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A novel method for grafting polymers on carbon blacks

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A simple and effective impregnation method to graft polymers on carbon blacks without any coupling agent or complicated pretreatment is reported. Dispersibility measurements, acidity measurements, infrared spectra and surface functional group effects on the grafting efficiency suggest that the acidic surface functional groups on carbon blacks are key factors in controlling the grafting efficiency of the impregnation process.

Introduction

Carbon blacks are important materials that have been widely used as fillers in elastomers, plastics, paints, inks, *etc.* However, unmodified carbon blacks cannot be used directly for certain applications. The desired surface properties of carbon blacks cannot always be obtained by the traditional manufacturing processes. Therefore, the modification of carbon black surfaces by chemical and physical methods, such as oxidation,[1–6] plasma treatment,[7,8] polymer grafting,[9–19] *etc.*, in particular polymer grafting, have been intensively studied.

Most carbon blacks produced are used in combination with polymers, especially with elastomers in the rubber industry. The compatibility of carbon blacks in elastomer matrices is markedly improved by grafting polymers onto the surface of carbon blacks. Grafting polymers on carbon blacks not only enables carbon blacks to have good dispersibility in solvents and polymers, but also enables carbon blacks to acquire useful properties, such as cross-linking ability, bioactivity, and photosensitivity.

Several methodologies have been developed to graft polymers onto carbon black surfaces.[19] Polymers can be grafted onto carbon surfaces *via* a termination reaction between growing polymer radicals and functional groups on the carbon surfaces, and by a polymerization reaction initiated from initiating groups that have been previously introduced on the carbon surfaces. Polymers may also be grafted onto carbon surfaces by reaction between carbon surface groups and functional polymers. Some complicated pretreatments and multiple steps with special coupling agents are required for all the methods of grafting polymers onto carbon blacks mentioned above.

In this paper, we report a simple impregnation method that can effectively graft polymers onto carbon blacks without a coupling agent. Polymers and organic compounds with functional groups such as hydroxy or amine groups can be grafted onto carbon blacks by this method. The nature of the polymer grafted carbon blacks was analyzed and characterized by Fourier-transform infrared spectroscopy (FT-IR), ultraviolet spectroscopy and thermogravimetric analysis (TGA) under a helium atmosphere.

Table 1 Specific surface areas and volatilities of carbon blacks

Carbon black	Specific surface area[a]/m^2 g^{-1}	Volatility[b]/wt%
FW200	460	20.0
N330	83	0.8
BP2000	1475	1.8

[a]Measured by BET method with nitrogen at 77 K. Data provided by the supplier. [b]Measured *via* TGA under helium flow between 25 and 900 °C.

Experimental

Carbon blacks used in this study were FW200 (Degussa Co.), BP2000 (Cabot Co.), and N330 (CSRC Co.). Their physical properties are shown in Table 1. The carbons were prewashed with deionized water using an ultrasonic cleaner for 10 min and dried in an oven at 90 °C before use. Nitric acid pretreatment of carbon blacks was done by heating the carbon blacks in 3.6 M nitric acid solution at 80 °C for 1 h. The nitric acid treated carbon blacks were then washed with deionized water in an ultrasonic cleaner for 10 min and dried in an oven at 90 °C before use. Polyethylene glycol (PEG), poly(vinyl alcohol) (PVA), 1-aminopropan-2-ol, monoethanolamine (MEA) and diethanolamine (DEA) have been used to test the grafting efficiency.

Grafting onto carbon black surfaces was obtained *via* an impregnation method. For a typical run, 1 g of carbon black was mixed with the desired amount of polymer dissolved in 2 ml of water or other solvent described in the text. It was then stirred at room temperature for 5 min, and finally dried in an oven at 100 °C overnight.

The thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7A instrument. About 10 mg of carbon black sample was loaded into the instrument in a platinum sample pan. The temperature was ramped from room temperature to 950 °C with a rate of 60 °C min^{-1} under a helium flow (150 ml min^{-1}).

Infrared (IR) spectra were taken with a Digilab FT 175 FT-IR spectrometer and were recorded in absorbance mode with a resolution of 2 cm^{-1} and 32 scans at room temperature. The 10 mm diameter sample disk was prepared by mixing of 0.01 g of the carbon black with KBr powder in a ratio of 1:300.

The pH of polymer grafted carbon blacks was measured with a standard combination electrode immersed in an aqueous slurry prepared with 1.5 g carbon black in 20 ml of distilled water. The slurry was ultrasonically agitated and stirred for 3 min before introduction of the electrode.

The percentage of polymer grafted onto carbon black surfaces was determined from the difference in weight of carbon black before and after the impregnating treatment. To eliminate the non-grafted polymer and the physisorbed polymer, the reaction products were washed with 100 ml of deionized boiled water using an ultrasonic cleaner for 10 min before measurement of the grafting percentage. The percentage of

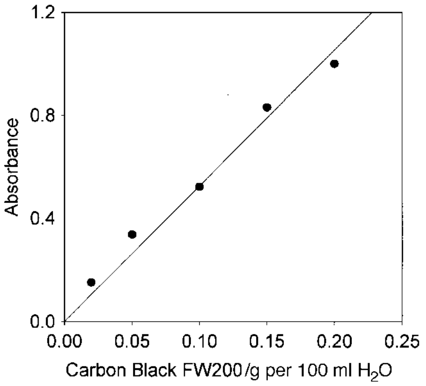

Fig. 1 The calibration curve plot of 2 wt% PEG6000 grafted FW200 carbon black concentration in water *versus* 249 nm ultraviolet light absorbance.

grafting was calculated *via* eqn. (1).

$$\text{Grafting }(\%) = 100 \times [\text{Polymer grafted (g)}/\text{carbon black charged (g)}] \qquad (1)$$

The dispersibility of polymer grafted carbon black in water was estimated as follows. Water washed polymer grafted carbon black (0.1 g) was dispersed in 100 ml of deionized water and stirred with a magnetic stirrer for 10 min. Then the dispersions were allowed to stand at room temperature. After a given time, 2 ml of dispersion liquid was removed with a pipette, and the content of the dispersed carbon black was determined. The amount of the dispersed carbon black was estimated by measuring the absorbance of carbon blacks in the ultraviolet (UV) spectrum at a wavelength where the carbon black shows a peak absorbance, *i.e.* 249 nm for FW200. A calibration curve plot of the concentration of carbon black in water *vs.* UV absorbance is shown in Fig. 1. The linear relationship between the carbon black concentrations and the UV absorbance suggests that the UV method is adequate for the dispersed carbon black contents measurement. The dispersibility of carbon blacks in water was estimated using eqn. (2).

$$\text{Dispersibility }(\%) = 100 \times \frac{\text{Carbon blacks dispersed after standing}}{\text{Carbon blacks dispersed before standing}} \qquad (2)$$

Results

Polymers with functional groups, such as hydroxy or amine moieties, can be grafted onto carbon blacks by the impregnation method. Polyethylene glycol (PEG, a hydrophilic polymer) with average molecular weight of 6000 (PEG6000) grafted on FW200 carbon black was used as a model to demonstrate the grafting efficiency of the impregnation method. The maximum amount of PEG6000 that can be grafted onto FW200 carbon black by the impregnation method is about 78% of the weight of FW200 carbon black.

The results of dispersibility measurements, surface functional group effects on grafting efficiency, TGA and infrared spectra confirmed that the polymer has been successfully grafted onto carbon surfaces through an interaction between the surface functional groups and the polymers. The interaction can be described as a chemisorption process where the surface functional groups on carbon are the active sites. Chemisorption, by definition, is a process where particles stick to the surface by chemical (usually covalent) bonding, and then find sites which maximize their coordination number with the substrate. The sites used for chemisorption within our impregnation method are most likely the acid surface functional groups on carbon blacks. These results are shown in Fig. 2–6.

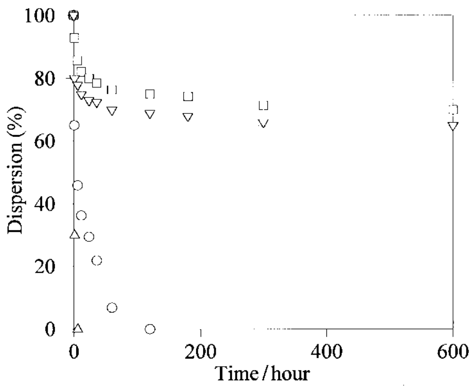

Fig. 2 Stability of PEG6000 grafted carbon black dispersion in water at room temperature: (△) 2% PEG6000 on N330, (○) FW200, (▽) 2% PEG600 on nitric acid treated N330 carbon black and (□) 20% PEG6000 on FW200 carbon black. All grafted carbon blacks were washed with boiled water before stability measurements.

PEG6000 grafted carbon blacks produced stable colloidal dispersion in water. The stability of PEG6000 grafted carbon black dispersions was compared with those of untreated carbon blacks in Fig. 2. As shown in Fig. 2, FW200 carbon black readily precipitated after five days. N330 carbon blacks completely precipitated within an hour. N330 carbon black (without nitric acid pretreatment) coated with PEG6000 also precipitated within an hour, suggesting that PEG6000 cannot be grafted onto N330 (without nitric acid treatment). However, more than 60% of the PEG6000 grafted FW200 black and the PEG6000 grafted N330 black (nitric acid pretreated) remained dispersed in water after a month.

Fig. 3 shows the TGA results of PEG6000 on FW200 carbon black. A weight loss peak at 406 °C was observed when a pure PEG sample was tested [Fig. 3(a)], suggesting that the pure PEG volatilized or decomposed at 406 °C in the He flow. Three weak weight loss peaks at 73, 276 and 700 °C were observed when the pure FW200 carbon black sample was

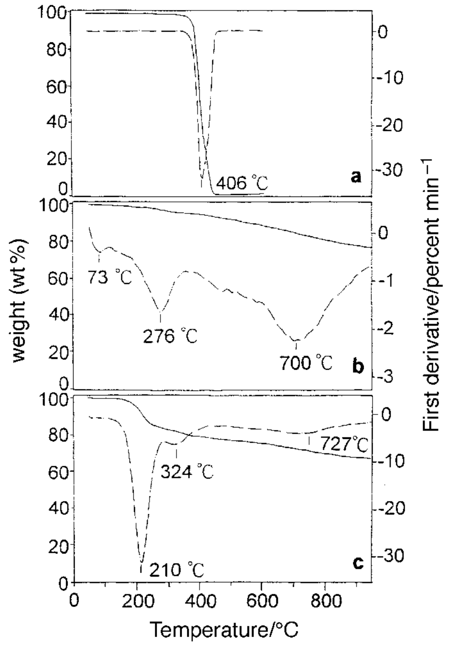

Fig. 3 TGA of (a) pure PEG6000, (b) pure FW200 carbon black and (c) 20 wt% PEG6000 on FW200 carbon black in He atmosphere. The He flow rate is 150 ml min^{-1}. The heating rate is 2 °C min^{-1} when the weight loss is higher than 2 wt% min^{-1}, and is 100 °C min^{-1} when the weight loss is lower than 0.3 wt% min^{-1}. (—) Weight loss and (–·–) first derivative.

tested [Fig. 3(b)]. The strong interaction between PEG6000 and FW200 carbon black led to a decrease of the PEG6000 decomposition peak temperature from 406 °C to as low as 210 °C [Fig. 3(c)].

The quantity of functional groups on a carbon black surface is an important factor in controlling the grafting efficiency of the impregnation method. Here we choose N330 and BP2000 carbon blacks to demonstrate the effect of surface functional groups on the grafting efficiency of the impregnation method. Table 1 shows some physical properties of carbon blacks used in this study. The number of surface functional groups (demonstrated as volatilized contents of carbon blacks in Table 1) on BP2000 and N330 is lower than 2% of the weight of the carbon blacks. A simple nitric acid pretreatment can increase the quantity of oxygen-containing functional groups, especially the carboxylic groups on a carbon black surface.[1,6,20] The dispersibility of N330, BP2000 and PEG6000-coated N330 and BP2000 (without nitric acid pretreatment) in water was poor (see Table 2). Good dispersibility in water can be obtained when PEG6000 was impregnated on nitric acid treated N330 and BP2000 carbon blacks. We also used ethylene glycol as a model to study the effect of functional groups of PEG polymers on the grafting ability. When the two hydroxy groups of ethylene glycol were replaced by methoxy groups, the grafting ability was reduced from 94% (ethylene glycol on FW200 carbon black) to 6% (1,2-dimethoxyethane on FW200). These results suggest that the interactions between polymers and carbon blacks most likely take place through the reaction between the oxygen-containing surface functional groups on carbon blacks and functional groups on the polymers. Fig. 4 shows the TGA results of PEG6000 on BP2000 and N330 carbon blacks and on nitric acid pretreated BP2000 and N330 carbon blacks. The peak decomposition temperatures of PEG6000 coated on N330 [398 °C, Fig. 4(a)] and on BP2000 [383 °C, Fig. 4(c)] are similar to the peak decomposition temperature (406 °C) of pure PEG6000. However, the peak decomposition temperatures of PEG6000 shifted down to 358 and 246 °C, respectively, when PEG6000 was grafted onto nitric acid pretreated N330 [Fig. 4(b)] and BP2000 [Fig. 4(d)] carbon blacks.

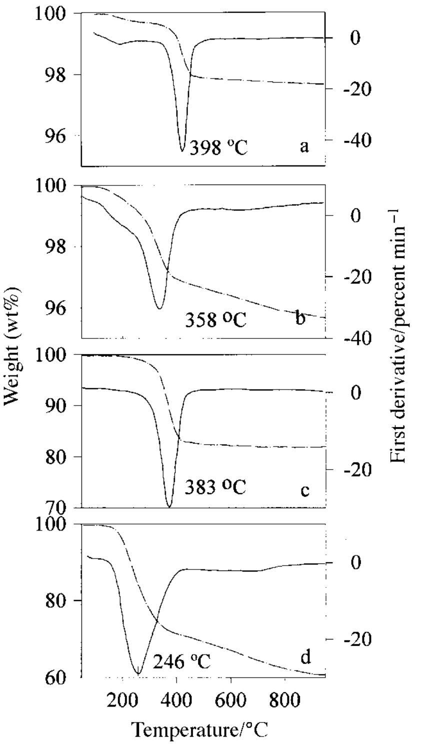

Fig. 4 TGA of (a) 2 wt% PEG6000 on N330 carbon black, (b) 2 wt% PEG6000 on nitric acid treated N330 carbon black, (c) 20% PEG6000 on BP2000 carbon black and (d) 30% PEG6000 on nitric acid treated BP2000 carbon black. (–·–) Weight loss and (—) first derivative.

Infrared spectra were used to examine the interaction between polymer and carbon black. Fig. 5 shows infrared spectra of PEG6000 and PEG6000 grafted FW200 carbon black. Four major bands were observed for FW200 at 3426, 1720, 1596 and 1261 cm^{-1}. These bands have been assigned to be the O–H (3450 cm^{-1}), C=O (1720, 1596 cm^{-1}) and C–O (1261 cm^{-1}) vibrations from the hydroxy, carboxylic, carboxylic anhydride and lactone functional groups on the carbon surface.[21] Part of the 1596 cm^{-1} band may also be due to a contribution from the C=C stretch of the aromatic rings on the carbon surface.[22] Fig. 5(c) is the IR spectrum of PEG6000 grafted FW200 carbon black. The IR bands of PEG6000 appear as fine structures on the broad IR bands of carbon black located at 2868, 1469, 1281, 1090, 943 and 835 cm^{-1}. The grafting effect of PEG6000 on carbon black shifts the C=O and C–O IR bands of FW200 carbon black from 1720, 1596 and 1261 cm^{-1} to 1742, 1576 and 1238 cm^{-1}, respectively, suggesting that the bond strength of the oxygenated functional groups, such as C=O and C–O, are altered in the grafted polymer.

The effect of the grafted polymer on the acidity of the carbon black is shown in Fig. 6. The pH of the carbon black dispersion solution increases with increases in the amount of polymer grafted on the carbon black surface until the pH value approaches 4. The shape of the pH plot curve is interesting. The variation of the pH curve of carbon black with respect to the amounts of grafted polymer may correlate with the quantity of various kinds of acidic functional groups that are available on the carbon black surface to interact with the impregnated polymers. The grafting efficiency of PEG6000 polymer on the FW200 black can only be enhanced a little when the pH value of the carbon black dispersion is higher than 4.5. This result suggests that the grafting reaction between PEG and carbon black occurs largely through the acidic functional groups on the carbon black surfaces.

Table 2 Dispersibilities of polymer/monomer grafted carbon blacks in water[a]

Grafting materials	FW200	N330	Acid-treated N330	BP2000	Acid-treated BP2000
Poly(vinyl alcohol)	+	—	+	—	+
1-Aminopropan-2-ol	+ (35%)	—	+	—	+
Ethylene glycol	+ (94%)	—	+	—	+
PEG600	+	—	+	—	+
PEG3000	+	—	+	—	+
PEG6000	+ (78%)	—	+	—	+
Monoethanolamine	+ (89%)	—	+	—	+
Diethanolamine	+ (52%)	—	+	—	+

[a] + = More than 50% dipersibility in water was observed after the carbon black dispersion slurry had stood for 1 month.— = Carbon blacks precipitated within one day. Numbers in parentheses are the maximum amounts of polymers or monomers that can be grafted on to the carbon surfaces.

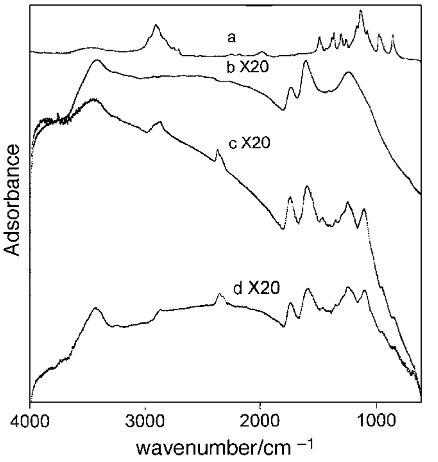

Fig. 5 FT-IR spectrum of (a) pure PEG6000, (b) FW200 carbon black, (c) 20 wt% PEG6000 on FW200 carbon black and (d) 20% PEG6000 impregnated FW200 carbon black after a water-wash procedure to remove any physically coated PEG6000.

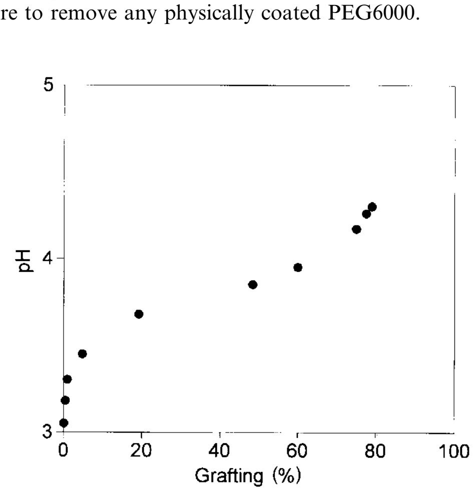

Fig. 6 Relationship between pH and PEG6000 grafting level on FW200 carbon black.

Discussion

Several aspects of the dispersion measurements, TGA and the effect of surface functional groups on the grafting efficiency data support the conclusion that the PEG6000 has been successfully grafted onto the carbon surfaces after the impregnating process. First, FW200 carbon blacks acquired a hydrophilic property after the grafting process. The PEG6000 grafted carbon blacks can produce stable colloidal dispersions in water, suggesting that the PEG6000 has been successfully grafted onto carbon surfaces by the impregnation method; carbon blacks are hydrophobic materials. A stable colloidal dispersion of carbon blacks in water could not be acquired if the hydrophilic polymer was just physisorbed on the surface.[11,15] In physisorption processes there is only a van der Waals interaction (for example, a dispersion or dipolar interaction) between the adsorbate and the substrate. The total amounts of physisorbed species is insensitive to the surface properties of the substrate. The polymer-grafted carbon blacks have been washed with deionized boiled water before the dispersibility measurement. Most, if not all, of the polymers would be washed out from the carbon black systems if the impregnated polymers were simply physisorbed on the carbon black surface. Physisorption can occur on all kinds of surfaces. The low dispersibility of PEG grafted N330 carbon black in water further proved that the colloidal stability of PEG grafted carbon black cannot be obtained by the physical adsorption mechanism alone.

Second, the positive relationship between the grafting efficiency and the amount of volatile species on carbon supported the premise that the polymer had been grafted on the carbon surface. A chemical bond can be easily formed between an organic acid group and an alcohol group. The higher grafting efficiency of PEG6000 on carbon black surfaces with higher amounts of volatile species suggests that the sites available for the chemisorption reaction on the carbon surfaces are the surface functional groups. The surface functional groups involved in the grafting reaction are most likely the acidic functional groups on carbon blacks. The acidity effects, infrared spectra and the polymer grafting on nitric acid pretreated carbon blacks support this hypothesis. The acidity of the carbon black dispersion solution decreases with an increase in the quantity of the polymer grafted, suggesting that the acid sites on the carbon black surfaces were occupied by the grafted polymers. PEG6000 can be grafted on nitric acid pretreated N330 black, but not on N330 black. It is well known that the quantity of acidic functional groups, especially the carboxylic acid groups, on a carbon black surface increases with nitric acid treatments.[6,20] The positive effect of nitric acid treatment on the grafting efficiency confirmed that the interaction between PEG6000 and carbon blacks takes place *via* the acidic surface functional groups, especially the carboxylic group. The shifting of the C=O and C–O bonds absorption wavelengths in the polymer-grafted black infrared spectra is consistent with this conclusion.

The grafting reaction between PEG and carbon blacks takes place largely on the functional groups on surfaces through a chemisorption process. Carbon surface structures, like defects and pore structures, may also contribute to the grafting behavior during the impregnation process. However, these properties are not solely responsible for the success of the impregnation method. This is proved by the zero or low yield of the grafting reaction between PEG and carbon blacks that have a low percentage of surface functional groups (below 1% of the weight of the carbon blacks). Little grafting yield was observed when N330 black was impregnated with PEG6000. The quantity of surface functional groups on N330 carbon black is lower than 0.9 wt% (see Table 1). BP2000 black has wide pore size distributions and high pore volumes[23] but the grafting efficiency of PEG6000 on BP2000 black is low. Note that defects and pore structures exist on all kinds of carbon black surfaces. However, the grafting efficiency is low on carbon blacks with few surface functional groups.

Although only a small fraction of commercially available blacks have a significant density of surface groups, the impregnation method is still good for grafting polymers on blacks. The successful grafting of polymer on nitric acid pretreated N330 black suggest that the impregnation method is applicable to carbon blacks with low amounts of surface functional groups after a simple nitric acid treatment.

The decomposition temperature of PEG6000 shifts about 200 °C after the grafting process. The grafting effect on the thermal stability of PEG6000 on FW200 carbon black can be easily noted by comparing the TGA of carbon black before and after the impregnation treatment, shown in Fig. 3. This result again supports the premise that a chemical bond has been formed between the polymer and the carbon black. Physical adsorption of the polymer on the carbon surface would not induce such a strong influence on the thermal stability of a polymer. An increase in the thermal degradability of a polymer can be beneficial in terms of environmental protection. A lot of research has been devoted to developing degradable polymers in order to reduce the environmental pollution caused by large amounts of nondegradable polymers.[24] The weakening of the thermal stability of a polymer by modifying the polymer with a functional end group has been reported.[24] The weakening of the thermal stability of chemisorbed species is also commonly observed in adsorptiondesorption systems. Consider, for example, that acetophenone is stable in inert atmosphere at temperatures higher than 200 °C. However, acetophenone decomposes at temperatures as low as 50 °C when chemisorbed on transition metal surfaces.[25]

The grafting of PEG onto carbon black surfaces by the impregnating procedure is a general method that can be extended to monomers and polymers containing hydroxy or amine groups with different average molecular weights. The dispersibilities of some polymer-grafted carbon blacks in water are shown in Table 2. Poly(vinyl alcohol), monoethanolamine, diethanolamine, triethanolamine and PEG with average molecular weight between 600 and 8000 have been successfully grafted onto FW200 and nitric acid treated carbon blacks by the simple impregnation method. The nitric acid treatment effect and the functional group effect of the monomer on the grafting ability suggest that ester or amide formation is also the most likely mechanism for the binding of low molecular weight –OH/–NH_x species on carbon surfaces.

Conclusions

Polymers and organic compounds with functional groups such as hydroxy or amine groups can be grafted onto carbon black surfaces by a simple impregnation method. The quantity of acidic surface functional groups on the carbon black is an important factor in controlling the grafting efficiency of the impregnation process. Nitric acid pretreatment can improve grafting efficiency on carbon blacks with a low density of surface functional groups. From acidity measurements, infrared spectra and nitric acid effects on the grafting reaction, we conclude that acidic surface functional groups, especially carboxylic groups, play a major role in the grafting reaction of the impregnation process.

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