Grafting Polyimides from Nanodiamonds

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Received October 11, 2007
Revised Manuscript Received December 6, 2007

Diamond is one of the most important materials from both a fundamental and practical standpoint due to its unique combination of properties, including superior hardness and wear resistance.[1−4] These outstanding intrinsic properties make diamond particularly attractive for advanced materials at micro- and nanoscales. The chemical modification of diamond or diamond-like surfaces is difficult under common conditions due to their almost inert nature. In the past years, however, several research groups successfully functionalized diamonds including oxidation,[5,6] bromination,[6] fluorination,[7,8] Diels−Alder reaction,[9] and ultraviolet (UV) irradiation.[10] To efficiently transfer the superior properties of diamond to polymer matrix in lightweight and ultrastrong composites for use in hi-tech fields, critical challenges lie in achieving desirable interfacial adhesion between diamond particles and organic polymers.

Aromatic polyimides are one of the most important subset of high-performance and high-temperature polymers and have been widely used as coatings, matrices of composites, and adhesives in aerospace industry.[11−15] For space-born systems, their service lives in orbit largely depend on the abrasion degree of movable devices and endurance of materials. The rigorous environments of space application demand materials with higher performance. Recent studies revealed that polymer systems containing nanoparticles, such as sheetlike layered silicates,[16,17] rodlike carbon nanotubes,[18−21] and spherical particles,[22] represent a new class of polymeric materials. Integrating of nanodiamond particles into polyimide is of particular interest to create polymer-based materials with higher performance by taking advantages of diamonds. Pioneering work on polymer/diamond nanocomposites by Dolmatov showed nanodiamonds are highly effective to enhance the modulus and strength of elastomers.[23] Recently, Shenderova and Zhang et al. reported improved thermal stability and mechanical properties of polyimide/diamond nanocomposites prepared via physical mixing of nanodiamond particles and a poly(amic acid) (PAA) precursor solution.[24,25] However, the interfacial adhesion between diamonds and polyimide matrix might be not desirable if interfacial chemical bonding is weak or absent. Chemically attaching polyimides onto diamonds to form stronger lightweight composite materials still remains a challenge.

In this report, a facile method to chemically grafting polyimides from diamonds will be presented. The hardness of resulting diamond-based nanocomposites was evaluated by an ultra-microindentation technique. The whole process, as shown in Scheme 1, consists of two steps, namely, acyl chloride functionalization of nanodiamonds and grafting polyimides from diamond surface. A commercially available nanodiamond (ND) powder fabricated via detonation method was used in this study. Under high-temperature and high-pressure detonation and oxidation purification process, some functional groups, e.g., −COOH, could be created on diamond surface,[26−28] which is confirmed by FT-IR as shown in Figure 1. The ND particles were first refluxed in thionyl chloride achieving acyl chloride groups on the ND surfaces and yielded acyl chloride-functionalized nanodiamonds (F-ND). The F-NDs were recorded by FT-IR as shown in Figure 1. Both the untreated and functionalized nanodiamonds show an absorption at 1725 cm^{-1} which is due to the C=O stretching, while the broad absorption band in the spectral area of 1620−1640 cm^{-1} is attributed to the OH vibration of adsorbed water.[27] Another strong peak at 805 cm^{-1} for F-ND is due to C−Cl stretching,[29,30] implying the successful functionalization and formation of acyl chloride groups on diamond surface. The acyl chloride functionalization of diamonds is also examined by EDAX analysis (Figure 2) as indicated by the Cl Kα peak at 2.65 keV.

Two approaches are generally used to attach polymers onto particle surface, namely, "grafting-to" and "grafting-from". "Grafting-to" means attaching polymer chains onto particle surface, while "grafting-from" means polymer chains grow from particle surface. The disadvantages of "grafting-to" approach are the following: (1) It is only suitable for soluble polymers; however, most polyimides are not dissoluble. (2) The viscosity of polyimide or polyimide precursor solutions is extremely high which brings more difficulties to disperse particles homogenously, particularly for nanoparticles because of their high surface free energy. (3) Reacting activities of polymer macromolecules are much weaker than their small monomer molecules which requires higher temperature or longer time to attach polymers onto particle surface. Therefore, the "grafting-from" approach was employed in this study. First, an aromatic diamine, 4,4′-(*m*-phenylenedioxy)dianiline (APB), was reacted with an appropriate amount of F-ND in anhydrous *N*-methyl-2-pyrrolidinone (NMP) and formed ND−APB with amine-terminated ends, and then 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) was added in and yielded poly(amic acid) (PAA) precursor grown from the diamond surface. The viscous PAA precursor solution was then cast on clean glass slides and formed polyimide/diamond nanocomposites by followed thermal cyclodehydration at elevated temperatures (100 °C for 1 h, 200 °C for 1 h, 300 °C for 1 h, and 400 °C for 10 min). Finally, polyimide nanocomposite with 1 wt % F-ND was prepared as well as the composites with 1 and 5 wt % untreated ND for comparison.

Figure 3a shows the dispersion of F-ND particles in the polyimide matrix. Though the F-ND particles are not dispersed individually, it presents a high degree dispersion and the size of particle agglomerates is less or around 100 nm. No serious agglomerations, such as microsize agglomerates, are observed for the polyimide/diamond nanocomposite which is important as the effect of serious agglomeration is obviously deleterious on final material performance. Moreover, it should be noted the dispersion of F-ND is better than that of unmodified NDs (Figure 3b). This improvement might be attributed to the acyl chloride functionalization of nanodiamond which not only breaks the ND agglomerations during chemical functionalization and mixing but also anchors polyimide chains on diamond surface,

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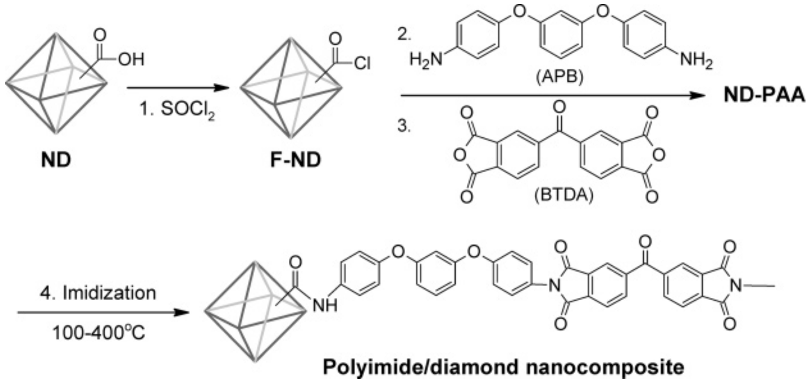
10.1021/ma702268x CCC: $40.75

Scheme 1. Acyl Chloride Functionalization of Nanodiamonds and Grafting Polyimide from Diamond Surface



which results in reduced surface free energy and facilitates particle dispersion.

Nanoparticles are generally supplied as agglomerated powder because of their high surface free energy, and particle dispersion has been an important issue for fabricating desirable polymer nanocomposites. Because of the small particle size, a larger percentage of atoms in nanodiamonds are contributing to the defect sites on grain boundaries than in natural single diamond crystals or microcrystalline synthetic diamonds. Some functional groups such as −COOH and the like are able to be grafted with carbon atoms on diamond defect sites. As a result, some soft agglomerations caused by van der Waals forces among diamond particles appeared, while some hard ones bonded by chemical bonds, such as carbonyl (−C═O) or ester (−COO) groups, also took place during fabrication and storage which impart more difficulties to disperse them individually, especially for the latter. The self-organized clusters or primary agglomerations might further form larger weakly bonded secondary agglomerations ranging from hundreds of nanometers to micrometer size. Furthermore, nanodiamond agglomerations have a fractal nature.[23] This hierarchy of nanodiamond agglomeration needs to be taken into account in the interpretation of experimental results.

Hardness is the characteristic of a solid material expressing its resistance to indentation, scratching, or penetration. An ultramicroindentation technique was employed to evaluate the effect of nanodiamonds on the hardness of polyimide. For the purpose of clarity, normalized hardness is present in Figure 4. As seen, the hardness of polyimide increases with increasing diamond content. Respectively, the hardness is enhanced by 15 and 26% with 1 and 5 wt % diamonds loading. The hardness does not increase linearly with diamond loading level. The reason is that particle agglomeration might become more serious when particle loading is high such as 5 wt %, leading to reduced reinforcement effect. Surprisingly, the hardness of polyimide with 1 wt % F-ND is increased by ∼30%, which is even higher than that of polyimide containing 5 wt % untreated ND. This significant improvement should be ascribed to the acyl chloride functionalization of ND particles because of the strong chemical bonding between diamonds and polyimide. The diamond particles play an important role not only as physical reinforcer but also as chemical cross-linker contributing to the significant improvement in hardness. The above results manifest that the acyl chloride functionalization is an effective method to enhance interfacial adhesion and achieve sufficient load transfer from the polymer to nanodiamond particles.

The methods of achieving acyl chloride groups on ND surface and further amidation (ND-APB) have some potential applications. The presence of the acyl chloride groups on the diamond particles makes them very good electrophiles, which means even a weak nucleophile can attack the acyl chloride group leading to high reactive diamond surface. Nanodiamond is also considered as a potential medical agent because of its high absorbing activities with respect to pathogenic viruses and microbes. The acyl chloride-functionalized diamonds can be attached to some biomaterials (e.g., carbohydrates) by bonding with their hydroxyl groups, allowing diamonds to be used for biotechnological applications. In the field of polymer science, the proposed method provides polymer researchers with an efficient method to covalently link nanodiamond to polymer matrices. For example, polyamides with amine groups are ideally suited to react with the acyl chloride groups on diamonds, and epoxy resins can be easily linked with the amine groups of ND-APB since amines are very active cross-linkers for epoxies.

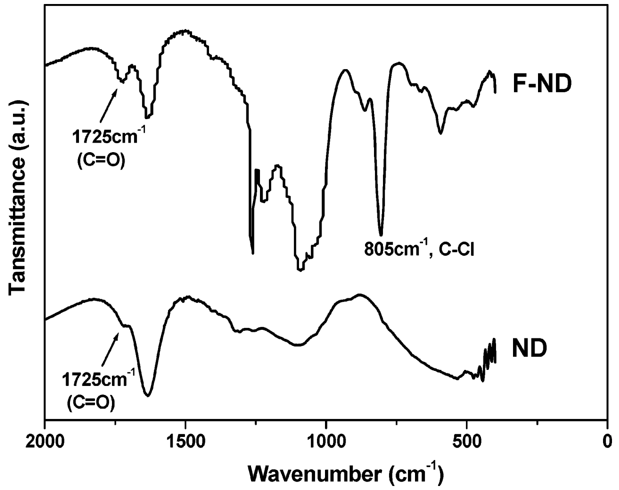


Figure 1. FT-IR spectra of acyl chloride-functionalized nanodiamonds (F-ND) and untreated nanodiamonds (ND).

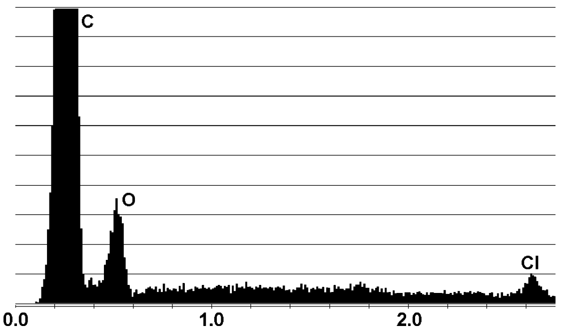


Figure 2. EDAX of acyl chloride-functionalized nano diamonds (F-ND).

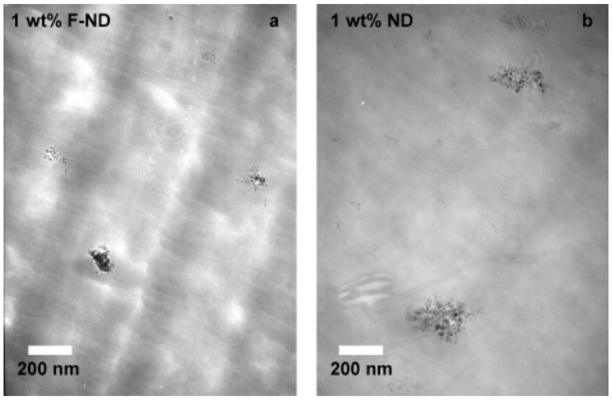


Figure 3. TEM micrograph of polyimide containing 1 wt % acyl chloride-functionalized nanodiamonds (F-ND) (a) and 1 wt % pristine ND (b).

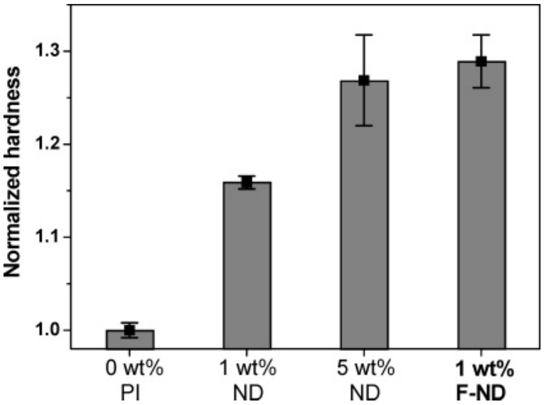


Figure 4. Normalized hardness of polyimide/diamond nanocomposites.

In conclusion, we present a facile approach to grafting polyimides from diamond surface via acyl chloride functionalization. The hardness of polyimide is significantly enhanced with small amount of nanodiamond loading. The research on using nanodiamonds in polymers is emerging, and it is expected that polymer/diamond nanocomposites will attract more attention from both the point of view of fundamental research and the current and promising perspective applications considering the superior properties of diamonds.

Acknowledgment. This work was supported in part by the Japan Society for the Promotion of Science (JSPS). Technique assistance from NIMS and RCAST is gratefully acknowledged.

Supporting Information Available: Experimental details, X-ray diffractions, and ultramicroindentations. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA702268X