ADSORPTION OF POLYMERS ON CONTACT LENS SURFACES IN RELATION TO BIOLUBRICATION

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SUMMARY

For the past few years, the Center for Surface Science and Engineering has carried out extensive research on adsorption/desorption of polymers on contact lens surfaces. The main objective of this research is to quantify the adsorption/desorption properties of ophthalmic polymers using a wide variety of lenses such as polymethylmethacrylate, silicron acrylate, etc.

We have carried out well coordinated research using a variety of ophthalmic polymers. Solutions of these polymers were prepared in 0.9% saline at pH 7. The concentrations of solutions were in the order of 0.1% - 2%, maintaining viscosity up to 100 cp. The lenses were dipped in these solutions for different time variations and were rinsed 0-50 times in saline and air dried in horizontal position. Adsorption of these polymers on these polymer treated contact lenses was measured by using contact angle measurements and ESCA. The silicon acrylate lens treated with polyvinyl alcohol showed correlation of contact angle and ESCA measurements. It was found that the degree of adsorption is inversely related to contact angle and coefficient of friction measurements.

INTRODUCTION

Nature has designed a very effective lubrication mechanism for the blinking process. Generally a person blinks 4000 to 5000 times per day (ref. 1). The fact that we do not experience a significant discomfort or wear due to the blinking process is in part due to a very effective lubricating mechanism operating in the eyelid-cornea system. Surface phenomena such as the spreading of meibomian oil at the air/tear interface, the kinetics of thinning of 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 the processes occur every time we blink (ref. 2) (Figure 1).

There are more than 20 million contact lens users in the United States today. When one wears contact lenses, the structure of the sliding surfaces in the eye is modified. In contrast to the natural eyelid-cornea system, the eyelid slides against the contact lens surface and a small movement also occurs between the contact lens and the corneal surface (Figure 2). Thus, it is expected that the surface properties of the contact lens material would
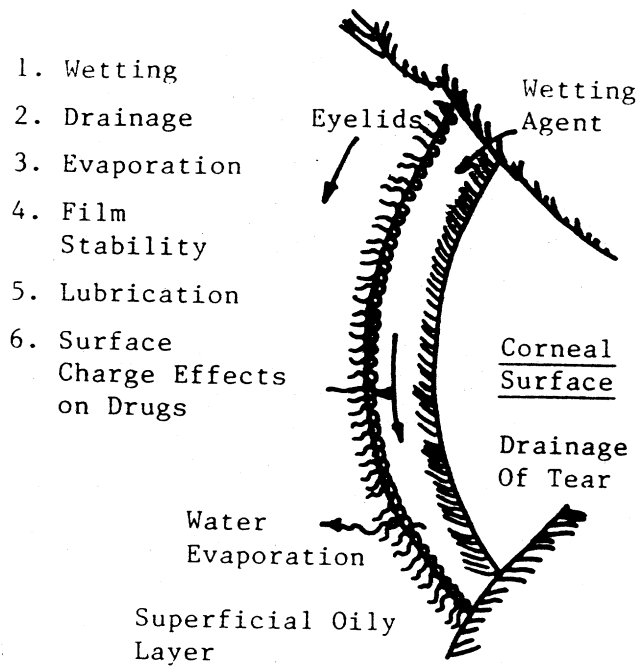
1. Wetting
2. Drainage
3. Evaporation
4. Film
   Stability
5. Lubrication
6. Surface
   Charge Effects
   on Drugs

Eyelids

Wetting
Agent

Corneal
Surface

Drainage
Of Tear

Water
Evaporation

Superficial Oily
Layer

Fig. 1 Surface phenomena in the eye.

Eyelid
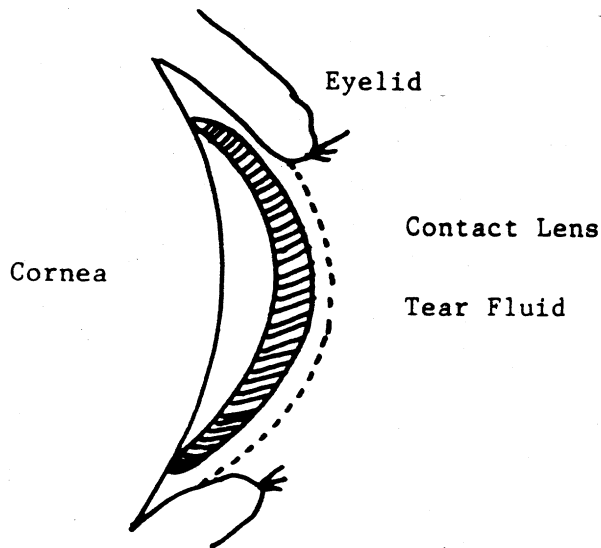
Contact Lens

Tear Fluid

Cornea

Fig. 2 Sliding of the eyelid against the contact lens surface during the blinking process.

significantly modify the friction and lubrication in the eye. The eye
produces mucin, a mucopolysaccharide which is a surface active macromolecule
and is likely to adsorb on the corneal as well as eyelid surfaces (refs. 3,4).
Adsorbed mucopolysaccharide will stabilize on aqueous boundary layer on the
sliding surface. During the blinking process, the friction is minimized
presumably by the adsorbed film of macromolecule. Although we recognize that
the mechanism by which macro-molecules provide lubrication in the cornea-
eyelid system is unknown, we propose that the adsorption of polymers to the
sliding surfaces has to be a very important and required step in the mechanism
of lubrication in the eye. Figure 3 schematically illustrates the adsorption
of polymer molecules on corneal and eyelid surfaces. It is obvious that the
structure of polymers molecules, their hydrodynamic radii, the conformation of
the adsorbed molecules, and the interaction of polymer molecules with the
surface (i.e., the strength of adsorption) would influence the frictional
forces generated during the sliding of the surfaces.
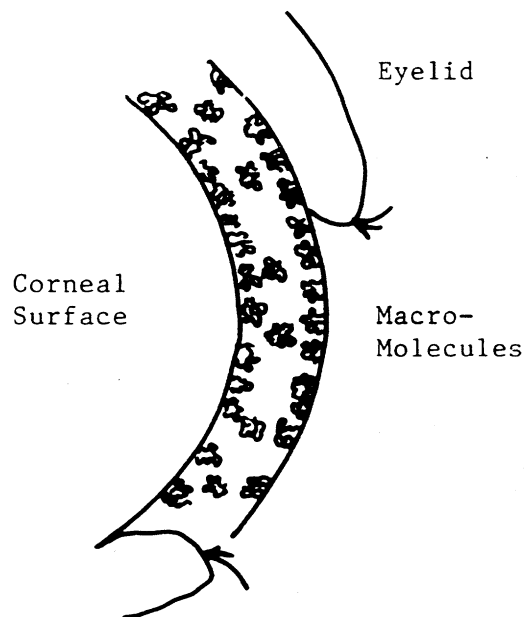
Eyelid

Corneal
Surface

Macro-
Molecules

Fig. 3 Adsorption of polymers and biolubrication of the corneal surface.

The subject of lubrication is concerned with the process of reducing frictional resistance occurring between two sliding solid surfaces. Any substance inserted between two sliding surfaces for the purpose of reducing the friction is called a "lubricant". There are two types of operating conditions in lubrication, namely boundary lubrication and hydrodynamic lubrication (ref. 5). In the former case, the lubricant film cannot support the load and contact occurs between the two surfaces (ref. 5). In this case, the coefficient of friction decreases with viscosity and speed and increases with load. In the case of hydrodynamic lubrication, the two sliding surfaces are separated with a thin film of lubricant. The frictional drag is entirely due to the rheological properties of the lubricant film. The coefficient of friction in this region increases with viscosity and speed and decreases with load. The friction between cornea and lid has been assumed to be of the boundary type. The surfaces, in this case, are likely to contact each other (ref. 6).

This paper focuses on the adsorption of polymers and commercial ophthalmic solutions on contact lens surfaces in relation to biolubrication.

MATERIALS, METHODS, INSTRUMENTS AND MEASUREMENTS

Materials

* Ophthalmic Polymers - Polyvinyl Alcohol (different molecular weights), Hydroxy methyl cellulose, Hydroxy ethyl cellulose, Chondroitin sulfate, Dextran, etc. have been used on Polymethylmethacrylate and Silicon acrylate lens surface for adsorption studies. These polymers were bought from Polyscience, Inc. or Aldrich Chemical Company, Inc.

* Commercial Ophthalmic Solutions - The following commercial ophthalmic solutions have been used for studies.

    1. AdsorboTear (Alcon) 2. Tears Plus (Allergan) 3. Lens Mate (Alcon)
    4. Adapettes (Alcon) 5. Tear Gard (Bio Products) 6. Tears Naturale (Alcon) 7. Muro Tears (Muro Pharmaceutical) 8. Neo-Tears (Barnes Hind)
    9. Hypotears (CooperVision) and 10. Liquifilm Tears (Allergan)

Methods

* Preparation of Polymer Solutions: Polymers were weighed based on their required concentration in the solution and added to a beaker containing 100 ml saline having a pH of 7. The mixture was stirred using a magnetic stirrer. The high molecular weight polymers had to be heated between 35° - 50° C until the polymer was completely dissolved.

* Preparation of Lens Material for Contact Angle, Coefficient of Friction and ESCA measurements: Three different size plates from big pieces of lens material were cut:

  a. 1/2 cm x 1/2 cm for ESCA measurements

  b. 2.5 cm x 2.5 cm for Adsorption/desorption studies and contact angle measurements

  c. 12.5 cm x 12.5 cm for coefficient of friction measurements

Lens plates for ESCA and contact angle measurements were dipped in polymer solutions for different time frames (3 hours, 8 hours and 24 hours).

Rinsing and drying processes

The plates were rinsed in saline. Depending on the experiment, the lens plates were rinsed in the following sequence: First plate was not rinsed while the second, third, fourth, fifth and sixth plates were rinsed 10, 20, 30, 40 and 50 times and dried in a horizontal plane laid on the tracks.

Instruments and Measurements

Contact Angle Measurements: A Rame-Hart goniometer was used to measure the advancing contact angle (θ) of solutions at equilibrium (approximately 3-5 minutes after a saline drop was deposited). The contact angle is the angle formed between the edge of a drop of the liquid and the surface upon which the drop is placed and is a measure of a solution's wetting ability. For example, water completely wets glass which is a hydrophilic surface and consequently the contact angle is zero. Water will not completely wet plexiglass and forms a contact angle of 65°. A solution is said not to wet at all if its contact angle is greater than 90°. Solutions with contact angles below 90° are said to wet incompletely. Under dynamic conditions, solutions with contact angles less than 90° can form a continuous liquid layer on some solid surfaces.

Surface Tension Measurements: The surface tension of polymer solutions and ophthalmic solutions was measured using Wilhelmy plate method. A platinum plate is suspended from one area of a balance and dipped into the liquid. One then gradually lowers the container holding the liquid and notes the pull on the balance when detachment occurs. A pressure transducer is used to determine the surface tension. The force is then converted into surface tension upon calibration of the instrument (ref. 7).

Viscosity Measurements: Viscosity measurements were taken by a Brookfield viscometer.

Coefficient Of Friction Measurements: A device has been developed in our lab (Figure 4) which measures the coefficient of friction and the scuff load of opthalmic solution for polymeric surface (ref. 8). A strain gauge bridge. employed to measure the stability of the lubricant film.

Horizontal Force Measurements: 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 the plate rotation applying definite force (0-1 gm, etc.) by means of a spring scales 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.

Frictional Force   Strain Gauge Bridge

Removable Weights For Vertical Force

Copper Foil Thermal Equalizer

Nylon Stylus

Lubricant Film

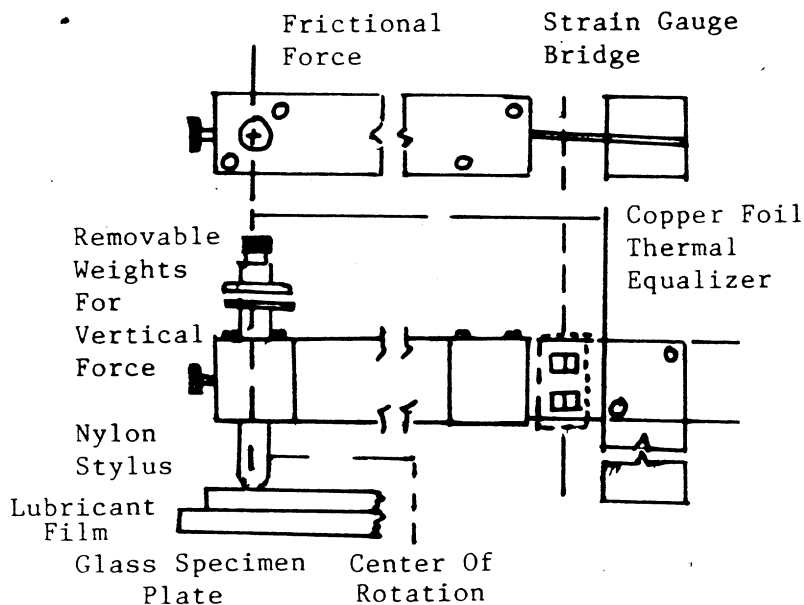Glass Specimen Plate   Center Of Rotation

Fig. 4 Friction test apparatus, stylus and specimen geometry.

Vertical Force Adjustment: After installation of a clean specimen plate and stylus, the stylus is adjusted for a minimal clearance from the plate. In a dry condition, this can be achieved by lowering the stylus until no contact sound is heard when the stylus is depressed towards the plate. When 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 component increase initially in a nonlinear fashion up to a certain load. Beyond this minimum load (1 or 2 gm 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 measurements of vertical force (ΔF_V) and horizontal force ΔF_H, i.e.

$$\Delta F_H / \Delta F_V \qquad\qquad\qquad (1)$$

ESCA measurement: Electron spectroscopy for chemical analysis (ESCA) utilizes a monochromatic source of low energy x-ray to produce a core level ionization (ref. 9). The energies of the ejected photoelectrons are measured and subtracted from that of the incident photon to obtain their binding energies. These energies identify the elements present and from slight but readily detectable shifts in energy also contain information on the chemical states of the atoms. The collected electrons derive only from the sample surface, thus ESCA reflects the characteristics of the sample surface. This technique is expected to probe 5 to 30 A° thick surface zone of materials.

SPECIFIC EXPERIMENTS AND RESULTS

1. PMMA and silicon acrylate lens plates were treated with (dipped in) 1% hydroxypropyl methyl cellulose for 24 hours. Solutions was prepared in saline.

2. The lens plates were rinsed in saline.

3. Rinsed lens plates were air dried in horizontal position, laid on tracks.

4. Contact angle on above treated plates were studied with a drop of saline and distilled water.

Table 1 represents the data of contact angle and coefficient of friction measurements on silicon acrylate and PMMA lens plates treated with Hydroxypropyl methyl cellulose.

TABLE 1

Contact Angle and Coefficient of Friction Measurements on Silicon Acrylate and PMMA Lens Plates Treated with 1% Hydroxypropyl Methyl Cellulose (HPMC) (Solution Prepared in Saline)

* pH of 1% HPMC solutions – 7.45
* Surface Tension – 72.695 dyne/cm
* Coefficient of Friction was measured between PMMA plate and PMMA ball of 0-25 inches in radius at a stylus velocity of 400 mm/sec with a vertical load of 10 gm.

Serial No.	Number of Rinses in Saline	Contact Angle with saline Silicon Acrylate Lens plate	Contact Angle with saline PMMA lens plate	Contact angle with distilled water on PMMA plate	Coefficient of friction Measurement on PMMA plate
1	Control (Clean plate)	59°	56°	66°	0.220
2	0	20°	21°	30°	
3	10	25°	23°	31°	
4	20	30°	23°	31°	
5	25	35°	23°	31°	0.12825
6	30	40°	23°	31°	
7	40	40°	23°	32°	
8	50	44°	25°	32°	0.1325
9	75	45°	39°	---	0.180
10	100	48°	56°	---	0.222

HPMC used for the experiment is from Aldrich Chemical Company, Inc. Cat #20,032-8, Lot #0112AL

Correlation of ESCA and Contact Angle Measurements of Polyvinyl Alcohol Adsorbed on Silicon Acrylate Surface

As shown in Figure 5, we have established that for a silicon acrylate surface, both the ESCA studies and contact angle measurements show that almost 50 rinses are required to remove the adsorbed polymer molecules from the surface.
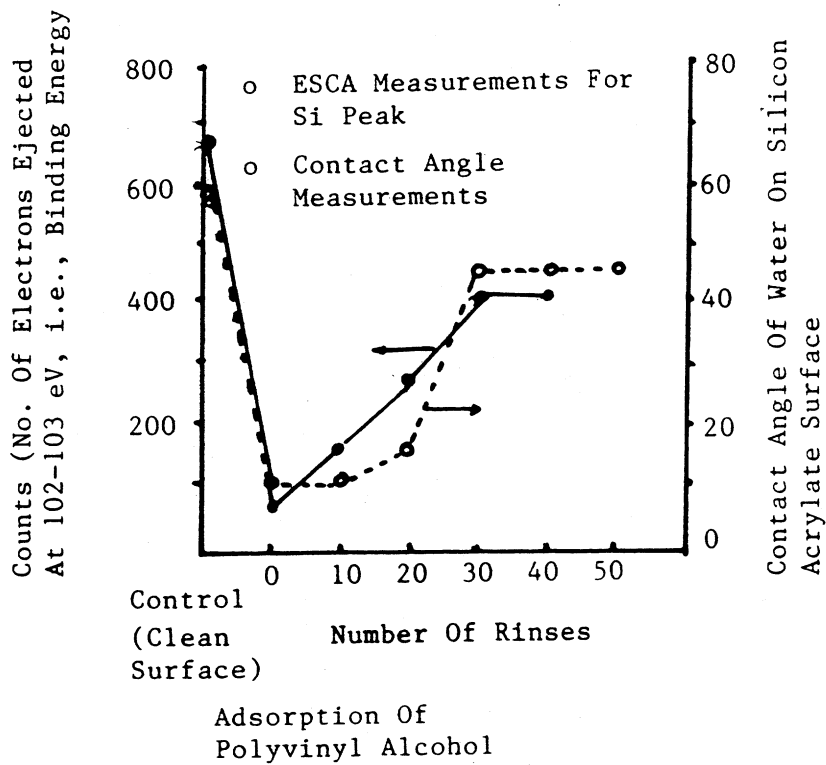
POLYVINYL ALCOHOL (M.W. 25000, 88% HYDROLYZED)

Fig. 5 A correlation of ESCA and contact angle measurements for polyvinyl
alcohol adsorbed on a silicon acrylate surface.

Coefficient of Friction Measurement of Commercial Ophthalmic Solutions

Table II represents the data of Coefficient of Friction, Viscosity,
surface tension and contact angle for ten commercial solutions (ref. 10),
Figures 6, 7, 8, 9.

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TABLE 2

Surface Chemical and Lubrication Properties of Various Ophthalic Solutions

Commercial Tear Substitute	Coefficient of Friction*	Viscosity (cp)	Surface Tension (dyne/cm)	Contact Angle of the solution on clean PMMA
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 Op.)	0.161	21.53	41.7	45°
Tears Naturale (Alcon)	0.164	7.03	30.8	26°
Muro tears (Muro Pharm.)	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.
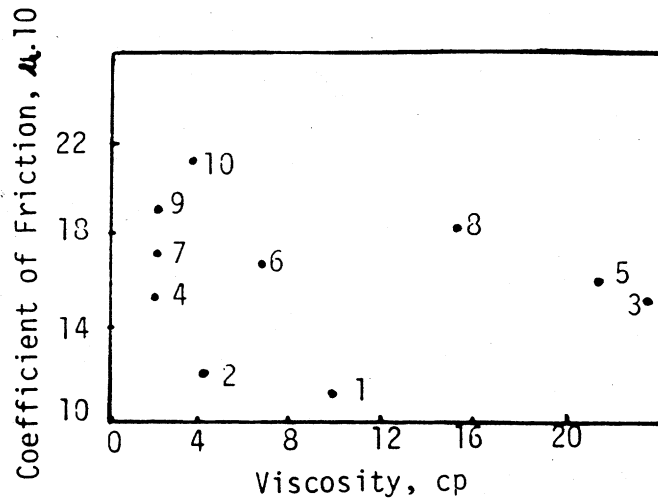
† PMMA = polymethyl methacrylate

Fig. 6 Coefficient of friction as a function of viscosity of various ophthalmic solutions between polymethylmethacrylate with a vertical load of 5g 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 and 10) Liquifilm.
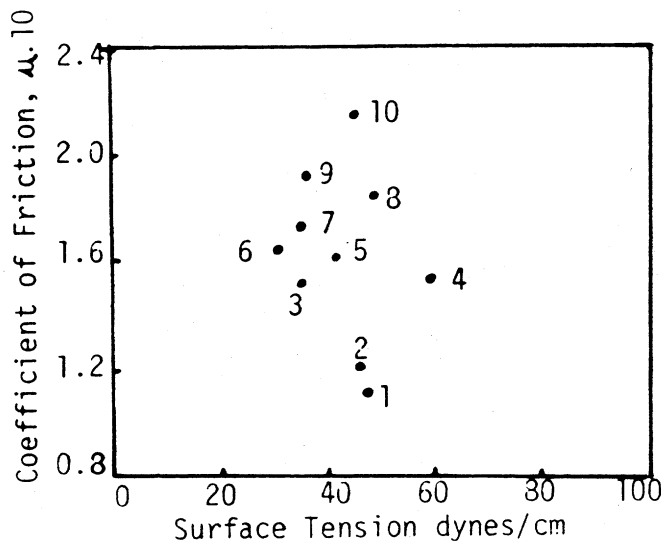

Fig. 7 Coefficient of friction for polymethylmethacrylate surfaces as a function of surface tension for various ophthalmic solutions: 1) Adsorbotear, 2) Tears Plus, 3) Lens Mate, 4) Adapettes, 5) Tear Gard, 6) Tears Naturale, 7) Muro Tears, 8) Neo-Tears, 9) Hypotears and 10) Liquifilm.
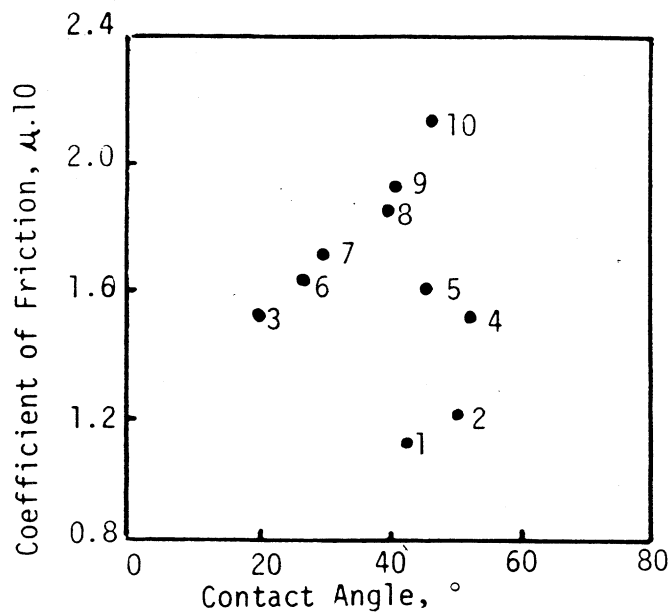
Fig. 8 Coefficient of friction of polymethyl methacrylate surfaces
as a function of contact angle for various opthalmic solutions:
1) Adsorbotear, 2) Tears Plus, 3) Lens Mate, 4) Adapettes, 5) Tear
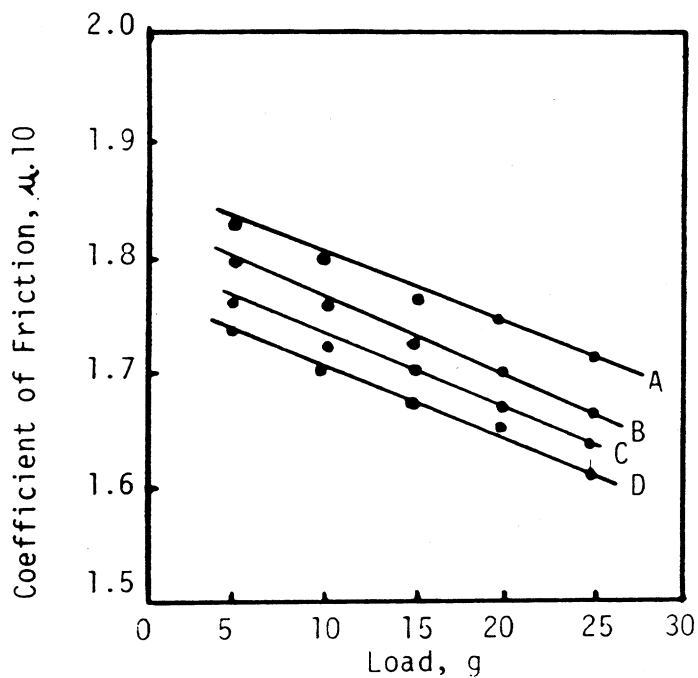Gard, 6) Tears Naturale, 7) Muro Tears, 8) Neo-Tears, 9) Hypo-tears
and 10) Liquifilm.

Fig. 9 Coefficient of friction between polymethyl methacrylate/
nylon at different loads and speeds for Tears Naturale.

    A. 400 mm/s
    B. 500 mm/s
    C. 600 mm/s
    D. 700 mm/s

DISCUSSION

The rationale behind studying adsorption of polymers on contact lens surfaces in relation to its biolubrication is to develop better understanding of biolubrication occurring between polymer molecules and corneal or contact lens surfaces. It is better to use low energy model surfaces such as PMMA, etc. to simulate a situation similar to that of the corneal surface with its critical surface tension of dyne/cm (ref. 11). The strongly adsorbed polymer on the lens surface will reduce friction of the sliding surfaces because of the increased thickness and stability of the tear film. Different polymers can adsorb at air/tear interface and the cornea/tear interface or both.

The ophthalmic solutions, comfort drops, cushioning agents and wetting agents are made with the blends of different ophthalmic polymers and other components. The interaction among the ingredient of these formulations will influence the surface properties, adsorption characteristics and coefficient of friction.

The solution with low surface tension and low contact angle will have the best wetting properties on contact lens and ocular surfaces (ref. 12). The ophthalmic solutions should have strong affinity for ocular surface, prolonged reaction time and low viscosity (ref. 13) since high viscosity could have undesirable side effects, such as blurring or vision and tendency to pull of epithelial filament.

In summary, the results presented in this paper establish that ophthalmic polymers have a wide range of coefficient of friction. Adsorption of ophthalmic polymers on lens surfaces is inversely related to contact angle and coefficient of friction measurements. Therefore, the polymers which are adsorbed strongly can be used for preparation of improved eye care products.

Acknowledgments

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