Diamond & Related Materials 20 (2011) 439–444

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Suface grafting of polymers onto nanodiamond by ligand-exchange reaction of ferrocene moieties of polymers with polycondensed aromatic rings of the surface

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ARTICLE INFO

Article history:
Received 30 May 2010
Received in revised form 19 November 2010
Accepted 6 January 2011
Available online 25 January 2011

Keywords:
Nanodiamond
Polymer grafting
Ligand-exchange reaction
Polycondensed aromatic ring
Vinyl ferrocene
Dispersibility

ABSTRACT

To improve the dispersibility of nanodiamond (ND) in solvents and polymer matrices, the grafting of copolymers containing vinyl ferrocene (Vf) onto the surface by a ligand-exchange reaction with ferrocene moieties of the copolymer and polycondensed aromatic rings of ND surface was investigated. The copolymer containing Vf was prepared by the radical copolymerization of Vf with vinyl monomers, such as methyl methacrylate (MMA), styrene (St), and *N*-isopropylacrylamide (NIPAM), using 2, 2′-azobisisobutyronitrile as an initiator. It was found that by heating of ND with poly(Vf-*co*-MMA), poly(Vf-*co*-St), and poly(Vf-*co*-NIPAN) in the presence of $AlCl_3$ and Al powder as catalysts, the corresponding copolymer was successfully grafted onto the surface. On the contrary, in the absence of $AlCl_3$, no grafting of these copolymers was observed. The grafting of polymers onto the ND surface was confirmed by FT-IR. These polymer-grafted NDs were found to give stable dispersions in solvents for the grafted polymer. In addition, the dispersibility of poly(Vf-*co*-NIPAM)-grafted ND uniformly dispersed in water below 32 °C but precipitated above the temperature. Therefore, it was concluded that the dispersibility of ND in water could be controlled by the temperature of water.

1. Introduction

Nanodiamond (ND) is a new class of carbon material with a diameter of nm orders and excellent properties, such as chemical and mechanical stability, higher thermal conductivity, and higher hardness. ND core has diamond crystalline structure, but the surface of ND is coated by amorphous carbon and has many oxygen containing functional groups, such as carboxyl, hydroxyl, and carbonyl groups. The addition of ND into polymers results in an increase in mechanical strength, wear-resistance, and heat-aging resistance [1–3]. However, it is hardly achieved to disperse ND in various solvents and polymer matrices uniformly due to the unique morphology. It is expected that the surface treatments of conventional carbon material, such as oxidative treatments [4–8], electrochemical treatments [9], coating, and grafting [10,11], can be used for the modification of the surface of ND. Gibson and his coworkers have reported the dispersibility of ND in water by chemical and physical modifications [12].

We have reported the surface grafting of polymers onto carbon materials, such as carbon blacks, carbon nanotubes, carbon micro coils, and carbon fibers [10,11]. In general, the surface grafting was achieved by the use of functional groups on the surface, such as carboxyl and phenolic hydroxyl groups. For example, it has been reported that the radical graft polymerization of vinyl monomers is initiated from surface radicals formed by the thermal decomposition of azo groups previously introduced onto carbon black [13] and silica nanoparticle [14]. We have also reported the radical graft polymerization of vinyl monomers initiated by the system consisting of $Mo(CO)_6$ and trichloroacetylchloride group on carbon black and silica nanoparticle [15,16].

Recently, it has been reported that by surface initiated living radical polymerization, polymers with well defined molecular weight and narrow molecular weight distribution can be grafted onto carbon materials, such as carbon nanotube and carbon black. Grafting density on the surface is considerably high. For example, Li et al have achieved the surface modification of ND by atom transfer radical polymerization [17].

On the other hand, we have reported the grafting of polymers by a ligand-exchange reaction of ferrocene moieties of polymers with polycondensed aromatic rings of carbon black, carbon fiber, and carbon nanofibers [18–21]. We have pointed out that the surface grafting by the ligand-exchange reaction between ferrocene moieties of the copolymer and the polycondensed aromatic rings of carbon materials is very effective for the grafting of polymers onto carbon materials having few functional groups.

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doi:10.1016/j.diamond.2011.01.014

In this paper, we investigated the grafting of copolymers containing vinyl ferrocene (Vf) onto ND surface by ligand-exchange reaction of ferrocene moieties of polymer with polycondensed aromatic rings of ND surface as shown in Scheme 1. The dispersibility of polymer-grafted ND will be also discussed.

2. Experimental

2.1. Materials and reagents

NDs used were cluster nanodiamond (CND) and polycrystalline nanodiamond (PCND). CND was supplied from Vision Development Co., Ltd. The particle diameter and the specific surface area of CND are 2–6 nm and 200–400 m^2/g, respectively. PCND was supplied from Sumitomo Coal Mining Co., Ltd. The particle diameter and specific surface area of PCND are 5–20 nm and over 120 m^2/g, respectively. These NDs were dried in vacuo at 50 °C before use.

Methyl methacrylate (MMA), styrene (St), *N*-isopropylcrylamide (NIPAM), vinyl ferrocene (Vf), 2,2′-azobisisobutyronitrole (AIBN), and 1,4-dioxane, which were obtained from Aldrich Chem. Co., were purified by the ordinary methods before use. $AlCl_3$ and Al powder (particle size: 53–150 μm) obtained from Aldrich Chem. Co. were used without further purification.

2.2. Preparation of poly(Vf-co-Vinyl Monomer)

Poly(Vf-*co*-MMA), poly(Vf-*co*-St), and poly(Vf-*co*-NIPAM) were prepared by the radical copolymerization of Vf with MMA, St, and NIPAM respectively. The detailed procedures were described in the previous paper [18–21].

The composition of the copolymer was determined by the maximum absorbance at 440 nm, assignable to ferrocene moiety in the copolymer. Ferrocene was used as a standard substance for the composition determination. The number-average molecular weight (*Mn*) and molecular weight distribution of the copolymer were determined by the use of a size exclusion chromatography (SEC), using polystyrene standards. For SEC, a Tosoh CCPD instrument equipped with TSK-GEL $G3000H_{XL}$ column was used.

2.3. Grafting of poly(Vf-co-vinyl monomer) onto ND surface

Into a flask, 0.05 g of ND, 0.05 g of poly(Vf-*co*-vinyl monomer), $AlCl_3$, Al powder, and 10.0 mL of 1,4-dioxane were charged and the mixture was stirred for a definite time with a magnetic stirrer under nitrogen. After the reaction, the quenching of $AlCl_3$ was achieved by the addition of methanol into the reaction mixture.

To separate the copolymer-grafted ND from the reaction mixture containing ungrafted copolymer and Al powder, the product was dispersed in 1,4-dioxane under the irradiation of ultrasonic wave. Then, the dispersion of copolymer-grafted ND was allowed to stand at room temperature for several minutes and Al powder precipitated was removed by decantation. The dispersion of copolymer-grafted ND was filtrated off and the resulting copolymer-grafted ND was dispersed again in 1,4-dioxane. The procedures were repeated several times to remove most of ungrafted copolymer. To remove adsorbed $AlCl_3$ on the copolymer-grafted ND surface, the copolymer-grafted ND was washed for 30 min in 1.0 mol/L HCl under stirring with a magnetic stirrer.

2.4. Percentage of grafting

The percentage of copolymer grafting onto ND surface was determined by the following equation.

$$\text{Grafting}\ (\%) = (A\,/\,B) \times 100,$$

where *A* is copolymer grafted (g) and *B* is the ND used (g). The amount of copolymer grafted onto the ND surface was determined by weight loss when the copolymer-grafted ND was heated from room temperature to 500 °C under nitrogen at 10 °C/min by using a thermo gravimetric analyzer (TGA-50, Shimadzu Co.). Considering iron which formed during the thermal decomposition of the copolymer, the weight of grafted copolymer (*A*) was calculated.

2.5. Dispersibility of copolymer-grafted ND

The dispersion state of poly(Vf-*co*-vinyl monomer)-grafted ND in THF was observed by a digital microscope (VHX-900, Keyence Co.) and an UV–visible spectrophotometer (UV-1600, Shimadzu Co.). The dispersion of ND for the observation by a digital microscope was prepared as follows: dispersion of copolymer-grafted ND (50 mg) in 10 mL of THF was dropped onto a slide glass and the drop was covered with a cover glass.

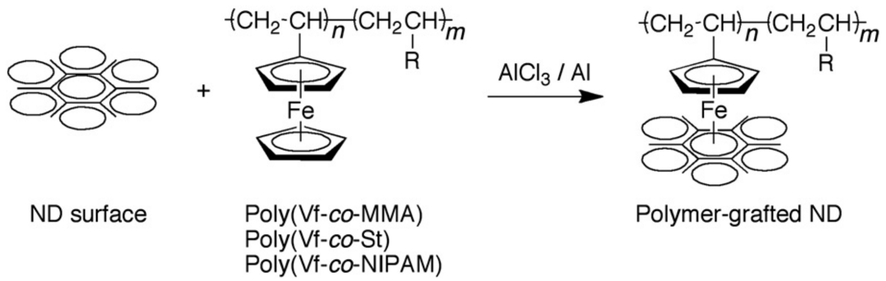
2.6. Characterization

The surface structure of grafted polymer on ND was confirmed by a FT-IR spectrophotometer (FTIR-8400 S, Shimadzu Co.) and a Laser Raman spectrophotometer (NRS-3100, JASCO Co.). Particle size distribution was estimated by a nanoparticle size analyzer (Shimadzu Manufacturing Co., Ltd. SALD-7100).

3. Results and discussion

3.1. Preparation poly(Vf-co-vinyl monomer) and characterization

Poly(Vf-*co*-MMA), poly(Vf-*co*-St), and poly(Vf-*co*-NIPAM) were prepared by the copolymerization of Vf with MMA, St, and NIPAM, respectively, using AIBN as an initiator[22,23]. Table 1 shows the number-average molecular weight, molecular weight distribution (*Mw*/*Mn*), and Vf content of poly(Vf-*co*-MMA), poly(Vf-*co*-St), and poly(Vf-*co*-NIPAM) determined by SEC using polySt standards. The molecular weight distribution of these copolymers was considerably narrow. The content of ferrocene moieties of poly(Vf-*co*-MMA), poly



Scheme 1. Grafting of poly(Vf-*co*-vinyl monomer) onto NDs by ligand-exchange reaction of the copolymer with polycondensed aromatic rings of the surface.