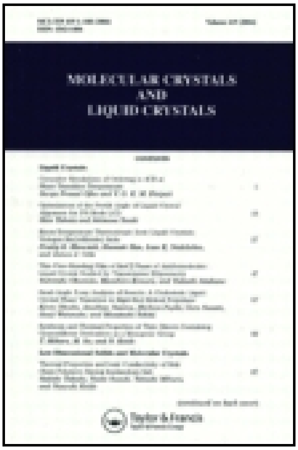

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Studies of Exfoliated Graphite (EG) for Heavy Oil Sorption

Beata Tryba [a], Ryszard J. Kalenczuk [a], Feiyu Kang [b], Michio Inagaki [c] & Antoni W. Morawski [a]

[a] Dept. of Water Technology and Env. Protection, Technical University of Szczecin, ul. Pulaskiego 10, 70-322, Szczecin, Poland

[b] Dept. of Materials Science and Engineering, Tsinghua University, Beijing, 100084, China

[c] Aichi Institute of Technology, Dept. ofAppl. Chem., Yakusa, Toyota, 470-0392, Japan

Version of record first published: 24 Sep 2006

To cite this article: Beata Tryba, Ryszard J. Kalenczuk, Feiyu Kang, Michio Inagaki & Antoni W. Morawski (2000): Studies of Exfoliated Graphite (EG) for Heavy Oil Sorption, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 340:1, 113-119

To link to this article: http://dx.doi.org/10.1080/10587250008025452

Mol. Cryst. and Liq. Cryst., 2000, Vol. 340, pp. 113-119
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Studies of Exfoliated Graphite (EG) for Heavy Oil Sorption

BEATA TRYBA[a], RYSZARD J. KALEŃCZUK[a], FEIYU KANG[b],
MICHIO INAGAKI[c] and ANTONI W. MORAWSKI[a]

[a]*Dept. of Water Technology and Env. Protection, Technical University of Szczecin, ul. Pułaskiego 10, 70–322 Szczecin, Poland,* [b]*Dept. of Materials Science and Engineering, Tsinghua University, Beijing 100084, China and* [c]*Aichi Institute of Technology, Dept. of Appl. Chem., Yakusa, Toyota, 470–0392 Japan*

Electrochemically intercalated graphite with H_2SO_4 was thermally expanded at 1000°C. Exfoliated samples of GIC-H_2SO_4 with different times of expansion revealed different expansion volumes. Both the surface area and the chemical character of samples also depend on the exfoliation time. A low density of the exfoliated graphite is demanded for the oil sorption. The oil sorption is restricted by the surface area and the bulk density.

Keywords: expanded graphite; exfoliation; heavy oils sorption

INTRODUCTION

Exfoliated graphite was found to have excellent capabilities for oil sorption[1, 2]. Inagaki et al. reported that the maximum sorption capacity for exfoliated graphite reached 86 g of oil per gram of the sample. This is a very promising result in comparison with other sorbents.

The maximum sorption capacity of exfoliated graphite is found to be strongly depend on its bulk density. For all the heavy oils used the capacity decreases drastically with an increase of the bulk density of the exfoliated graphite[1].

Under conditions of thermal shock (950-1000°C) the surface area of the exfoliated graphite rapidly increases to the value of 50-200 m^2/g[2]. It has been found that if the bulk density of the exfoliated graphite decreases during exfoliation the surface area of these samples increases[1].

In this paper we studied the influence of exfoliation time on the properties of EG.

EXPERIMENTAL

Natural graphite was intercalated electrochemically in 98% wt. sulfuric acid. Details of this procedure has been reported in the literature[3]. The characteristics of the samples are given in table 1. Sample I6 was superoxidised. All the samples were thermally expanded in a muffle furnace at 1000°C for a residence time that varied from 20 to 60 sec.

TABLE 1. Characteristic of the GIC-H_2SO_4 samples.

Sample Number	**I10**	**I6**	**I5**	**I3**	**IX**
Moisture [%]	1.06	2.18	0.1	0.53	-
Volatile [%]	5.24	19.32	15.85	9.7	-
Ash [%]	0.66	2.4	0.4	0.15	-
Average flake size [mm]	0.3	0.3	0.3	0.3	0.18
Consumed electrical quantity [A· hr / kg]	4.6	7.7	5.7	5.5	6.1

The surface area BET of the exfoliated graphite was determined from measurements of nitrogen adsorption - desorption isotherms performed at a temperature of -196°C in an ASAP2010 Micromeritics instrument. Porosity was calculated using the classical Kelvin equation.

X-ray diffraction analysis was performed using a HZG-4 diffractometer (Germany) with filtered CuKα radiation.

The residual sulphur in exfoliated graphite samples was estimated by the XRFS method using a VRA-30 spectrofotometer (Germany).

The performance of oil sorption was examined for various grades of oils: two engine oils (synthetic Havoline formula 3 5W-40 and 15W-40), petrol and crude oil which were characterized by both a different viscosity (134, 178, 0.5 and 3.1cP respectively) and density (847, 883, 723 and 798 kg/m^3 respectively). Moreover, they possessed various sorption capacity. The experiments for oil sorption on the exfoliated graphite were performed using selected adsorbents with the following notation: 6E40 (GIC No. 6 exfoliated for 40 sec.), 10E60 (GIC No. 10 exfoliated for 60 sec.), 5E50 (GIC No. 5 exfoliated for 50 sec.), and 5E60 (GIC No. 5 exfoliated for 60 sec.). The samples 6E40 and 10E60 differ strongly in surface area, whereas the samples 5E50 and 5E60 exhibit the similar values of the surface area but 5E60 was more oxidised than sample 5E50.

RESULTS AND DISCUSSION

The exfoliation time influences the expansion volume. Generally, if the time of exfoliation increases the surface area of the exfoliated graphite increases and the bulk density decreases, but prolonged time of exfoliation reduces the surface area and increases the burn-out of the graphite. Some data are listed in table 2. The maximum of the surface area is achieved for 40-50 sec. of exfoliation. According to the literature[4] an increase of the bulk density of the exfoliated graphite results in a decrease of both the specific surface area and the total pore volume.

TABLE 2. The bulk density and surface area of exfoliated graphite samples.

Sample	20 sec.		30 sec.		40 sec.		50 sec.		60 sec.	
	[g/cm^3]	[m^2/g]	[g/cm^3]	[m^2/g]	[g/cm^3]	[m^2/g]	[g/cm^3]	[m^2/g]	[g/cm^3]	[m^2/g]
3	0.015	33.0	0.010	37.2	0.009	40.8	0.007	48.2	0.008	47.6
5	0.017	31.7	0.008	41.5	0.007	55.0	0.006	39.9	0.007	36.7
6	0.015	39.6	0.005	65.5	0.004	86.8	0.004	73.9	0.004	53.5
10	0.035	15.2	0.026	16.7	0.019	18.3	0.027	19.5	0.028	14.8
X	0.021	29.5	0.007	55.7	0.005	53.9	0.006	42.9	0.006	50.3

Scanning electron micrographs obtained in a SEM for sample 6 are shown in figure 1.

A graphite sample subjected to exfoliation can be observed in fig. 1a,b which displays very puckered graphite sheets with the honeycomb structure[5]. A prolonged time of exfoliation (50-60 sec.) causes peripheral melting of graphite (spheres on the micrograph, figure 1d) and creates craters in some regions of graphite (figure 1c).

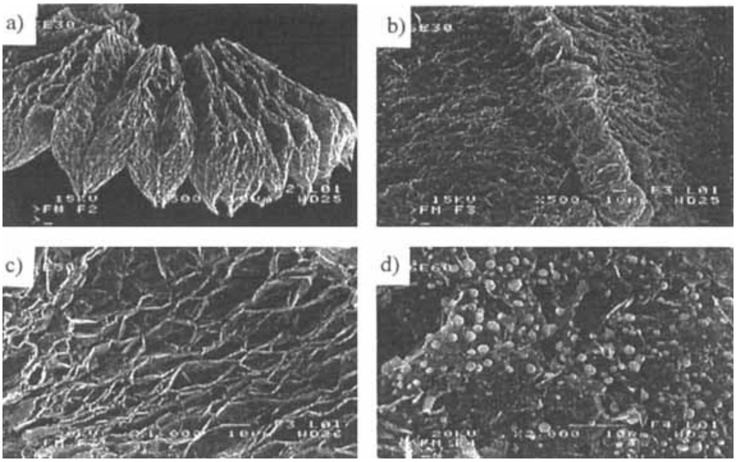

FIGURE 1 Scanning Electron Micrographs of sample 6 exfoliated for a) 30 sec., b) 30 sec., c) 50 sec., d) 60 sec.

The X-ray diffraction patterns obtained for the intercalates No. 6 and 10 are illustrated in figure 2a. This diffractogram shows many peaks which are overlap near the diffraction angle $2\theta = 26°$. This is regarded as proof of the existence of residual sulphur in these intercalates[4]. It can be seen in this figure that the intercalated sample 110 is ordered to a lower degree in comparison with the others. This may be attributed to the distribution of the intercalate in the graphite structure which may be localized beyond the centre of a flake.

The diffractograms of the samples No. 6 and 10 after heat treatment are shown in fig. 2b. A single sharp peak (002) emerged and revealed the graphite structure in addition to other peaks of (101), and (100) of graphite.

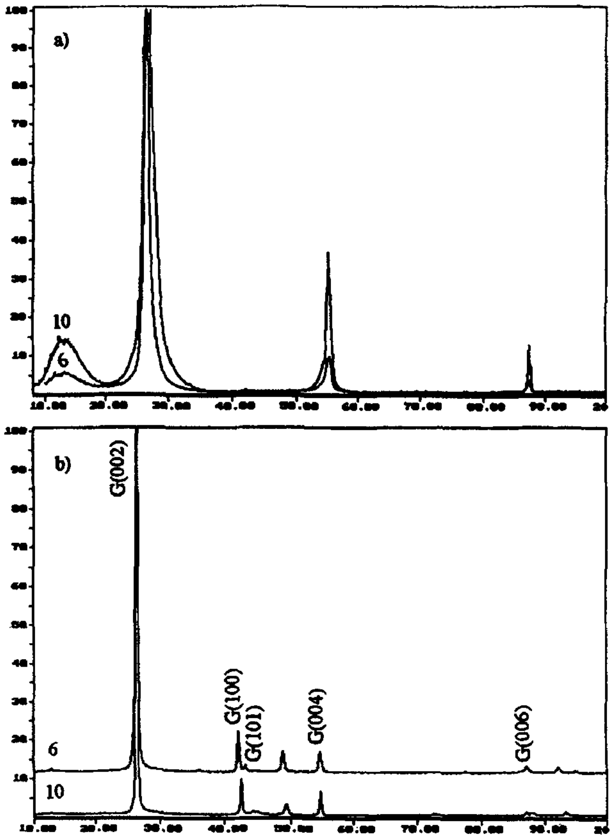

FIGURE 2 XRD patterns of samples No. 6 and 10 a) intercalated, b) exfoliated in 40 sec.

X-ray fluorescence spectroscopy analysis demonstrates that a small amount of sulphur still remained after the heat treatment. The sample 6 of both intercalated and exfoliated graphite contains the highest amount of sulphur in comparison with the other samples. The weight percentage of sulphur in the GIC-H_2SO_4 samples was estimated as 5.3% for sample 3, 5.7% for sample 5, 7.3% for sample 6, 4.5% for sample 10 and 6.4% for sample X. After 30 sec. of exfoliation the amount of residual sulphur decreased substantially, the weight percentage of sulphur was estimated respectively as 0.5% for sample 3, 0.8% for sample 5, 3.5% for sample 6, 0.7% for sample 10 and 1.1% for sample X. The amount of sulphur in the intercalates reflects a different percentage of intercalation because of different preparation conditions. Higher intercalate percentage results in a higher expansion volume and surface area.

In the case of thermal exfoliation the opening of these pockets start from their centre as an effect of the gas overpressure[5]. It may be assumed that sample 10 with the lowest sulphur acid concentration does not possess an intercalate localized in the inner regions of flakes – it is poorly exfoliated in comparison with the other samples, and has the lowest amount of intercalated compound. The other samples are readily exfoliated as expected from the amount of intercalated compound and their ordered structure.

The highest sorption capacity (51.1g/g of EG sample) was noticed for sample 6E40 for oil having both the highest viscosity and density. Sorption of Havoline Formula 3 5W/40 was also high, however petrol exhibited a sorption of only 0.2-2 g per gram of sorbent. After petrol sorption the exfoliated graphite did not form a solid in the shape of sphere as it did in the case of the other oils. On the contrary, after contact with petrol the exfoliated graphite was collapsed. Table 3 summarises the results from the measurements of oil sorption.

TABLE 3. Maximal oil sorption for studied samples.

Sample	Havoline Formula 3 5W/40 [g/g]	Havoline Formula 3 15W/40 [g/g]	Crude oil [g/g]	Petrol [g/g]
6E40	40.3	51.1	38.2	0.2
10E60	13.7	14.2	6.8	0.5
5E50	33.3	35.2	19.3	0.5
5E60	35.5	35.3	30.1	2.0

CONCLUSIONS

The high consumption of current during the intercalation results in a high volatility of the samples and therefore imparts a high expansion volume and a significant development of surface area during the exfoliation. The sample 6 which was superoxidised was characterised by the highest expansion volume and possesses the highest value of surface area. The ash content in the intercalates does not influence the expansion volume. Thus, it may be assumed that flake sizes of GIC samples in the range 0.3 – 0.18 mm does not affect the final product of exfoliation but the intercalate percentage and its localization in the graphite structure might be important.

As the exfoliation time increases the surface area increases and the bulk density rapidly decreases. An exfoliation time in the range of 40-50 sec. is sufficient to produce a good material for oil sorption. A large amount of the intercalated compound gives more exfoliated product.

Oil sorption increases as the surface area of the exfoliated graphite increases and its bulk density decreases. The mezo and macroporous structure of the exfoliated graphite fits very well for oil sorption.

It was proved that heavy oils with both high viscosity and density are preferentially sorbed on the exfoliated graphite.

References

[1] M. Toyoda, J. Aizawa, M. Inagaki, *Desalination,* **115,** 199 (1998).

[2] N. Z. Cao, W. C. Shen, S. Z. Wen, J. L. Gu, Z. D. Wang, *The European Carbon Conference "Carbon 96"- Newcastle, UK,* **114** (July 1996).

[3] F. Kang, T. Zhang, Y. Leng, *J. Phys. Chem. Solids,* **57,** 883 (1996).

[4] J. H. Han, K. W. Cho, K. H. Lee, H. Kim, *Carbon,* **36,** 1801 (1998).

[5] J. M. Skowroński, *J. Mat. Science,* **23,** 2243 (1988).

[6] S. Shin, J. Jang, S.-H. Yoon, I. Mochida, *Carbon,* **35,** 1739 (1997).

[7] S. Eser, *Carbon,* **34,** 539 (1996).

[8] H. H. Willard, L. L. Merritt, Jr., J. A. Dean, F. A. Settle, Jr., *Instrumental Methods of Analysis,* 7th Edition, Wadsworth Publishing Company (1988).