

Vol. 35, No. 2 (2013) 128-133

Tribology in Industry

www.tribology.fink.rs

RESEARCH

Tribological Study of Biocompatible Hybrid Organic Molecules Film with Antibacterial Effect

J.H. Horng^a, C.C. Wei^a, S.Y. Chern^a, W.H. Kao^b, K.W. Chen^a, Y.S. Chen^a

^a Department of Power Mechanical Engineering, National Formosa University, Taiwan, ^b Institute of Mechatronoptic Systems, Chienkuo Technology University, Taiwan.

Keywords:

Self-assembled monolayer Adhesion force Antifouling Contact angle Anti-bacterial

Corresponding author:

J. H. Horng National Formosa University, Department of Power Mechanical Engineering, No.64, Wenhua Rd., Huwei Township, Yunlin County 632, Taiwan, E-mail: jhhorng@gmail.com

ABSTRACT

Optical glass is widely used in bioengineering and various utilities such as public touchscreen displays and mobile devices. This work evaluates the features of anti-bacterial and anti-adhesion on Octadecyltrichlorosilane (OTS) material that was mixed with a biocompatible antibacterial agent coated on the optical glass. Test samples were allocated to different bath and drying temperatures as well as reaction times. Results show that in angle contact experiments, pure OTS films and mixed antibacterial films have almost the same contact angle of about 105° under the conditions of a 12 hour reaction time and 80 °C reaction temperature. The antibacterial test indicated the following order: antibacterial agent> OTS+ antibacterial agent (50 %) > OTS+ antibacterial agent (10 %) > OTS. At the same operation condition, OTS mixed with 50 % antibacterial agent was able to increase the adhesion force between the OTS film and lens. This suggests that surface treatment of optical lenses involving OTS with 50 % antibacterial solution is the most effective for increasing antifouling and antibacterial functions while simultaneously- enhancing the adhesion function between films and lens surfaces.

© 2013 Published by Faculty of Engineering

1. INTRODUCTION

The uses of self-assembled monolayer (SAMs) in biomedicine utilities have been increasing rapidly, such as in biosensors, non-fouling surfaces, bioactive surfaces, and drug delivery [1,2]. The OTS monolayer is one of the most extensively studied self-assembled monolayers [3-5]. Therefore, how to improve the adhesion and anti-bacterial performance of SAM films has become an attractive topic in order to enhance device application and reliability. Bierbum [6,7] noted that the substrate surface water layers are an important factor in the formation of OTS films. Bierbum explained that OTS molecules initially spread vertically on substrate surfaces and then cluster after locating activation positions. Subsequently, other OTS molecules spread to cluster edges and form islands. The molecules then spread outwards and cause adsorbed molecules to form connections, finally forming tightly connected monolayers. In 1998, Vaillant et al. [8] used atomic force microscopy (AFM) and a Fourier-transform infrared

spectrometer (FTIR) to observe the process by which OTS molecules form films on substrate surfaces. Results showed that a larger amount of water in the solutions cause the OTS molecules to undergo a hydrolysis reaction and produce polymerization within the solution, cloud-shaped or island-shaped leading to molecular films being formed throughout the solution. In contrast, solutions with comparatively low proportions of water exhibit point distributions and chaotically grown OTS molecules that organize into a liquid-like form. While surface diffusion renders OTS molecules as absorbing molecules within a solution, the tightly knit, island-shaped structures are formed by messy molecule films.

Resch [9] also used AFM and found that OTS molecules initially grow chaotically and irregularly. With the passage of time, molecules covering the surface spread horizontally and ultimately form tightly arranged molecular films. Carraro et al. [10] examined the formation of OTS SAMs under different ambient temperatures. They discovered that when the ambient temperature falls below 16 °C, OTS first forms islands or clouds and then films; by contrast, when the ambient temperature rises above 40 °C, the films grow evenly instead of forming islands. However, films form more quickly at lower temperatures. The formation of an OTS monolayer on a material surface is highly sensitive to several factors, including the density of surface hydroxyl groups, reaction temperature, reaction environment, reaction time, solvent used to deposit OTS, water content of the solvent, concentration of OTS, solution age, roughness of the underlying substrate, and cleaning procedures after SAM deposition [11].

The main requirements that must be satisfied by all bioengineering surfaces are corrosion resistance, biocompatibility, bioadhesion, and particular. biofunctionality [12]. In for lubrication motion devices, the biodegradable, bioadhesion and anti-bacterial functions of the surface and lubricant have become topics of great research interest for industrial application [13,14]. Therefore, how to improve the biocompatibility, adhesion and anti-bacterial performance of SAM films has become an attractive task in order to enhance device application and reliability.

2. EXPERIMENTAL

The optical lenses were ultrasonicated in acetone and sequentially rinsed with tetrahydrofuran solvent and deionized water (DI) and then immediately dipped in the OTS solution containing approximately 40 ml. For the preparation of SAM films, OTS was dissolved in alcohol and prepared to a molar concentration of 10 mM, and then mixed with different proportions of antibacterial agent (10 % and 50 %). The test pieces were placed in the solutions at different bath temperatures and duration times, but both with a drying time of 10 min. The test pieces were then removed and set aside for 12 hrs before being ultrasonicated in acetone for 5 min to remove any loosely bound material; after which, they were rinsed in DI water and blown dry with nitrogen gas. The molecular structure of OTS is shown in Table 1, which reveals that its hydrophobic properties come from the terminal group (CH₃). The main composition of the biocompatible antibacterial agent is bioflavonoids and citric acid, which come from plants.

Table 1. The molecular structure of OTS.

| SAMs | Molecular formula | Head group | Terminal group |
|------|--|--------------------|------------------|
| OTS | CH ₃ (CH ₂) ₁₇ SiCl ₃ | -SiCl ₃ | -CH ₃ |



Fig. 1. Contact angle equipment.

For the experimental investigation of hydrophobic properties for the different surface films on the lens, FTA contact angle equipment was used to measure the contact angle, as shown in Fig. 1. A larger contact angle indicates better hydrophobic and anti-fouling properties of surfaces, and contact angles were measured on both sides of the water drop. Droplet profiles were captured using a video comprised of digital frames over a period of 12 seconds and transferred to а computer for angle measurement. The adhesion force between surface films and substrates were measured using atomic force microscopy (AFM) in scratch mode. AFM was also used to examine samples' topography before and after SAM deposition by the non-contact mode.

3. RESULTS AND DISCUSSION

In the contact angle analysis of various operation conditions, the measurement data of each test piece was obtained from the mean of five measurements. Figure 2(a) is a photo of the contact angle for the original lens, while Fig. 2(b) is a photo of the contact angle for the OTS material. One can find that the OTS film can effectively increase the lens surface contact angle. Figure 2(c) shows that the contact angle changes with various reaction times and bathe temperatures. More specifically, it shows that the higher the bath temperature, the higher the contact angle; and further, the longer the reaction time, the higher the contact angle. However, the variation of contact angles for the OTS+50 % antibacterial agent films under various reaction time conditions are all quite low. The difference in contact angle between reaction times of 12 hours and 24 hours is very small, so this is not shown in the figure. Bathing OTS+50 % agent films at a bath temperature of 80 °C gradually increased the contact angle to approximately 105 degrees. The various reaction times and bath temperature have very little influence on the contact angle.



(a)



Fig. 2. Contact angles (a) photo of original lens; (b) photo of OTS film; and, (c) comparison chart for different reaction times and temperatures.

X-ray photoelectron spectroscopy (XPS) detection, as shown in Fig. 3, confirmed that OTS material bonds on the lens surface [11]. In summary, a bath temperature of 80 °C and duration time of 12 hours was chosen as the operation condition order to investigate the antibacterial in characteristics of the surface film on lenses.



Fig. 3. XPS spectrum diagram of the OTS film at the bath temperature of 80 °C and duration time of 12 hours.

The various roughness values of different surface materials are shown in Fig. 4. Roughness tests were conducted in air at a relative humidity of about 50 % using AFM in the noncontact mode, where the scanned detection range was 40 μ m × 40 μ m. The various surface roughness values of different surface materials are shown in Fig. 4(a). The comparison chart shows that the antibacterial agent can decrease the surface roughness value of pure OTS films. The surface roughness value of the OTS film incorporating 10 % antibacterial agent is approximately 175 nm, whereas the OTS film roughness value with 50 % antibacterial agent decreased to approximately 100 nm. The 3-D topography image for the hybrid organic molecular film (OTS + 50 % agent) is shown in Fig. 4(b). Island-shaped structures formed on the surface, as mentioned in Vaillant's work [8], which shows that hybrid organic films exhibit uniform surface coverage with regular patterns of island formations. This indicates that the antibacterial agent was absorbed and stored in the topographic valleys of the OTS film.



Fig. 4. (a)Roughness values of the different surface films; and, (b) 3-D topography image of the OTS + 50 % antibacterial agent film.

The reliability and beauty requirements of the display elements for manufacture become important in their service life. The light transmittance and film adhesion properties are one of the key performance indices of lenses. In order to explore the relation between surface film and light transmittance of a lens, Fig. 5 shows that transmittance of the OTS film and antibacterial agent on the lens. Results indicate that the OTS surface film slightly decreases the light transmittance of the original lens; however, the antibacterial agent has very little influence on transmittance. The minimum value of transmittance is 93.6 % for the film of OTS + 50 % agent film. This verifies that all transmittances of surface films are acceptable for industrial applications and life utilities in our work.



Fig. 5. Light transmittance of different surface films on lenses.



Fig. 6. Critical loads between surface films and substrate.

Film adhesion is another key performance index of lenses for reliability. Figure 6 shows the effect of the antibacterial agent on the critical load of surface films on the lens. The scratch tests indicate that high critical loads of films have high resistance against film wear out. It shows that the antibacterial agent increases the critical load between the OTS film and lens. Mixing the antibacterial agent (50 %) in the OTS material increases the critical load to approximately 104 μ N. In summary, the surface treatment of optical lenses involving OTS+ Agent (50 %) is the most capable of effectively increasing the anti-adhesion function between films and lens surfaces.



Fig. 7. (a)Bacterial growth situation on original lens; (b) bacterial growth situation on the OTS film; (c) effect of surface film material with antibacterial.

In the antibacterial tests, staphylococcus aureus (SA) were inoculated with different selfassembled films; and then after 24 hours, bacteria values were measured (Japan standard: JISZ 2801:2010). Figures 7(a) and (b) show the growth situation of SA on the general lens and the OTS + 50 % agent film. The SA number on the mixed film is less than that on the general lens. Figure 7(c) is the comparison chart of the bacteria count for the different surface films. For the general lens surface, the bacteria count is about 135,000 after 24 hours. The pure OTS film also has little antibacterial function, and shows that the bacteria count on OTS with 50 % antibacterial agent and the pure antibacterial agent surface is less than 10. This is far lower than the bacteria value of 5.3×10^4 on the OTS film.

4. CONCLUSION

This work studied the features of anti-bacterial and anti-adhesion on OTS self-assembled monolayers mixed with a biocompatible antibacterial agent coated on optical lenses. The results can be concluded as follows:

- 1. Both OTS and mixed OTS film can effectively increase the contact angle of a lens surface at various bath temperatures as well as duration times, and effectively reduce the device adhesion force.
- 2. The addition of the antibacterial agent has little effect on the contact angle and light transmittance of pure OTS films.
- 3. The antibacterial agent can effectively reduce the surface roughness and increase the adhesion force and antibacterial abilities of pure OTS film on lens surfaces (reaction time = 12 hrs, reaction temperature = 80 °C).

Acknowledgement

The author gratefully acknowledges National Science Council (NSC 102-2218-E-150-001) and Common Lab. for Micro-Nano Science and Technology of NFU.

REFERENCES

- [1] M. Masuko, H. Miyamoto, A. Suzuki: *Tribological characteristics of self-assembled monolayer with siloxane bonding to Si surfac*, Tribology International, Vol. 40, pp. 1587-1596, 2007.
- [2] G. Mani, D.M. Johnson, D. Feldman, D. Patel, A.A. Ayon, C.M. Agrawal: Drug delivery from gold and titanium surfaces using self-assembled monolayers, Biomaterials, Vol. 29, pp. 4561-4573, 2008.

- [3] A.N. Parikh, D.L. Allara, I.B. Azouz, F. Rondelez: *An Intrinsic Relationship between Molecular Structure in Self-Assembled n-Alkylsiloxane Monolayers and Deposition Temperature*, Journal of Physical Chemistry, Vol. 98, pp. 7577-7590, 1994.
- [4] C. Carraro, O.W. Yauw, M.M. Sung and R. Maboudian: Observation of Three Growth Mechanisms in Self-Assembled Monolayers, Journal of Physical Chemistry B, Vol. 102, pp. 4441-4445, 1998.
- [5] R. Brambilla, F. Silveira, J. Santos: *Investigating morphological changes on octadecyl modifiedsilicas by SEM and AFM*, Modern Research and Educational Topics in Microscopy, pp. 626-633, 2007.
- [6] P. Silberzan, L. leger, D. Auserre, J.J. Benatter: Silanation of Silica Surfaces. A New Method of Constructing Pure or Mixed Monolayers, Langmuir, Vol. 7, pp. 1647-1651, 1991.
- [7] K. Bierbaum, M. Grunze, A.A. Baski, L.F. Chi, W. Schrepp, H. Fuchs: Growth of self-assembled nalkyltrichlorosilane films on Si (100) investigated by atomic force microspcopy, Langmuir, Vol. 11, pp. 2143-2150, 1995.
- [8] T. Vallant: Formation of Self-Assembled Octadecylsiloxane Monolayers on Mica and Silicon Surfaces Studied by Atomic Force Microscopy and Infrared Spectroscopy, Journal of Physical Chemistry B, Vol. 102, pp. 7190-7197, 1998.

- [9] R. Resch, M. Grasserbauer, G. Friedbacher, T.h. Vallant, H. Brunner, U. Mayer, H. Hoffmann: In situ and ex situ AFM investigation of the formation of octadecylsiloxane monolayer, Applied Surface Science, Vol. 140, pp. 168-175, 1999.
- [10] C. Carraro, O.W. Yauw, M.M. Sung, R. Maboudian: Observation of Three Growth Mechanisms in Self-Assemble Monolayers, Journal of Physical Chemistry B, Vol. 102, pp. 4441-4445, 1998.
- [11] G. Mani, D.M. Feldman, O. Sunho, C.M. Agrawal: Surface modification of cobalt-chromiumtungsten-nickel alloy using octadecyltrichlorosilanes, Applied Surface Science, Vol. 255, pp. 5961-5970, 2009.
- [12] F. Zivic, M. Babic, N. Grujovic, S. Mitrovic: *Tribometry of Materials for Bioengineering Applications*, Tribology in Industry, Vol. 32, No. 1, pp. 25-32, 2010.
- [13] N.J. Fox, G.W. Stachowiak: *Vegetable oil-based lubricants - a review of oxidation*, Tribology International, Vol. 40, No. 7, pp. 1035–1046, 2007.
- [14] B. Chen, N. Zhang, K. Liang, J. Fang: Enhanced Biodegradability, Lubricity and Corrosiveness of Lubricating Oil by Oleic Acid Diethanolamide Phosphate, Tribology in Industry, Vol. 34, No. 3, pp. 152-157, 2012.