Contents lists available at ScienceDirect

Tribology International

journal homepage: www.elsevier.com/locate/triboint

Impact of reinforcing fillers' properties on transfer film structure and tribological performance of POM-based materials



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ARTICLE INFO

Keywords: Reinforcements POM Transfer film Tribology

ABSTRACT

Series of polyoxymethylene (POM) composites filled with three kinds of micro-sized reinforcing fillers, i.e. short carbon fibers (SCF), aramid particles (AP) and short glass fibers (SGF), with addition of polytetrafluoroethylene (PTFE) and/or silica nanoparticles were prepared. The tribological properties and transfer film structures were comprehensively investigated. It was revealed that mechanical properties of the micro-sized reinforcing fillers influenced significantly the tribological mechanisms of PTFE and silica nanoparticles in POM hybrid composites in aspect of transfer film formation. In comparison to SCF and SGF, AP played a better synergetic role with PTFE and SiO₂ nanoparticles in enhancing the tribological performance. It is assumed that tribo-physical and -chemical actions occurring on the reinforcements' asperities are important for tribological behaviors of the composites.

1. Introduction

In order to fulfill the increasing demands for optimal tribological designs of numerous motion systems, more and more attentions have been focused on polymer composites owing to their light weights and self-lubrication capabilities especially under dry sliding conditions [1–4]. Polyoxymethylene (POM) is one of the most widely used engineering thermoplastics providing good mechanical properties and outstanding self-lubricating characteristics [5–8]. Numerous efforts have been dedicated to the development of POM composites for applications where low coefficient of friction (COF) and wear rate (W_s) are required [6–9].

It was identified that addition of reinforcing fillers was an effective way enhancing dramatically the wear resistance of numerous polymer matrixes [8–14]. It is believed that the high load-carrying capability and abrasion resistance of the reinforcements imparted reinforced polymers high anti-wear properties [8,9,13,14]. In order to develop composites for tribo-engineering applications, various reinforcing fillers were added into POM matrix [8–12,14]. Zou et al. [9] reported that both aramid fibers and aramid particles enhanced significantly the wear resistance of POM. Yang et al. [14] declared that short carbon fibers (SCF) treated with nitric acid improved the anti-wear properties of POM exposed to reciprocating sliding. Benabdallah [15] revealed that POM filled with glass fiber was found to be more abrasive than the matrix in the reciprocating sliding tribological tests. In addition, it was

evidenced that formation of a transfer film, or namely tribofilm, separated the direct rubbing of sliding pairs and therefore provided lubricating action depending on its structure-related properties [3,16,17]. Addition of solid lubricants is a conventional way promoting the formation of a lubricating transfer film [5–7,18].

In the last decade, it has been demonstrated that further addition of ceramic nanoparticles into SCF-reinforced polymer composites improved the tribological performance [19–22]. Bahadur et al. [23] reported that addition of CuO nanoparticles into polyphenylenesulfide (PPS) composites enhanced its tribological performance. The authors ascribed the enhancement of tribological performance to the generation of a homogeneous transfer film. Chang et al. [24–26] proposed that the rolling of TiO₂ particles was responsible for the improved tribological performance of SCF-reinforced epoxy (EP). Our previous researches [17,27,28] revealed that the addition of nano-SiO₂ into SCF-reinforced EP led to the formation of a thin transfer film mainly consisting of silica. Note that the reinforcing fillers in these hybrid nanocomposites are mainly carbon fibers.

As well accepted, tribology is a system behavior governed by complex tribo-physical and -chemical actions occurring on the friction interface. It is believed that, among various influencing factors, reinforcing fillers' properties can play a role in mechanical rubbing and flash temperature on the interface, and therefore affecting transfer film formation as well [17,28]. Although the tribological performance of POM composites filled with various reinforcing fillers has been

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http://dx.doi.org/10.1016/j.triboint.2016.12.005

Received 1 November 2016; Received in revised form 1 December 2016; Accepted 3 December 2016 Available online 06 December 2016 0301-679X/ © 2016 Elsevier Ltd. All rights reserved.





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Table 1

Physical parameters of raw materials utilized.

Materials	Mohs' Hardness	E-Modulus (GPa)		
POM AP SCF SGF PTFE SiO ₂	- < 4.5 [29] 4 [29] 6 [29] - 7	2.85^{a} $60-120^{b}$ 230^{c} 86^{d} 0.65^{e} $72-78^{f}$		
-				

Table 2

Compositions of composites investigated in the present work.

Composites	Compositions					
	POM (vol%)	AP (vol%)	SCF (vol%)	SGF (vol%)	PTFE (vol%)	SiO ₂ (vol%)
POM+AP	85	15	-	_	_	_
POM+AP+SiO ₂	83	15	-	-	-	2
POM+AP+PTFE	65	15	-	-	20	-
POM+AP+PTFE+SiO ₂	63	15	-	-	20	2
POM+SCF	90	-	10	-	-	-
POM+SCF+SiO ₂	88	-	10	-	-	2
POM+SCF+PTFE	70	-	10	-	20	-
POM+SCF+PTFE+SiO ₂	68	-	10	-	20	2
POM+SGF	90	-	-	10	-	-
POM+SGF+SiO ₂	88	-	-	10	-	2
POM+SGF+PTFE	70	-	-	10	20	-
$\rm POM+SGF+PTFE+SiO_2$	68	-	-	10	20	2



Fig. 1. Schematic illustration of POD tribological tests.

extensively studied, the effect of various reinforcements on transfer film formation was not systematically compared yet. In particular, the tribological mechanisms of solid lubricants and nanoparticles in POM hybrid composites with various reinforcements have not been directly compared.

In the present work, series of POM composites, i.e. POM filled with (including combination) SCF, AP, SGF, PTFE (PT for short) and silica nanoparticles, were prepared. The tribological properties of POM composites and structures of transfer films formed on the counterpart were comprehensively investigated. The main objective of this work is to reveal how reinforcing fillers' properties affect transfer film structures and tribological properties of POM-based materials. It is expected that the output of this work can provide insight into the tribological behaviors of POM composites.

2. Materials and Methods

2.1. Materials and specimens preparation

Granular POM copolymer (trade mark C9021) was supplied by Hostaform (Celanese, Germany). The softening temperature and melting point of the POM copolymer are 155 °C and 178 °C, respectively. Three kinds of micro-sized reinforcements were utilized, i.e. AP, SCF and SGF. AP was provided by Teijin Twaron (Twaron 5011, Japan). Polyacrylonitrile-based SCF (SY-PCF-8005), with diameter of 7 μ m and length-diameter ratio of 10:1–5:1, was purchased from Nantong Senyou (China). E borosilicate type glass fiber, with a diameter of 12–14 μ m and length-diameter ratio of about 4:1, was commercially available from Nanjing Lvzhou Building Materials (China). PTFE particles with an average size of 4 μ m (TF9207z, Dyneon) were employed as the solid lubricant. SiO₂ nanoparticles with an average diameter of 20 nm were supplied by Zhoushan Nanomaterials (China). The Mohs' hardness and E-modulus of the raw materials utilized were listed in Table 1.

The data obtained from Celanese (a), Teijin (b) and the relevant manufacturers (*c*-f), respectively.

POM granulates and all the fillers were dried at 90 °C for 5 h prior to compounding. POM was compounded with various fillers using a laboratory-scale melting mixer (PolyLab QC, Haake). The processing temperature, rotor speed and blending time were set at 185 °C, 80 rpm and 10 min, respectively. The compounded materials were then hot pressed into plates with a dimension of 80×80×4 mm³ by compression molding at 190 °C and 10 MPa. Afterwards, the polymer plates were cut into pin specimens with required sizes for tribo-tests. The compositions of the composites prepared were listed in Table 2. It should be pointed out that the content of AP was selected as 15 vol%, which displayed the best wear resistance property in POM based composites as reported [9], and the volume fractions of SCF and SGF, i.e. 10 vol%, were the same as our previous work [17,28].

2.2. Tribology tests

Tribology tests were performed using a Pin-On-Disc (POD) tribometer (Wazau TRM 1000, Germany) according to the standard ASTM D3702-94 (1999). Schematic illustration of the POD test was displayed in Fig. 1. Polymer specimens had a dimension of 4×4×12 mm³. The counterpart was a GCr15 (GB/T18254-2002) standard steel disc



Fig. 2. COF (a) and W_s (b) of pure POM and POM composites reinforced with AP. The sliding velocity: 1 m/s.

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