



# Facile synthesis of biosourced graphitic nanoparticle anchored silica nanoparticle hybrid for the development of functional polyurethane composite

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## ABSTRACT

The present work demonstrates a facile approach for the generation of functional polyurethane coatings using a biosourced graphitic nanoparticle anchored silica nanoparticle hybrid. Hence, 3-aminopropyl triethoxysilane was reacted with silica nanoparticles to obtain amino groups on the surface and was further reacted with a carboxyl terminated graphitic nanoparticle obtained from the incineration of camphor. The formation of hybrid structure was established through the electron microscopy images and other spectroscopic techniques. The infrared spectroscopic measurements reveal the successful formation of carbon–silica nanohybrid through amide linkages. The synthesized hybrids were dispersed in different weight percentages into a polyether polyol and then reacted with diisocyanate to form polyurethane nanocomposite. The presence of unreacted amino groups in the carbon–silica nanohybrid is helpful in urea linkage formation, which leads to uniform dispersion in the polymer matrix. The prepared polyurethane composite possess exceptional physico-chemical properties owing to the presence of nanoparticulates. Interestingly, the resulting composite showed shape recovery behavior. The shape recovery behavior of the obtained coating under temperature of 60 °C was found to correlate with the increase in the nanomaterial content. It is also found that storage modulus of the composite at room temperature increases from 183 MPa to 432 MPa in the case of neat and 1.5% carbon–silica nanohybrid incorporated polyurethane respectively.

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## 1. Introduction

In the recent years, nanomaterials have gained significant interest in the polymer industry owing to their geometry and the exceptional properties they offer [1,2]. They were initially used merely as filler in a polymer matrix to increase the strength and other physicochemical properties of the materials. However, recently there has been a paradigm shift in the way nanomaterials are used in polymer coatings [3]. The current trend focuses on making versatile coatings which cater the technological needs like scratch resistance, self cleanability, super-amphiphobicity etc. [4–6], which pose potential industrial usage. Nanoparticles all by itself cannot accommodate the present need for functional coatings. Therefore a demand for a highly functional nanomaterial

exists [7]. For this reason, a mixture of hybrids using either organic or inorganic nanomaterials was developed. Amongst these hybrids, carbon–silica based composites have gained prominence in the recent years [8]. This is because; the combination of silica and carbon together instills unique properties like low thermal expansion, exceptional durability, excellent optical absorptivity and purity [9].

Several methods for the preparation of carbon–silica composites have been reported in the recent years [10–12]. In view of potential methods for industrial applications, silica nanoparticles within a carbon matrix were produced by employing polymer dissolving pyrolysing methods [10]. However, maintaining the homogeneous dispersion prior to pyrolysis is difficult to obtain. As a result, there is a possibility of severe agglomeration of nanoparticles. Other methods like spray pyrolysis of a mixture of nanocrystalline silica powder and citric acid in ethanol was reported by Ng et al. for the synthesis of spherical carbon coated silica nanoparticles [11]. Hydrothermal treatment was also reported by Hu et al. to obtain the composite [12]. Though several methods exist, most

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of them are time consuming, require high end equipments, high temperature and stringent conditions. Therefore a requirement for the production of economic and structure optimized carbon–silica nanoparticle hybrid (CSH) exists. Therefore there exists a requirement to blend natural nanocarbons and silica to develop versatile, eco-friendly and economic CSH.

It is also a common observation that incorporation of CSH into polymeric matrix could inscribe additional properties of both silica and carbon, therefore providing an insight into the structure–property relationship. Dispersion of CSH into the polymers could be a difficult task owing to the kinetic barriers which restrain their proper dispersion [13]. Therefore, there is a necessity to chemically link the CSH with the polymer matrix. The chemical linkage is generally achieved through covalent bonding between the CSH and matrix. The enhancement in physico-chemical properties of such a nanocomposite is credited to the surface to volume ratio offered by the CSH, which leads to domination of surface atoms than that of the interiors [14]. These surface atoms are the main cause for increase in the potential properties of polymer matrix like hydrophobicity, corrosion resistance, scratch resistance etc. [15].

Considering the fact that the previously reported works utilize carbon materials which are not ecofriendly and economic, we put forth a new approach to use a biosourced carbon nanoparticle derived from camphor which is a naturally occurring hydrocarbon [16]. This nanoparticle is highly water-soluble, non-toxic and cost effective. Therefore, we utilize this nanoparticle to prepare a new inorganic nano-hybrid by covalently reacting it with silica nanoparticle and further inscribe them into polyurethanes. For this purpose, we initially terminated silica nanoparticles with an amino group by treating it with aminopropyl triethoxysilane (APTES) to obtain amine terminated silica nanoparticles (Si–NH<sub>2</sub>). Following this, we synthesized carboxyl terminated carbon nanoparticle (GNP–COOH) from camphor. GNP–COOH and excess Si–NH<sub>2</sub> were reacted at optimal temperature to form carbon silica nanohybrid via amide linkages. The resulting CSH consist of left over aminogroups, which were reacted with diisocyanate to form urea linkages. The various steps involved in engineering CSH were confirmed by thermogravimetric analysis (TGA), transmission electron microscopy (TEM), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), Fourier transform infrared (FTIR) and Raman spectroscopic techniques. The obtained CSH was loaded in different weight percentages such as 0.5, 1 and 1.5 into poly (tetramethylene ether) glycol (PTMG) matrix. These pre-polymers were reacted with 1-isocyanato-4-[(4-isocyanatocyclohexyl)methyl] cyclohexane (H<sub>12</sub>-MDI) at NCO:OH ratio of 1.2:1 and cured under atmospheric moisture to obtain functional polyurethane–urea–CSH composites. The resulting polyurethane–urea–CSH along with pure polyurethane were analyzed by TGA, atomic force microscopy (AFM), XRD, FTIR, FESEM and water contact angle measurements.

## 2. Experimental

### 2.1. Materials

Camphor, silica nanoparticles (~5–15 nm size, >99.5% pure), poly tetramethylene glycol (PTMG-1000), trimethylol propane (TMP), 1-isocyanato-4-[(4-isocyanato cyclohexyl) methyl] cyclohexane (H<sub>12</sub>-MDI), Dibutyl tin dilaurate, AR grade toluene were purchased from Sigma–Aldrich. Cellosolve acetate, concentrated sulphuric acid, Hydrochloric acid, 30% hydrogen peroxide solution, AR grade ethanol were purchased from SD Fine chemicals, Mumbai. All the chemicals were used as received without any purification.

### 2.2. Synthesis of biosourced oxidized graphitic nanoparticles

The graphitic carbon nanoparticles (GNP) were synthesized according to a method developed at our laboratory which was then treated with strong oxidizing agents so as to terminate it with a carboxyl group. The typical procedure involves incineration of 5 g camphor in a copper crucible in the presence of atmospheric oxygen. The obtained soot was collected on a polished copper sheet clamped above the burning camphor. The soot deposited on the copper sheet was allowed to cool to room temperature. Then the GNPs were carefully scraped out and treated with a solution of piranha (mixture of sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in the ratio of 7:3 respectively) for 5 h. The obtained mixture was vacuum filtered and washed with acetone several times. The oxidized-GNPs (GNP–COOH) were placed in oven at 60 °C overnight.

### 2.3. Synthesis of amine terminated silica-nanoparticles

Typically 0.6 g of SiO<sub>2</sub> nanoparticles was initially dispersed in a round bottom flask containing toluene and was sonicated for 15 min. Then 0.1 g APTES and catalytic amount of conc. HCl was added. The reaction was carried out at a temperature of 110 °C under atmospheric pressure for 24 h. Inert atmosphere was maintained throughout the experiment to facilitate the reaction. Amine terminated silica-nanoparticles (Si–NH<sub>2</sub>) were obtained by washing with ethanol and water followed by drying.

### 2.4. Synthesis of carbon–silica nanoparticle hybrid (CSH)

0.12 g of GNP–COOH was taken in a round bottom flask containing 60 ml of toluene and was sonicated for 30 min followed by flushing with nitrogen thrice. Then the prepared Si–NH<sub>2</sub> was added to the above solution and was refluxed at 110 °C under inert conditions for 72 h. Carbon–silica hybrid composites (CSH) were obtained finally by washing with ethanol and water several times.

### 2.5. Synthesis of polyurethane–CSH (CSH–PU) hybrids

Calculated amount of CSH (0.5%, 1.0% and 1.5% with respect to total weight), H<sub>12</sub>-MDI (0.98 g, 3.73 mmol) and 2.5 g of cellosolve acetate were taken in a round bottom flask. The mixture was sonicated for half an hour and stirred at 60 °C for 3 h. To this solution a mixture of PTMG-1000 (1 g, 1 mmol) and TMP (0.15 g, 1.1 mmol) dissolved in cellosolve acetate was added drop wise slowly. In all the hybrids, OH and NCO ratio was maintained as 1:1.2. The mixture was stirred at 65 °C for 8 h under inert atmosphere. After adding one drop of 5% DBTDL in MIBK as catalyst and one drop of Tagostab as surfactant, the CSH–PU hybrid films were casted on a tin foil by a manual driven square applicator. The excess NCO present in the hybrid films were moisture cured at 30 °C and laboratory humidity conditions (25–30%) for 15 days. The supported films were extracted after amalgamation of tin and cleaning.

### 2.6. Characterization

Fourier Transform Infrared spectra (FTIR) of synthesized samples were recorded by Thermo Nicolet Nexus 670 spectrometer. X-ray Diffraction (XRD) patterns for all the samples were obtained using a Siemens D-5000 X-ray diffractometer with Cu K $\alpha$  radiation of wavelength 1.54. The thermo gravimetric analysis (TGA) was conducted on TGA Q500 Universal TA instrument (U.K.) at temperature ramp rate of 10 °C min<sup>-1</sup> from 25 to 600 °C. Raman spectra were recorded using Horiba JobinY von Raman spectrometer with a laser excitation wavelength of 632.81 nm. Field emission scanning electron microscope (FESEM) using S4300 SEIN HITACHI Japan at

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