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Synthesis and characterizations of poly(ethylene oxide) methyl ether grafted on the expanded graphite with isocyanate groups

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Abstract

Introducing isocyanate (NCO) groups onto the surface of expanded graphite (EG) was achieved by treatment of the EG with excess toluene-2,4-diisocyanate in dimethyl sulfoxide (DMSO). The reaction of NCO group on the EG with the hydroxyl group in the poly(ethylene oxide) methyl ether (MPEO) to yield MPEO-grafted EG was carried out for modifying the surface properties of graphite. The influence factors, such as reaction time, temperature and the ratio of the reactants, on the grafting reaction and grafting ratio were investigated.

Keywords: Composite; Grafting; Poly(ethylene oxide) methyl ether; Graphite

1. Introduction

In the recent decades, the conductive composites made of polymers and graphite has received great attention [1–3]. Most of studies on this subject focused on the intercalation of polymers into graphite to afford polymer-intercalated graphite composites [4–9]. When the polymer/graphite composites are prepared by blending polymer with graphite particles, their electrical conductivity is improved, but their mechanical properties decrease due to the incompatibility of polymers with graphite. One of the best methods to solve this problem is the surface modification of graphite by grafting polymers on the graphite particles, which has been investigated [10–13]. Tsubokawa [10] reported that the grafting polymerizations of methyl methacrylate (MMA) and styrene (St) were carried out in the presence of the graphite treated with *n*-butyllithium, and the grafting ratio for PMMA and PSt were 52.8% and 37.2% respectively. Daoulas KC[11] studied that graphite particles were grafted by three different polyethylenes (PEs) with number-average chain length = 78, 156 and 250, forming the products with grafting densities ranging from 0.54 to 2.62 nm^{-2}. We reported that St was polymerized to form PS-grafted EG in presence of the expanded graphite (EG) with cationic initiating sites, $CO^{+}ClO_4^{-}$ or/and $C^{+}ClO_4^{-}$ on its surface [12].

Compared with the intercalation of polymers into graphite, grafting polymers on the surface of graphite was less studied. Here we reported a new method to prepare polymer-grafted EG. As we know, when nature graphite is oxidized, functional groups, such as C–O–C, C–OH and COOH, are formed on the surface of graphite oxide [12,13]. The same functional groups could be remained on the surface of EG made from the graphite oxide [12]. Thus, addition reactions of hydroxyl or/and carboxylic acid groups with isocyanate group

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should be taken place. When an excess of toluene-2, 4-diisocyanate (TDI) is mixed with EG, the graphite particles with isocyanate groups can be obtained, subsequently react with those functional polymers having hydroxyl groups, resulting in polymer-grafted EG.

Since both poly(ethylene oxide) and graphite are good electrolyte materials, it should be valuable to study the preparation and characterizations of the graphite particles grafted with poly (ethylene oxide) methyl ether (MPEO).

2. Experimental

2.1. Materials

Natural graphite purchased from Shanghai Colloid Chemical Factory was oxidized with $KMnO_4$ in a solution of acetic anhydride and nitric acid at 30 °C for 40 min. The graphite oxide (GO) obtained was extracted with benzene for removing the impurities. The EG was prepared by heating GO at 500 °C for 15 min under N_2 atmosphere. Toluene-2,4-diisocyanate (TDI, The Shanghai First Chemical Reagent Plant) was distilled under reduced pressure before use. Toluene (The Shanghai First Chemical Reagent Plant) was dried over CaH_2 and distilled. Dimethyl sulfoxide (DMSO, The Shanghai Chemical Reagent Company) was dried over CaH_2 and distilled under reduced pressure. MPEO with only one terminal hydroxyl group ($M_n = 5000$) was purchased from Fluca, and dried in vacuum at 50 °C before use.

2.2. Preparation of EG with NCO group (EG-NCO)

Two methods were used to prepare EG-NCO. Method 1: TDI (0.06 ml) and toluene (50 ml) were mixed with 0.5 g of dried EG under nitrogen atmosphere at room temperature. The suspension solution was stirred at 25 °C for 48 h. The solid product was obtained by filtration, and then washed with toluene three times.

Method 2: TDI (0.06 ml) and toluene (50 ml) were mixed with dried EG (0.5 g) under nitrogen atmosphere at room temperature. The suspension solution was refluxed with stirring at 110 °C for 48 h, and then unreacted TDI and solvent were distilled completely under reduced pressure. The EG having NCO group on its surface (EG-NCO) was produced.

2.3. Grafting reactions of MPEO with EG-NCO

There were two methods to carry out the grafting reactions of MPEO with EG-NCO. Method A: MPEO (3.5 g) was added into the suspension solution of EG-NCO (0.5 g) made by Method 1 in 50 ml toluene. The mixture was stirred under nitrogen atmosphere at 25 °C for 30 h.

Method B: MPEO (3.5 g) was added into the suspension solution of EG-NCO (0.5 g) made by Method 2 in 50 ml DMSO. The mixture was refluxed with stirring under nitrogen atmosphere at 110 °C for 30 h. The products obtained from both methods were filtered, washed with alcohol, and dried in vacuum at 50 °C.

2.4. Determination of grafting ratio

The products obtained were extracted with alcohol in Soxhlet extractor for removing unreacted MPEO completely. After the product was dried in vacuum at 50 °C for 24 h, MPEO-grafted EG was weighted (W_C). The grafting ratio is calculated according to Eq. (1).

$$\text{Grafting ratio } (\%) = (W_C - W_{EG})/W_{EG} \times 100\% \quad (1)$$

where W_{EG} is the weight of EG.

2.5. Characterization and measurement

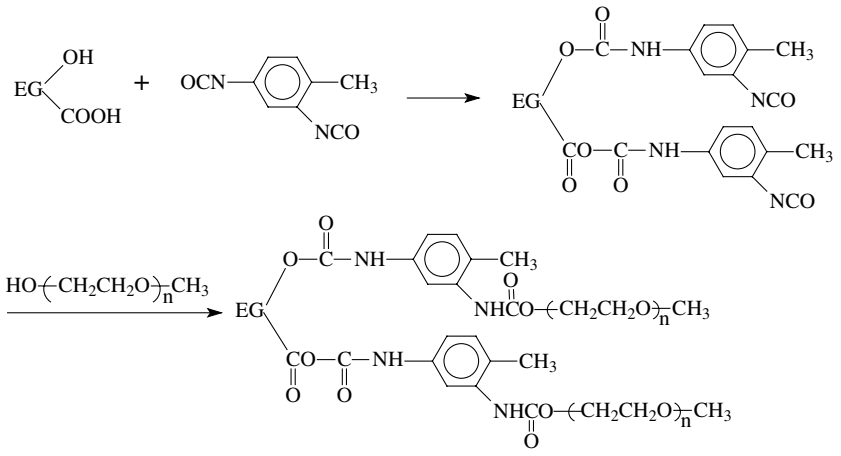
Elementary analysis of the sample was performed on a Vario ELIII Elementary Analyzer. The XPS spectra was measured on a VG ESCALAB MK-II X-ray photoelectron spectrometer at 25 °C using Mg/K as X-radiation source. The sample chamber was pumped to about 10^{-9} Pa. FTIR spectra were recorded on a VECTOR-22 Fourior Transform Infrared Spectrophotometer.

3. Results and discussion

3.1. EG with NCO groups

It is expected that the hydroxyl and carboxyl groups in the EG particles will react with isocyanate group according to Scheme 1. An excess of TDI was reacted with the hydroxyl and carboxyl groups of EG, and after the reaction was completed, the product was isolated by filtration. The IR spectra were measured, and the typical IR spectra of EG and EG-NCO are shown in Fig. 1. When comparing with the IR spectrum of EG in Fig. 1A, we can find a peak at $v = 2269\ cm^{-1}$ ascribed to the isocyanate group, and another peak at $1708\ cm^{-1}$ corresponding to carboxyl group of urethane in Fig. 1B, indicating that isocyanate groups of TDI are connected to the surface of EG particles through urethane linkages.

Another evidences for the reactions of hydroxyl and carboxylic acid with isocyanate groups are the results from elementary analysis and XPS measurements. They are summarized in Table 1. The existence of N in the



Scheme 1.

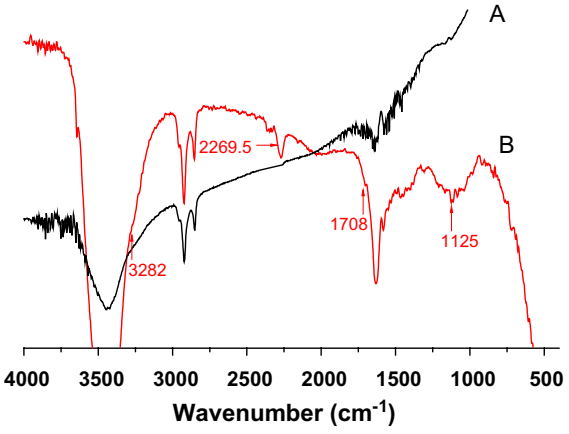


Fig. 1. IR spectra of A: EG and B: EG-NCO (the same samples with that in Table 1).

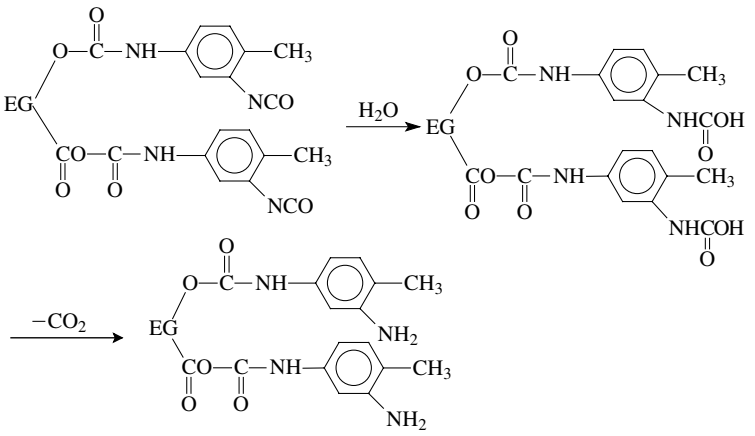
EG-NCO (see Table 1) demonstrates that the reaction of EG with TDI occurred, since there is no N in EG. Theoretically, if only hydroxyl groups in EG react with one isocyanate group of TDI, the ratio of oxygen to nitrogen atoms in EG-NCO is 1.5/1. If similar reactions between carboxylic acid and isocyanate groups occurs, this ratio will be 2/1. However, the much higher ratio of O/N = 4.8/1 (Table 1) was obtained from elementary analysis. The probable reasons are that the ether linkage (C–O–C) cannot react with isocyanate group, and/or some of the hydroxyl groups inside the EG particles cannot participate in this reaction, and still remain after reactions. However, the ratio of O/N from XPS measurement is 1.07/1 (Table 1), which is much lower than theoretical value of 1.5/1. Probably, some of isocyanate groups on the surface of EG-NCO reacted with H_2O in air, forming amine group as shown in Scheme 2, which was also observed by Tsubokawa et al. [14].

In order to confirm the existence of amino groups, the XPS spectra of EG-NCO were measured, and a typical XPS spectrum is shown in Fig. 2. We can find three peeks, C1S: 284–286 eV, N1S: 399.4–401.7 eV, O1S: 531.5–533.5 eV. The nitrogen peak can be divided into three peaks as shown in Fig. 3. A main peak at 400.5 eV is ascribed as N in carbamate group (–NH–COO). Another two peaks at 401.7 and 399.4 indicate the existence of isocyanate and amine ($–NH_2$) groups in EG-NCO respectively. This confirms further that the NCO groups on the surface of EG-NCO are moisture-sensitive.

Table 1
The compositions of EG and EG-NCO

Sample	Elementary analysis (wt%)				O/N (AT ratio)	XPS (AT%)			O/N (AT ratio)
	C	N	O	H		C	N	O	
EG[a]	98.81	0.012	0.852	0.326		98.24	0.00	1.58	
EG-NCO[b]	93.69	0.735	4.062	0.973	4.8/1	82.87	8.27	8.86	1.07/1

[a] EG is expanded graphite.
[b] EG-NCO is the product from the EG treated with TDI.



Scheme 2.

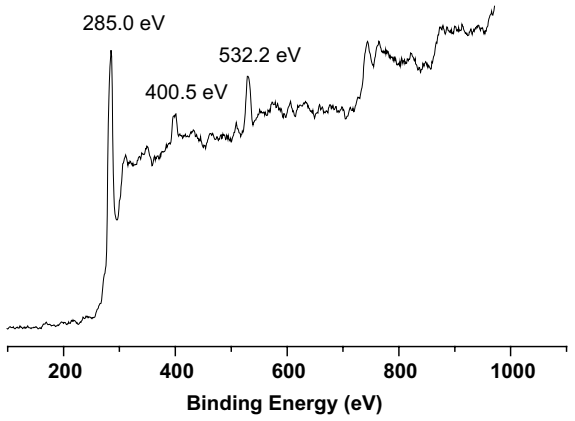


Fig. 2. XPS spectrum of EG-NCO (the same sample with that in Table 1).

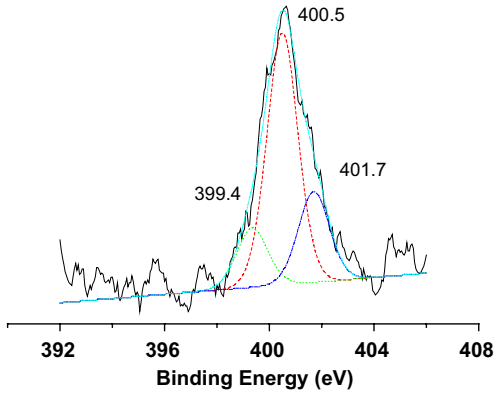


Fig. 3. XPS spectrum of nitrogen in EG-NCO (the same sample with that in Table 1).

3.2. Grafting reaction of EG-NCO with PEO

The addition reaction of NCO groups in the EG-NCO particles with hydroxyl groups of poly (ethylene oxide) methyl ether (MPEO) was carried out. The results are listed in Table 2. No weight increase for the reaction of EG with MPEO (Table 2) indicates that no active sites in EG can react with hydroxyl of MPEO. The weight increase for sample 1 in Table 2 must be due to the reactions of isocyanate groups with hydroxyl groups of MPEO. Although isocyanate group has higher reactivity toward hydroxyl group, the effect of reaction time on the grafting ratio was investigated in order to get higher grafting ratio of MPEO on the surface of EG-NCO. The results are shown in Fig. 4. We can find that the grafting ratios in Fig. 4A are lower than that in Fig. 4B, this must be the result that more addition reactions took place in method B. Before 18 h, the grafting ratio increased rapidly with increase of reaction time, and then leveled off as shown in Fig. 4, probably due to big decrease of NCO group content in EG-NCO. In order to confirm further the reaction of EG-NCO with MPEO, the IR spectrum of EG grafted with MPEO (EG-MPEO) was measured. Its typical IR spectrum is shown in Fig. 5B. Comparison with Fig. 5A, the peak at $v = 2269\ \mathrm{cm}^{-1}$ ascribed as isocyanate group is absent in

Table 2
The effect of feed ratio on grafting ratio[a]

No.	Feed ratio			Grafting ratio (%)
	EG (g)	TDI (ml)	MPEO (g)	
1	0.497	0. 06	3.6	23.4
2	0.506	0	3.6	2.1
3	0.508	0. 06	0	4.4

[a] The conditions of grafting reactions: DMSO: 50 ml; temperature: 100 °C; time: 30 h.

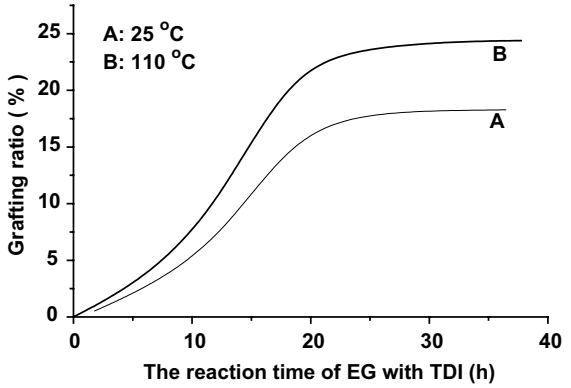


Fig. 4. The effect of reaction time between EG and TDI on grafting ratio. A: reaction conditions: see Method A in experimental part. B: reaction conditions: see Method B in experimental part.

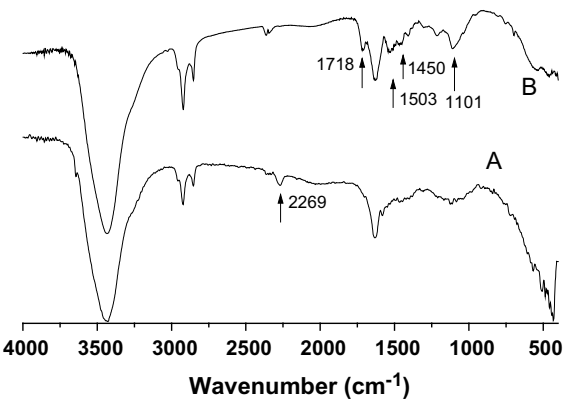


Fig. 5. IR spectra of A: EG-NCO (in Table 1) and B: EG/MPEO (sample 1 in Table 2).

Fig. 5B, indicating complete reaction of the NCO groups on the surface of EG-NCO with MPEO.

For getting high grafting ratios, it is necessary to study the effect of the reaction time on grafting reaction of MPEO with EG-NCO. The results are shown in Fig. 6. It was found that the grafting ratio increased with the increase of the reaction time. Before reaction time of 25 h, rapid increase of grafting ratio was observed with the increase of reaction time. After 25 h, the grafting ratio approached 24.9% gradually.

Another influencing factor on the grafting ratio is the feed weight ratio of MPEO to EG-NCO. Thus, grafting ratios of the EG-MPEO obtained from various amounts of MPEO added were measured, and the results are in Fig. 7. The grafting ratio did not approach the maximum until the weight of MPEO used was 3.5 g. Assume that only one of the two NCO groups in a TDI molecule was reacted with hydroxyl or carboxylic acid, another one remained, we can calculate the content of NCO in

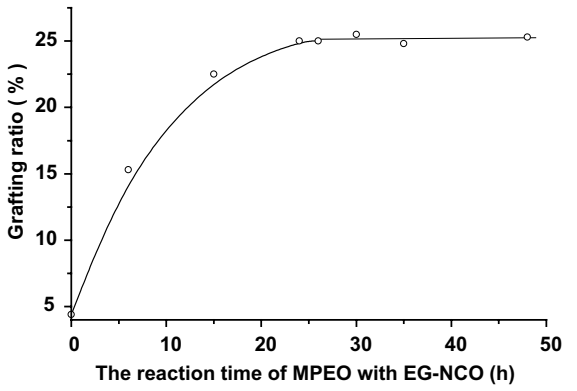


Fig. 6. The effect of reaction time of EG-NCO with MPEO on grafting ratio. Preparation of EG-NCO: reaction time: 25 h; other conditions: the same with that in Fig. 4B.

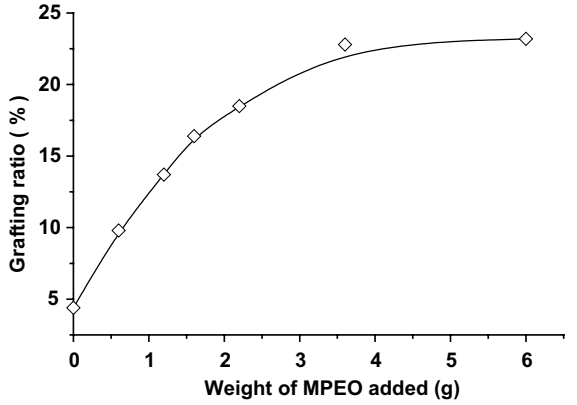


Fig. 7. The relationship between grafting ratios and the amount of MPEO used. Grafting reaction time: 25 h; other conditions: the same with that in Fig. 4B.

EG-NCO, which is 0.263 mM/g based on N content from elementary analysis. MPEO (0.69 g) can react completely with NCO group in 1 g of EG-NCO (0.263 mM/g) used, thus the theoretical grafting ratio is 132%. However, the grafting ratio was about 9.8% for 0.6 g of MPEO used, and 18.5% for 2.2 g of MPEO used from Fig. 7. Most of the MPEO added was not grafted onto EG-NCO. Probably, many NCO groups were covered by MPEO, and cannot react with hydroxyl groups in MAPEO. However, the excess of MPEO is necessary for getting higher grafting ratio of EG.

4. Conclusion

The hydroxyl or/and carboxylic acid groups on the surface of EG can react with NCO group of TDI to

form the EG with active NCO group. The concentration of NCO groups on the surface is higher than that inside EG, and they are very moisture-sensitive. The EG grafted with MPEO was successfully prepared by the reaction of NCO group in EG-NCO with hydroxyl group in MPEO. For getting higher grafting ratio, an excess of MPEO is necessary. Higher reaction temperature is favorable to form EG-NCO with higher concentration of the NCO group, and then to produce MPEO-grafted EG with higher grafting ratio. The reactions of EG with TDI and NCO in EG-NCO with MPEO are almost completed in 24 h at 110 °C.

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