One-pot synthesis of nitrogen containing carbon nanomaterials in CVD reactor enhanced with plasma

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Abstract - *In this paper, we present a one step method to synthesize carbon nanomaterials (CNM) with a 3% nitrogen content. The presence of nitrogen in CNM in the form of different functional groups provides high zeta potentials which exceed +30 mV. This is adequate to ensure a stable dispersion of CNM in water with concentration up to 3 mg/mL, without any additional physical or chemical treatment of the material. Air was used as the nitrogen source, which was transformed into a reactive state by means of plasma or arc discharge. The properties of CNM synthesized in common CVD reactors and industrially manufactured CNM were studied for comparison. It is shown that the CVD reactor enhanced by arc discharge is a more suitable platform for manufacturing CNM with high nitrogen content. Such nanomaterials form stable dispersions in water which is much needed in the building and composite materials industries. This effective method has another advantage, as the synthesis and functionalization are realized in a single step directly in the reactor, and air is used as a source for the functionalizing reagent.*

Key Words: Carbon nanomaterials, plasma, arc discharge, dispersion in water, zeta potential, nitrogen

1. INTRODUCTION

Dispersions of nanotubes and nanofibers in water or solvents are in high demand for the fabrication of high performance composite materials, especially in the production of polymer composites [1] and high performance concrete [2-5]. The concentration of carbon nanomaterials in water does not need to be extremely high. In most cases, the amount of carbon nanotubes (CNT), which yields better mechanical properties in composite materials, are added in the range of 0.1 - 0.5%. The important requirement is a stable dispersion which can be sustained for at least several hours. However, pristine nanotubes and nanofibers do not have the capability to form stable dispersions. Typically, the solubility of carbon nanomaterials (CNM) is improved by the application of surfactants [6], by wrapping them in water-soluble polymers [7], or by surface functionalization [8]. The methods of CNM functionalization can be divided into two categories – (1) treatment of nanotubes with oxidative agents, such as sulfuric or nitric acids, ozone or plasma; (2) grafting of chemicals with specific functional groups. CNM are often subjected to preliminary oxidative treatment for the creation of carboxyl and hydroxyl groups on the surface followed by grafting.

Oxidative treatment, however, is detrimental to the mechanical properties of CNM as it causes structural damage. In addition, CNM functionalization through grafting by organic compounds is unsuitable for some applications, especially in the case of concrete, as the introduction of organics into the concrete composition may significantly reduce its mechanical properties [9]. Moreover, the additional step of CNM functionalization on an industrial scale could add significant production cost.

Hence, the ability to functionalize CNM in a single step during its synthesis in a reactor is of great interest. Functionalization of CNM during synthesis can be achieved by introducting additional components into the gas mixture. For example, the addition of small amounts of water, alcohols or organic acids, coupled with the feeding gas, into a reactor during the synthesis process could lead to different functional groups on the CNM surface [10]. The addition of organic chemicals containing silica is also of strong interest because the silica functional groups would be embedded in the concrete structure during the curing time [11].

Based on our past works, the addition of organic acids into the reactor gave highly negative zeta potential values which benefit dispersion stability, but the size of of the CNM becomes smaller as compared to those synthesized in standard conditions. This in turn negatively impacts the mechanical properties of concrete. The addition of small amounts of water gave similar results as the organic acids. The addition of organic compounds containing silica into the reactor will result in the successful insertion of silica into the CNM structure with zeta potentials below -30 mV. However, pyrolysis brought about by the silica containing organic compounds contaminated the walls of the reactor that it became unsuitable for industrial applications.

Besides oxygen and silica, there is significant interest to use nitrogen for CNM functionalization to improve the material's

solubility in solvents and water. The introduction of nitrogen on CNM surface results in high zeta potential values and creates defects on the surface, which in turn enhances the linkage between CNM and the matrix of the composite material. The usage of nitrogen containing compounds for CNT functionalization in dispersions of water or organic solvents is quite common. For example, in the works [7, 12-13], polymers containing imidazole were employed to achieve stable dispersions of nanotubes in organic solvents. Imidazolium-rich surfactants or polymers end-functionalized by another chemical with extremely rich amounts of nitrogen, such as 2,6-diamino-1,3,5-triazine were used to make stable dispersions of CNT in water and solvents [14-15]. Chemical functionalization of CNT by lysine or grafting by thymine also produced good dispersions in water [15-16]. Microwave functionalization of nanotubes by diamines created stable dispersions in water [17]. Oxidative modification of CNT by refluxing in HNO_3 also provided insertion of nitrogen elements of up to 3% in CNM [18]. Successful infusion of nitrogen into the CNM structure during synthesis was demonstrated by supplying nitrogen which contained chemicals (ammonia or acetonytrile) in a chemical vapour deposition (CVD) reactor [19-20].

There has been much interest to use nitrogen from the air for CNM doping as it is a safe, abundant and cheap source of nitrogen. However, nitrogen is inactive below 900°C, which impairs its chemical reaction with CNM in classical CVD reactors of lower working temperatures. The introduction of plasma in reactors may eliminate this issue.

CNT have been shown to be doped by different heteroatoms and functional groups thorough PECVD reactors [21]. For example, a wide range of possible chemical and radical transformations of hydrocarbon, ammonia and nitrogen containing chemicals were highlighted in the work by M. Mao and A. Bogaerts [22]. However, the introduction of nitrogen, in the form of air, for doping CNT has not been accentuated in the field.

Using different types of CVD reactors, we studied the possibility of obtaining CNM which has high zeta potentials and are able to form stable dispersions in water. The other objective is to ensure that the synthesis could be easily scaled up for industrial purposes. We used nitrogen from the air to create different functional groups on the CNM surface and synthesized functionalized CNM in a one step process. Concurrently, we studied and compared the stability of commercially available CNM in water dispersions.

2. EXPERIMENTAL

2.1 Materials

Sodium hydroxide (0.1 M) and hydrochloric acid (0.1 M) were purchased from Fluka and Sigma Aldrich respectively.

Sodium hydroxide (0.01 N) and hydrochloric acid (0.01 N) were purchased from VWR Analytical. Anhydrous calcium chloride was purchased from Alfa Aesar. Salicylaldehyde > 98%, diethyl oxalate > 99%, benzene 99.9% HPLC grade and sodium ethoxide were purchased from Sigma Aldrich. All chemicals were used as purchased.

To compare the properties of our synthesized product with commercially available CNM, three different CNM were purchased: VGCF-X from Showa Denko; C150p from Bayer and Chengdu IG from Chengdu Organic Chemicals Co. Ltd. All CNM references were produced in catalytic reactors without application of arc discharge or plasma.

2.2 Methods of analysis

Fourier Transform Infrared Spectroscopy (FTIR).

Perkin Elmer FTIR Spectrum GX Spectrometer was used to analyze the functional groups of CNM. 1-3 mg of CNM were mixed with KBr for pellet preparation.

Gas-chromatography mass spectrometry (GC-MS).

Analyses of gas samples were performed using the Agilent GC equipped with the Quadruple Waters detector. Capillary column: DB-5MS (30 × 0.25 mm × 0.25 μm). Ionization mode: electron impact. Injector temperature: 250°C. Oven temperature ramp: from 50°C up to 300°C with heating rate 10°C/min.

Elemental analysis.

Elemental analysis of the CNM was conducted using the CHN628 LECO elemental analyzer.

Zeta potential measurement.

Zeta potential was obtained using a Malvern Zetasizer ZS (Malvern, UK) equipped with a He/Ne ion laser (633 nm). Milli-Q water was used to prepare dispersions of CNM. Samples were dispersed in water by ultrasonication for 15 minutes.

Analysis of hydroxyl and carboxyl functional groups.

Carboxyl and hydroxyl functional groups were determined by titrimetric analysis according to the following procedure. 25 mL NaOH (0.1 M) was added to 20 mg of CNM under argon and the mixture was ultrasonicated for 10 minutes. The sample was then filtered with cellulose acetate filter (0.45 μm) under argon. The filter was washed with 10 mL of milli-Q water, and the filtrate and washing solution were combined. 25 mL of HCl (0.1 M) was added to the combined volume of filtrate. Dissolved CO_2 was removed from the solution by vibration and vacuum, which was achieved by

putting the sample into a small desiccator placed on the vibration table for 2 hours. The final sample was titrated by NaOH (0.1M). The same procedure was carried out as a reference without CNM. The amount of –COOH and –OH groups in mol/g of CNM was determined using the amount of mol of NaOH used for the titration, taking into account the reference results.

Another portion of the same CNM was subjected to chemical interaction with sodium ethoxide (1 M) in anhydrous THF overnight at room temperature. The rationale is to protect the carboxyl groups and to make them unavailable for the titration. After the reaction, the sample was carefully washed with milli-Q water and dried for 12 hours at 105°C. The amount of unprotected hydroxyl groups was determined by the same procedure described above. The amount of carboxyl groups was calculated based on the results of two titrations: Amount (COOH) = Amount (COOH + OH) –Amount (OH).

Analysis of amino groups.

Primary, secondary and tertiary amino groups in CNM were determined by the modified method stated previously [23]. 500 mg of CNM were suspended in 100 mL of milli-Q water using ultrasonication, followed by removal of CO_2 under vacuum in a desiccator placed on the shaker for 2 hours. Analysis was realized in three steps – (1) total amount of amino groups was titrated by a 0.01 M HCl solution using pH meter. Ethylene glycol and isopropanol mixed in the ratio of 1:1 was used as a solvent for the preparation of HCL solution; (2) blocking of primary amines by salicylaldehyde, which will only yield secondary and tertiary amines when titrated; (3) the procedure was modified to block the primary and secondary amino groups. Diethyl ester of oxalic acid was used instead of acetic anhydride. Also, 5 mL of diethyl ester of oxalic acid was added to the dispersion of CNM in benzene. After the evaporation of benzene, the residue was washed with ethanol and water and dried in the oven at 105°C overnight. Only tertiary amines were available for the titration after the reaction of CNM with diethyl ester of oxalic acid. The amount of secondary amines was obtained by the subtraction of results from the third and second step. The amount of primary amines was determined by the subtraction of secondary and tertiary amines from the total amount of amines.

Preparation of CNM water dispersion.

Water dispersion of CNM was prepared using milli-Q water. The amount of CNM used for dispersion was calculated to create a concentration of 5 mg/mL. Also, 250 mL of the suspension was treated in ultrasonic bath for 30 minutes. The dispersion was kept for at least 24 hours. The concentration of CNM in water was then measured by UV-Vis

spectroscopy (Shimadzu UV 2401 PC) using the protocol published by Hyung et al. [24-25].

2.3 Synthesis of CNM

The synthesis was performed in three types of catalytic reactors – (1) plasma enhanced; (2) arc discharge; (3) catalytic tubular CVD reactor. The most significant difference between the plasma enhanced and arc discharge reactors is that high current (150-160 A) and relatively low voltage (60-70 V) are applied in the plasma enhanced reactor, whereas high voltage (2-7 kV) and low current (0.1-0.3 A) are applied in the arc discharge reactor. A catalytic reactor, enhanced with the arc discharge, was equipped with a Ni-Fe (10% Ni) tube (46 mm diameter), and the inner wall was used as a surface for the CNM to grow. The length of the reactor tube was 1 m. The arc discharge was created between a tungsten cathode and a tubular copper anode. The starting distance between the two electrodes at the igniting moment was 35 mm with successive increment of up to 50 mm in the working mode. The temperature of the reactor wall was maintained by an external heating device and was varied in the range of 640°C to 680°C. The flows of gases supplied to the reactor are 175 L/h and 425 L/h for natural gas and air respectively. The CNM obtained in the reactor with arc discharge is called AD CNM.

The synthesis condition of CNM in a plasma enhanced reactor was published by Zhdanok S.A et al. [26-27]. A distinctive feature of this synthesis is the use of a low-temperature plasma generated between the hollow anode and the rod shape cathode. This CNM is called P CNM.

CNM grown in simple CVD reactor was used for comparison. For this synthesis, the temperature used was 650°C. The flow rate of natural gas was 75 L/min. 1 g of nickel oxide catalyst was distributed in the zone of synthesis (20 cm) of the quartz tube which has an internal diameter of 8 cm. The quartz tube was placed in a tubular oven to maintain the required temperature in the zone of synthesis. The synthesis duration was 2 hours and the obtained material from this reaction is called catalytic CNM (C CNM).

3. RESULTS AND DISCUSSION

3.1. GC-MS study and elemental analysis of exhausted gases from reactors

We expect that the high temperatures generated by the arc discharge or plasma would make nitrogen chemically active, allowing for its infusion into the CNM structure. To validate this assumption, we carried out GC-MS analysis (Fig. 1) of exhausted gases from the arc discharge reactor and from the simple catalytic reactor working at 650°C. Exhausted gases were absorbed by 50 mL of tetrahydrofurane (THF) for 20

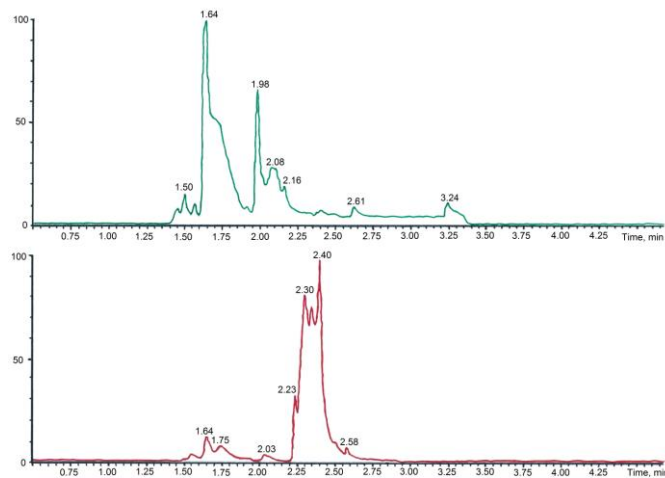minutes in both cases. The final volume of THF was less than 10 mL.

Fig-1: GC-MS chromatograms of gases absorbed by THF. Top: Catalytic reactor. Bottom: Arc discharge reactor

It should be noted that the chemicals detected by THF do not reflect the composition of exhausted gases because volatile compounds cannot be absorbed effectively by the solvent. This characterization aims to provide a qualitative analysis of possible differences in the by products between the two reactors. The compounds detected by THF from the exhausted gases from both reactors are presented in Tables 1 and 2.

Table-1: Products absorbed from exhausted gases from the catalytic reactor

Elution time (minutes)	Area (%)	Name (formula)
1.45	1.13	Carbon dioxide (CO_2)
1.50	2.56	Acetaldehyde (C_2H_4O)
1.57	1.68	Methane, Nitroso (CH_3NO)
1.64	18.30	Acetone (C_3H_6O)
1.70	26.25	Cyclopropanecarboxaldehyde (C_4H_6O)
1.98	7.56	Not identified
2.08	22.10	Hexane (C_6H_{14})
2.16	1.84	Pentane, 3-methyl (C_6H_{14})
2.40	3.80	2,4-Hexadiyne (C_6H_6)
2.61	8.01	2-Butanone, 3-methyl ($C_5H_{10}O$)
3.24	6.77	2-Pentene, 4-methyl-, (Z) (C_6H_{12})

Table-2: Products absorbed from exhausted gases from the arc discharge reactor

Elution time (minutes)	Area (%)	Name (formula)
1.51	0.53	Acetaldehyde (C_2H_4O)
1.54	1.12	1,3-Butadiyne (C_4H_2)
1.64	5.30	Acetone (C_3H_6O)
1.74	5.47	2-Propenenitrile (C_3H_3N)
1.87	0.68	2,3-Dimethyl-aziridine (C_4H_9N)
1.94	0.91	Pentanedinitrile ($C_5H_6N_2$)
2.03	1.06	N-Aminopyrrolidine ($C_4H_{10}N_2$)
2.23	2.67	Not identified
2.34	38.17	Not identified
2.40	42.64	2,4-Hexadiyne (C_6H_6)
2.58	1.45	3-[N-Aziridyl]-2-methylpropionitrile ($C_6H_{10}N_2$)

It is evident that exhausted gases from the arc discharge reactor contain a significantly larger variety of organic compounds containing nitrogen. This data supports the expectation that nitrogen would be infused into the CNM structure. Elemental analyses of synthesized and commercially available CNM were performed to confirm and compare the presence of nitrogen in their structures (Table 3).

Table-3: Elemental analysis of CNM

Type of CNM	C	H	N
Synthesized samples			
P CNM	92.6	0.82	0.63
AD CNM	85.1	1.63	2.86
C CNM	95.81	0.95	0.11
Industrial samples			
Bayer C150p	96.5	0.65	0.18
Changdu IG	94.35	0.64	0.26
SD VGCF-X	91.2	0.54	0.05

From the table, it is evident that nitrogen is present in significant amounts in the two samples, P CNM and AD CNM, obtained in catalytic reactors enhanced with arc discharge and plasma. It is worthy to note that the amount of nitrogen in the AD CNM is 5-6 times higher as compared to the P CNM. At this point, there is no sufficient explanation for this effect as temperatures in both reactors and their gas supplies were approximately the same. However, we propose an explanation based on data obtained from the FTIR analysis (Fig. 2).
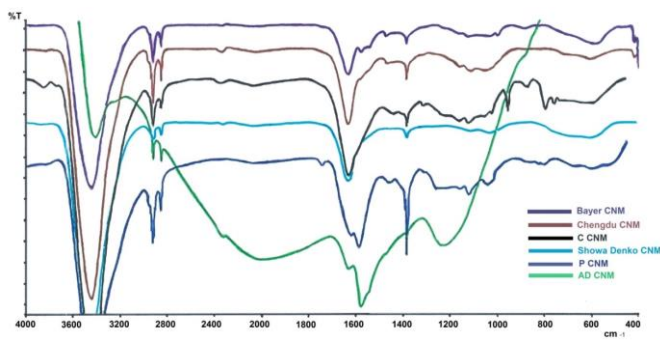
Fig- 2: FTIR spectra of CNM

All the FTIR spectra for the various CNM revealed typical structural formation which is generally observed in carbon nanomaterial compositions. We can assume that the AD CNM with a higher amount of nitrogen was synthesized in a reductive atmosphere as compared to P CNM. The small peak in the P CNM spectrum at 1742 cm^{-1} may indicate the presence of carbonyl groups, which is not present in AD CNM. It can be postulated that the plasma promotes the formation of an oxidative atmosphere in the reactor. The converse occurs for arc discharge reactor, which results in reductive reactions. Due to this reductive potential in the arc discharge reactor, the atmosphere is favorable for the interaction of activated nitrogen with carbon-containing compounds and for the appearance of relevant building blocks in CNM. On the other hand, the oxidative environment in the plasma enhanced reactor resulted in the formation of oxidated forms of nitrogen. Due to the lower reactivity, the amount of bound nitrogen in CNM from the plasma CVD reactor was less when compared to CNM obtained from the arc discharge reactor.

There are a few peaks in the P CNM and AD CNM FTIR spectra which highlight the potential inclusion of nitrogen in the structures of both nanomaterials. Both materials exhibit depressions in the range of 2000-2300 cm^{-1}, which may be due to nitrogen (C≡N) but this observation is unconclusive. The peaks at 1626 cm^{-1} and 1586 cm^{-1} point to the presence of the C=N structure. The peak at 1626 cm^{-1} may also be due to amide-like structures. For the arc discharge material, its largest peak at 1229 cm^{-1} could be due to C-N chemical bonds.

An interesting result was obtained from simulation using the Bio-Rad FTIR library. The database showed a huge similarity between the FTIR spectrum of P CNM with a few other compounds. The first match being graphite fibers (probability: 0.526) that is logical, the second match being polybenzimidazol (probability: 0.489) and the third match being 2,4-dinytro-1-naphtol (probability: 0.477). A comparison of the FTIR spectra of P CNM and polybenzimidazol from the library is presented in Figure 3.
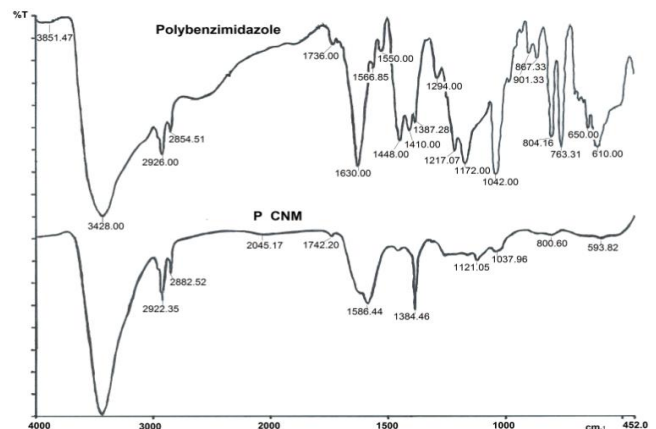

Fig-3: Comparison of FTIR spectra of P CNM and polybenzimidazol

Imidazole is water soluble and 60 times more basic than pyridine. It is also very easy to protonate and provides high positive zeta potential. The FTIR simulation coincides with another observation made during the treatment of P CNM and AD CNM with nitric acid. After the treatment, P CNM and AD CNM lost their capabilities to form dispersions in water and possess zeta potentials in the range of +6 mV to -10 mV. Prior to the nitric acid treatment, both materials possessed zeta potentials above +30 mV. Imidazol shares the same traits as it provides high zeta potential and may be destroyed in an oxidative acidic environment. To confirm these hypotheses and observations from the FTIR data, we analyzed the amount of nitrogen and oxygen containing functional groups in CNM by analytical methods.

3.2 Functional groups in CNM

Analyses of amino groups in CNM gave high standard deviations (Fig. 4). Despite this, some differences could be detected in how nitrogen was infused into the CNM structures.
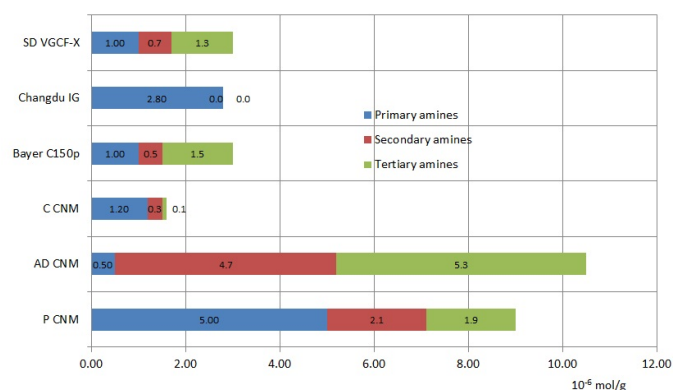

Fig-4: Composition of amino groups in CNM (10^{-6} mol/g)

The analysis of amines by titration deviated from the amounts detected by elemental analysis but similar trends are witnessed. We attribute this difference to the assumption that only nitrogen from the surface could be available for detection by the titration method. Based on the results in Fig. 4, the first observation is that the amount of secondary and tertiary amines in the materials obtained from plasma and arc discharge reactors are similar. It is typical for the cyclic nitrogen containing structures to consist of one secondary and one tertiary nitrogen atom. It corroborates with the FTIR simulation and high zeta potentials for these samples, which is associated with imidazol residue. Comparing the samples from plasma and arc discharge reactors, the second interesting observation is related to the amount of primary amines. It seems that the majority of nitrogen in P CNM is in a primary form, whereas more complicated nitrogen structures exist in AD CNM due to a large amount of secondary and tertiary amines. This indicates that the atmosphere and conditions in an arc discharge reactor are more favorable for formation of a large variety of building blocks containing nitrogen.

Analysis of hydroxyl and carboxyl groups.

The distribution of carboxyl and hydroxyl functional groups in CNM samples are presented in Fig. 5.
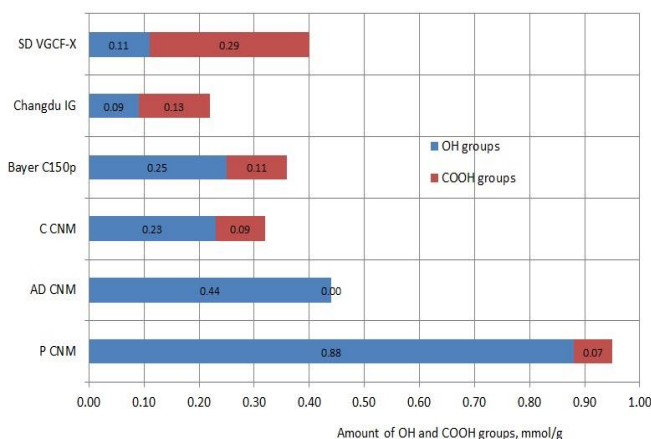

Fig-5: Amount of hydroxyl and carboxyl groups in CNM

From the data presented in Figure 5, the difference between samples obtained with plasma, arc discharge and catalytic reactors is clearly seen. The hydroxyl group is the major functional group in CNM synthesized with plasma and arc discharge reactors, whereas the other samples have significant amounts of carboxyl groups. The higher amount of carboxyl groups in the first three samples in Figure 5 correlates with the low zeta potential values which are negative for the two last samples.

3.3. Correlation between properties of CNM and dispersion in water

The physical properties of CNM and their concentrations in water are presented in Table 4.

Table-4: Size, zeta potential, specific surface area and maximum concentration in dispersion

Type of CNM	Size (µm)	Specific surface area (m²/cc)	Zeta potential (mV)	Dispersion in water (mg/mL)
Synthesized samples				
P CNM	3.1±1.4	2.97	+32.0±0.6	2.15
AD CNM	4.3±2.1	2.56	+31.1±0.92	3.05
C CNM	23.7±4.8	0.34	+23.8±1.04	0.14
Industrial samples				
Bayer C150p	30.4±5.5	0.75	+8.23±1.37	0.10
Changdu IG	39.2±6.3	0.22	-12.5±1.22	0.04
SD VGCF-X	30.8±5.5	0.25	-11.6±1.57	0.06

As shown in Table 4, the sizes of all catalytic CNM vary from 23 to 39 µm. The P CNM and AD CNM are ten times smaller compared to the three industrial samples. A possible explanation for this phenomenon is that plasma and arc discharge reactors produce a large variety of building blocks for CNM, which lead to irregular structures and non-uniformity. As a result, smaller nanomaterials are obtained. The high specific surface areas of P CNM and AD CNM validate the non-uniform structures of these two nanomaterials.

The zeta potentials of all synthesized CNM are above +20 mV but samples obtained with plasma and arc discharge reactors gave higher concentrations when dispersed in water as compared to all other studied materials. This could be due to the following two reasons – (1) Both AD CNM and P CNM have the highest zeta potentials which are above +30 mV; (2) Small AD CNM and P CNM particles allow for easy formation of stable suspensions as compared to larger particles which have the tendency to precipitate.

It is evident that the physical properties of CNM and the chemical structure of their surfaces play significant roles in the stability of the dispersions [28]. The coefficients of correlation were calculated to quantitatively reflect the influence of CNM properties on their capability to be dispersed. This allowed a clear view of the relationship

between the amount of soluble materials in water and their chemical properties (Table 5).

Table-5: Correlation coefficients between CNM properties and concentration in water dispersion

Property	Coefficient of correlation
Size of CNM	-0.95
Specific surface area	0.94
Bulk density	0.64
Zeta potential	0.75
Amount of OH groups	0.74
Amount of COOH groups	-0.68
Amount of nitrogen (elemental analysis)	0.88
Amount of primary amines (-NH$_2$ group)	0.18
Amount of secondary amines (-NH group)	0.96
Amount of tertiary amines (-N= group)	0.87
Total amount of amines	0.98

The amount of nitrogen in the studied samples correlates with the capabilities of the CNM to form stable dispersions in water. The coefficient of correlation between the nitrogen amount in CNM and the concentration of CNM in water was 0.88. The concentration of CNM in water also significantly correlates with the zeta potential values of CNM with a correlation coefficient of 0.75. These two coefficients of correlation are considered high by the Chedoke scale. This corroborates with the general knowledge of colloid chemistry, where stable dispersions can be obtained if the zeta potential values are above +30 mV or below -30 mV.

The size of particles has a negative correlation with their stability as dispersions in water, simply because large particles sink. High specific surface areas of CNM positively influence their stability to disperse in water due to their irregular structures, presence of nitrogen and smaller densities. Evidently, higher zeta potentials also increase the stability of CNM dispersion in water. Interestingly, primary amines are not related to good dispersion. On the other hand, secondary and tertiary amines, which we assume reflect cyclic, imidazole-like structures, favor formation of good dispersions. The presence of hydroxyl functional groups gives good dispersion of CNM, whereas carboxyl groups do not support dispersion. However, it is believed that this effect is mostly related to negative or low zeta potentials, rather than the amount of carboxyl groups.

4. CONCLUSIONS

By utilizing different CVD reactors for CNM synthesis, we discovered that the application of plasma changes not only the structure of CNM and the productivity of the reactor, but also positively influences the dispersion of CNM in water. Our research shows that the enhancement of catalytic reactors with plasma or arc discharge allows for direct infusion of nitrogen from the air into the CNM structure during synthesis. Ambient nitrogen can be incorporated into CNM to form different functional groups due to the high temperature impact of plasma which chemically activates nitrogen. We speculate that the arc discharge in the CVD reactor leads to the presence of imidazole-like structures on the CNM surface. This provides high zeta potential values which ensure stable dispersion of CNM in water of up to 3 mg/mL. Water dispersions of CNM obtained from the plasma or arc discharge reactors are more stable when compared that from a simple CVD reactor, regardless of the same working conditions in the zone of synthesis. High concentrations of CNM can be obtained directly during synthesis without any additional chemical treatment, such as the application of surfactants, which would be beneficial for composite materials and concrete industry today.

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