Highly Aqueous-dispersible Carbon Black Grafted with SAS and AA Copolymers

Jian-Yi Zhao[†,††] and Cheng-Yang Wang[†]
[†]*Key Laboratory for Green Chemical Technology of State Education Ministry,*
School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, P. R. China
[††]*North China Engineering Institute, Taiyuan 030008, P. R. China*

(Received December 17, 2004; CL-041553)

Carbon black grafted with copolymer of AA and SAS exhibits significant dispersibility in water. Although the grafting ratio is low, sulfonic groups of SAS can effectively stabilize carbon black when dispersed in aqueous media. The advantage of this method is that only low grafting ratio is needed, thus avoiding the complex procedure for high grafting ratio.

Carbon black (CB) is extensively used in pigments and paints. Generally, these reagents should be dispersed in organic solvent for better performance. Increasing environmental concerns require more environmental-safe solvent, for example, water. Unfortunately, CB particles are strongly hydrophobic and prone to aggregate when dispersed in water.[1] Surface modification of CB, such as oxidation and grafting, can improve its dispersibility in aqueous media.[2–5] Specifically, polymer-graft is more effective because hydrophilic groups can be introduced onto the surface.[3–5] The dispersibility of such polymer-grafted CB depends on the grafting ratio and properties of grafted polymer. When dispersed in aqueous media, polymers on CB surface will expand and this steric hindrance can prevent the contact and aggregation of CB particles. At the same time, grafted groups will ionize and form electric double layer that can help to form stable colloid system. However, the efficiency for grafting polymerization is low according to the limited number of active sites on CB surface. Pre-introduction of initiating groups onto CB can improve the grafting ratio but the process is too complex with increased cost.[3–5] We think that, if excellent hydrophilic polymers are grafted on CB, desired dispersibility could be obtained even with low grating ratio. There is report for acrylic acid (AA) grafting on CB but such modified CB could not stably disperse in aqueous solution with low grafting ratio.[6] We notice that the copolymer of AA and sodium allyl sulfonate (SAS) is excellent water absorbing resin.[7] Sulfonic group is strong electrolyte and thus can improve the dispersibility of CB. Herein we report the copolymer-grafting of AA and SAS on CB surface exhibiting excellent dispersibility in water.

The reaction was firstly optimized by AA grafting reaction and the optimal reaction conditions was: 0.5 g of CB, 0.04 g of ammonium persulfate, 2 mL acrylic acid mixed in 10 mL of water with pH value as 3.5. For copolymer-grafting, definite SAS were added in the mixture. Prior to reaction, the surrounding of the mixture was purged with N_2 for 0.5 hour to eliminate O_2. Then it was placed in ultrasonic bathing at room temperature for 2 h meanwhile AA and SAS copolymerized and grafted onto CB surface. After reaction, the polymer-grafted CB was separated, washed, and dried at 100 °C for 10 h. The grafting ratio was calculated by the following equation:

$$\text{Grafting ratio} = \frac{A - B}{B}$$

Where A is weight of grafted CB, and B is weight of CB before grating.

The FT-IR spectra of copolymer-grafted CB were recorded on IR spectrophotometer using KBr pellet. The surface composition was analyzed by XPS. The dispersibility of grafted CB in water was determined by transmission of 510-nm light. 0.04 g of samples were dispersed in 20 mL of water under ultrasonic bathing for 20 min. Then the suspension was centrifugalized under 3000 r/min for definite time. Finally 0.5 mL of upper suspension was take out and diluted to 25 mL for analysis.

Figure 1 shows that addition of SAS can not improve the grafting ratio when the amount of SAS is too less. The highest grafting ration of 7.04% is obtained when 0.4 g of SAS is added, which is still lower than the 7.12% of pure AA grafting. This result suggests that the polymerizing ability of SAS is relatively lower than that of AA, thus the copolymerization is necessary to graft SAS on CB.

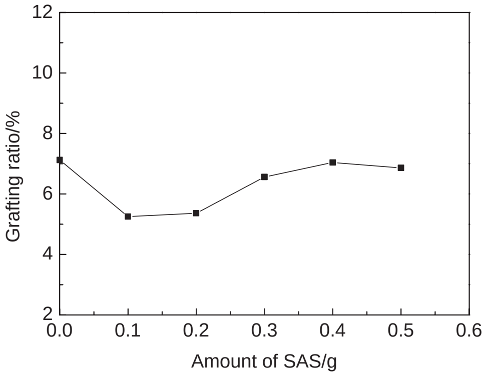


Figure 1. Grafting ratio versus the amount of added SAS.

To identify the groups grafted on CB, IR spectra are shown in Figure 2. For ungrafted CB, two strong and wide peaks appear at 3439 and 1235 cm^{-1}, belonging to stretching vibration of surface OH and C–O bond, respectively. A peak at 1700 cm^{-1} is observed for AA-stretching vibration. This means that AA is grated on CB surface. It is shown that the monomer of SAS shows strong peaks at 3508, 1643, 1211, and 1054 cm^{-1}. Although these peaks are overlapped with the peaks of CB, the stronger and wider peaks at 3450, 1563, and 1210 cm^{-1} can be clearly seen, identifying that SAS is grafted on CB. To further identify the sulfonic groups. XPS analysis is conducted as show in Figure 3. The surface atomic composition of sulfur is 0.1%. The S_{2p} XPS profile (absent in the present paper) also reconfirms that sulfonic groups are grafted on CB. Therefore, AA and SAS

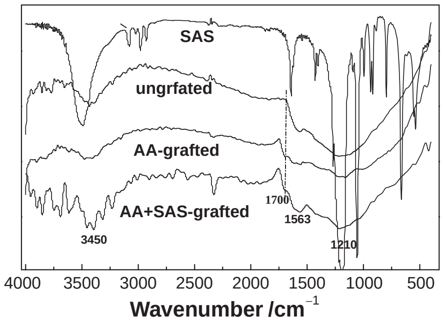


Figure 2. IR spectra of samples.

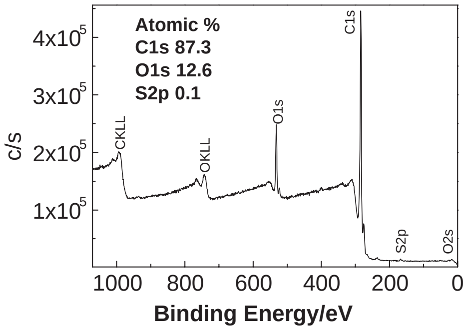


Figure 3. XPS profile of AA + SAS-grafted carbon black.

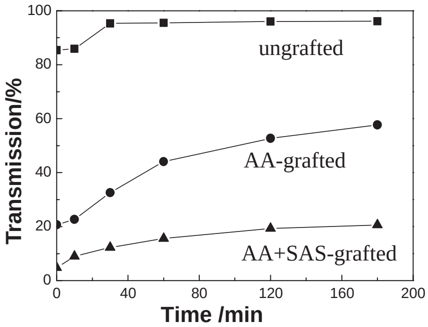
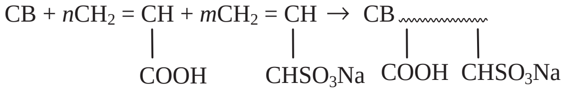


Figure 4. Dispersibility of samples determined by light transmission.

are effectively grafted on CB:



$$\mathrm{CB} + n\mathrm{CH_2} = \underset{\displaystyle \mathrm{COOH}}{\mathrm{CH}} + m\mathrm{CH_2} = \underset{\displaystyle \mathrm{CHSO_3Na}}{\mathrm{CH}} \rightarrow \mathrm{CB}\!\sim\!\sim\!\sim \; \underset{\mathrm{COOH}}{|} \;\; \underset{\mathrm{CHSO_3Na}}{|}$$

Figure 4 is the dispersibilty of polymer-grafted CB determined by light transmission. It can be seen that ungrafted CB shows significantly high transmission because only a little CB are dispersed in water. The dispersibilty of copolymer grafted CB is much higher than that of AA-grafted CB despite its lower grafting ratio. Furthermore, analysis indicates that CB grafted with copolymer of AA and SAS can stably disperses in water for a long time. The transmission of copolymer grafted CB with 3 hours' centrifugation remains at 41.2% after 70 days. However, the transmission of AA-grafted CB increases to 80.3% by the deposition of CB.

Table 1. Effects of pH value and KNO_3 on light transmission of grafted CB dispersed in water/%

pH	1.3	6.0	12	KNO_3/0.1 mol/L
AA-grafted	84.2	20.0	3.1	95.5
AA + SAS-grafted	74.5	2.3	1.8	78.8

Above result shows the dramatic difference in dispersibilities of AA-grafted CB and AA + SAS-grafted CB. The first one shows bad dispersibility because of its low grafting ratio. The later one has an excellent dispersibility with similar grafting ratio. Therefore, the significant improvement in CB stability in water should be attributed to the sulfonic groups of SAS. CH_2SO_3Na groups of SAS grafted on CB can easily ionize into $CH_2SO_3^-$ and Na^+ ions, thus electric double layer is formed around CB particles. The repulsion between electric double layer of different CB particles can prevent the contact and aggregation of CB. In addition, the ionized sulfonic groups on the polymers will repulse with each other, resulting in the branches of polymer expanding with greatest degree. Therefore, CB is well dispersed in water like stable colloid.

It was also noticed that the hydrophilicity of AA and SAS on CB is related with their dissociation in water, as seen in Table 1, with the decrease of pH value or the addition of KNO_3 the light transmission of grafted CB dispersed in water is becoming increased, it means that the hydrophilicity of grafted CB is becoming weaker.

In conclusion, CB grafted with copolymer of AA and SAS exhibits high stability when dispersed in water. This dispersibility is due to the excellent hydrophilicity of sulfonic groups on SAS. Previous researches focused on improving grafting ratio for better dispersibility. This study shows that the dispersibility of CB can be improved by grafting hydrophilic groups even with low grafting ratio, which suggests a more practical way for industrial application.

References

1 Y. Lin, T. W. Smith, and P. Alexandrids, *J. Colloid Interface Sci.*, **255**, 1 (2002).
2 P. E. Fanning and M. A. Vannice, *Carbon*, **31**, 721 (1993).
3 N. Tsubokawa, *Prog. Polym. Sci.*, **17**, 417 (1992); E. Papirer, R. Lacroix, and J.-B. Donnet, *Carbon*, **34**, 1521 (1996).
4 E. Papirer, R. Lacroix, and J.-B. Donnet, *Carbon*, **34**, 1521 (1996).
5 Y. Wu, A. Liu, L. Shao, and Z. Jiang, *Gaofenzi Xuebao*, **6**, 745 (1994).
6 A. Gao and J. Huang, *J. Tianjin Inst. Technol.*, **2**, 33 (1991).
7 Y. Shirai and N. Tsubokawa, *React. Funct. Polym.*, **32**, 153 (1997).

Published on the web (Advance View) March 19, 2005; DOI 10.1246/cl.2005.580