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HEAT-RESISTANT POLYMER-GRAFTED CARBON BLACK: GRAFTING OF POLY(AMIDE-IMIDE) ONTO CARBON BLACK

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ABSTRACT

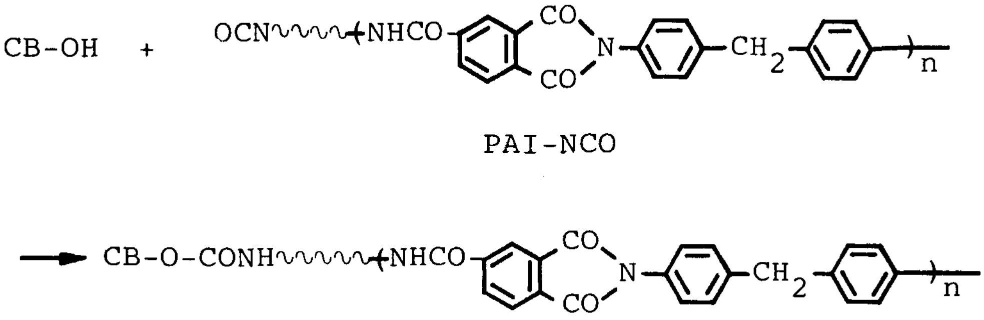
Aromatic poly(amide-imide) with terminal isocyanate groups (PAI-NCO) was prepared by the polycondensation of trimellitic anhydride and a slight excess of 4,4′-diphenylmethane diisocyanate in *N*-methyl-2-pyrrolidone (NMP) at 160°C for 20 h. PAI was effectively grafted onto the surface by the reaction of PAI-NCO with carbon black: the percentage of grafting onto FW 200 and Neospectra II was determined to be 41.2 and 39.5%, respectively. When the carboxyl and phenolic hydroxyl groups on carbon black were blocked by treatment with diazomethane, the grafting of PAI-NCO onto the treated carbon black does not proceed. Therefore, it is concluded that PAI-NCO reacts with the carboxyl and phenolic hydroxyl groups on carbon black and PAI is grafted through amide and urethane bonds, respectively. The reaction of PAI-NCO with carbon black was accelerated by the addition of amines as catalyst and by raising of the reaction temperature. Thermogravimetric analysis indicated that PAI-grafted carbon black was stable in air up to about 300°C. The PAI-grafted carbon black was found to give a stable colloidal dispersion in NMP.

INTRODUCTION

In a series of papers we have reported the grafting of various polymers, such as vinyl polymers [1], polyesters [2, 3], polyethers [4, 5], and polyamides [6], onto carbon black surfaces. Furthermore, the grafting of polyurethane onto carbon black was achieved by reaction of polyurethane having terminal isocyanate groups with carboxyl and phenolic hydroxyl groups on the surface [7].

However, the grafting of heat-resistant polymers has hardly been investigated. In a previous paper we demonstrated that, during the polyaddition of diepoxides with diisocyanates initiated by lithium phenolate groups on carbon black, poly-2-oxazolidone, a well-known heat-resistant polymer, was effectively grafted onto the surface [8]. In addition, we succeeded in the grafting of poly(oxymethylene) by the cationic ring-opening polymerization of trioxane initiated by acylium perchlorate groups introduced onto carbon black [9]. The poly(oxymethylene)-grafted carbon black was found to be stable up to 200°C [9].

On the other hand, aromatic poly(amide-imide) (PAI) is known to be a heat-resistant polymer and is generally synthesized by the polycondensation of trimellitic anhydride (TMAH) with 4,4′-diphenylmethane diisocyanate (MDI) [10-12]. Therefore, in the present paper, we wish to report the grafting of PAI onto carbon black by the reaction of PAI having terminal isocyanate groups (PAI-NCO) with carboxyl and phenolic hydroxyl groups on the surface. In addition, the thermal stability and the dispersibility in an organic solvent of PAI-grafted carbon black were studied.



EXPERIMENTAL

Materials

Carbon blacks used were both furnace black and channel black. Furnace black Philblack O (Philips Petroleum Co., BET specific surface area, 79.6 m^2/g) was extracted with benzene before use to remove resinous substances present on the surface. Channel blacks FW 200 (Degussa A.G., 460 m^2/g) and Neospectra II (Columbian Carbon Co., 906 m^2/g) were used without extraction because they contain no resinous substances. These carbon blacks were dried in vacuo at 110°C before use.

Trimellitic anhydride (THAH) obtained from Amoco Chemical Co. was sublimed under reduced pressure. 4,4′-Diphenylmethane diisocyanate (MDI) was distilled under reduced pressure.

N-Methyl-2-pyrrolidone (NMP) and *N,N*-dimethylformamide (DMF) were dried over calcium hydride and distilled under reduced pressure.

Poly(Amide-imide) with Terminal Isocyanate Groups (PAI-NCO)

PAI having terminal isocyanate groups (PAI-NCO) was prepared by the polycondensation of TMAH with a slight excess of MDI. A typical example was as follows. Into a 100-mL flask equipped with a nitrogen inlet and a calcium chloride tube, 4.3 mmol TMAH, 4.6 mmol MDI, and 10.0 mL NMP were charged. The reaction was conducted at 120°C for 20 h under nitrogen. The polymer solution thus obtained was used for the reaction with carbon black without isolation of the polymer to avoid quenching of the terminal isocyanate groups.

Reaction of PAI-NCO with Carbon Black

To a flask that contained NMP solution of PAI-NCO, 0.30 g carbon black was added. The reaction mixture was stirred with a magnetic stirrer at 160°C under nitrogen. After the reaction, the content of the flask was poured into acetone to precipitate PAI-grafted carbon black and ungrafted polymer. The precipitate was filtered, washed with acetone, and dried *in vacuo* at 40°C.

Treatment of Carbon Black with Diazomethane

The treatment of carbon black with diazomethane was carried out as previously reported [13]. Both carboxyl and phenolic hydroxyl groups on the carbon black were blocked by the treatment with diazomethane.

Percentage of Grafting of PAI

The product was dispersed in DMF at room temperature, and the dispersion was centrifuged at 1.2×10^4 rpm until carbon black was precipitated completely. Subsequently, the precipitated carbon black was extracted with DMF by use of a Soxhlet extractor for 50 h. The percentage of grafting of PAI onto carbon black was calculated by

$$\text{percentage of grafting} = \frac{\text{PAI grafted (g)}}{\text{carbon black used (g)}} \times 100.$$

Molecular Weight of PAI

The molecular weight of PAI was calculated by the following equation from viscosity measurements in NMP at 30.0°C [14]:

$$[\eta] = 2.48 \times 10^{-4}\, M^{0.60}$$

Dispersibility of PAI-Grafted Carbon Black

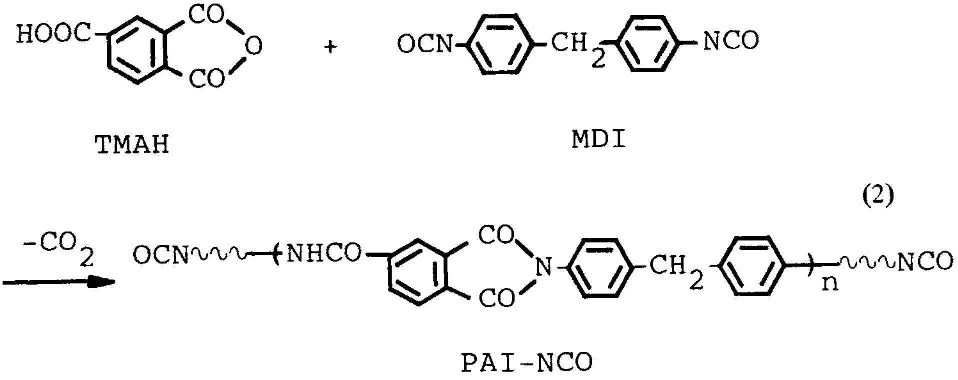
PAI-grafted carbon black (0.30 g) was dispersed in 100 mL DMF with a magnetic stirrer, and the dispersion was allowed to stand at room temperature. After the desired time, 5.0 mL dispersion liquid was taken out with a pipet, and the content of carbon black dispersed in DMF was determined. The dispersibility was determined by the following equation [5]:

$$\text{dispersibility (\%)} = \frac{\text{carbon black dispersed after standing (g)}}{\text{carbon black dispersed before standing (g)}} \times 100$$

RESULTS AND DISCUSSION

Preparation of PAI-NCO

The preparation of PAI-NCO was carried out by the reaction of TMAH with a slight excess of MDI:



(2)

When the polymerization of 4.3 mmol TMAH with 4.7 mmol MDI in 10.0 mL of NMP was carried out at 160°C for 20 h, the conversion went to about 100%. The IR spectra of the polymer exhibited absorptions at 1780 and 1380 cm^{-1} (imide bond), 1660 and 1525 cm^{-1} (amide bond), and 1510 and 1590 cm^{-1} (aromatic ring). Its molecular weight was determined to be 3.5×10^5. The content of NCO groups of the PAI was determined to be 1.4×10^{-5} equivalent/g by titration [15].

Based on the above results, it is concluded that PAI-NCO can be prepared by the polymerization of TMAH with a slight excess of MDI.

Reaction of PAI-NCO with Carbon Black

It has been reported that urethane prepolymer having terminal isocyanate groups reacts with carboxy and phenolic hydroxyl groups and that the polymer was grafted onto the surface through amide and urethane bonds [7]. Therefore, the reaction of PAI-NCO with carbon black was carried out under several conditions, and the grafting of PAI onto the surface was examined.

The results are shown in Table 1, which clearly shows that PAI-NCO was grafted onto the carbon black surface by the reaction of PAI-NCO with the surface (No. 2), because less than 10% of PAI, which has no isocyanate groups, adsorbed on the surface (No. 1). Therefore, it is concluded that by the reaction of PAI-NCO with carbon black, PAI was effectively grafted onto the surface.

On the other hand, it was found that, when the polycondensation of TMAH with MDI was carried out in the presence of carbon black, no polymer was grafted onto the surface (Table 1, No. 3). This may be due to the fact

TABLE 1. Reaction of PAI-NCO with Carbon Black under Several Conditions

No.	Reaction mixture	Conversion, %	Percentage of grafting
1[a]	PAI + CB	–	9.4
2[a]	PAI-NCO + CB	–	39.5
3[b]	TMAH + MDI + CB	92.1	11.6

[a] Neospectra II, 0.30 g; polymer, 1.80 g; NMP, 10.0 mL; 160°C; 20 h.

[b] Neospectra II, 0.30 g; TMAH, 4.3 mmol; MDI, 4.7 mmol; NMP, 10.0 mL; 160°C; 20 h.

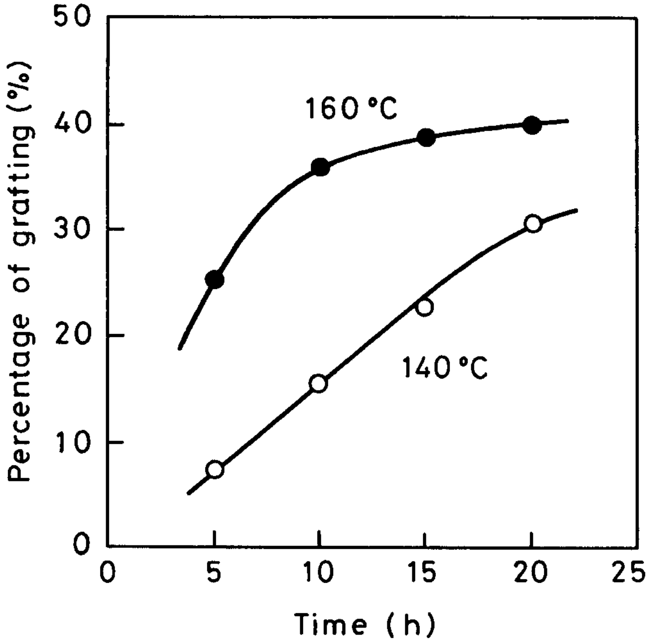


FIG. 1. Grafting of PAI by the reaction of PAI-NCO with carbon black. Neospectra II, 0.30 g; PAI-NCO, 1.80 g; NMP, 10.0 mL.

that carboxyl and phenolic hydroxyl groups on the carbon black are preferentially blocked by the reaction with MDI.

Figure 1 shows the relationship between the percentage of grafting of PAI and reaction time. It was found that the percentage of grafting increased with increasing reaction time.

Grafting of PAI onto Several Carbon Blacks

To clarify the grafting sites on carbon black, the reaction of PAI-NCO with several carbon blacks were carried out and the relationship between the functional group content of carbon black and the percentage of grafting was examined. The results are shown in Table 2.

Similarly to Neospectra II, PAI was effectively grafted onto the surface of FW 200 by the reaction of PAI-NCO with the surface. However, the grafting of PAI-NCO onto Philblack O, which has fewer functional groups, was scarcely observed. In addition, when carboxyl and phenolic hydroxyl groups on FW 200 were blocked by the treatment with diazomethane [14], the percentage of grafting of PAI onto the surface was remarkably decreased.

Based on these results, it is considered that terminal isocyanate groups of PAI react with carboxyl and phenolic hydroxyl groups on carbon black and the polymer is grafted through amide and urethane bonds, respectively.

Effect of Temperature on the Grafting

Figure 2 shows the effect of temperature on the grafting of PAI by the reaction of PAI-NCO with carbon black. It was found that the grafting reac-

TABLE 2. Grafting of PAI-NCO onto Several Carbon Blacks[a]

Carbon black	COOH, meq/g	OH, meq/g	Percentage of grafting
FW 200	0.61	0.10	41.2
Neospectra II	0.40	0.24	39.5
Philblack O	0	0.02	9.1
CH_2N_2-FW 200	0	0	10.8

[a] CB, 0.30 g; PAI-NCO, 1.80 g; NMP, 10.0 mL; 160°C; 20 h.

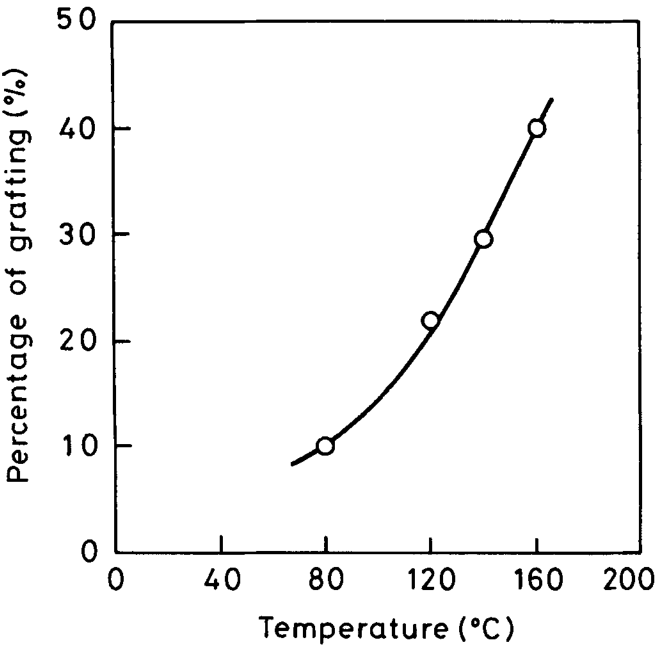


FIG. 2. Effect of temperature on the reaction of PAI-NCO with carbon black. Neospectra II, 0.30 g; PAI-NCO, 1.80 g; NMP, 10.0 mL; 20 h.

tion was accelerated at higher temperature. The result indicates that relatively higher temperature is required for the preparation of PAI-grafted carbon black with a higher percentage of grafting.

Effect of Catalyst on the Grafting

It is well known that the reaction of isocyanates with carboxylic acids and alcohols is accelerated by the addition of amines as catalysts [16]. Therefore, the effect of amines on the grafting of PAI-NCO onto carbon black was examined. The results are shown in Table 3. It was found that amines such as pyridine, α-picoline, and triethylamine act as effective catalysts for the reaction of PAI-NCO with carbon black.

TABLE 3. Effect of Amines on the Reaction of PAI-NCO with Carbon Black[a]

Amine	Percentage of grafting
None	10.2
Pyridine	22.0
α-Picoline	26.3
Triethylamine	23.4

[a] Neospectra II, 0.30 g; PAI-NCO, 1.80 g; amine, 5 mmol; NMP, 10.0 mL; 80°C; 8 h.

Thermal Stability of PAI-Grafted Carbon Black

It has been reported that PAI's are stable in air up to about 300°C [10-12]. Thus, the thermal behavior of PAI-grafted carbon black was examined by thermogravimetric analysis.

As shown in Fig. 3, polyester-grafted carbon black exhibited an initial weight loss at about 200°C in air. However, the initial inflection point on the thermogravimetric curve of PAI-grafted carbon black occurred at about 300°C. This may be due to the difference in thermal stability between these grafted polymers, because Neospectra II is stable up to 600°C in air.

Dispersibility of PAI-Grafted Carbon Black

PAI-grafted carbon black produced a stable colloidal dispersion in NMP and DMF. The dispersibility of PAI-grafted carbon black and PAI-adsorbed carbon black is compared with that of untreated carbon black in Fig. 4.

As shown in Fig. 4, it was found that PAI-grafted carbon black scarcely precipitated even after 1 month at room temperature. On the contrary, untreated carbon black and PAI-adsorbed carbon black were readily precipitated. These results clearly show the effect of grafting of PAI onto the surface on the dispersion of carbon black particles in organic solvent.

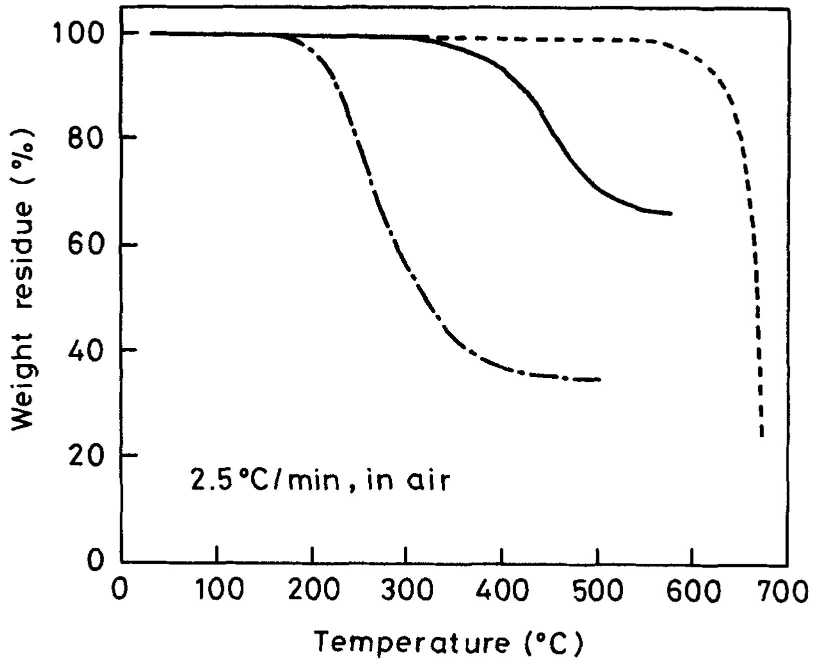


FIG. 3. Thermogravimetric curves of PAI-grafted carbon black. (- - -) untreated Neospectra II; (—) PAI-grafted Neospectra II (percentage of grafting = 39.5); (– – –) polyester-grafted Neospectra II [3] (145%). Heating rate 25°C/min in air.

CONCLUSIONS

PAI was effectively grafted onto the surface through amide and urethane bonds by the reaction of PAI-NCO with carboxyl and phenolic hydroxyl groups on carbon black. The grafting reaction was accelerated by the addition of amines as catalysts and by raising the reaction temperature. PAI-grafted carbon black was stable in air up to about 300°C and produced a stable dispersion in organic solvents such as NMP and DMF.

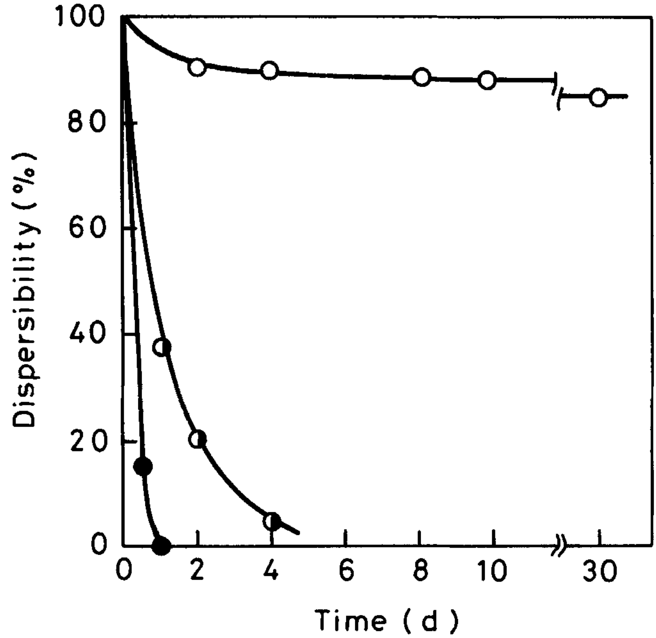


FIG. 4. Dispersibility of PAI-grafted carbon black in DMF at room temperature. (○) PAI-grafted Neospectra II (percentage of grafting = 39.5); (◐) PAI-adsorbed Neospectra II; (●) untreated Neospectra II.

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