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Preparation of amphiphilic carbon black by postgrafting of polyethyleneimine to grafted polymer chains on the surface

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Summary

To prepare amphiphilic carbon black, we investigated the postgrafting reaction of polyethyleneimine (PEI) with pendant glycidyl groups of grafted polymer on carbon black surface. The grafting of polymers having pendant glycidyl groups onto carbon black surface was achieved by the copolymerization of glycidyl methacrylate (GMA) with methyl methacrylate (MMA) initiated by azo groups introduced onto the surface. Pendant glycidyl groups of poly(GMA-co-MMA)-grafted carbon black was found to react with PEI, and the corresponding polymers postgrafted to the grafted copolymer chains on carbon black surface: the percentage of PEI-postgrafting was readily controlled by the reaction conditions. PEI-postgrafted to poly(GMA-co-MMA)-grafted carbon black, whose PEI postgrafting is 3.9% showed amphiphilic nature and acted as an emulsifier.

Introduction

To improve the surface properties of carbon black, the grafting of polymers onto the surface is known to be one of the effective method. The aggregation of carbon black particles is interfered and the dispersion stability of carbon black in an organic solvent is effectively improved by the grafting of polymers onto the surface (1-3). In addition, grafting of polymers onto carbon black surface enables us to give various functions to carbon black, such as photosensitivity, pH sensitivity, and crosslinking ability (1-3).

The grafting of polymers onto carbon black surface is achieved by various methods. The most effective method is the graft polymerization of monomers initiated from the surface initiating groups because of the growth of polymer chains from the surface (1-3). For example, radical, cationic, and anionic graft polymerizations of various monomers were reported to be initiated by azo or peroxyester (4,5), acylium perchlorate (6), and potassium carboxylate (7) groups, respectively, introduced onto carbon black surface.

We have reported that the postpolymerization of vinyl monomers is initiated by pendant azo (8), peroxycarbonate (9), potassium carboxylate (10), and acylium perchlorate (11) groups introduced to grafted polymer chains on the carbon black surface. More recently, we have reported the postgrafting of polymers having terminal amino groups, such as polyethyleneimine (PEI), with glycidyl groups of grafted polymer on carbon black surface as shown in Scheme 1 (12).

By the above postpolymerizations, highly branched polymer-grafted carbon black with higher percentage of grafting is obtained. In addition, it is pointed out that the postgrafting to polymer-grafted carbon black is able to control the dispersibility and the

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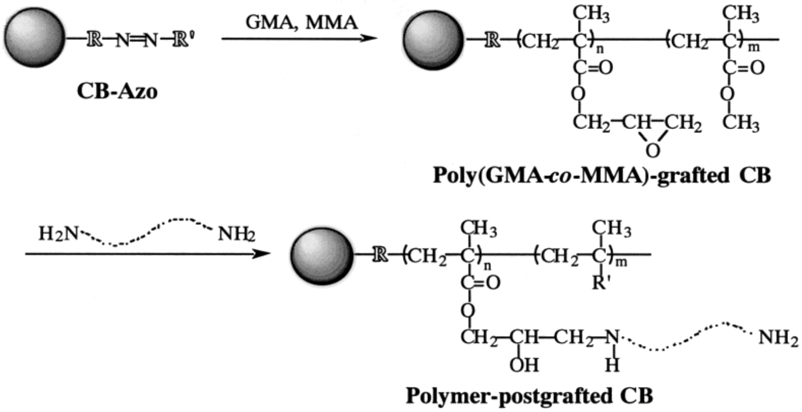

Scheme 1 Postgrafting of PEI onto poly(GMA-co-MMA)-grafted CB

wettability of carbon black surface and to give carbon black new functions, such as compatibilizer.

In the present paper, the effect of PEI-postgrafting onto carbon black on the hydrophilic and hydrophobic nature of carbon black surface was discussed.

Experimental

Materials and Reagents

Carbon black used was channel black FW 200 (Degussa A. G.). Specific surface area and particle size were 460 m^2/g and 13 nm, respectively. The amount of phenolic hydroxyl and carboxyl group was determined to be 0.10 mmol/g and 0.61 mmol/g, respectively. The carbon black was dried in vacuo at 110°C before use.

Glycidyl methacrylate (GMA) and methyl methacrylate (MMA) were purified by ordinary methods (12). Polyethyleneimine (PEI) (Mn=1800) was obtained from Nippon Shokubai Chemical Ind. Co. Ltd., Japan. PEI was dried in vacuo at 75°C before use.

Grafting of poly(GAM-co-MMA) onto Carbon Black Surface

The grafting of poly(GMA-co-MMA) was achieved by the copolymerization of GMA with MMA initiated by azo groups introduced onto carbon black surface (4,12).

Postgrafting Reaction of PEI with Poly(GMA-co-MMA)-grafted Carbon Black

Into a 100 mL flask, 0.30 g of poly(GMA-co-MMA)-grafted carbon black, 2.5 mmol of PEI, 10 mL of DMF, and a stirrer bar were charged. The mixture was stirred with a magnetic stirrer under nitrogen at 80°C. After a definite time, the resulting mixture was poured into a large excess of methanol (12).

Determination of Percentage of Grafting, Postgrafting and Overall Grafting

To isolate poly(GMA-co-MMA)-grafted carbon black and PEI-postgrafted carbon black from the reaction mixture containing ungrafted polymer, the reaction product was dispersed in a good solvent for the grafted polymer, and the dispersion was centrifuged at 1.5×10^4 rpm until carbon black was precipitated completely. Methanol was used for the solvent of PEI, and THF was used for poly(GMA-co-MMA). The carbon black precipitated was dispersed in a good solvent and centrifuged again. The procedures were repeated until no more ungrafted polymer could be detected in the supernatant solution. After the above procedure, the resulting carbon black was dried in vacuo at

60°C. The percentage of grafting, postgrafting and overall grafting were calculated by the following equations:

$$\text{Grafting (\%)} = (A/B) \times 100$$
$$\text{Postgrafting (\%)} = (C/D) \times 100$$
$$\text{Overall grafting (\%)} = (E/F) \times 100$$

where A is weight of copolymer grafted, B is weight of carbon black charged, C is weight of PEI postgrafted, D is weight of copolymer-grafted carbon black charged, E is weight of total polymer grafted, and F is net weight of carbon black charged. The weight of polymer grafted onto the carbon black surface, *i.e.*, A, C, and E, were determined by weight loss when polymer-grafted carbon black was heated at 500°C by use of a thermal analyzer (Thermogravimetric Analyzer TGA-50, Shimadzu Manufacturing Co., Ltd.).

Wettability of Polymer-grafted Carbon Black

The wettability of polymer-grafted carbon black was estimated by the penetrating rate of water through a column packed with polymer-grafted carbon black. A typical example is as follows. Into a glass column (inside diameter: 2.0 mm), 0.30 g of polymer-grafted carbon black was packed, and water was added from the top of the column. Then the penetrating rate of water through the column was determined.

Results and discussion

Postgrafting of PEI to Poly(GMA-co-MMA)-grafted Carbon Black

In the previous paper, we have reported that PEI is successfully postgrafted to poly(GMA-co-MMA)-grafted carbon black by the reaction of amino and imino groups of PEI with pendant glycidyl groups of the grafted poly(GMA-co-MMA) on the surface to give branched polymer-grafted carbon black: in the postgrafting reaction of PEI with ester groups of MMA moieties was scarcely observed (12).

In this study, PEI-postgrafted carbon black with different PEI postgrafting was prepared by control of reaction conditions: the composition of the grafted copolymer was GMA:MMA=44.5:55.5 and the percentage of grafting was 25.0%.

The percentage of PEI-postgrafting onto carbon black and reaction conditions are given in Table 1. The percentage of glycidyl groups reacted with PEI was estimated to be only 5% (12).

Relationship between PEI-postgrafting and Wettability of Carbon Black Surface

The wettability of carbon black surface was readily controlled by the grafting of hydrophilic and hydrophobic polymers onto the surface (13). Therefore, the relationship between wettability of carbon black surface and PEI postgrafting was

Table 1 Postgrafting of PEI onto poly(GMA-*co*-MMA)-grafted CB

Temperature (°C)	Time (h)	Postgrafting of PEI (%)	Overall grafting (%)
80	2	7.5	31.5
40	8	9.8	37.3
80	8	13.7	42.1
120	8	21.1	51.3

Poly(GMA-*co*-MMA)-grafted CB (GMA:MMA=44.5:55.5, grafting=25.0%), 0.30 g; PEI (Mn=1800), 2.5 mmol; DMF, 10 mL.

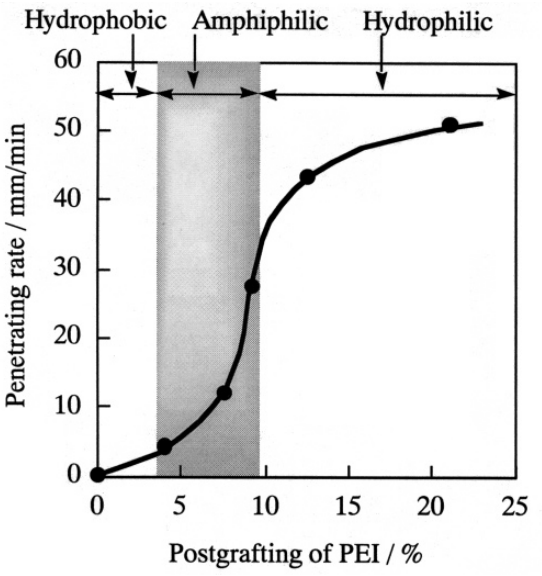

Fig.1 Relationship between percentage of PEI postgrafting and penetrating rate of water through the column packed with PEI-postgrafted CB

Grafting, 25.0%; g rafted copolymer, GMA:MMA=44.5:55.5.

examined. The wettability of carbon black surface was estimated by penetrating rate of water through the column packed with various carbon blacks.

Figure 1 shows the relationship between percentage of PEI-postgrafting and penetrating rate of water through the column packed with PEI-postgrafted carbon black. It was found that the penetrating rate of water increased with increasing percentage of postgrafting of PEI. The surface of PEI-postgrafted carbon black, whose PEI-postgrafting is 0-3.0%, shows hydrophobic nature. On the contrary, PEI-postgrafted carbon black surface shows hydrophilic nature when PEI-postgrafting exceeded 9.5%. It is interesting to note that the surface of PEI-postgrafted carbon black, whose PEI-postgrafting is 3.0-9.5%, shows amphiphilic nature.

Therefore, it is concluded that hydrophobic and hydrophilic nature of carbon black

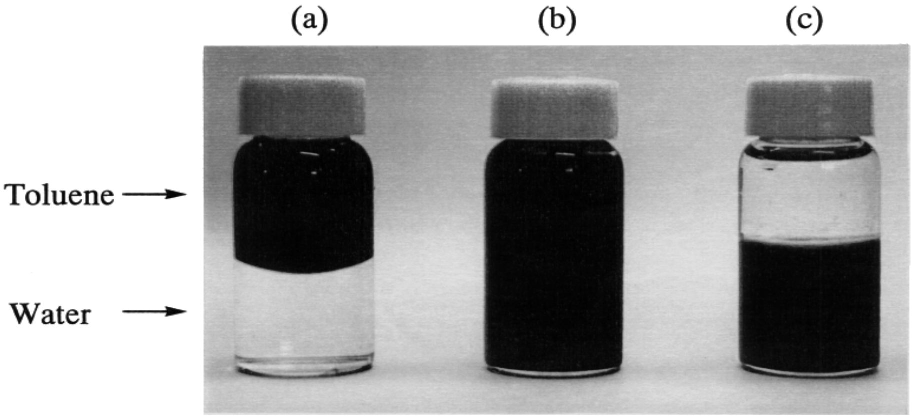

Fig. 2 Dispersibility of (a) poly(GMA-co-MMA)-grafted (grafting=24.3%), (b) PEI-postgrafted (postgrafting=3.9%), and (c) PEI-postgrafted CB (postgarfting=13.7%) in binary mixture of toluene/water

surface can be controlled by the postgrafting of hydrophilic PEI to poly(GMA-co-MMA) grafted on the surface.

Dispersibility of PEI-postgrafted Carbon Black in Binary Mixture (Toluene/Water)

The dispersibility of PEI-postgrafted carbon black in binary mixture (toluene/water) was examined. Polymer-grafted carbon black was added into toluene/water binary mixture and the mixture was shaken vigorously and allowed to stand. The results are shown in Figure 2.

Poly(GMA-co-MMA)-grafted carbon black dispersed in toluene phase only and no carbon black in water phase was observed (Figure 2 (a)), because of hydrophobic nature of the poly(GMA-co-MMA)-grafted carbon black. On the contrary, PEI-postgrafted carbon black, whose percentage of PEI postgrafting is 9.1% gave a stable dispersion in water, but not in toluene (Figure 2 (c)).

It is interesting to note that PEI-postgrafted carbon black, whose percentage of PEI postgrafting is 3.9%, suspended homogeneously in toluene/water mixture for a long time (Figure 2 (b)).

Furthermore, this solution was confirmed to be O/W (oil in water) type-emulsion by microscope observation as shown in Figure 3.

These results suggest that PEI-postgrafted carbon black whose percentage of postgrafting of PEI is 3.9% possesses surface activity. This may be due to the fact that PEI-postgrafted carbon black shows amphiphilic nature and has the most suitable value of the hydrophile-lipophile balance (HLB) to emulsify toluene and water.

In addition, PEI-postgrafted carbon black particles were found to gather at the interface between toluene and water from Figure 3. Therefore, these carbon black particles are considered to arrange in the same manner as surfactant molecules on the basis of affinity of grafted poly(GMA-co-MMA) chains for toluene and of postgrafted PEI chains for water as shown in Figure 4.

Conclusions

1. Pendant glycidyl groups of poly(GMA-co-MMA) grafted onto carbon black surface were readily reacted with amino or imino groups of PEI to give branched polymer-grafted carbon black.

2. PEI-postgrafted carbon black with different percentage of PEI-postgrafting was prepared by control of reaction conditions.

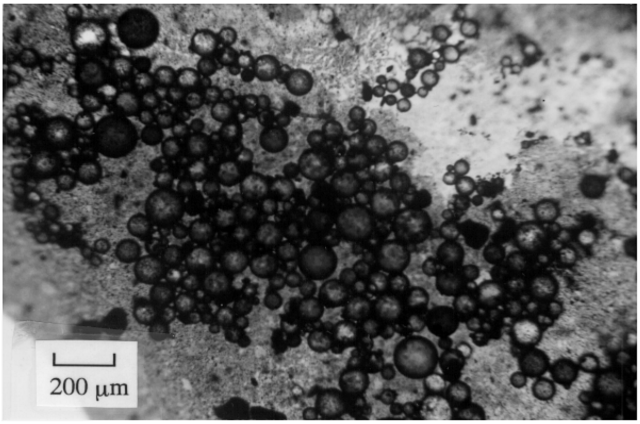

Fig.3 Aspect of O/W type emulsion of toluene and water in the presence of PEI-postgrafted CB (PEI-postgrafting=3.9%)

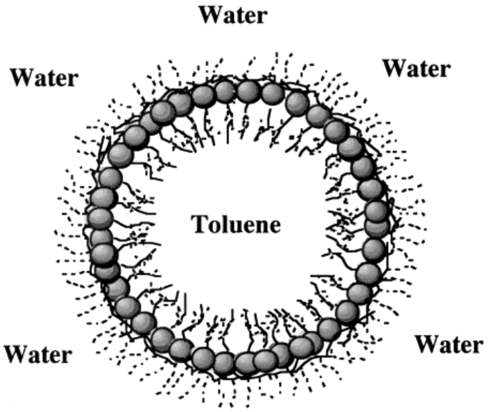

Fig.4 O/W type-emulsion of toluene and water in the presence of PEI-postgrafted CB

3. The hydrophilic and hydrophobic nature of carbon black surface was controlled by PEI-postgrafting.
4. PEI-postgrafted carbon black, whose PEI-postgrafting is 3.9%, shows amphiphilic nature and acted as a emulsifier.

Acknowledgment

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References

1. Tsubokawa N (1992) Prog Polym Sci 17: 417.
2. Tsubokawa N (1995) Kobunshi (High Polymer) 45: 412.
3. Tsubokawa N (1996) Nippon Gomu Kyokaishi (J Soc Rubber Ind, Japan) 70: 378.
4. Fujiki K, Tsubokawa N, Sone Y (1990) Polym J 22: 661.
5. Tsubokawa N, Fujiki K, Sone Y (1988) Polym J 20: 213.
6. Tsubokawa N (1984) J Polym Sci, Polym Chem Ed 22: 1515.
7. Tsubokawa N, Funaki A, Hada Y, Sone Y (1982) J Polym Sci, Polym Chem Ed 20: 3297.
8. Hayashi S, Iida T, Tsubokawa N (1997) J Macromol Sci -Pure Appl Chem A34: 1381.
9. Hayashi S, Tsubokawa N (1994) Preprints 5th International Polym Conf: 293.
10. Tsubokawa N, Fujiki K, Sasaki T (1993) Kobunshi Ronbunshu 50: 235.
11. Fujiki K, Motoji N, Tsuchida H, Tsubokawa N (1994) Polym J 26: 571.
12. Hayashi S, Naitoh J, Takeuchi Y, Tsubokawa N (1997) Nippon Gomu Kyokaishi (J Soc Rubber Ind, Japan) 70: 404.
13. Yoshikawa S, Iida T, Tsubokawa N (1997) Prog Org Coatings 31: 127.