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Heat-Resistant Polymer-Grafted Carbon Black: Grafting of Poly(Organophosphazenes) onto Carbon Black Surface

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HEAT-RESISTANT POLYMER-GRAFTED CARBON BLACK: GRAFTING OF POLY(ORGANOPHOSPHAZENES) ONTO CARBON BLACK SURFACE

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ABSTRACT

The grafting of poly(organophosphazenes) onto carbon black surface by the reaction of poly(dichlorophosphazene) (PDCP) with carbon black having sodium phenoxide groups was investigated. PDCP was prepared by the ring-opening polymerization of hexachlorocyclotriphosphazene in solution using sulfamic acid as a catalyst. The introduction of sodium phenoxide groups onto carbon black was achieved by treatment of phenolic hydroxyl groups on the surface with sodium hydroxide in methanol. Poly(diphenoxyphosphazene) (PDPP) was successfully grafted onto carbon black by the reaction of PDCP with sodium phenoxide groups introduced onto the surface followed by the replacement of chlorine atoms in PDCP with phenoxy groups. The percentage of grafting onto carbon black increased to 206% at 30°C after 12 h. It was found that only 1.4% of sodium phenoxide groups on carbon black surface was used for the grafting of PDCP because of the blocking of the surface by grafted polymer chains. Poly(diaminophenylphosphazene) and poly(diethoxyphosphazene) were also grafted onto carbon black surface by the treatment of PDCP-grafted carbon black with aniline and sodium ethoxide, respectively. Poly(organophosphazenes)-grafted carbon blacks produced stable colloidal dispersions in good solvents for grafted polymers. Furthermore, thermogravimetric analysis indicated that poly-

(organophosphazenes)-grafted carbon blacks were stable in air about 300°C.

INTRODUCTION

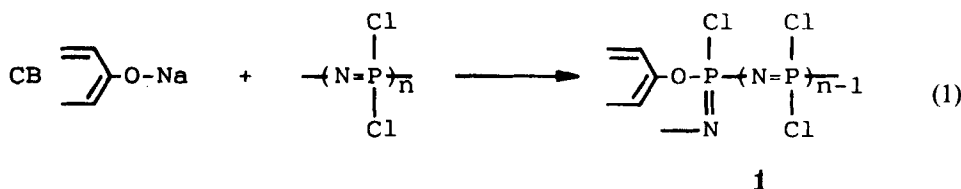
To modify the surface properties of carbon black, the grafting of polymers onto the surface was widely investigated [1]. In a series of our papers, we have reported the graft polymerization of various monomers from carbon black initiated by functional groups, such as azo, potassium carboxylate, and acylium perchlorate groups, introduced onto the surface: vinyl polymers [2, 3], polyesters [4-6], polyethers [7], and polyacetals [8] were effectively grafted by this method.

Furthermore, we achieved grafting onto carbon black by the reaction of functional groups on the surface with functional polymers: poly(propylene glycol), poly(ethylene glycol), poly(ethyleneimine), isocyanate-capped polyurethane, isocyanate-capped polyamide-imide, and hydroxyl-terminated poly(dimethylsiloxane) were successfully grafted onto the surface [1, 9-11].

However, the grafting of heat-resistant polymers has rarely been investigated. In a previous paper, we demonstrated that during the polyaddition of epoxides with diisocyanates using lithium phenoxide groups introduced onto carbon black as catalyst, poly-2-oxazolidone, a well-known heat-resistant polymer, was effectively grafted onto the surface [12].

On the other hand, poly(organophosphazenes) are well-known heat-resistant inorganic polymers having excellent mechanical properties and are generally synthesized by ring-opening polymerization of hexachlorocyclotriphosphazene followed by replacement of the chlorine atoms by alkoxy, aryloxy, and amino groups [13-19].

In the present study, the grafting of poly(organophosphazenes) onto carbon black by the reaction of poly(dichlorophosphazene) (PDCP) with sodium phenoxide groups introduced onto the surface [Eq.(1)] followed by the replacement of chlorine atoms in PDCP with alkoxy, aryloxy, or amino groups [Eq.(2)] was investigated. In addition, the thermal stability and the dispersibility in organic solvents of poly(organophosphazenes)-grafted carbon blacks were compared with those of untreated carbon black.



EXPERIMENTAL

Materials

Carbon black used was channel black Neospectra II (Columbian Carbon Co.). The content of phenolic hydroxyl, carboxyl, and quinonic oxygen groups on the surface was determined to be 0.24, 0.40, and 0.92 mmol/g, respectively. Determination of phenolic hydroxyl, carboxyl, and quinonic oxygen groups was carried out by use of 2, 2-diphenyl-1-picrylhydrazyl [20], sodium bicarbonate [21], and sodium borohydride [22], respectively. The carbon black was dried *in vacuo* at 110°C before use.

Hexachlorocyclotriphosphazene was obtained from Nippon Soda Co. and purified by sublimation under reduced pressure. *n*-Hexane, toluene, benzene, tetrahydrofuran (THF), and *N,N,N',N'*-tetramethylethylenediamine were refluxed over sodium and distilled before use. Aniline was purified by distillation under reduced pressure.

Sodium phenoxide and sodium ethoxide were prepared by the reaction of sodium with phenol and ethanol, respectively, in mixed solvent of toluene and diethylene glycol dimethyl ether (2/1 in volume).

All other reagents and solvents were purified by ordinary methods.

Treatment of Carbon Black with Sodium Hydroxide

Introduction of sodium phenoxide groups onto the surface was achieved by the treatment of carbon black with sodium hydroxide in methanol [21]. A typical example was as follows. Three grams of carbon black was reacted with methanol solution of sodium hydroxide under stirring with a magnetic stirrer at 30°C for 24 h. The treated carbon black was filtered, washed with absolute methanol, and dried *in vacuo*.

Poly(dichlorophosphazene) (PDCP)

Poly(dichlorophosphazene) was prepared by the ring-opening polymerization of hexachlorocyclotriphosphazene in solution using sulfamic acid as a catalyst. A typical example was as follows. Into a four-necked flask equipped with an agitator, a thermometer, a reflux condenser, and a nitrogen inlet, 2.4 g of hexachlorocyclotriphosphazene, 25.0 cm³ of 1,2,4-trichlorobenzene, and 0.05 g of sulfamic acid were charged. The monomer was dissolved by heating in a stream of nitrogen, and the reaction was conducted at 210°C under nitrogen. When the evolution of bubble and the Weizenberg effect was observed (after about 3 h), the reaction mixture was cooled below 100°C. Then 200 cm³ of *n*-hexane was added to the reaction mixture to remove unreacted monomer and oligomer. The rubber-like product thus obtained was washed three times with *n*-hexane and dissolved in toluene. The toluene solution of PDCP was kept in a refrigerator and used for the grafting reaction within 2 days.

Partial Replacement of Chlorine Atoms in PDCP with Phenoxy Groups (Preparation of PDCP-s)

To reduce the reactivity of PDCP, the partial replacement of chlorine atoms in PDCP with phenoxy groups was carried out by the reaction of PDCP with about 50 mol% of sodium phenoxide based on chlorine atoms of PDCP. Into a flask that contained toluene/diethylene glycol dimethyl ether (2/1 in volume) solution of sodium phenoxide, toluene solution of PDCP was added from a dropping funnel at 100°C. After the addition of PDCP solution, the mixture was refluxed for 48 h. After the reaction, sodium chloride precipitated was filtered off and the polymer was precipitated with *n*-hexane. The polymer thus obtained was purified by reprecipitation.

Grafting Reaction of PDCP with Carbon Black

Into a 100-cm³ flask that contained 0.10 g of carbon black having sodium phenoxide groups, 15.0 cm³ of PDCP (0.70 g) toluene solution was added. The reaction mixture was stirred with a magnetic stirrer at 30°C under nitrogen. After the reaction, carbon black was isolated by centrifugation and washed with THF.

Replacement of Chlorine Atoms in Grafted PDCP on the Surface with Phenoxy, Ethoxy, or Amino Groups

To replace chlorine atoms in grafted PDCP on the surface with phenoxy, ethoxy, or amino groups, the resulting carbon black was refluxed with excess of sodium phenoxide (in mixed solvent of toluene and diethylene glycol dimethyl ether), sodium ethoxide (in mixed solvent of toluene and diethylene glycol dimethyl ether), or aniline (in *N,N,N',N'*-tetramethylethylenediamine), respectively [13–19]. After treatment for 48 h, to remove unreacted sodium phenoxide, sodium ethoxide, or aniline, dilute hydrogen chloride was added and the resulting carbon blacks were washed with water, extracted with THF for 48 h, and dried *in vacuo*.

Percentage of Grafting

The amount of polymer grafted onto the carbon black surface was determined from the difference in weight of carbon black before and after the reaction. The percentage of grafting (the proportion of grafted polymer to carbon black) of poly(organophosphazene) onto carbon black was calculated by the following equation.

$$\text{Grafting (\%)} = \frac{\text{polymer grafted (g)}}{\text{carbon black charged (g)}} \times 100$$

Stability of Poly(organophosphazene)-Grafted Carbon Black Dispersion

The procedures for estimation of stability of polymer-grafted carbon black dispersion in solvents were described in detail in the previous paper [12].

RESULTS AND DISCUSSION

Introduction of Sodium Phenoxide Groups onto Carbon Black

Carbon black has carboxyl and phenolic hydroxyl groups on the surface, and these functional groups undergo general chemical reactions: for instance, neutral-

ization with alkali, methylation with diazomethane, and esterification with acid anhydrides[23]. Therefore, sodium phenoxide groups can be introduced by the reaction of phenolic hydroxyl groups on the surface with sodium hydroxide [21, 23].

Figure 1 shows infrared spectra of (A) untreated and (B) sodium hydroxide-treated carbon black. The infrared spectra of untreated carbon black exhibited absorptions at 3460, 1726, and 1636 cm^{-1} , which are characteristic of phenolic hydroxyl, quinonic oxygen, and carboxyl groups. On the other hand, after treatment of carbon black with sodium hydroxide, the absorption of phenolic hydroxyl groups at 3460 cm^{-1} had almost disappeared and the absorption of carboxyl groups was replaced by new absorption at 1592 cm^{-1} , which is characteristic of carboxylate anion. Based on the above results, it is concluded that sodium phenoxide groups are successfully introduced onto carbon black surface.

Reaction of PDCP with Carbon Black

It is well known that PDCP has active chlorine atoms and these atoms can be replaced with phenoxy, alkoxy, and amino groups to give poly(organophosphazenes). These poly(organophosphazenes) are heat-resistant polymers with excellent mechanical properties [13–19].

Therefore, the grafting of poly(organophosphazenes) onto carbon black by the reaction of PDCP with sodium phenoxide groups introduced onto the surface was examined. Table 1 shows the results of the reaction of PDCP with carbon black under several conditions. As mentioned above, the percentage of grafting was determined after the replacement of active chlorine atoms in grafted PDCP with phenoxy groups.

As shown in Table 1, the percentage of grafting of PDPP onto carbon black was determined to be 206% when PDCP was reacted with carbon black having

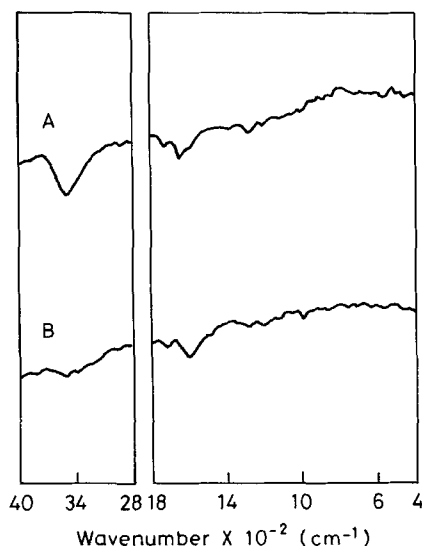


FIG. 1. Infrared spectra of (A) untreated and (B) sodium hydroxide-treated carbon black.

TABLE 1. Reaction of PDCP with Carbon Black Under Several Conditions^a

Run	Carbon black	Poly(phosphazene)	Grafting (%)
1	Untreated	PDCP	45.0
2	CB-ONa ^b	PDPP	30.1
3	CB-ONa ^b	PDCP	206

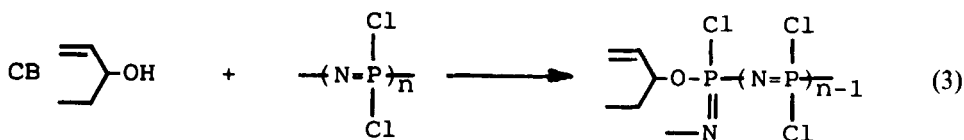
^aCarbon black; 0.10 g; poly(phosphazene), 0.70 g; toluene, 15.0 cm³; 30.0°C; 12 h.

^bCarbon black having sodium phenoxide groups.

sodium phenoxide groups at 30°C for 12 h (run 3). When carbon black having sodium phenoxide groups was mixed with PDPP (active chlorine atoms are blocked with phenoxy groups) in toluene, however, unextractable PDPP remaining on the surface was determined to be 30.1% after the Soxhlet extraction (run 2). This value was much smaller than that obtained from the reaction of PDCP with carbon black having sodium phenoxide groups.

Therefore, these results indicated that PDCP reacts with sodium phenoxide groups on carbon black to give PDCP-grafted carbon black as shown in Eq.(1).

On the other hand, the percentage of grafting onto carbon black obtained from the reaction of PDCP with untreated carbon black was 45.0% (run 1). This value is larger than that obtained from the reaction of untreated carbon black with PDPP. This indicates that PDCP also reacts with phenolic hydroxyl groups on carbon black [Eq.(3)], but the reactivity of phenolic hydroxyl groups was much smaller than that of sodium phenoxide groups introduced onto the surface.



The molecular weight of PDCP used in the above grafting reaction was determined to be 9.0×10^5 by GPC using standard polystyrene. Therefore, 206% grafting of PDCP means that the number of grafted PDCP on carbon black is 2.3×10^{-6} mol/g. This indicates that one PDCP-grafted chain occupies about 1000 sodium phenoxide groups on the surface, because the sodium phenoxide group content of carbon black was 0.24 mmol/g. This suggests that sodium phenoxide groups on the surface are readily blocked by grafted polymer chains.

Effect of Temperature on the Grafting

The grafting reaction of PDCP with sodium phenoxide groups on carbon black was carried out at 0, 15, and 30°C, and the effect of temperature on the grafting was examined. The results are shown in Fig. 2.

Figure 2 clearly shows that the grafting reaction was accelerated at higher temperature: the grafting reaction at 0°C was extremely retarded. During the graft-

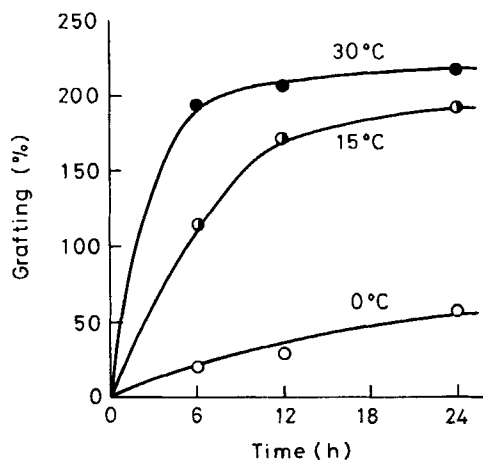


FIG. 2. Effect of temperature on the grafting of PDCP by the reaction of PDCP with carbon black having sodium phenoxide groups. Carbon black, 0.10 g; PDCP, 0.70 g; toluene, 15.0 cm³.

ing reaction below 30°C, no formation of gel was observed. This indicates that chlorine atoms of grafted PDCP on carbon black scarcely reacted with another carbon black, because carbon black was reacted with a large excess of PDCP.

On the other hand, when the grafting reaction was carried out above 30°C, gelation of PDCP was observed. This may be due to side reaction of PDCP with the small amount of water contained in the reaction of mixture, because the toluene solution of PDCP was gelled by heating above 30°C even in the absence of carbon black.

Effect of Chlorine Atom Content of PDCP on Grafting

By use of PDCP whose chlorine atoms were partly replaced with phenoxide groups, i.e., PDCP-s, the effect of the chlorine atom content of PDCP on the grafting reaction with carbon black having sodium phenoxide groups was examined. The results are shown in Fig. 3. The amount of chlorine atom of PDCP-s replaced with phenoxide group was 44.0 mol%.

The grafting reaction was found to decrease with decreasing chlorine atom content. Gelation of PDCP above 30°C, however, was retarded by use of PDCP-s.

Grafting of Several Poly(organophosphazenes) onto Carbon Black

Poly(diaminophenylphosphazene) (PDAPP) and poly(diethoxyphosphazene) (PDEP) were grafted onto carbon black surface by treatment of PDCP-grafted carbon black with aniline and sodium ethoxide, respectively. Figure 4 shows the infrared spectra of (A) PDPP-grafted, (B) PDAPP-grafted, and (C) PDEP-grafted carbon black.

In comparison with infrared spectra of untreated carbon black and sodium hydroxide-treated carbon black shown in Fig. 1, infrared spectra of PDPP-grafted

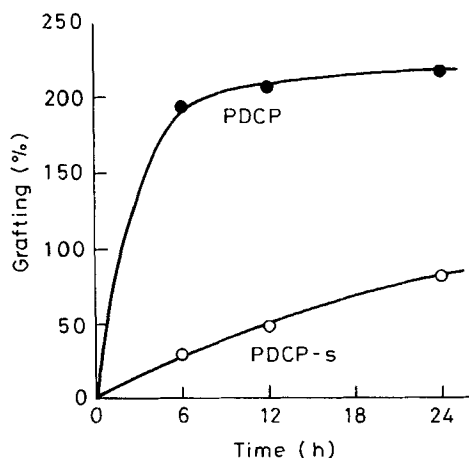


FIG. 3. Effect of chlorine atom content of the grafting of the grafting of PDPP at 30°C. Reaction conditions are given in Fig. 2.

carbon black show new absorptions characteristic of PDPP at 774 cm^{-1} ($-\text{N}=\text{P}-$ bond), 1200 cm^{-1} ($-\text{N}=\text{P}-$ and $\text{P}-\text{O}-\text{C}$ bond), 1458 cm^{-1} (phenyl), and 1594 cm^{-1} (phenyl).

On the other hand, infrared spectra of PDAPP-grafted carbon black exhibited new absorptions at 750 cm^{-1} and 1244 cm^{-1} , 1504 cm^{-1} and 1606 cm^{-1} , and 3490 cm^{-1} , which are characteristic of the $-\text{N}=\text{P}-$ bond, phenyl group, and $\text{Ph}-\text{NH}-$ group, respectively.

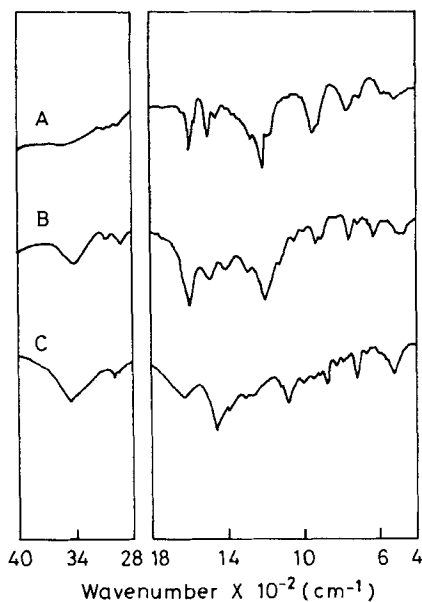


FIG. 4. Infrared spectra of (A) PDPP-, (B) PDAPP-, and (C) PDEP-grafted carbon black.

In addition, infrared spectra of PDEP-grafted carbon black show absorptions characteristic of PDEP at 764 cm^{-1} , 1252 cm^{-1} , and 1448 cm^{-1} .

Based on these results, it is concluded that various kinds of poly(organophosphazenes) can be grafted onto carbon black surface by treatment of PDCP-grafted carbon black with sodium phenoxide, sodium ethoxide, and aniline.

Stability of PDPP-Grafted Carbon Black Dispersion

Poly(organophosphazenes)-grafted carbon blacks produced stable colloidal dispersions in THF. The stability of PDPP-grafted carbon black dispersion was compared with that of untreated carbon black in Fig. 5.

As shown in Fig. 5, untreated carbon black was readily precipitated after 1 day. On the contrary, it was found that about 50% of PDPP-grafted carbon black was dispersed in THF even after 30 days. These results clearly show the effect of grafting of PDPP onto the surface on the dispersibility of carbon black particles in organic solvents.

Thermal Stability of PDPP-Grafted Carbon Black

It is well known that poly(organophosphazenes) are stable in air about 300°C . Thus, the thermal behavior of PDPP-grafted carbon black was examined by thermogravimetric analysis.

As shown in Fig. 6, ungrafted PDPP exhibited an initial weight loss about 300°C . The initial inflection point on the thermogravimetric curve of PDPP-grafted carbon black occurred at about 300°C . Therefore, PDPP-grafted carbon black shows excellent heat resistivity as well as poly(amide-imide)-grafted carbon black [11].

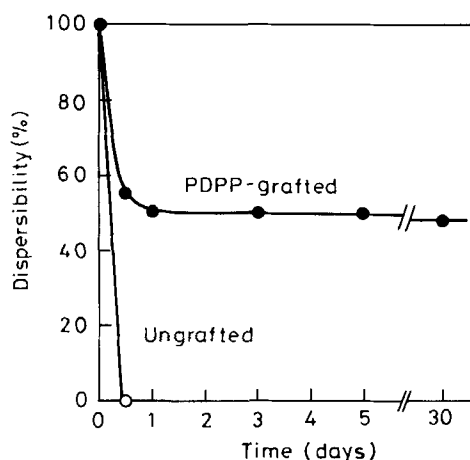


FIG. 5. Stability of PDPP-grafted carbon black dispersion in THF at room temperature.

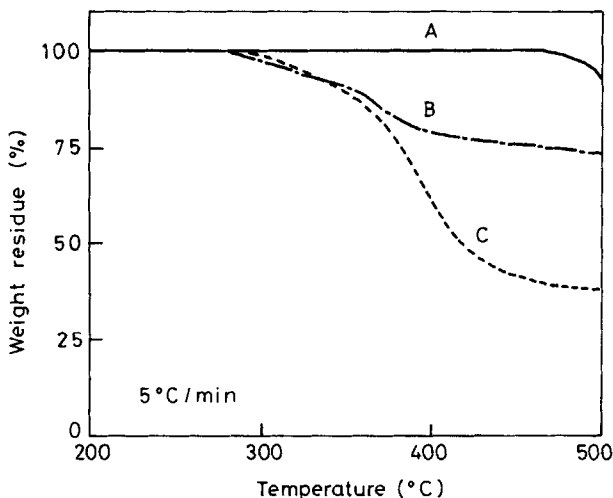


FIG. 6. Thermogravimetric curves of (A) untreated carbon black, (B) PDPP-grafted carbon black, and (C) PDPP in air.

CONCLUSIONS

Poly(organophosphazenes) were successfully grafted onto carbon black surface by the reaction of PDPCP with carbon black having sodium phenoxide groups followed by treatment with sodium phenoxide, sodium ethoxide, and aniline. Poly(organophosphazenes)-grafted carbon blacks thus obtained produced stable colloidal dispersions in THF and showed excellent heat resistivity.

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