

# Synthesis of Fullerene-Acrylamide Copolymer Nanoball and Its Lubrication Properties

JIANG, Gui-Chang<sup>\*,a,b</sup>(江贵长)    GUAN, Wen-Chao<sup>a</sup>(官文超)    ZHENG, Qi-Xin<sup>a</sup>(郑启新)

<sup>a</sup> Department of Chemistry, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China

<sup>b</sup> Department of Chemistry, Huainan Teachers college, Huainan, Anhui 232001, China

A novel fullerene-acrylamide copolymer was synthesized via radical polymerization. It is soluble in polar solvents such as water, dimethyl sulfoxide *etc.* The product was characterized by FTIR, UV-Vis and GPC. TEM analysis shows that the average particle diameter is about 46 nm. Four-ball tests show that the addition of a certain concentration of the fullerene copolymer to base stock (2 wt% triethanolamine and 0.5 wt% OPZ aqueous solution) can effectively raise the load-carrying capacity ( $P_B$  value) and the antiwear ability. SEM analysis shows that the addition results in reducing diameter of wear scar and decreasing wear.

**Keywords** fullerene-acrylamide copolymer, water solubility, lubrication property, nanoball

## Introduction

The lubricating properties of fullerene C<sub>60</sub> have been speculated since the time of its discovery because of its unique spherical shape with cage diameter of 0.71 nm, high load-bearing capacity, low surface energy, high chemical stability, weak intermolecular and strong intramolecular bonding,<sup>1-4</sup> and it was expected to act as tiny ball bearing.<sup>5,6</sup> Theoretical simulations found that C<sub>60</sub> molecule was able to roll between graphite sheets, as well as, between hydrogen-terminated surfaces of diamond under relatively low load.<sup>7</sup> The tribological properties of fullerene particles as an additive to liquid lubricants were studied by a few groups.<sup>8,9</sup> 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 some physical or mechanical ways (such as solid grinding, solvent evaporation, ultrasonic, *etc.*) since they are only soluble in few non-polar solvents (such as benzene, toluene, carbon disulfide, *etc.*), so fullerene particles were present in the form of molecular cluster or super-corpuscle.<sup>8,9</sup> Up to this date, the tribological properties of soluble fullerene and its derivatives have seldom been studied. In this paper, a novel water-soluble fullerene-acrylamide copolymer was synthesized, and the frictional behavior of soluble fullerene copolymer was studied for the first time.

## Experimental

### Materials

Fullerene (C<sub>60</sub>) was obtained from Wuhan university (purity > 99.99%). Acrylamide (A.R.) was obtained from Hubei university. Benzoyl peroxide was obtained from Hubei university. The other solvents are analytically pure reagents.

### Preparation of fullerene-acrylamide copolymer

The fullerene-acrylamide copolymer was synthesized by typical free radical polymerization. A solution of C<sub>60</sub> in *o*-dichlorobenzene (*o*-DCB) or toluene was mixed with acrylamide. The mixture (dark red color) was deoxygenated by bubbling dry nitrogen gas for *ca.* 25 min, followed by the addition of benzoyl peroxide. The polymerization reaction was carried out in a sealed glass bottle at 70 °C. The reaction products were precipitated from the *o*-DCB solution into methanol. The precipitation procedure was repeated several times, yielding a solid sample with almost black color. The solid sample was further purified by washing with dimethyl sulfoxide /CH<sub>3</sub>OH and dimethyl sulfoxide/C<sub>6</sub>H<sub>14</sub>. After drying under vacuum, the final copolymer sample was obtained. Polymer of neat acrylamide was prepared under the same conditions to be used as a reference.

### Measurement of tribology properties

Base stock was 2 wt% of triethanolamine and 0.5 wt% of OPZ (prepared by ourselves) aqueous solution. The fullerene-acrylamide copolymer prepared above was used as lubricant additive in the base stock. The tribological measurements were carried out by using an

\* E-mail: wangzhiqing1978@163.com

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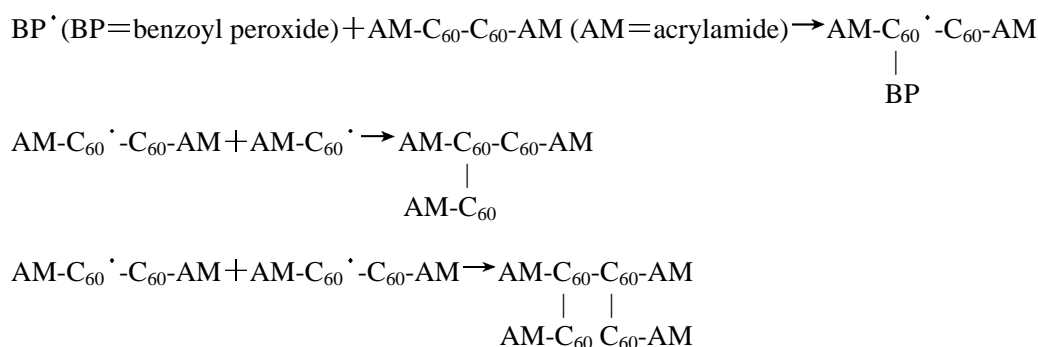
MQ-800 four-ball tribotester at a rotational speed of 1450 r/min and at a temperature of 20 °C. The maximum nonseized load was obtained by GB3142-82, similar to ASTM D2783; wear scar diameter was measured under a load of 400 N and a test duration of 30 min; dependence of wear scar diameter on load was also measured at 0.2 wt% additive content and test duration of 30 min for wear scar diameter. The stainless steel balls used in the tests were made of GCr15 (AISIE52100) bearing steel with the 64–66 surface HRC hardness and 0.012 μm of surface roughness Ra. In order to study the effect of fullerene in the fullerene-acrylamide copolymer, the same concentration of the polyacrylamide reference as additive was measured under the same conditions. For comparison, the C<sub>60</sub> used as additive was measured under the same conditions as a reference.

## Results and discussion

### Fullerene-acrylamide copolymerization reactions

The results presented here clearly show that C<sub>60</sub> and acrylamide can be copolymerized under different conditions (Table 1). With a constant benzoyl peroxide amount, C<sub>60</sub> contents in the copolymers increase with increasing initial C<sub>60</sub> : acrylamide reactant ratio (Table 1). There is no apparent reduction in the polymer yield at high initial C<sub>60</sub> : acrylamide reactant ratios, which is probably due to relatively small [C<sub>60</sub>]/[initiator] values. In addition, solubility in water of the copolymers prepared with different initial C<sub>60</sub> : acrylamide reactant ratios is not significantly different (Table 1). In a classi-

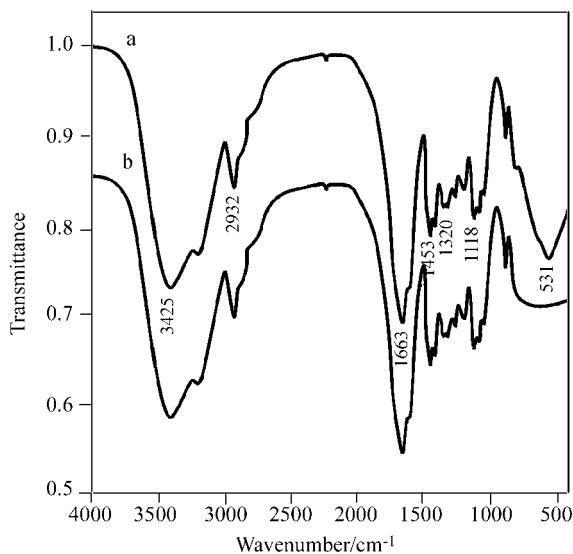
cal mechanism of radical polymerization, propagation of C<sub>60</sub>• radicals is critical to the formation of true C<sub>60</sub>-acrylamide copolymers.<sup>10</sup> However, it has been suggested<sup>10</sup> that propagation of C<sub>60</sub>• radicals is slow in general because of their relatively high stability. It has also been suggested that C<sub>60</sub> competes effectively with acrylamide for initiator radicals and, as a logical extrapolation, for AM• radicals as well. In this regard, C<sub>60</sub> may act as a radical inhibitor in the copolymerization reaction. Evidence for the inhibiting effect includes the observation<sup>10</sup> that at high [C<sub>60</sub>]/[initiator] ratios polymerization yields are low in comparison with those in neat acrylamide polymerization. Thus, the mechanism of C<sub>60</sub>-acrylamide copolymerization may be different from the classical mechanism of radical polymerization of acrylamide such that there is a significant population of C<sub>60</sub> radicals and their propagation is relatively slow. However, even with the suggested inhibiting effect of C<sub>60</sub> in the copolymerization reaction, contributions of polyacrylamide structures are substantial even in the copolymers with high C<sub>60</sub> contents, as shown in the observed FT-IR spectra of the copolymers (Figure 1). By assuming that C<sub>60</sub> radicals participate in termination processes only, the average number of C<sub>60</sub> cages per polymer (*N*<sub>C<sub>60</sub></sub>) should be 1–2. However, in the copolymers with high C<sub>60</sub> contents (Table 1), the estimated *N*<sub>C<sub>60</sub></sub> values are apparently larger. The high C<sub>60</sub> populations might be explained by considering the possibility that functionalized C<sub>60</sub> cages may also compete for initiator radicals. The results could be used to support a proposed copolymer mechanism as follows.



**Table 1** Results of fullerene-acrylamide copolymerization reactions<sup>a</sup>

| ID  | C <sub>60</sub> : acrylamide (mg : g) | Ben. peroxide/mg | Yield <sup>b</sup> /% | C <sub>60</sub> /wt% | Solvent         | Product <sup>c</sup> |
|-----|---------------------------------------|------------------|-----------------------|----------------------|-----------------|----------------------|
| I   | 30 : 4.0                              | 200              | ~45                   | ~1.7                 | Pyridine        | Not good             |
| II  | 50 : 1.3                              | 200              | ~65                   | ~5.7                 | Dioxane         | Good                 |
| III | 70 : 1.1                              | 200              | ~67                   | ~8.9                 | Dichlorobenzene | Not good             |
| IV  | 100 : 1.0                             | 200              | ~70                   | ~14                  | Toluene         | Good                 |
| V   | 100 : 0.5                             | 200              | ~60                   | ~30                  | Toluene         | Good                 |
| VI  | 100 : 0.1                             | 200              | ~95                   | ~53                  | Toluene         | Not good             |

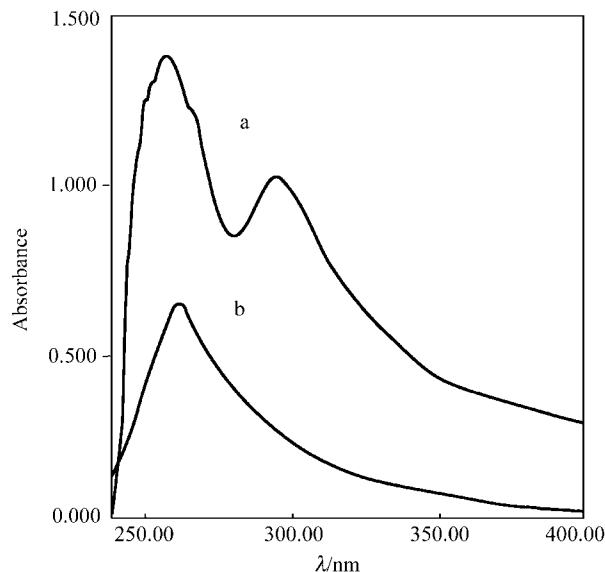
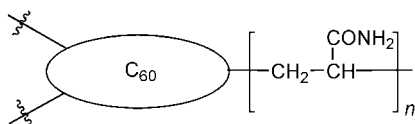
<sup>a</sup> Reaction temperature 70 °C, reaction time 10 h. <sup>b</sup> Calculated without considering the contribution of initiator fragments. <sup>c</sup> Solubility in water.



**Figure 1** FTIR spectra of  $C_{60}$ -acrylamide copolymer (a) and polyacrylamide (b).

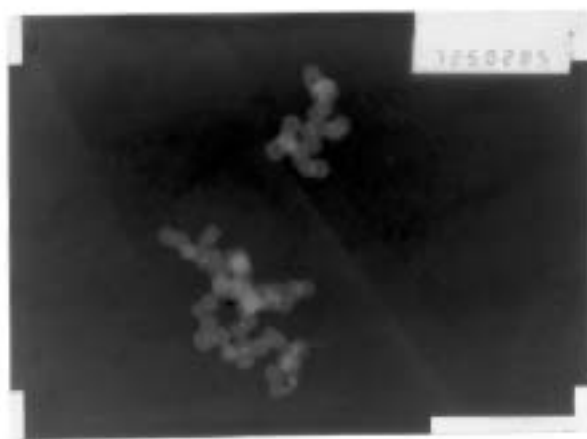
### Characterization of fullerene-acrylamide copolymer

The copolymer was characterized by FTIR, UV and GPC. FT-IR spectra were measured in KBr matrices, and the results were compared with those of neat polyacrylamide samples prepared under the same experimental conditions. As shown in Figure 1, observed FT-IR spectra of the copolymers with  $C_{60}$  contents are very similar to those of neat polyacrylamide. However, for the copolymer with  $C_{60}$  contents, the FT-IR spectrum shows extra absorption in the  $531\text{ cm}^{-1}$  region, which is typical with respect to substituted  $C_{60}$ .<sup>10</sup> UV absorption spectra were measured in THF, and the results were compared with those of polyacrylamide. As shown in Figure 2, observed UV absorption spectra of copolymer with  $C_{60}$  contents are very different from those of polyacrylamide. The somewhat structured absorption band of free  $C_{60}$  is replaced by a steadily decreasing band, typical for substituted  $C_{60}$ .<sup>10</sup> UV absorption wavelength maximum of copolymer with  $C_{60}$  contents is 252 nm, different from that of free  $C_{60}$  and polyacrylamide, which is typical with respect to substituted  $C_{60}$ .<sup>11,12</sup> The emission can be attributed to the  $C_{60}$ -containing sites in the polyacrylamide structure. The average molecular weight ( $M_w$ ) was obtained by GPC (Voria 5060 model).  $M_w$  of copolymer with  $C_{60}$  contents is 3360. The molecular structure of the copolymer may be star polymer with fullerene as core and a grafting of one or several polyacrylamide chain segments. The results could be used to support a proposed copolymer structure as follows:



**Figure 2** Comparison of  $C_{60}$ -acrylamide copolymer UV absorbance (a) with that of polyacrylamide (b). All in THF.

Morphology and size of the fullerene copolymer in water were measured using a JEM 100CXII model transmission electron microscope (TEM) 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 40–80 nm, as shown in Figure 3. For comparison, the appearance of the polyacrylamide in water is lamellar shape. The physical structure of the fullerene copolymer nanometer tiny balls may be described as follows: the core is very hard fullerene, and the shell is polyacrylamide, which may be relatively soft but very elastic.<sup>12</sup>



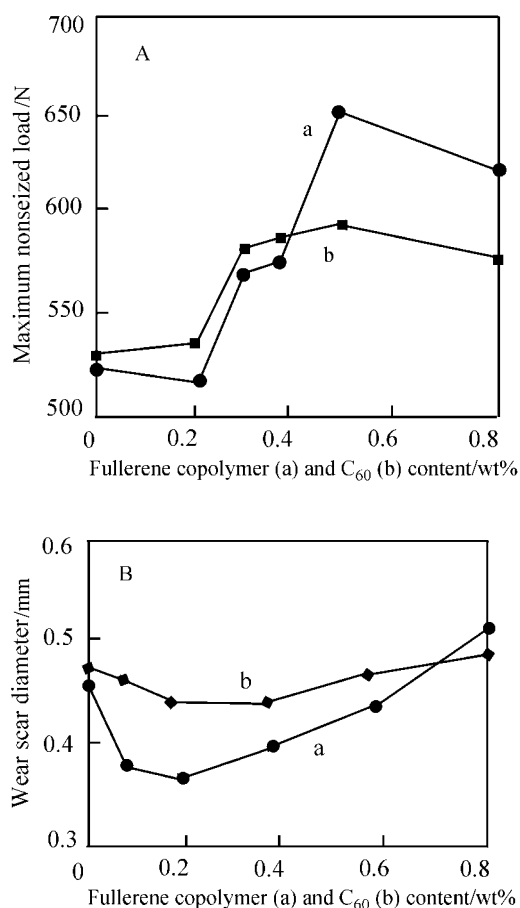
**Figure 3** Morphology of nanometer balls of the fullerene copolymer in water. Magnification:  $72000\times$ .

### Tribology properties of fullerene-acrylamide copolymer

The maximum nonseized load ( $P_B$  value) 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 higher maximum non-seized load than the base stock and C<sub>60</sub>. In other words, the fullerene copolymer could strengthen the load-carrying capacity of the base stock. When the fullerene copolymer content reaches 0.5 wt%, the P<sub>B</sub> value is maximum. Then excessive fullerene copolymer resulted in a decrease of load-carrying capacity of the base stock.

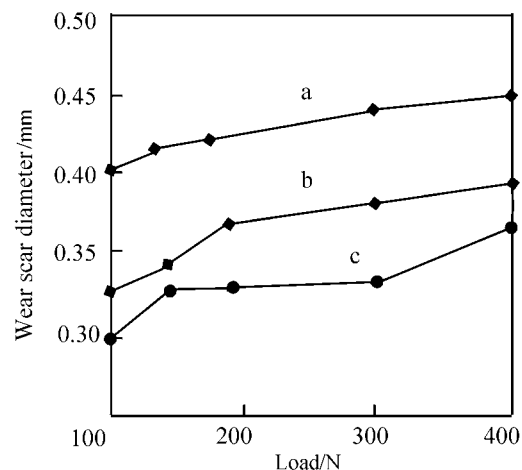
The wear scar diameter data are given in Figure 4 (B). It is seen that the addition of the fullerene copolymer can decrease the wear scar diameter of the base stock. The base stock with the fullerene copolymer exhibits a smaller wear scar diameter than that with C<sub>60</sub>. When the fullerene copolymer content reaches 0.2 wt%, the wear scar diameter is minimum. But excessive fullerene copolymer exhibits a larger wear scar diameter than the base stock and C<sub>60</sub>. Decrease in load-carrying capacity and wear resistance at excessive additive may be attributed to the corrosive wear, since the fullerene-acrylamide copolymer additive may react with the surface of the metal.



**Figure 4** Effect of the fullerene copolymer and content on (A) maximum non-seized load and (B) wear scar diameter.

The dependence of wear scar diameter on load is shown in Figure 5.

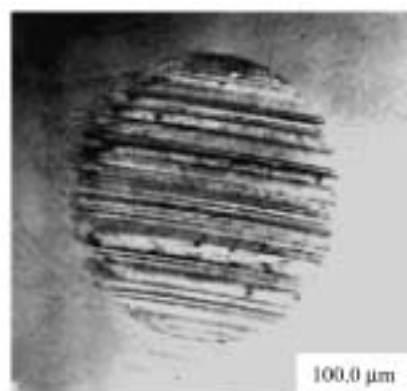
Under testing loads, the wear scar diameter of base



**Figure 5** Effect of load on wear scar diameter. a. Base stock with 0.2 wt% polyacrylamide; b. base stock with 0.2 wt% C<sub>60</sub>; c. base stock with 0.2 wt% fullerene-acrylamide copolymer.

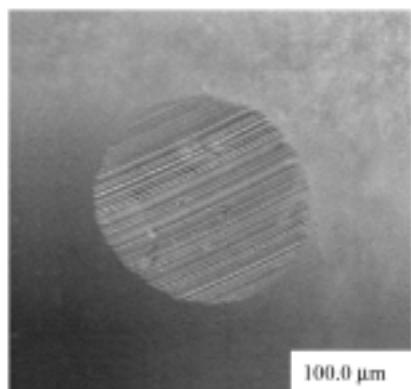
stock with 0.2 wt% fullerene-acrylamide copolymer is smaller than that with 0.2 wt% polyacrylamide and that with 0.2 wt% C<sub>60</sub>. It means that the presence of fullerene copolymer can strengthen the wear resistance of base stock.

The worn surface in four-ball machine testing, which was obtained under a load of 400 N and a testing time of 30 min, was observed by SEM. The wear scar of base stock with 0.2 wt% polyacrylamide and that with 0.2 wt% fullerene-acrylamide copolymer are shown in Figures 6 and 7, respectively. It was indicated that the wear scar obtained with the fullerene copolymer additive is obviously smaller and exhibits mild scratches, but in comparison, larger wear scar and sharp tracks were observed in the presence of base stock with polyacrylamide additive. In other words, the fullerene-acrylamide copolymer can improve microcosmic wear condition.



**Figure 6** Morphology of the wear scar lubricated by base stock with 0.2 wt% polyacrylamide (100×).

Based on the above tribological measurements and worn surface analyses, the lubrication mechanism of the fullerene-acrylamide copolymer additive can be deduced. The fullerene copolymer plays the role of a solid



**Figure 7** Morphology of the wear scar lubricated by base stock with 0.2 wt% fullerene-acrylamide copolymer (100 $\times$ ).

lubricant. Since fullerene has very high load-carrying capacity and the fullerene copolymer is nanometer tiny balls with core-shell structure, which can penetrate into rubbing surfaces and deposit there, it is reasonable to speculate that the fullerene copolymer nanometer balls may be more effective than polyacrylamide and C<sub>60</sub> to support and isolate two relative motion surfaces, and therefore, the load-carrying capacity and anti-wear 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 polymer of neat acrylamid, which is relatively soft but very elastic, thus microcosmic condition of wear is improved.

## Conclusions

A novel fullerene-acrylamide copolymer was pre-

pared. It is completely soluble in water, yielding a clear brown solution. TEM analysis shows that it presents an ideal spherical shape in water with a diameter ranging from 40 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 anti-friction ability of base stock. Excessive additive was disadvantageous for the wear resistance and load-carrying capacity.

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