Wear 309 (2014) 43–51

Contents lists available at ScienceDirect

Wear

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

Enhanced wear resistance of high-density polyethylene composites reinforced by organosilane-graphitic nanoplatelets

Tian Liu, Bin Li, Brooks Lively, Allen Eyler, Wei-Hong Zhong*

School of Mechanical and Materials Engineering, Washington State University, Pullman, WA 99164, USA

ARTICLE INFO

Article history:
Received 7 May 2013
Received in revised form
21 October 2013
Accepted 26 October 2013
Available online 13 November 2013

Keywords:
Sliding wear
Polymer–matrix composite
Graphite nanoplatelet
Solid lubricants

ABSTRACT

It is known that graphite has excellent lubricant properties due to the 2D graphene layers bonded via van der Waals forces. Thus, graphite nanoplatelets (GNPs) should have high lubricating efficiency during contact frictional movement of sliding parts. However, GNPs have rarely been used to improve the tribological properties of polymeric materials. In this study, we aimed to improve wear resistance of GNP–reinforced high-density polyethylene (HDPE) composites via the synthesis of organosilane-modified GNPs. Wear resistance of the HDPE/GNP composites was examined on a pin-on-disc wear testing apparatus under various sliding velocities. The results revealed that compared to the composites without filler surface modification, significant enhancements in wear resistance under different sliding velocities were realized in silanized-GNP–reinforced HDPE composites. In particular, 97% wear resistance improvement under 1.3 m s^{-1} sliding velocity was obtained. Furthermore, the organosilane-modified GNPs minimized the influence of sliding velocity on wear resistance of the composite and thereby maintained excellent wear resistance in a broad range of sliding velocities, and even at very high velocity (2.0 m s^{-1}). Both superior wear resistance and good stability of wear performance at various sliding velocities suggest silanized-GNP/HDPE composites are promising materials with great potential for a wide range of tribological applications.

1. Introduction

Tribological properties of polymeric materials are significant to the performance and service life in many applications, including load-bearing total joint replacements, airplane interiors, machinery parts of automobiles, medical devices, and other grinding systems. However, many polymers do not possess satisfactory tribological properties [1,2]. In order to improve tribological performance of polymers including the increase in wear resistance and the reduction of the friction coefficient, numerous attempts have been undertaken, typically involving the addition of different additives into the base polymers [3,4]. Although the reported results showed that better tribological performances could be achieved for composite materials under general wear conditions, the increased elastic modulus and the reduced crack resistance led to failure of the composites under severe wear [4]. In addition, the thermal effect caused by wear process is another potential threat to the performance of polymeric materials. The increasing temperature during wear, especially at high wear sliding velocity, can affect the structures and properties of polymer matrices, owing to the nature of their viscoelasticity. The generated heat will speed up the damage of the material. Therefore, to meet the demand for good wear performance stability and maintain life expectancy of friction elements, development of reinforced polymeric composites by adding appropriate reinforcements is necessary.

Graphite nanoplatelets (GNPs) are an ideal reinforcement for polymeric materials because of their superior physical and mechanical properties, multi-functionalities, and the abundance of the necessary raw materials in nature. The resulting GNP–reinforced polymer nanocomposites benefit the creation of next-generation materials for broad applications, such as automotive, aeronautical and biomedical manufacturing [5,6]. In recent years, studies of polymeric nanocomposites with GNPs have primarily focused on the development of electrically and thermally conducting composites, gas storage, sensors, etc., showing extraordinary accomplishments in enhancing electrical, mechanical and thermal properties [7–9]. To date, very little work has been demonstrated on the tribological benefits of GNP–polymer nanocomposites.

With unique structure and exceptional properties, GNPs have the potential to improve wear resistance of polymer composites while minimizing the thermal effect generated by wear. However, very few studies have related to the resultant tribological performance of GNP–reinforced polymer composites thus far. GNPs consist of stacked 2D graphene layers bonded via van der Waals forces. These multilayered 2D structures allow strong interlayer sliding motion with GNPs under external force, which provides GNP with an outstanding lubricant property, resulting in lesser wear [10]. Moreover, on each graphene basal plane, there exists plenty of sp^2 hybridized carbons which are conducive to the storage and dissipation of frictional heat. The high thermal

---

* Corresponding author. Tel.: +1 509 335 7658; fax: +1 509 335 4662.
E-mail address: katie_zhong@wsu.edu (W.-H. Zhong).

0043-1648/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.wear.2013.10.013

stability and conductivity of GNP–reinforced polymer composites can be exploited to diminish the negative effect on polymer matrix resulting from heat generated during wear [11]. Furthermore, functional groups on commercial GNP surfaces, which are produced as a result of oxidation processes during manufacturing, can serve as active sites for surface modification to strengthen interfacial bonding and reinforce the composites. Hence, GNP is an ideal nano-reinforcement to improve tribological properties of polymers.

To make high performance polymer composites, reinforcements that can be homogenously dispersed and strongly bonded to the polymer matrix are the essential prerequisites. Research on tribological properties of polymer composites has demonstrated that effective filler treatment can contribute to the improved wear resistance of the composites through uniform filler dispersion and enhanced interfacial interaction [12]. For GNP–reinforced polymer composites, the strengthened interactions between GNP and polar polymer matrices can be easily achieved through the reactive sites along the edges of commercial GNPs, such as hydroxyl, carbonyl and epoxide groups [13]. Hence, the fabrication of the composites with uniform GNP dispersion and strong GNP–matrix interaction is more facile. For non-polar polymers, the functional groups on commercial GNP surfaces are incompatible with hydrocarbon polymer matrices, such as polyethylene (PE), which have high wear resistance. In this case, the surface modification for GNPs has been commonly applied to improve the interfacial bonding in polymer composites [11,13]. In general, various chemicals can be selected, such as diaminoalkanes, poly(sodium 4-styrene sulfonate), aryl diazonium salts, etc. [14–16] However, these agents do not significantly contribute to a homogeneous GNP dispersion. The restacking of GNP sheets can compromise their effectiveness [8].

In the current work, we studied various GNPs to reinforce high-density polyethylene (HDPE) for tribological applications. As-received, thermally purified and surface-modified GNPs were selected. The organosilane coupling agent was used to modify GNPs. As a popular surface modification approach, a variety of silane coupling agents have been applied to various fillers [17,18]. To date, the studies on tribological performance of polymer composites with silane-modified carbon-based nanofillers have been mainly focused on carbon nanofibers (CNF) and carbon nanotubes (CNT) [18,19]. The relevant investigations of GNPs have been rarely reported to authors' knowledge. In this study, octadecyltrimethoxysilane (ODMS) was selected as a modifier to treat GNPs to achieve the desired uniform filler dispersion and strong interaction with the HDPE matrix. Qualitative morphological study and quantitative filler dispersion analysis showed that the HDPE/GNP composite with homogerously dispersed nanofillers and enhanced interfacial interaction was realized by silane modification of GNPs. The wear testing results revealed that the use of silanized GNP in composites was capable of improving wear resistance dramatically and maintaining the outstanding wear resistance at various sliding velocities. A significant enhancement on wear resistance was found in the silanized GNP composites, which was up to 97% at 1.3 m s^{-1} wear sliding velocity. This work suggests that the lubrication effect of GNPs can be successfully transferred to the nanocomposites after silane surface modification.

2. Experimental procedures

2.1. Materials

High-density polyethylene (HDPE) (HP54-60 Flake) was supplied by Bamberger Polymers Inc. with a density of 0.954 g cm^{-3}. The as-received graphitic nanoplatelet (*as*-GNP) used in this study was purchased from XG Science Inc., which was pre-exfoliated with dimensions approximately 5 μm in diameter and 5 nm thickness. Octadecyltrimethoxysilane (ODMS) (90% technical grade) was used as the organosilane coupling agent and was purchased from Sigma-Aldrich. Sodium hydroxide (NaOH) (5% w/v aq. Soln.) was supplied by Alfa Aesar Johnson Matthey.

2.2. Method of synthesis for silanized GNPs

2.2.1. High-temperature purification of as-received GNPs

The as-received GNPs (*as*-GNPs) were pre-exfoliated via an acid intercalation approach by the supplier. This is a highly oxidative process and can create an abundant amount of chemically active sites on the particle surface, typically hydroxyl and carbonyl groups [13]. After exfoliation, small amounts of acid residuals still exist in GNP particles. To remove the acid impurities for further surface modification and composite fabrication, the *as*-GNPs were thermally purified in a muffle furnace at 1000 °C for 5 min to obtain high-temperature purified GNPs (*ht*-GNPs).

2.2.2. Surface modification of thermally purified GNPs

Octadecyltrimethoxysilane (ODMS) was used as the coupling agent to modify the *ht*-GNPs further, as its end groups with long hydrocarbon chains could lead to good interaction with HDPE matrix. The *ht*-GNPs were first bath sonified in 95% ethanol for 1 h. Next, 5×10^{-5} mol/L NaOH to be used as a catalyst was then added and mixed with the *ht*-GNPs/ethanol solution. ODMS was diluted in 100% ethanol and added to the *ht*-GNP suspension slowly in 0.5 ml increments after the suspension started to reflux. The whole reaction was under reflux for 5 h. Finally, the silane-modified GNPs were vacuum dried, washed with 100% ethanol to remove the unreacted silane coupling agent, and then the silanized-GNPs (*s*-GNPs) were dried in oven at 70 °C for 24 h.

2.3. Manufacturing of HDPE/GNP composites

The 3 wt% *as*-GNPs, *ht*-GNP and *s*-GNPs were melt-blended with HDPE by a Haake Torque Rheometer. Mixing was set at 170 °C with a rotator speed of 7.3 rad s^{-1} for 15 min. The resulting nanocomposites are named as Comp-*as*GNP, Comp-*ht*GNP and Comp-*s*GNP, respectively. A reference sample of neat HDPE was also prepared under identical conditions. All samples were subsequently hot-pressed into 2.5 mm thick panels at 180 °C for 15 min on a hydraulic compression molding machine. The panels were allowed to cool down to room temperature naturally after turning off the heat. All manufacturing parameters for graphitic nanofiller reinforced HDPE composites were selected based on our previous studies [19]. The specimens for pin-on-disk wear testing were cut from the compression molded panels. The detailed descriptions of each prepared sample are shown in Table 1.

2.4. Characterization

2.4.1. TGA (Thermogravimetric analysis)

A Thermogravimetric Analyzer (TA Instruments, SDT Q600, USA) was used to verify the removal of acid residuals in the *as*-GNPs after thermal purification, as well as the wt% of organosilane coating on the surface of *s*-GNPs. The temperature range for TGA

Table 1
Detailed description for each sample.

Sample	Reinforcement	Filler content
Pure HDPE	–	–
Comp-*as*GNP	As-received GNPs	3 wt%
Comp-*ht*GNP	High-temperature purified GNPs	
Comp-*s*GNP	Silanized GNPs	