ANALYSIS OF MOLECULAR CONFORMATION OF PFPE ON HARD DISK SURFACES BY CONSIDERING THE DIP-COATING PROCESS

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ABSTRACT

The paper provides some new insight of the molecular conformation of the PFPE with functional end groups on hard disk surfaces by considering the dip coating process. It is proposed that the change in the molecular conformation during the dip coating process can be divided into three stages: adsorbing stage, developing stage and drying stage. A formula of predicting the monolayer thickness of the PFPE lubricant on hard disk surfaces is also proposed.

INTRODUCTION

The quality of the lubricant film depends greatly on its molecular conformation on the hard disk surface. Extensive studies, both experimentally and numerically, have been carried out. Ma et al. [1] show that functional perfluoropolyether (PFPE) lubricants tend to adopt the loop conformation whereas the nonfunctional PFPE tends to have the train conformation. Monte Carlo (MC) simulations based on the simple reactive sphere model [2] and the bead-spring model [3], and molecular dynamics simulation using the bead-spring model [4] have been developed to analyze the PFPE film structure on hard disk surfaces.

All the existing studies confine their attention to the behavior of the PFPE molecules on a solid surface only, and ignore the possible effects of dip coating process completely. It is well known that the solvent [5, 6], the concentration, the pull rate and the temperature etc. have great effects on the dip-coated PFPE lubricant film on magnetic recording media [5]. In this paper, the conformation of PFPE molecules with functional end groups was analyzed by taking the dip-coating process into consideration, and a formula of predicting the monolayer thickness of the PFPE lubricant film was also proposed.

MOLECULAR CONFORMATION

The dip-coating process for hard magnetic recording media is such a process in which the media is inserted within a dilute solution of PFPE lubricant, of which the concentration is about 0.1%, and pulled out at a slow speed of less than several mm/s. The molecular conformation of PFPE lubricant on the medium surface is closely related to the conformation within the solution. The PFPE lubricant has the chemical structure of X-[(OCF₂CF₂)ₚ-(OCF₂)ₚ]-O-X (p/q~2/3). The end group, -X is –CF₃ (nonfunctional) in PFPE Z, and –CF₃CH₂OH (functional) in PFPE Z dol. The functional end group is preferentially adsorbed onto the medium surface while the main chain segments with lower adsorption affinity are largely excluded from the surface, thereby forming a dangling loop. The adsorbed molecule density of PFPE with functional end groups is determined by the balance between the adsorption energy of the functional end group and the repulsion of the dangle loops. Because the distance between the two functional end groups of a PFPE molecule within the solution determines the coverage area of an adsorbed molecule, the distance is the most important in determining the adsorbed molecule density. As a first order of approximation, the molecules of PFPE in a dilute solution may be assumed to be a free rotation chain. For such a molecule the end-to-end distance \( R \) is given by the following equation

\[
R = \sqrt{N \frac{1+\cos \theta}{1-\cos \theta} b},
\]

where \( N \) is the segment number of a molecule, \( b \) the average bond length, and \( \theta \) the average bond angle. It is supposed that the two functional end groups of a molecule will be absorbed to a solid surface without changing their distance.

The actual distance of the end groups will be larger than that given by Eq. (1) since the rotational energy barrier exists and therefore the rotation will be hindered. It is shown that the rotational energy barrier decreases in an order of CF₃O—CF₂CF₂OCF₃, CF₂OCF₃—CF₂OCF₃, and CF₂O—CF₂OCF₃ [7].

In addition to the rotational energy barrier the distance \( R \) will also be affected by the solution and it is expected that a good solvent will give an increased distance. Therefore Eq. (1) can be considered as the lower limit of the end-to-end distance.

The change in the molecular conformation of PFPE lubricant during the dip-coating process is schematically shown in Fig. 1. After being absorbed to the medium surface the PFPE molecules is stretched due to the chemical potential across the adsorbed film thickness as shown in Fig. 1. In the idea condition the medium surface will be covered completely by the dangling loop of the PFPE molecules. The occupied area...
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In summary the change in the molecular conformation in the dip coating process can be divided into three different stages: adsorbing stage, developing stage and drying stage. In the adsorbing stage the lubricant molecules are adsorbed onto the hard disk surface with no or little change in its spherical conformation as in the solution. After being adsorbed the molecules will be stretched in the thickness direction due to the chemical potential across the adsorbed film thickness, and therefore vacancy is generated and more lubricant molecules are adsorbed. This process will continue until the adsorbed film is saturated. This is the developing stage which is followed by the drying stage. In the drying stage the disk is pulled out from the solution, the solvent is vaporized and only the lubricant molecules remain on the medium surface.

**CONCLUSION**

(1) The change in the molecular conformation of PFPE lubricant during the dip-coating process can be divided into three different stages: adsorbing stage, developing stage and drying stage.

(2) The monolayer thickness may be estimated by Eq. (4), which suggests that the monolayer thickness is proportional to the square root of the molecular weight of PFPE lubricant.

**REFERENCES**


