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# *Grafting*

## Reactive Carbon Black Having Isocyanate or Acyl Azide Group
### Preparation and Reaction with Polymers Having Hydroxyl Group

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## SUMMARY

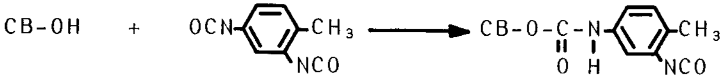
Introduction of isocyanate (NCO) group onto carbon black surface was achieved by the treatment of carbon black with toluene-2,4-diisocyanate. In addition, carbon black having acyl azide ($CON_3$) group, a precursor of NCO group, was prepared by the reaction of COCl or $COOCOOC_2H_5$ group on carbon black with $NaN_3$. The $CON_3$ group on carbon black was relatively stable at below 20°C but readily decomposed to NCO group by heating (Curtius rearrangement). By the reation of NCO group on carbon black with hydroxyl group of polymers, such as polypropylene glycol, polyethylene glycol, and polyvinyl alcohol, these polymers were found to be grafted onto carbon black.

## INTRODUCTION

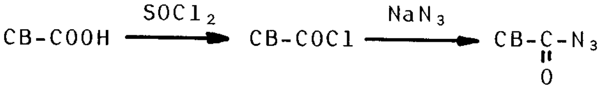
The grafting of various kinds of polymers onto carbon black surface has been extensively studied in our laboratory (1). For instance, we have reported the anionic grafting of polyesters (2∿4) and poly-β-alanine (5), the cationic grafting of polystyrene (6), polyesters (7), polyethers (8), and polyacetals (9), and the radical grafting of vinyl monomers from carbon black (10). Furthermore, it became apparent that phenolic hydroxyl and carboxyl groups on the surface of carbon black react with prepolymer having a terminal NCO group to give polymer-grafted carbon black (11). Moreover, carbon black was found to be able to gelatinize urethane prepolymer having two-terminal NCO groups (12) and epoxy resin (13).

However, the grafting of polymers onto carbon black by the reaction of carbon black having reactive surface groups, such as NCO groups, with functional groups of various kinds of polymers has not been investigated.

In the present paper, the introduction of NCO groups onto carbon black by the reaction of toluene-2,4-diisocyanate (TDI) with phenolic hydroxyl and carboxyl groups on carbon black (Eq. 1) and that of $CON_3$ groups, the precursor of NCO groups, according to Eqs. 2 and 3 were examined. Furthermore, the reactions of these reactive carbon black samples with functional polymers such as polypropylene glycol, polyethylene glycol, polyvinyl alcohol, and soluble starch were carried out.

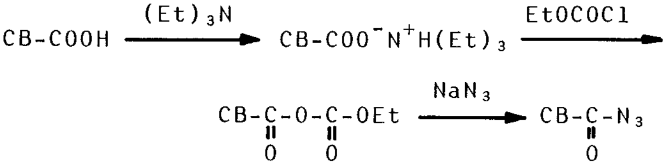


(Eq. 1)



$$\mathrm{CB{-}COOH} \xrightarrow{\mathrm{SOCl_2}} \mathrm{CB{-}COCl} \xrightarrow{\mathrm{NaN_3}} \mathrm{CB{-}\underset{\underset{O}{\|}}{C}{-}N_3}$$

(Eq. 2)



$$\mathrm{CB{-}COOH} \xrightarrow{\mathrm{(Et)_3N}} \mathrm{CB{-}COO^-N^+H(Et)_3} \xrightarrow{\mathrm{EtOCOCl}}$$

$$\mathrm{CB{-}\underset{\underset{O}{\|}}{C}{-}O{-}\underset{\underset{O}{\|}}{C}{-}OEt} \xrightarrow{\mathrm{NaN_3}} \mathrm{CB{-}\underset{\underset{O}{\|}}{C}{-}N_3}$$

(Eq. 3)

## EXPERIMENTAL

### *Materials*

Carbon black used was color channel black Neospectra II (Columbian Carbon Co., specific surface area; 906 $m^2/g$). It was dried *in vacuo* at 110°C before use. The content of phenolic hydroxyl and carboxyl groups was 0.24 mequiv./g and 0.40 mequiv./g, respectively.

Toluene-2,4-diisocyanate obtained from Wako Pure Chemical Co. Ltd., Japan, was distilled under reduced pressure before use. Sodium azide (Kanto Chemical Co. Inc., Japan) was activated according to the method of Iwakura *et al.* before use (14).

*m*-Xylene was washed with concentrated $H_2SO_4$, refluxed over sodium, and distilled. Dimethyl sulfoxide (DMSO) was dried over $CaH_2$ and distilled under reduced pressure. All other reagents and solvents were also used after ordinary purification.

### *Polymers*

Diol-type polypropylene glycol (PPG) and polyethylene glycol (PEG) obtained from Wako Pure Chemical Co. Ltd. were dried *in vacuo* at 110°C before use. The average number molecular weight of PPG and PEG was 2000 and 6000, respectively. Polyvinyl alcohol (PVA: molecular weight=$6.6 \times 10^4$) and soluble starch were also dried *in vacuo* at 50°C.

### *Introduction of NCO Group onto Carbon Black*

Introduction of NCO group onto carbon black surface was achieved by the treatment of carbon black with an excess of TDI. A typical example was as follows. Into a three-necked flask equipped with a reflux condenser and an inlet of nitrogen, 3.0g of Neospectra II, 0.7g of TDI, and 60ml of *m*-xylene were added. The mixture was refluxed for 30h with stirring using a magnetic stirrer under nitrogen. After the reaction, the carbon black was filtered and extracted with benzene using a Soxhlet apparatus under dry nitrogen for 50h. The carbon black was dried *in vacuo* at 90°C.

### *Introduction of $CON_3$ Group onto Carbon Black*

Method 1 (Eq. 2): Carbon black having COCl group (CB-COCl) was prepared by the reaction of carboxyl group with $SOCl_2$. The procedure was described in detail in the preceding paper (6).

Then, CB-COCl was treated with activated $NaN_3$ as follows. To a dispersion of CB-COCl (3.0g) in 50ml of tetrahydrofuran (THF), 1.6g of $NaN_3$ in 10ml of water was added and the mixture was stirred at 0°C for 2h. After the reaction, the resulting carbon black was filtered, washed with ice-cold water, and dried *in vacuo* at room temperature.

Method 2 (Eq. 3): To a dispersion of Neospectra II (5.0g) in 50ml of THF was added a solution of 0.6g of triethylamine in 10ml of THF. After the reaction at 0°C for 2h, the reaction mixture was cooled to -10°C and the 0.56g of ethyl chloroformate was added. The resulting reaction mixture was stirred for 10h at -10°C and then a solution of 0.4g of activated $NaN_3$ in 10ml of water was added. After the treatment at -2∿0°C for 10h, the resulting carbon black was filtered, washed with ice-cold water and THF, and dried *in vacuo* at room temperature.

### *Determination of NCO Group on Carbon Black*

Carbon black having NCO group was reacted with 10ml of 0.025N di-*n*-butylamine toluene solution at room temperature for 3h with stirring. After the reaction, unreacted di-*n*-butylamine was titrated with 0.02N HCl using bromophenol blue as an indicator (15).

### *Determination of $CON_3$ Group on Carbon Black*

Acyl azide group on carbon black was rearranged to NCO group by heat treatment at 130°C for 1h. Then, the content of NCO group was determined by titration described above.

### *Reaction of Carbon Black Having NCO Group with Polymers Having Hydroxyl Group*

The reaction of carbon black having $CON_3$ group (CB-$CON_3$) with PPG and PEG was carried out in bulk. For instance, a mixture of CB-$CON_3$ (0.35g) and 5.0g of polymer was heated at 130°C in an electric oven. On the other hand, the reaction of CB-$CON_3$ with PVA and soluble starch was carried out in solution using DMSO as solvent. Thus, CB-$CON_3$ (0.25g) was added to a solution of PVA (1.0g) in 7.0ml of DMSO and the mixture was stirred with a magnetic stirrer under dry nitrogen at 130°C.

### *Determination of Grafting Ratio*

After the reaction, the carbon black reacted with PPG was dispersed in benzene, and the dispersion was centrifuged at $10^4$ rpm. The carbon black precipitated was extracted with benzene to remove unreacted polymer and dried *in vacuo* at 100°C. The extracting solvent for PEG was methanol and that for PVA and soluble starch was water. The grafting ratio of polymer onto carbon black was calculated by the following equation.

$$\text{Grafting ratio} = \frac{\text{Weight of polymer grafted(g)}}{\text{Weight of carbon black used(g)}} \times 100$$

## RESULTS AND DISCUSSION

### *Carbon Black Having NCO Group*

In the previous paper, we have described that phenolic

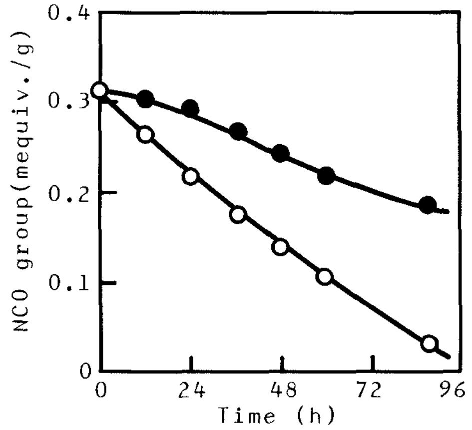


Figure 1. Stability of NCO group on the surface of carbon black

(○): stored in a desiccator (silica-gel) at room temperature.

(●): stored in vacuum at room temperature.

hydroxyl and carboxyl groups on the surface of carbon black react with a terminal NCO group of prepolymer and the prepolymer was grafted onto carbon black surface with amide or urethane bond (11,12). Therefore, it was expected that when carbon black was treated with TDI, one of the two NCO groups of TDI reacts with phenolic hydroxyl or carboxyl group on carbon black and that TDI is fixed on the carbon black surface as shown in Eq. 1.

Accordingly, carbon black Neospectra II was treated with an excess of TDI in *m*-xylene at 130°C. After the purification by Soxhlet extraction with benzene to remove unreacted TDI, the content of NCO group on the surface of carbon black was determined to be 0.31 mequiv./g by titration. The result indicates that the amount of NCO group introduced onto carbon black was about one-half of the total functional groups, *i.e.*, phenolic hydroxyl and carboxyl groups.

It is well known that NCO group is very moisture-sensitive. Therefore, the stability of NCO group on carbon black was investigated. CB-NCO was stored in a desiccator (silica-gel) or in vacuum (0.1∿0.5 mmHg). Then, the content of NCO groups on carbon black was determined at given intervals. The results are shown in Figure 1.

As shown in Figure 1, the content of NCO group on carbon black decreased rapidly in desiccator (silica-gel). Even if it was stored in vacuum desiccator, the content of NCO group gradually reduced to two-third of the initial content after 90h. Therefore, these results indicate that CB-NCO is unable to store for a long time and has to be used as soon as possible.

### *Carbon Black Having $CON_3$ Group*

In general, acyl azide group is relatively stable at room temperature, but undergo facile fragmentation to produce NCO group and nitrogen by heating (Curtius rearrangement). Therefore, we have examined two routes (*c.f.* Eqs. 2 and 3) for the introduction of $CON_3$ group onto carbon black surface.

The usual procedure of obtaining acyl azide consists of treating acid chloride with $NaN_3$ (16). Boehm has introduced $-NHCOOC_2H_5$ group onto carbon black by the reaction of carbon black having COCl group with $NaN_3$ in ethanol (17). However,

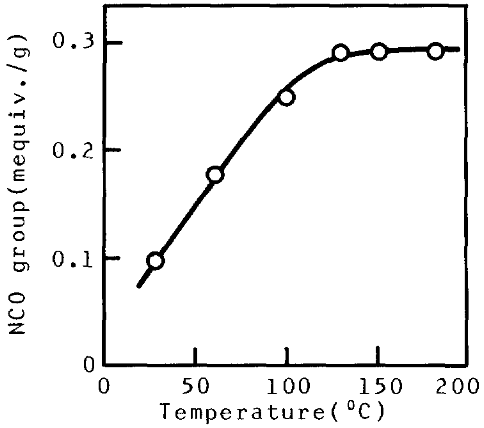


Figure 2. Formation of NCO group by rearrangement of $CON_3$ group on carbon black by heating for 1h

carbon black having $CON_3$ group was not isolated.

The first method to introduce $CON_3$ group onto carbon black is essentially analogous to that of Boehm (17). As shown in Eq. 2, this involves two stages: (i) introduction of COCl group onto carbon black by the reaction of carboxyl group with $SOCl_2$ and (ii) reaction of COCl group with $NaN_3$.

The second method, as shown in Eq. 3, is an adaptation of the method of Weinstock (18). This involves three stages: (i) treatment of carboxyl group on carbon black with triethylamine, (ii) reaction with ethyl chloroformate, and (iii) reaction with $NaN_3$.

The carbon black having $CON_3$ group (prepared by the second method) was heated at various temperature for 1h and then NCO group content of carbon black was determined by titration. Figure 2 shows the relationship between the temperature of the heating and the amount of NCO group formed on the carbon black by the rearrangement of $CON_3$ group. The result indicates that $CON_3$ group introduced onto carbon black was rearranged completely into NCO group by heating at 130°C for 1h.

The content of $CON_3$ group on carbon black obtained from

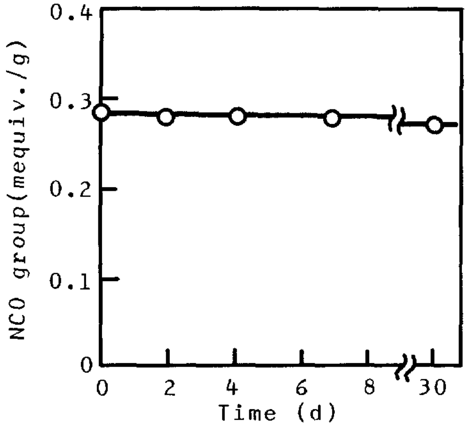


Figure 3. Stability of $CON_3$ group on the surface of carbon black

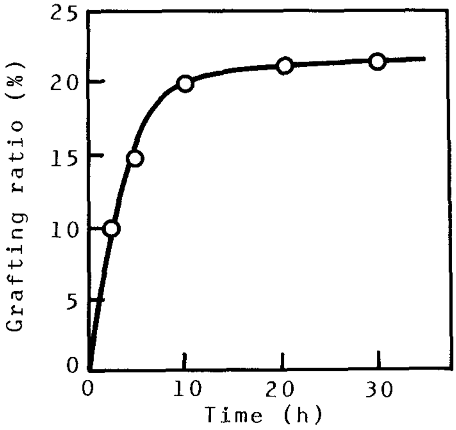


Figure 4. Grafting of PPG by the reaction of CB-CON$_3$ with PPG

Neospectra II-CON$_3$, 0.35g; PPG, 5.0g; 130°C.

the methods 1 (Eq. 2) and 2 (Eq. 3) was 0.27 mequiv./g and 0.28 mequiv./g, respectively. Therefore, no difference in the content of CON$_3$ group introduced onto carbon black between two methods was observed. Moreover, the amount of CON$_3$ group introduced onto carbon black was about 70% of the carboxyl group content of carbon black surface.

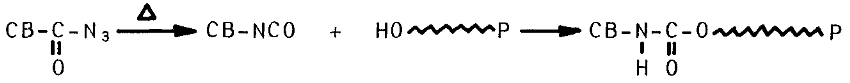
Furthermore, the stability of CON$_3$ group on carbon black upon storage was examined. The result is shown in Figure 3. In contrast with NCO group on carbon black, as shown in Figure 3, CON$_3$ group on carbon black was scarcely decomposed in a desiccator at below 20°C after 30 days.

### *Grafting onto Carbon Black by the Reaction of NCO Group on Carbon Black with Polymers Having Hydroxyl Group*

It has been reported that glass fiber having NCO group, which was prepared by the reaction of silanol group on the fiber surface with TDI, reacts with diol-type polyester (19).

The reaction of NCO group on the carbon black surface, which was formed by the heating of CB-CON$_3$, with PPG (diol-type, $\overline{M}n$=2000) was carried out and the grafting of the polymer onto carbon black was examined. The result is shown in Figure 4.

Figure 4 shows that NCO group on carbon black reacts with terminal hydroxyl group of PPG to give PPG-grafted carbon



$$\mathrm{CB\text{-}}\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{\text{-}N_3} \xrightarrow{\Delta} \mathrm{CB\text{-}NCO} + \mathrm{HO}\sim\sim\sim\mathrm{P} \longrightarrow \mathrm{CB\text{-}}\underset{\underset{\displaystyle \mathrm{H}}{|}}{\mathrm{N}}\text{-}\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{\text{-}O}\sim\sim\sim\mathrm{P}$$

black. The grafting ratio after heating at 130°C for 30h was determined to be 21.9%. This indicates that 41% of NCO group is reacted with hydroxyl group of PPG.

Table I shows that PEG, PVA, and soluble starch are able to graft onto carbon black by the reaction of NCO group on carbon black with hydroxyl group of these polymers.

In conclusion, by the use of carbon black having CON$_3$ group, it became feasible to graft various kinds of polymers having hydroxyl groups onto carbon black surface. This

TABLE I
Grafting onto Carbon Black by the Reaction of $CB-CON_3$ with Polymers Having Hydroxyl Group

| Polymer | $\overline{Mn}\times10^{-3}$ | DMSO (ml) | Temp. (°C) | Time (h) | Grafting ratio (%) |
|---|---|---|---|---|---|
| PPG | 2.0 | - | 130 | 10 | 21.9[a] |
| PEG | 6.0 | - | 130 | 5 | 26.7[a] |
| PEG | 6.0 | - | 130 | 10 | 29.7[a] |
| PVA | 66.0 | 7.0 | 130 | 10 | 32.4[b] |
| PVA | 66.0 | 7.0 | 130 | 30 | 43.4[b] |
| Starch | - | 7.0 | 130 | 30 | 23.0[b] |

[a] Polymer, 5.0g; $CB-CON_3$, 0.35g.
[b] Polymer, 1.0g; $CB-CON_3$, 0.25g.

grafting method enabled us to control the molecular weight of grafted polymer chains. Further application to various kinds of functional polymers is now under investigation.

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