due to surface-active polymers may be attributed to a dragged boundary layer associated with spreading of a film at the air/tear interface.

The subject of lubrication is concerned with the art of reducing frictional resistance occurring between two sliding, solid surfaces. Any substance inserted between two sliding surfaces for the purposes of reducing the friction is called a lubricant. There are two types of operating conditions in lubrication, namely, boundary lubrication and hydrodynamic lubrication.[5] In the former case, the lubricant film cannot support the load, and contact occurs between the two surfaces.[5] In this case, the coefficient of friction

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decreases with viscosity and speed and increases with load. In the case of hydrodynamic lubrication, the two sliding surfaces are separated by a thin film of lubricant. The frictional drag is entirely due to the rheologic properties of the lubricant film. The coefficient of friction in this region[5] increases with viscosity and speed and decreases with load. The friction between the cornea and the lid has been assumed to be of the boundary type. The surfaces, in this case, are likely to contact each other.[6]

The purpose of this paper is to report surface chemical and lubrication properties of some commercial ophthalmic solutions.

Materials and Methods

Commercial Ophthalmic Solutions

The following ten commercial ophthalmic solutions have been employed in the study involving measurement of coefficient of friction, viscosity, contact angle, and surface tension: (1) Adsorbotear (Alcon); (2) Tears Plus (Allergan); (3) Lens Mate (Alcon); (4) Adapettes (Alcon); (5) Tear Gard (Bio Products Ophthalmics); (6) Tears Naturale (Alcon); (7) Muro Tears (Muro Pharmaceutical); (8) Neo-Tears (Barnes-Hind); (9) Hypotears (Coopervision); and (10) Liquifilm Tears (Allergan). The tear substitutes were obtained from their respective manufacturers or from retail stores.

The viscosity (η) of all solutions was measured with a viscometer. A contact-angle goniometer was used to measure the advancing contact angle (θ) of solutions at equilibrium (approximately three to five minutes after a drop is deposited), and a pressure transducer was employed to measure the surface tension (γ) by the Wilhelmy plate method. The contact angle is the angle formed between the edge of a drop of liquid and the surface upon which the drop is placed and is a measure of a solution's wetting ability. Water, for example, completely wets glass (e.g., quartz), which is a hydrophilic surface; consequently, the contact angle in this case is zero. Water will not completely wet PMMA and forms a contact angle of 65°. A solution is said to be nonwetting if its contact angle is greater than 90°. The coefficient of friction (μ) of the commercial tear substitutes was measured by a specially designed friction tester on different polymeric surfaces. The usefulness and capability of this instrument has already been successfully demonstrated by its sensitivity to low loading forces (1–10 g).[7] Friction measurements for these solutions at equilibrium were made approximately three to five minutes after the solution was delivered on the test surface. Vertical forces were applied to a nylon or a PMMA spherical stylus 0.25 inch in diameter, which runs in a track of lubricating solution applied to the rotating plate of PMMA. The plate rotates at constant speed with respect to the stylus. During the course of the experiment, the test solution is replenished every 1.5 minutes to maintain the same concentration of the solution. The values of the coefficient of friction were the average of at least six measurements of the same experiment. The standard deviation in the value of the coefficient of friction is not more than ±0.008.

Operating Procedure—Horizontal Force Measurement

The measuring circuit is stabilized by running the machine with its cover in place for about 30 minutes. The stylus is displaced horizontally in the direction of plate rotation applying definite force (0.1 g, etc.) by means of a spring scale when it is out of contact with the plate. This vertical force at a given sensitivity produces a corresponding horizontal component that can be registered and measured on a recorder chart. Coefficient of friction (μ) at a given vertical load and speed (under a set of experimental conditions) can be computed for a lubricant film from this calibration.

Vertical Force Adjustment

After installation of a clean specimen plate and stylus, the stylus is adjusted for a minimal clearance from the plate. In the dry condition, this can be achieved by lowering the stylus until no contact sound is heard when the stylus is depressed toward the plate. When the tear substitute is introduced, it will form a film whose upper surface will contact the stylus and, because of its viscosity, will produce a horizontal force when the plate is rotated. The horizontal component increases initially in a nonlinear fashion up to a certain load. Beyond this minimum load (1 or 2 g, which is required to bring the stylus in contact with the specimen plate) the horizontal force begins to increase linearly as a function of load. The coefficient of friction is determined as the slope of the linear portion of the plot between the increments of vertical force (ΔF_V) and horizontal force (ΔF_H), i.e.,

$$\mu = \frac{\Delta F_H}{\Delta F_V}$$

Results

In order to determine the accuracy of the method for measuring the coefficient of friction of the commercial solutions, the following technique was adopted. The experiment was carried out with a test solution on a PMMA plate at a uniform stylus velocity of 400 mm/sec (80.4 rev/min) with a constant load of 5 g. This experiment was repeated at least six times, and the measurements were made for the same test solution under similar set of conditions, but each on a different clean and dry PMMA plate (at least six plates). Reproducible data were obtained by this method on different PMMA plates, with a standard deviation of $\Delta\mu = \pm 0.008$.

Table I represents the data of coefficient of friction, viscosity, surface tension, and contant angle for the ten ophthalmic solutions, namely, (1) Adsorbotear; (2) Tears Plus; (3) Lens Mate; (4) Adapettes; (5) Tear

Table I Surface Chemical and Lubrication Properties of Various Ophthalmic Solutions

Commercial Tear Substitute	Coefficient of Friction* μ	Viscosity (cp) η	Surface Tension (dynes/cm) γ	Contact Angle of the Solution on Clean PMMA† θ
Adsorbotear (Alcon)	0.112	10.03	47.9	42°
Tears plus (Allergan)	0.121	4.52	46.4	50°
Lens mate (Alcon)	0.152	23.61	34.8	20°
Adapettes (Alcon)	0.153	2.13	60.0	52°
Tear gard (Bio Products Ophthalmics)	0.161	21.53	41.7	45°
Tears naturale (Alcon)	0.164	7.03	30.8	26°
Muro tears (Muro Pharmaceuticals)	0.172	2.34	35.5	29°
Neo-tears (Barnes-Hind)	0.184	15.51	48.8	39°
Hypotears (Coopervision)	0.191	2.43	38.6	40°
Liquifilm tears (Allergan)	0.213	3.91	45.0	46°

*Coefficient of friction was measured between PMMA plate and PMMA ball of 0.25 inch in radius at a stylus velocity of 400 mm/s (80.4 revs/min) with a vertical load of 5 g.
†PMMA = polymethyl methacrylate.

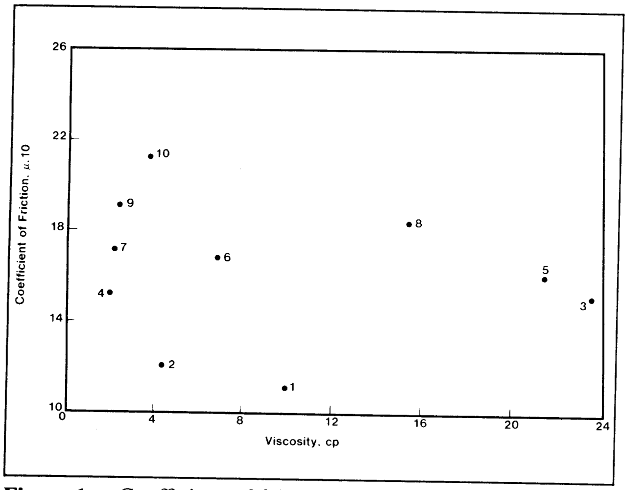

Figure 1. Coefficient of friction as a function of viscosity of various ophthalmic solutions between polymethylmethacrylate with a vertical load of 5 g at a speed of 400 mm/sec (stylus velocity). (1) Adsorbotear, (2) Tears Plus, (3) Lens Mate, (4) Adapettes, (5) Tear Gard, (6) Tears Naturale, (7) Muro Tears, (8) Neo-Tears, (9) Hypotears, (10) Liquifilm.

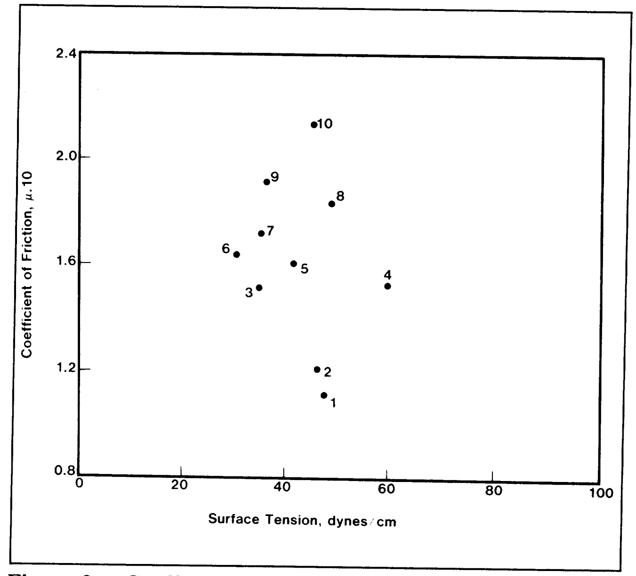

Figure 2. Coefficient of friction for polymethyl methacrylate surfaces as a function of surface tension for various ophthalmic solutions. (1) Adsorbotear, (2) Tears Plus, (3) Lens Mate, (4) Adapettes, (5) Tear Gard, (6) Tears Naturale, (7) Muro Tears, (8) Neo-Tears, (9) Hypotears, (10) Liquifilm.

Gard; (6) Tear Naturale; (7) Muro Tears; (8) Neo-Tears; (9) Hypotears; and (10) Liquifilm Tears.

Figure 1 shows the coefficient of friction (μ) of these commercial ophthalmic solutions and their corresponding viscosity (η) at a constant load of 5 g and a stylus velocity of 400 mm/sec (80.4 revs/min). It is seen from the data in the viscosity range studied that there is no correlation between the coefficients of friction and the corresponding viscosities of the ten ophthalmic solutions. In other words, the coefficients of friction of these ophthalmic solutions are independent of their viscosities.

Figures 2 and 3 reveal that there is no relationship between the coefficients of friction of these ophthalmic solutions and their corresponding values of surface tension and contact angle on clean and dry polymethylmethacrylate surface.

In contrast to our observation with regard to the coefficient of friction of the ophthalmic solutions and their nondependence on the corresponding values of viscosities, surface tension and contact angle, Benedetto and coworkers[8] demonstrated that the dynamic film thickness of the commercial ophthalmic solutions was strictly viscosity-dependent and did not depend upon

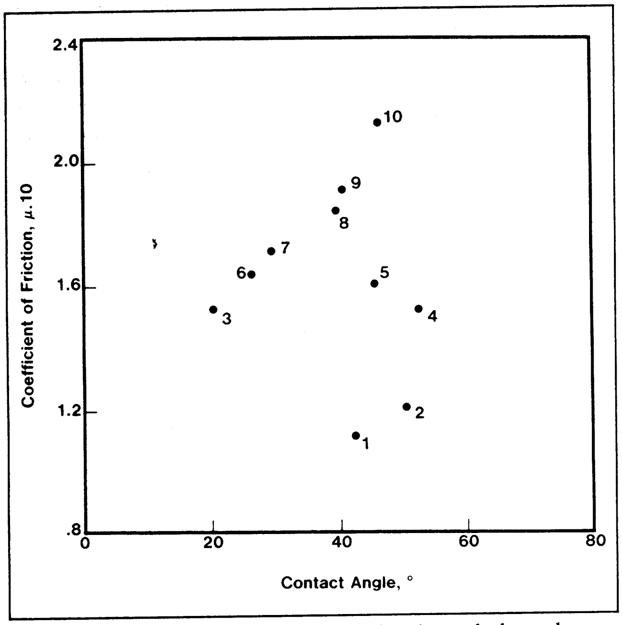

Figure 3. Coefficient of friction of polymethyl methacrylate surfaces as a function of contact angle for various ophthalmic solutions. (1) Adsorbotear, (2) Tear Plus, (3) Lens Mate, (4) Adapettes, (5) Tear Gard, (6) Tears Naturale, (7) Muro Tears, (8) Neo-Tears, (9) Hypotears, (10) Liquifilm.

Table II Coefficient of Friction μ Beteween PMMA and Nylon at Different Loads and Speeds of Tears Naturale

Vertical Load (g)	Coefficient of Friction μ at Speeds (Stylus Velocity mm/s)			
	400	500	600	700
5	0.183	0.180	0.176	0.174
10	0.180	0.176	0.173	0.170
15	0.177	0.173	0.170	0.167
20	0.175	0.170	0.167	0.165
25	0.171	0.166	0.164	0.161

PMMA = polymethylmethacrylate.

the contact angle or the surface upon which the solution was deposited. However, it was found that the thickness of the film increases as the surface tension of the solution decreases. The dynamic film thickness increases with the viscosity of the solutions having the same surface tension.[8]

Table II represents the data of coefficient of friction for Tears Naturale between PMMA plate and nylon sphere at different vertical loads (5, 10, 15, 20 and 25 g) and speeds (400, 500, 600, and 700 mm/sec). The analysis of the coefficient of friction (μ) data reveals that for a given test solution, Tears Naturale, the μ values decrease as the stylus velocity increases at a given vertical load. Figure 4 (Table II) demonstrates that the coefficient of friction (PMMA/nylon) for

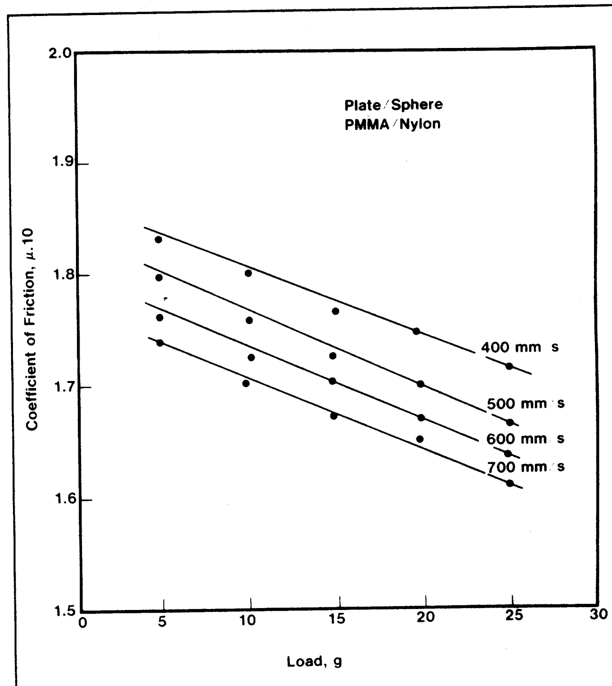

Figure 4. Coefficient of friction between polymethyl methacrylate/nylon at different loads and speeds for Tears Naturale.

Tears Naturale decreases with increasing speed at constant lubricant viscosity and load. This is the characteristic feature for a system in a region of boundary lubrication. Higher loads give lower values of coefficient of friction (Table II). For systems involving a constant area of contact, this observation would be rather anomalous, because speed and load should act in the opposite directions.[5] In our present system, however, the area of contact increases so rapidly with vertical load that doubling the load does not double the effective contact pressure. In other words, the effective contact pressure decreases rapidly as the load increases.[5] Figure 5 (Table III) shows the plots of coefficient of friction and the corresponding vertical loads at various uniform speeds, the test surfaces being PMMA and PMMA. These plots also demonstrate that the system is in the region of boundary lubrication.[5]

A comparison of results in Table II and III, obtained on different sets of sliding surfaces (namely, PMMA versus nylon and PMMA versus PMMA) for the same tear substitute reveals that a better lubrication is provided by the film for PMMA/PMMA rather than PMMA/nylon, perhaps because of the more effective adsorption occurring at these surfaces. In other words, the film formed between PMMA and PMMA is stable and uniform, producing lower friction, probably as a result of better adsorption of surface active ingredients of the ophthalmic solution on the sliding surfaces.

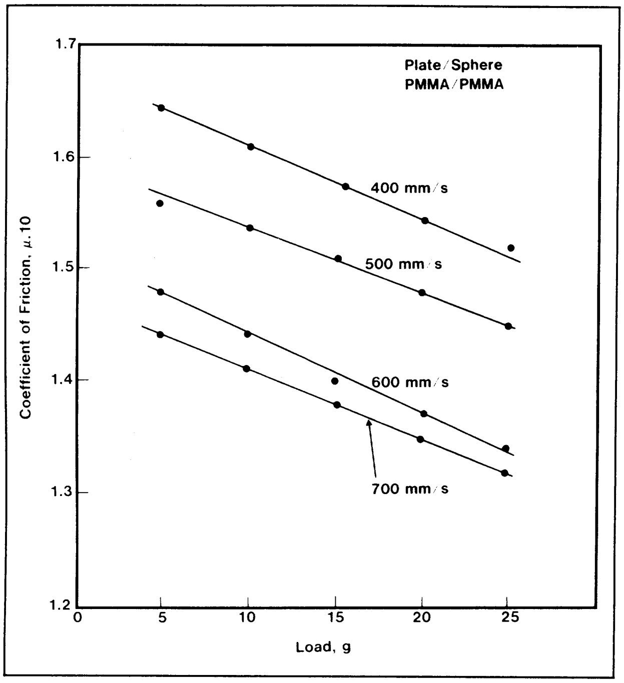

Figure 5. Coefficient of friction between polymethyl methacrylate/polymethyl methacrylate and speeds for Tears Naturale.

Discussion

The rationale behind employing low-energy model surfaces such as PMMA and nylon is to simulate a situation similar to that of the corneal surface with its critical surface tension (CST) of 28 dynes/cm.[9] Most of the low-energy surfaces employed in the present study have almost similar values of critical surface tension.[9]

The coefficient of friction is influenced by the state of the adsorbed film between the sliding surfaces (i.e., the structure and the conformation of the adsorbed macromolecules). The role of polymer in ophthalmic solutions is to increase the thickness and the stability of the tear film. Different polymers can adsorb at either the air-tear interface or the cornea-tear interface, or both.

It should be pointed out that ophthalmic solutions are prepared by employing blends of polymers and other components. The interaction among the ingredients of a formulation is likely to produce a combined effect that will strongly influence the surface properties, adsorption characteristics, and coefficient of friction.

In mucin-deficient states, the usefulness of surface properties is quite obvious.[10] The assumption that has been made is that a solution with low surface tension and small contact angle will have the best wetting properties on contact lens and ocular surfaces.[11]

It has been suggested[12] that the formulations of ophthalmic solutions should aim at having strong affinity for the ocular surface, prolonged retention time, and low viscosity, since high viscosities could have undesirable side effects, such as blurring of vision and the tendency to pull off epithelial filaments.

In summary, the results presented in this paper establish that commercially available ophthalmic solutions exhibit a broad range of values of the coefficient of friction from 0.11 to 0.21. It appears that the coefficient of friction is an intrinsic property that depends on the structure and conformation of the polymers; it does not show a direct correlation with viscosity, surface tension, or contact angle, and it depends on the components of ophthalmic solutions, the nature of the solid surfaces, and the experimental conditions (speed, load, etc).

Table III Coefficient of Friction μ Between PMMA and PMMA at Different Loads and Speeds for Tears Naturale

Vertical Load (g)	Coefficient of Friction μ at Speeds (Stylus Velocity mm/s)			
	400	500	600	700
5	0.164	0.156	0.148	0.144
10	0.161	0.154	0.144	0.141
15	0.158	0.151	0.140	0.138
20	0.154	0.148	0.137	0.135
25	0.152	0.145	0.134	0.132

PMMA = polymethyl methacrylate.

Acknowledgment

Alcon Laboratories, Inc, Fort Worth, Texas, provided the research grant that enabled the authors to undertake this project.

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