Synthesis and Application of New Fullerene Derivative

Guichang Jiang,[1,2] Qixin Zheng[1]

[1]*Department of Biology, Huazhong University of Science and Technology, Wuhan 430074, China*
[2]*Department of Chemistry, Huainan Teachers College, Huainan 232001, China*

ABSTRACT: A novel fullerene–maleic anhydride copolymer is synthesized via radical polymerization. It is soluble in polar solvents such as water, dimethyl sulfoxide, tetrahydrofuran, and so forth. The product is characterized by FTIR, UV–visible, and GPC. Transmission electron microscope analysis shows that it presents an ideal spherical shape in water with an average particle diameter of about 36 nm. Four-ball tests show that the addition of a certain concentration of the fullerene copolymer to the base stock (2 wt % triethanolamine and 0.5 wt % Alkylpolyoxyalkylene Phosphate Zinc (OPZ) aqueous solution) can effectively raise the load-carrying capacity (P_B value) and raise the antiwear ability. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 2182–2185, 2005

Key words: fullerene–maleic anhydride copolymer; water solubility; lubrication property; nanoball

INTRODUCTION

The lubricating properties of fullerene (C_{60}) have been the subject of speculation since its discovery because of its unique spherical shape with a cage diameter of 0.71 nm, high load-bearing capacity, low surface energy, high chemical stability, and weak intermolecular and strong intramolecular bonding.[1–4] Moreover, it was expected to act as a tiny ball bearing.[5,6] Theoretical simulations found that the C_{60} molecule was able to roll between graphite sheets, as well as between hydrogen-terminated surfaces of diamond under relatively low load.[7] The tribological properties of fullerene particles as an additive to liquid lubricants were studied by two groups.[8,9] The results indicated that the presence of fullerene was able to increase the load-carrying ability and decrease the friction coefficient and wear. However, in these experiments fullerene particles were dispersed in liquid lubricants by physical or mechanical methods (such as solid grinding, solvent evaporation, ultrasonic, etc.) because they are only soluble in a few nonpolar solvents (such as benzene, toluene, carbon disulfide, etc.), so fullerene particles were present in the form of molecular clusters or supercorpuscles.[8,9] Up to now, the tribological properties of soluble fullerene and its derivatives have seldom been studied. In this article, a novel water-soluble fullerene–maleic anhydride copolymer was synthesized and the frictional behavior of the soluble fullerene copolymer was studied for the first time.

EXPERIMENTAL

Materials

Fullerene (C_{60}) was obtained from Wuhan university (purity > 99.99%). Maleic anhydride and benzoyl peroxide were obtained from Fubai University. The other solvents are analytically pure reagents.

Preparation of fullerene–maleic anhydride copolymer

The fullerene–maleic anhydride copolymer was synthesized by typical free radical polymerization. A solution of 50 mg of C_{60} in 1,4-dioxane was mixed with 2 g of maleic anhydride. The dark red mixture was deoxygenated by bubbling dry nitrogen gas for ~25 min, followed by the addition of 200 mg of benzoyl peroxide. The polymerization reaction was carried out in a glass bottle at 70°C for 48 h. The reaction products were precipitated from the 1,4-dioxane solution into petroleum ether. The precipitation procedure was repeated several times, yielding a solid sample with a nearly black color. The solid sample was further purified by washing with acetone/petroleum ether and THF/C_6H_{14}. After drying under a vacuum, 1.5 g of the final copolymer sample was obtained.
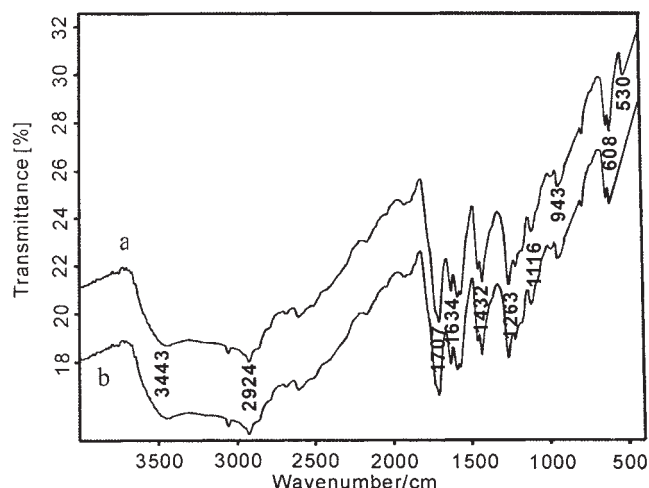
Figure 1 FTIR spectra of (a) C_{60}–maleic anhydride copolymer and (b) poly(maleic anhydride).

Measurement of lubrication properties of nanometer-scale fullerene copolymer

The base stack is 2 wt % triethanolamine and 0.5 wt % Alkylpolyoxyalkylene Phosphate Zinc (OPZ) (self-prepared) aqueous solution. The fullerene–maleic anhydride copolymer prepared above was used as a lubricant additive in the base stock. The tribological measurements were carried out by using an MQ-800 four-ball tribotester at a rotational speed of 1450 rpm and a temperature of 10°C. The maximum nonseized load was obtained by GB3142-82, similar to ASTM D 2783. The wear scar diameter was measured under a load of 400 N and a test duration of 30 min. The dependence of the wear scar diameter on the load was also measured at 0.1 wt % additive content and a 30-min test duration for the wear scar diameter. The stainless steel balls used in the tests were made of GCr15 (AISIE52100) bearing steel with 64-66 surface hardness and 0.012 μm of surface roughness. In order to study the effect of fullerene in the fullerene–maleic anhydride copolymer, the same concentration of the poly(maleic anhydride) reference as an additive was measured under the same conditions.

RESULTS AND DISCUSSION

Characterization of fullerene–maleic anhydride copolymer

The copolymer was characterized by FTIR, UV, and GPC. FTIR spectra were measured in KBr matrices, and the results were compared with those of neat poly(maleic anhydride) samples prepared under the same experimental conditions. As shown in Figure 1, the observed FTIR spectra of the copolymers with C_{60} contents are very similar to that of neat poly(maleic anhydride). However, for the copolymer with C_{60} con-
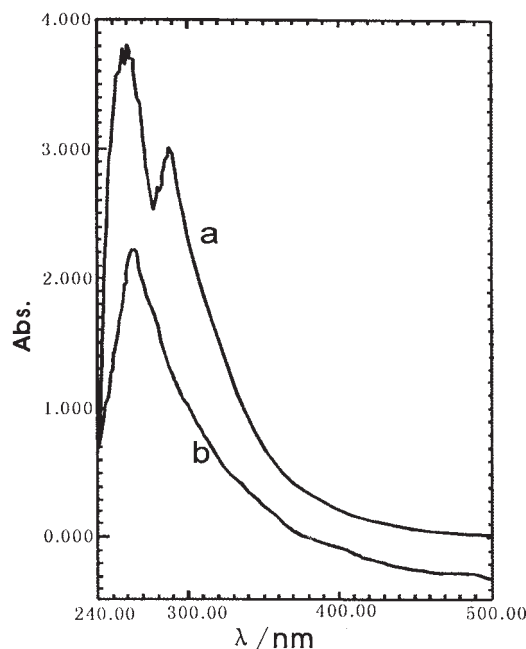

Figure 2 A comparison of (a) the C_{60}–maleic anhydride copolymer UV absorbance with (b) that of poly(maleic anhydride) (all in THF).

tents, the FTIR spectrum shows extra absorption in the 530 cm^{-1} region, which is typical with respect to substituted C_{60}.[10] UV absorption spectra were measured in THF, and the results were compared with that of poly(maleic anhydride). As shown in Figure 2, the observed UV absorption spectra of the copolymer with C_{60} contents are very different from that of poly(maleic anhydride). The somewhat structured absorption band of free C_{60} is replaced by a steadily decreasing curve, typical for substituted C_{60}.[10] The UV absorption wavelength maximum of the copolymer with C_{60} contents is 255 nm, which is different from that of free C_{60} and poly(maleic anhydride), which is typical with respect to substituted C_{60}.[11] The emission can be attributed to the C_{60}-containing sites in the poly(maleic anhydride) structure. The weight-average molecular weight (M_w) was obtained by GPC (Voria 5060 model). The M_w of the copolymer with C_{60} contents is 3560. The molecular structure of the copolymer may be a star polymer with fullerene as the core and grafting of one or several poly(maleic anhydride) chain segments. The results could be used to support a proposed copolymer structure as follows:
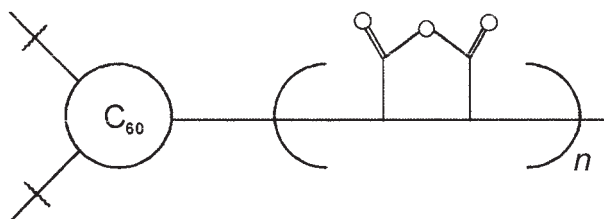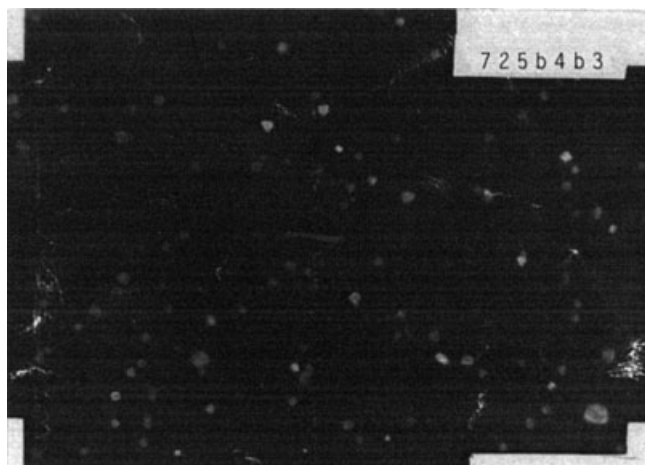
Figure 3 The morphology of nanometer balls of the fullerene copolymer in water. Original magnification ×72,000.

The morphology and size of the fullerene copolymer in water were measured using a JEM 100CXII TEM microscope with a voltage of 200 kV. The synthesized fullerene copolymer is soluble in water, giving a clear brown solution. TEM analysis indicates that the copolymer presents an ideal spherical shape in water with a diameter of about 10–80 nm, as shown in Figure 3. For comparison, the appearance of the poly(maleic anhydride) in water is a lamellar shape. The physical structure of the fullerene copolymer nanometer-sized balls may be described as follows: the core is very hard fullerene and the shell is poly(maleic anhydride), which may be relatively soft but very elastic.

Lubrication properties of fullerene–maleic anhydride copolymer

The maximum nonseized load (P_B) represents the load-carrying capacity of the lubricant. The P_B value

was measured and the results are given in Figure 4(a). The P_B value of the base stock (2 wt % triethanolamine and 0.5 wt % OPZ) is 520 N, and the base stock with the fullerene copolymer showed a higher maximum nonseized load than that of the base stock. In other words, the fullerene copolymer could strengthen the load-carrying capacity of the base stock. When the fullerene copolymer content reached 0.5 wt %, the P_B value was maximum. Then, excessive fullerene copolymer resulted in a decrease of the load-carrying capacity of the base stock.

The wear scar diameter data are given in Figure 4(b). It is shown that the addition of the fullerene copolymer can decrease the wear scar diameter of the base stock. When the fullerene copolymer content reaches 0.1 wt %, the wear scar diameter is minimum. However, excessive fullerene copolymer exhibits a larger wear scar diameter than the base stock. The decrease in the load-carrying capacity and wear resistance with excessive additive may be attributed to the corrosive wear, because the fullerene–maleic anhydride copolymer additive may react with the surface of the metal. The dependence of the wear scar diameter on the load is shown in Figure 5.

Under testing loads, the wear scar diameter of the base stock with 0.1 wt % fullerene–maleic anhydride copolymer is smaller than that with 0.1 wt % poly(maleic anhydride). This means that the presence of fullerene copolymer can strengthen the wear resistance of the base stock.

Based on the above lubrication measurements the lubrication mechanism of the fullerene–maleic anhydride copolymer additive can be deduced. The fullerene copolymer plays the role of a solid lubricant. Because fullerene has a very high load-carrying capacity and the fullerene copolymer is nanometer-sized balls with a core–shell structure, which can penetrate into rubbing
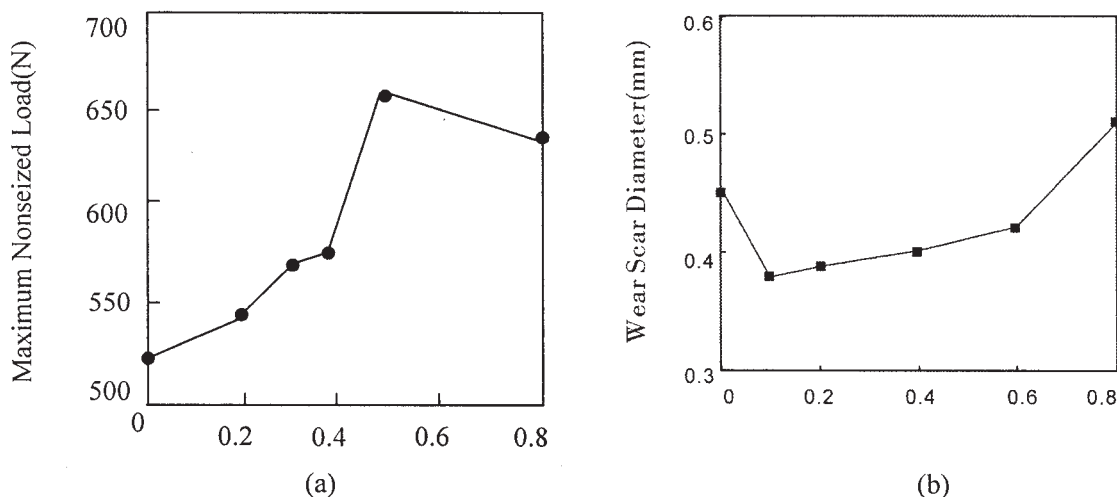

(a)

(b)

Figure 4 The effect of the fullerene copolymer and content on (a) the maximum nonseized load and (b) the wear scar diameter.
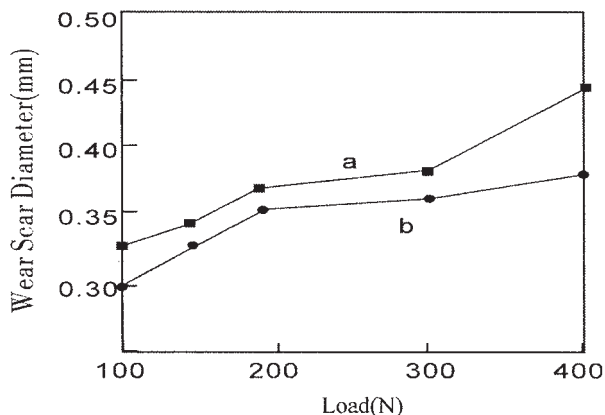
Figure 5 The effect of load on the wear scar diameter with base stock with (a) 0.1 wt % poly(maleic anhydride) and (b) 0.1 wt % fullerene–maleic anhydride copolymer.

surfaces and deposit there, it is reasonable to speculate that the fullerene copolymer nanometer balls may be more effective than poly(maleic anhydride) to support and isolate two relative motion surfaces. Therefore, the load-carrying capacity and antiwear performance of the base stock were improved. Moreover, the nanometer balls are expected to roll between two relative motion surfaces to reduce the friction coefficient. In addition, the shell is a polymer of neat maleic anhydride, which is relatively soft but very elastic. Thus, microcosmic wear is improved.

CONCLUSIONS

A novel fullerene–maleic anhydride copolymer was prepared. It was completely soluble in water, yielding a clear brown solution. TEM analysis showed that it presents an ideal spherical shape in water with a diameter ranging from 10 to 80 nm. As a lubricant additive in base stock (2 wt % triethanolamine and 0.5 wt % OPZ aqueous solution), it can improve the wear resistance, load-carrying capacity, and antifriction ability of base stock. Excessive additive was disadvantageous for the wear resistance and load-carrying capacity. The lubrication mechanism of the fullerene copolymer was likely attributable to its spherically shape structure, which can cause microcosmic elastic rolling as nanometer-sized balls between the two rubbing surfaces.

References

1. Kratschmer, W.; Lamb, L. D.; Fostiropoaulos, K. Nature 1990, 347, 354.
2. Kroto, H. W.; Heath, J. R.; O'Brien, S. C. Nature 1985, 318, 162.
3. Feng, B. Lubrication Sci 1997, 9, 181.
4. Bhushan, B.; Gupta, B. K.; Van Cleef, G. W. Tribol Trans 1993, 36, 573.
5. Blau, P. J.; Haberlin, C. E. Thin Solid Films 1992, 219, 129.
6. Gupta, B. K.; Bhushan, B.; Capp, C. J Mater Res 1994, 9, 2823.
7. White, C. T.; Mintmire, J. W.; Mowrey, R. C. Buckminster-fullerenes; VCH: New York, 1993; p 125.
8. Gupta, B. K.; Bharat, B. Lubrication Eng 1994, 50, 524.
9. Yan, F. Y.; Jin, Z. S.; Zhang, X. S. Tribology 1993, 1, 59 [in Chinese].
10. Bunker, C. E.; Lawson, G. E.; Sun, Y. P. Macromolecules 1995, 28, 3744.
11. Hirsch, A.; Lamparth, L.; Grosser, T. J Am Chem Soc 1994, 116, 9385.