

Generating Functionalized Nanocarbons and Polymer Nanocomposites in Poly(phosphoric acid)

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ABSTRACT

This overview presents the research results based on a versatile, covalent functionalization technique utilizing poly(phosphoric acid)/phosphorus pentoxide (PPA/P₂O₅, optimized w/w: 4:1) medium to promote dispersion, solubilization, and *in-situ* polymerization to generate functionalized 1D and 2D nanocarbon materials and polymer matrix nanocomposites. Highlights on such functionalized carbon nanotubes (CNT) & nanofibers (CNF) and generation of their nanocomposite materials illustrate the versatility and applicability to other members of nanocarbon raw materials. It also showcases the scientific fruition of an in-house research program at AFRL/RXAS and an interactive US-Korea collaboration (2003-2011) supported by US Air Force Research Laboratory.

Keywords: Friedel-Crafts, acylation, poly(phosphoric acid), P₂O₅, nanofiber, nanotubes, PEK, nanocomposites.

1 INTRODUCTION

For the proof-of-concept in developing the PPA/P₂O₅-based “chemical modification and *in-situ* nanocomposites” methodology, carbon nanofiber (CNF) was selected at the outset of our research mainly for the reason that vapor grown CNF contains significant amount of C-H defects, which were hypothesized to be susceptible to Friedel-Crafts acylation reaction under suitable reaction conditions. Further, in comparison to single-walled (SWNT) or multi-walled carbon nanotubes (MWNT), vapor-grown CNF were more attractive from the standpoint of practicality in terms of their relatively low cost and availability in larger quantities as the result of their more advanced stage in commercial production. These nanofibers are typically produced by a vapor-phase catalytic process in which a carbon-containing feedstock (e.g. CH₄, C₂H₄ etc.) is pyrolyzed in the presence of small metal catalyst (e.g. ferrocene, Fe(CO)₅ etc.) and have an outer diameter of 60-200 nm, a hollow core of 30-90 nm, and length on the order of 50-100 microns[1-3]. It follows that having aspect ratios (length/diameter) of greater than 800 should make them useful as nano-level reinforcement for polymeric matrices.

Furthermore, since their inherent electrical and thermal transport properties are also excellent, there are many possibilities imaginable for tailoring their polymer matrix composites into affordable, light-weight, multifunctional materials.

In our later work, we found that the “*in situ* nanocomposite” method is also applicable to MWNT, detonation nanodiamonds(DND[4], and graphite nanoplatelets(GNP)/graphene stacks[5].

2 RESULTS & DISCUSSION

Conceptually, there are three general techniques for dispersing chemically unmodified CNF in the polymer matrices: (1) melt blending (2) solution blending, and (3) reaction blending. For the reaction blending route, there are two scenarios: (a) *in-situ* polymerization of monomers (AB) or co-monomers (AA+BB) in the presence of dispersed CNF that occurs without forming any covalent bonding between the CNF and the matrix polymer, or (b) *in-situ* grafting of AB monomers that occurs with direct covalent bonds formed between the CNF and the matrix polymer. While melt-blending is perhaps the most cost effective approach to CNF-based nanocomposites, and has been applied to thermoplastic[1,6], thermosetting[7], and elastomeric[8] matrices, the resulting nanocomposite materials are, by and large, less than optimal, especially in the cases where polymer-CNF incompatibility adversely impact the desired level of dispersion and the breakage of the carbon nanofibers by high shear forces reduce the reinforcing aspect ratios[9]. The solution blending appears to have circumvented these problems, for example, the nanocomposite materials produced by this route have shown 2-3 orders of magnitude higher in electrical conductivity and much lower percolation threshold (<1 vol%) than similar materials prepared by the melt-blending route[10]. To our knowledge, we are not aware of any report in the literature prior to our disclosure that describes successful preparation of CNF-based nanocomposite materials via reaction blending[11]. However, similar non-grafting, reaction blending processes have been reported for unmodified SWNT[12] and MWNT [Error! Bookmark not defined.,13-17]. In addition, there are reports on the grafting of a polymer either to or from a SWNT or MWNT

that typically involved prior oxidation[18,19], or functionalization of the CNT with a reactive group (e.g. surface-bound acid chloride[20] or initiator for atom-transfer radical polymerization[21]).

2.1 Concept of In-situ Polymer-Matrix Nanocomposites

Our in-situ nanocomposite work is built on the following experimental results/conclusion first obtained at AFRL/RXAS[22,23]: (1) high molecular-weight, wholly aromatic poly(ether-ketones) could be easily generated from phenoxybenzoic acid type of AB-monomers in optimized poly(phosphoric acid)/phosphorus pentoxide (i.e. 4:1 w/w PPA/P₂O₅) medium; (2) strong evidence from FT-IR and elemental analysis that as-received CNF contains substantial amount of C-H defects (~ca.1 wt% hydrogen); (3) a model reaction of 2,4,6-trimethylphenoxybenzoic acid on the CNF surface via a direct Friedel-Crafts arylcarbonylation at the C-H defect sites in PPA/P₂O₅ resulted in isolating CNF with expected arylketo-moieties as covalently attached pendants, as proven by FT-IR, TGA and elemental analysis. It is worth mentioning that after experimental confirmation by spectroscopic methods (chiefly by strong and characteristic IR vibrational bands attributed to the covalently-bound moieties such as carbonyl and sp³C-H stretches), and high-resolution imaging techniques (SEM & TEM), the combination of TGA and elemental analysis is a rapid and easy way to quantify the degree of functionalization (DF).

Subsequently over the period (2003-2011), in a very productive collaboration with Jong-Beom Baek's research group, first at Chungbuk National University, and then at UNIST, South Korea, we have used the general approach of "in situ polymerization" in tandem to the preceding nano-surface modification via Friedel-Crafts carbonylation to generating a wide range of polymer nanocomposites with thermoplastic (linear and hyperbranched polymer architecture) and thermoset matrices.

Overall, our approach can be categorized as either a one-pot synthesis or a two stage synthesis process. In addition to poly(ether-ketones) that are formed nicely via Friedel-Crafts polymerization in PPA/P₂O₅ medium, the former approach would take advantage of various heterocyclic-ring forming reactions from a diacid and a suitable co-monomer and this allowed the use of as-received carbon nanofibers or nanotubes in the same polymerization vessel. An important advantage of this route is that the as-synthesized polymerization mixture (dope) could be directly spun into nanocomposite fibers with outstanding mechanical properties, as demonstrated recently for MWNT/para-poly(ether-ketone) by an AFOSR grantee's (Satish Kumar's) laboratory at Georgia Tech[24].

For a two-stage, in-situ nanocomposite approach, a pre-functionalized CNF/CNT was used together with the mixture of co-monomers in the same vessel. The pre-functionalized CNF/CNT was first chemically modified via Friedel-Crafts acylation reaction with benzoic acid containing an appropriate functional group (amine, halides, hydroxyl, thiol, etc.)[25] that are nonreactive or compatible with PPA/P₂O₅ medium, can promote dispersibility in organic solvents (e.g. chloride with respect to chlorinated solvents)[26], or can co-react with one of the monomeric functionalities during the in-situ polymerization process. For example, an amine-containing benzoic acid could be used to arylcarbonylate vapor grown carbon nanofibers and multiwalled carbon nanotubes via a Friedel-Crafts acylation reaction in an optimized PPA/P₂O₅ medium. The resulting H₂N-CNF with relatively high degree of functionalization was able to participate in the in situ polymerization of a dianhydride (2,2-bis(4-phthalic anhydride)-111,333-hexafluoroacetone or 6FDA) and a diamine (e.g. 1,3-bis(3-aminophenoxy)benzene or APB) to afford, after typical thermal curing (from precursor poly(amic acid)/DMAc solutions), a series of polyimide-based nanocomposite (CP2-g-CNF) films, which contained 0.1 to 5 wt % of the functionalized CNF. Therefore, while our previous work has shown the feasibility of directly grafting the defect sites on either CNF or MWNT via a Friedel-Crafts acylation reaction in poly(phosphoric acid) with a suitable, arylether-benzoic acid type AB or AB₂ monomer in a one-pot fashion, this work further demonstrates the feasibility of in situ grafting of prefunctionalized CNF (and MWNT as well) with a well-studied aromatic polyimide (CP2) under the conventional AA + BB polymerization and thermal (solid-state) imidization conditions. In this two-stage preparation of in situ nanocomposites, the presence of prefunctionalized CNF has little or no adverse effect on the molecular weight of the resulting polyimide. However, based on the comparative results from solvent extraction experiments, there was more free polyimide present in these nanocomposites than there were free poly(ether ketone)s in the previous cases[24]. This may be arisen from the kinetics of grafting polymerization. Last but not least, we confirm that the functionalized CNF has a better dispersion in and a stronger bonding with the matrix polymer in the CP2 films than the unfunctionalized counterpart, as evidenced by the better mechanical properties, THF-extraction results, and the comparison of SEM data. The electrical response of these nanocomposite films has also been investigated for use as high-temperature electrostatic dissipation (ESD) and electromagnetic interference (EMI) shielding films, and as thermal electric switches[27].

2.2 CNT/CNF Solubilization by Hyperbranched Polymer Grafts

Apart from being an efficient Friedel-Crafts catalyst, the PPA/P₂O₅ medium is moderately acidic but effective enough to promote homogeneous dispersion of CNF and

MWNT at relatively low temperature ($\sim 70^\circ\text{C}$), avoiding the premature onset of Friedel-Crafts reaction ($>100^\circ\text{C}$), and its relatively high viscosity provides shear field during mechanical stirring to assist in breaking up proton-weakened CNF/CNT bundles as well as impedes CNF/CNT reaggregation. As a result, a uniform grafting of linear PEK's onto CNF and MWNT has been achieved. However, these nanocomposites were found to be more soluble in strong acids than in common organic solvents. This finding has prodded us to explore the use of "aromatic hyperbranched polymer" approach to improving the solubilization of carbon nanofibers and nanotubes [28]. This is because solubility (or nano-dispersibility) in organic and aqueous solvents is an important pre-requisite to the processing and fabrication of these nanocomposites especially on large surface areas. Furthermore, the non-entangling nature of hyperbranched structures should also aid in controlling the solution or melt viscosity during the processing of the resulting of the resulting nanocomposites.

Various in-situ polymerization methods in grafting hyperbranched polymers to or from the surfaces of carbon nanofibers[29] and carbon nanotubes have been reported in the literature: (a) transfer radical polymerization (ATRP)[30]; (b) ring-opening polymerization[31]; (c) self-condensing vinyl polymerization (SCPV)[32]; (d) polycondensation [33]. In a recent example, SWNT was grafted with poly(aminoamine) dendrimers using a divergent methodology[34]. In all cases, (a) the CNF/CNT surfaces were prefunctionalized with appropriate functional groups for the subsequent polymerization processes; (b) either aliphatic or partially aliphatic hyperbranched polymers were resulted. In our case, no such prefunctionalization was required, and the resulting hyperbranched poly(ether-ketone) is wholly aromatic.

Thus, polymerization of 5-phenoxyisophthalic acid, in the presence of various amounts (1, 2, 5, 10, 20, 30 and 40 wt%) of vapor-grown carbon nanofibers (CNF) was performed under similar reaction conditions. The resulting (HPB-PEK)-g-CNF nanocomposites were insoluble in dichlorobenzene or toluene, but showed greatly improved solubility in polar solvents such as NMP, DMF, DMAc, ethanol, and even higher solubility in ethanol/triethylamine mixture or in aqueous ammonia solution, apparently stemming from the ionization of the numerous peripheral CO_2H groups. This is in contrast to our previous result that the nanocomposites derived from CNF similarly grafted with a linear meta-poly(ether-ketone), *m*PEK, with 1-30 wt% CNF content had much lower solubility in these polar solvents but are more soluble in methanesulfonic acid. As a way to determine both the ease in performing chemical transformation on the periphery of the hyperbranched component of the resulting (HPB-PEK)-g-CNF nanocomposites and the endgroup effect on some of their physical properties, the 10wt% (HPB-PEK)-g-CNF bearing carboxylic-acid endgroups were converted to

benzothiazole, dodecyl ester and amine endgroups. For example, the dodecyl-terminated nanocomposite displayed an excellent solubility in chloroform and a much lower T_g than the CO_2H -terminated analog. The overall evidence based on the data from elemental analysis, thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR), scanning electron microscopy (SEM) as well as transmission electron microscopy (TEM) of the resulting materials implicates that under our reaction conditions, HPB-PEK was grafted to the surfaces of CNF resulting in the formation of highly coated nanofibers. TGA, SEM and TEM data also support that CNF has remained more or less structurally intact under the mildly acidic, relatively high-shearing and hot polymerization conditions.

Our results show that (HPB-PEK)-g-CNFs have considerably better solubility (e.g. in aprotic polar solvents) than their linear analogs, *m*PEK-g-CNF, validating our concept in using an aromatic hyperbranched structure to enhance organo-solubility/dispersibility and widen the processing options of CNF/CNT materials. Because of the generally much lower viscosity behaviors as an attribute of hyperbranched polymers, the derived nanocomposites would be amenable to applications where speed and large-area coverage are required, e.g. spraying and painting techniques. In addition, we also show that the overall polarity of the nanocomposites could be synthetically controlled by converting the terminal CO_2H groups of the HPB-PEK grafts to amine, benzothiazole groups, and dodecyl esters groups. The former two cases could be conducted in a one-pot fashion by the addition of the respective endcapping agents after the A_2B polymerization in PPA has completed. A complementary approach that we have demonstrated to be successful in such polarity modification is via an *in-situ* A_3+B_2 polymerization with judicious stoichiometric variation of the triacid (A_3) and bis(phenyether), B_2 monomers [35]. As expected, the nature of chain ends can dramatically affect physical properties of the resulting nanocomposites. For example, the dodecyl-terminated nanocomposite displayed an excellent solubility in chloroform and a much lower T_g than the CO_2H -terminated analog. Perhaps, most importantly, we have demonstrated that aromatic hyperbranched polymers with its vast number of end-groups and random structures can be a very useful tool in enhancing solubility/nano-dispersibility, introducing application-specific functionality (e.g. lithium-hydrogen exchange for ion conductivity and battery applications)[35], and modulating thermal properties of the polymer nanocomposites with high contents of CNF/CNT materials for higher temperature applications.

3 CONCLUSION

In summary, we have found our version of "*in-situ* nanocomposite" approach to be very effective in dispersing

CNF/CNT nanoparticles, versatile and adaptable to a wide variety of polymer matrices, including high-temperature heterocyclic polymer[36], and conducting polymers such as poly(phenylene sulfide)[37], and polyaniline[38]. More importantly, we have demonstrated that polycondensation processes *vis-à-vis* the popular polyaddition processes [39] are a viable and complementary tool to synthesize polymer-matrix CNT/CNF nanocomposites with multifunctional capabilities.

4 REFERENCES

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