Review Article

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A review of current physical techniques for dispersion of cellulose nanomaterials in polymer matrices

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Abstract: Cellulose nanomaterials (CNMs) naturally exist in biomass. Recent developments in nanotechnology and extraction procedure of CNMs open up a new era in the polymer composites industry. Abundant, renewable, biodegradable, transparent, light weight, and most importantly, low cost make CNMs the ideal material for packaging, automotive, construction, and infrastructure applications. CNMs are generally used as materials for polymer matrix reinforcement in the composites industry. The industrial-scale manufacturing of CNM/thermoplastic composites remains an unsolved puzzle for both academics and industries. The dispersion of nanocellulose in polymer matrix is the central problem inhibiting the manufacturing of CNM/polymer composites at an industrial scale. Several attempts were made to disperse nanocellulose effectively in a polymer matrix and improve compatibility between the matrix and CNMs. Chemical-aided surface modification of CNMs has been effective in several cases; however, chemical toxicity, high price, and critical control of reactions make them unsuitable. This current review paper focuses on novel eco-friendly physical dispersion techniques of CNMs and their future scope of research. The physical dispersion techniques such as plasma-induced surface modification, ultrasonication, magnetic and electric field discharge, electrospinning, or drawing can visibly improve the dispersion state of CNMs. But several factors affect physical techniques' performance, e.g. CNM type and forms, process

conditions and parameters, etc. Moreover, the material-related factors interplay with the process-related factors. This review addresses the current state of knowledge on the physical dispersion techniques for CNMs and identifies challenges that are critical to adoption of these novel materials at commercial scale for future applications.

Keywords: polymer–matrix composites, dispersion of nanocellulose, chemical-aided surface modification, physical dispersion techniques

1 Introduction

Polymer materials are widely used in various industrial sectors for a variety of applications. Most petroleum-based materials are not biodegradable. The lack of biodegradability of fossil-based non-biodegradable products is a growing concern in today's world. Increased greenhouse gas emission, air and water pollution, and the severity of global climate change have compelled scientists to find eco-friendly alternatives to these petroleum-based materials. The most common and sustainable bio-based material is cellulose. Cellulose is the most abundant and natural polymer on earth [1]. Chemically, cellulose is a high molecular weight homopolysaccharide composed of β -1,4-anhydro-D-glucopyranose units. Each cellulose chain has a hemiacetal group, a chemically reducing functionality in one end. The other end has a pendant hydroxyl group as reducing group. The degree of polymerization of cellulose (DP) varies depending on its origin, starting from 10,000 to 15,000. Each monomer of cellulose contains three hydroxyl groups, which play a major role in fibrillar and semicrystalline packing governing important physical properties [2].

When cellulose is mechanically fibrillated or chemically hydrolyzed under specific conditions, nanoscale materials are generated as shown in Figure 1 [3–5]. There are three types of nanocelluloses: cellulose nanocrystals (CNC), cellulose nanofibrils (CNF), and bacterial nanocellulose (BNC).

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Figure 1: Types of nanocellulosic materials from woody/non-woody biomass.

In the following sections, the structure and properties of nanocelluloses are discussed briefly.

1.1 CNC

CNC, also known as nanocrystalline cellulose or cellulose nanowhiskers (CNWs), is a nanocellulose with high strength. Additionally, CNCs have limited flexibility because of their high crystallinity (54–88%). CNCs have a short rod-like or whisker-like shape with a diameter of 2–20 nm and length of 100–500 nm. The nanocrystalline cellulose is prepared by hydrolyzing and removing the amorphous part of cellulose using highly concentrated acids. The dimension of CNC and crystallinity depend on the conditions of extraction and source of cellulose. Higher crystallinity is exhibited by CNCs extracted from pure cellulosic materials. During hydrolysis, the nature of the acid used is extremely important because it affects the dispersion property. If hydrochloric or hydrobromic acid is used, the dispersion is very limited, and subsequently, the aqueous suspensions tend to flocculate. However, in case of sulfuric and phosphoric acids, the hydroxyl groups of cellulose surface yield sulfate or phosphate esters which improve dispersion of CNC in water [2–6].

CNC exhibits excellent mechanical properties as a result of higher crystallinity. The theoretical tensile strength of CNC is in the range of 7.5–7.7 GPa, which is much higher than steel and Kevlar and the elastic moduli is ~150 GPa. The experimental Young's moduli of cotton CNC's and tunicate CNC's are ~105 and ~143 GPa, respectively [7]. CNCs can be successfully functionalized to reduce their hydrophilicity and promote incorporation of modified nanoparticles in a hydrophobic matrix.

1.2 CNF

CNF are also known as nanofibrillated cellulose, cellulose microfibril, microfibrillated cellulose or cellulose nanofibre, etc. CNFs consist of long, flexible bundles of elementary nanofibrils composed of alternating amorphous and crystalline domains. CNFs can be of 1–100 nm in diameter and 500–2,000 nm in length. CNFs are generally extracted from pure cellulosic material such as wood pulp, by the cleavage of fibrils in High Pressure Homogenizer without any pretreatment, or after chemical or enzymatic pretreatment. In the amorphous domains of cellulose or hemicellulose, at first some of interfibrillar hydrogen bondings are broken due to mechanical shearing. Afterwards, the inter-molecular bondings of van der Waals' forces are also broken. CNFs having a spaghetti-like shape contain both cellulose and hemicellulose, with a medium range of crystallinity (51–69%) [2–6].

CNFs tend to show gel-like characteristics in aqueous solution even at low concentration (2 wt%). There are two reasons behind this phenomenon. The first one is a large number of hydrogen bond formation because of the surface hydroxyl groups present in its structure. The second one is significant increase in the surface area due to reduction in size. Agglomeration is induced in CNF suspension because of the strong hydrogen interaction and high hydrophilicity of the material by virtue of their structure. The effective dispersion and distribution of CNFs are the most crucial challenges faced, when they are used as reinforcement in polymer matrices [8]. The most feasible solution is to modify the surface functional groups of cellulose to avoid hydroxyl interactions and increase interfacial compatibility with different types of polymer matrices.

The axial strength and modulus of CNFs are estimated to be ~3 and ~136 GPa, respectively [9].

1.3 BNC

Unlike plant cellulose, BNC is produced in the pure form, devoid of lignin, hemicellulose, pectin, or any other compound commonly present in plant pulp. BNC does not contain any contaminant of animal origin [10]. The anhydroglucose units and various BNC fibrils interact to form a crystalline structure through internal and external hydrogen bondings. These thin nanofibres have a diameter range of 20–100 nm [11]. BNC is a highly crystalline linear polymer of glucose, synthesized mainly by *Gluconacetobacter xylinus*. During cellulose production, *G. xylinus* builds a nanofibrillar film with dense lateral

surface and a gelatinous layer on the opposite side [12]. Despite numerous studies, the metabolic pathways through which the microorganisms regulate BNC production remain unclear.

There are two main methods of BNC production using microorganisms: static culture and stirred culture. In case of static culture, there is an accumulation of a thick, leather-like white BNC pellicle at the air–liquid interface. In stirred culture, BNC is produced in a dispersed manner in the culture medium, forming irregular pellets or suspended fibres [13].

The high mechanical strength of BNC can be attributed to its fibrillar structure. BNCs exhibit a hydrogel-like behaviour as they can bind water. Additionally, BNC is not degradable in human bodies, making them suitable for biomedical applications [4].

1.4 Significance of surface modification

The excellent mechanical properties of cellulose nanomaterials (CNMs) comparable to conventional materials, like glass fibre, carbon fibre, and Kevlar fibre, make them potential candidates for green replacement of the synthetic fibres in composites industry [14]. Polymer matrix nanocomposites are the new age materials and are regarded as the future of composites industry. The main advantages of polymer composites are that they are flexible, stretchable, and even reconfigurable [15]. Polymer composites have gained special attentions from both researchers and industry for their unique properties such as high strength to weight ratio. During manufacturing, the major parameters to take care of are: filler/reinforcement alignment and loading, nature of reinforcement, nature of matrices, and good filler-to-matrix adhesion [16]. The incompatibility between filler and matrix materials may cause bond weakening or even debonding. Bond weakening will result in less effectiveness of the filler material, which in turn adversely affects the mechanical properties of the resultant composite material [1]. With the recent advancement of nanotechnology, CNMs are exploited as a reinforcement for polymer composites along with the other ones because of the special attributes such as biodegradability, light weight, transparency, and relatively low cost [17]. Thermoplastic polymers are used as the matrix materials in major cases (90%), and the rest are thermosets [18]. Though thermoplastics are recyclable in nature, they are not mechanically robust like thermosets. For this reason, fillers are used to reinforce the thermoplastics to create stronger composites [19]. The main issue regarding the mixing of CNMs with the thermoplastics is the limited dispersion of

CNMs in the polymer matrices. Thermoplastics are usually hydrophobic in nature and have low surface energy, while the CNMs are hydrophilic with high surface energy. Because of this reason, thermoplastics cannot adequately interact (wet) with the surface of CNMs and effectively disperse them throughout the polymer matrices [5]. All surface modifications are mainly conducted to (1) introduce stable negative or positive electrostatic charges on the surface of the CNMs, (2) tune the surface energy characteristics to enhance compatibility with the polymeric matrices, especially non-polar or hydrophobic ones, and (3) change only the surface characteristics of the CNMs keeping the original morphology intact to avoid any polymorphic conversion [4]. Surface modifications can induce charges or tune the surface energy characteristics of CNMs by decreasing energy consumption and clogging and also confer new properties to CNMs [20]. Therefore, many efforts have been spent on the surface modification of CNMs either by chemical or physical means. Currently, there is no single physical or chemical method available to improve dispersibility of CNMs in the polymer matrices for enhancement of the mechanical properties.

2 Rationale

In most review articles, CNMs have a broad coverage regarding the chemically aided dispersion methods of CNMs for polymer nanocomposites. For over 50 years, researchers have been discussing different types of chemical surface modification methods in detail. However, till date, there is no single review paper focused on physical/mechanically aided dispersion methods. A comprehensive summary and deep understanding in this field are highly desirable. This review solely focuses on efforts to enhance the dispersion of CNMs using the physical/mechanically aided dispersion methods. It is envisioned that this review will help to gain insight, guidance, clarity, and inspiration towards ongoing cellulose/polymer nanocomposites research, a step further into pilot/industrial-scale production.

3 Chemical-aided dispersion of CNMs

The chemical modification of the surface of CNMs can be divided into two categories depending on the locations of attack: either on the surface hydroxyl groups or AGU ring opening. In some cases, charged groups generate

repulsive forces to weaken the cohesion of hydrogen bonds. In other ones, osmotic pressure produced by the difference in ionic concentration facilitates fibre swelling and reduction in the interfibrillar cohesion which in turn enhances breakage of the cell walls [20]. There are different types of chemical surface modifications reported in recent years: polymer grafting, silanization, acetylation, esterification, etc. In the following section, a brief discussion on these methods is presented.

3.1 Polymer grafting

In polymer grafting method, functional polymer brushes are grafted on the surface of nanocelluloses by “grafting onto” and “grafting from” approaches. The “grafting onto” method involves attachment of pre-synthesized polymer chains with reactive groups onto the surface hydroxyl groups of cellulose. On the other hand, the “grafting from” approach uses ring opening polymerization method to grow polymer brushes *in situ* on nanocelluloses using the surface hydroxyl groups as initiating sites [21]. In “grafting onto” approach, high grafting densities cannot be obtained because of the steric hindrance of the polymer chains. The main advantage of this method is that the properties of the resulting material can be controlled judiciously as the molecular weight of the attached polymer can be characterized before grafting [22]. For example, Anirudhan and Rejeena [23] synthesized a novel multi-component superabsorbant polymer composite by grafting the vinyl monomers onto magnetite nanocellulose composite (MNCC). Methacrylic acid and vinyl sulfonic acid were chosen because of their anionic character, which increases the swelling capacity of the resultant material. The FTIR spectra showed the characteristic absorption bands of cellulose were retained in MNCC with a small decrease in intensity. This indicated the degradation of hydrogen bonds between the cellulose chains during the acid hydrolysis treatment [23]. The “grafting from” approach normally provides higher grafting efficiency due to lower steric hindrance produced by small monomers, compared to the shielding effect on reaction sites in “grafting onto” approach. Wang et al. grafted poly(methyl methacrylate) (PMA) from the CNC-macroinitiator achieving almost six times the mass of grafted PMA (with respect to CNC) within only 30 min. The resulting PMA-grafted CNC showed excellent dispersibility in a number of organic solvents. From FTIR spectra, it can be seen that the hydrogen absorption band showed a gradual decrease with reaction time, almost disappeared

at 30 min. This indicated that the CNC surface was covered gradually by the growing PMA chains [24]. In another study, polycaprolactone diol (PCL) was grafted on the surface of oxidized nanocelluloses to enhance the compatibility between the hydrophobic polymer matrix and hydrophilic cellulose. This grafting was done by using click chemistry. The reaction produced polycaprolactone-grafted oxidized nanocellulose (ONC-g-PCL), which improved the interfacial adhesion of composite material. The TEM image of the ONC-g-PCL shows significant increase in the width of the grafted ONC fibres (25–30 nm). The increase in width clearly indicates successful grafting of PCL chains onto the surface of the ONC fibrils [25]. There is no visual evidence of the improvement in dispersion of the CNMs in the polymer matrix in “grafting onto” method.

3.2 Silylation

Silanes are other widely used coupling agents which can be used for polymer composites to improve the interfacial compatibility between nanocellulose and the polymer matrix. One of the major benefits of using silane is that the reaction can be a water/alcohol-based system, instead of the harmful organic solvents. First, the alkoxy end group of the bifunctional silanes should be converted to silanols before reacting with the hydroxyl groups on cellulose [26]. Pohl and Osterholtz reported that the chemistry of the silanes can be rather complicated, depending on many factors such as the solvent, temperature, pH, concentration of silanes, etc. [27]. Salon et al. concluded that reaction time for the hydrolysis of silane and the following adsorption of silanol groups onto the cellulose surface should be carefully regulated to reduce the degree of self-condensation [28]. Xu et al. grafted nanocrystalline cellulose (CNC) with poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) using (3-amino-propyl) triethoxysilane (APES) as a coupling agent, resulting in a grafting degree of ~25 wt%. The fracture morphologies of the freeze-fractured surfaces (SEM images) (Figure 2) showed no or very little agglomeration of PHBH/CNC-g-PHBH blend, when CNC-g-PHBH content was 1.0 wt%. However, agglomeration was observed as the content of CNC increased. The Young's modulus of composites increased by 15% by the addition of 1.0 wt% CNC-g-PHBH [29].

Taipina et al. used a silane with isocyanate groups (isocyanatepropyltriethoxysilane) to modify the surface characteristics of CNC [30]. The aim of this study was to produce an oligomeric network of polysilsesquioxane,

Figure 2: SEM micrographs of freeze-fractured surfaces of (a) CNC-*g*-PHBH (1.0 wt%) blend and (b) CNC-*g*-PHBH (2.0 wt%) blend. Adapted from ref. [29].

which can result in an efficient nanocrystal surface covering. The modified CNCs showed less polar surface characteristics facilitating compatibility with the hydrophobic polymer matrices. The microscopic images of the modified CNC showed better dispersion in toluene than the pristine ones, which can be a result of the reduction in hydrophobic character of CNC [30]. Salon et al. found out that after solvent evaporation, the residual silanol groups may not only undergo further condensation reaction with the hydroxyl groups present in the cellulose surface, but also lead to self-condensation to form polysiloxane network on the solid surface [28]. This phenomenon can severely affect cellulose grafting, since in this system most of the silane linkages are engaged in siloxane bridges. Only the remaining small proportion of silane groups is available to undergo the reaction with the hydroxyl groups on the cellulose surface to yield chemical bonding between the silane coupling agents and cellulose substrate [28]. Qian et al. introduced silane compatibilized (triethoxyvinylsilane, A-151) bamboo cellulose nanowhiskers in poly(lactic acid) (PLA) matrix [31]. The elongation at break of the composites remarkably increased from $12.3 \pm 1.7\%$ (untreated) to $213.8 \pm 21.6\%$ (silane-treated). But there is no clear evidence of the improvement in dispersion of nanowhiskers in the polymer matrix [31]. As silanes are typically used at small addition levels to promote interfacial compatibility because of their high cost and high efficiency, the use of large doses of silane required for good dispersion is not commercially feasible.

3.3 Other chemical treatments

Substitution of the hydroxyl groups of cellulose with anionic-moieties from acid is another common practice of the surface modification of nanocellulose. Dhar et al. produced four varieties of CNC via hydrolysis using different acids with tailored physical, thermal, structural,

and surface characteristics. Here four different types of acids are used: sulfuric acid, hydrochloric acid, phosphoric acid, and nitric acid. All fabricated CNCs show cellulose I crystal structure with different degrees of substitution of the surface hydroxyl groups. CNC-PO₄ and CNC-Cl exhibited hydrophobic behaviour, which facilitated their enhanced dispersion in PLA matrix. The morphological analysis of the CNCs was done by FESEM (Figure 3) and AFM. The variable aspect ratio of different acid-functionalized CNCs affects the mechanical reinforcing efficiency and the crystallization behaviour of the fabricated nanocomposites. The CNC-PO₄ with higher aspect ratio and long needle-like morphology improved the elastic modulus and elongation behaviour of composites [32].

CNCs can also be modified by aliphatic and aromatic isocyanates. Morelli et al. fabricated nanocomposites of poly(butylene adipate-coterephthalate) (PBAT) with 5–10 wt% CNC content via solvent casting technique [33]. In case of the CNCs reacted with aromatic isocyanate (phenyl butyl isocyanate), the PBAT chains were more anchored due to a possible π - π interaction between the polymer aromatic rings and the phenyl rings grafted onto CNCs as shown in the schematic. This rigid percolated network enhanced the elastic modulus and yield stress up to 120 and 40%, respectively, of the composites in comparison to pure PBAT [33].

Acetylation is another popular method of the surface modification of CNMs. Peng et al. synthesized epoxy nanocomposites reinforced with acetyl, hexanoyl, and dodecanoyl-modified CNCs. Electron microscopy (Figure 4) showed that the acetyl-grafted CNC (CNC_a) and hexanoyl-grafted

Figure 3: FESEM micrographs of CNCs modified with different acids: (a) sulfuric acid, (b) hydrochloric acid, (c) phosphoric acid, and (d) nitric acid. Adapted from ref. [32].

Figure 4: Fracture surface of broken tensile specimens of (a) CNC_d, (b) CNC_h, and (c) CNC_a. Adapted from ref. [34].

CNC (CNC_h) had good dispersion in cured epoxy. CNC-reinforced epoxy exhibited highest increase in tensile modulus, tensile strength, and work of fracture [34].

Shojaeiarani et al. used masterbatch preparation techniques (film casting, spin coating) [35–37] for the esterification of CNCs. Though TEM images did not exhibit significant difference between the esterified and unmodified CNCs, there was a reduction in aspect ratio in case of the modified one. These modified CNCs are used as a reinforcement for PLA matrix. The thermal stability and tensile strength of the resultant composites are also enhanced. The spin-coated nanocomposites exhibited higher storage modulus than the film-casted samples in the glassy state.

The main drawbacks of the chemical-aided dispersion techniques are: use of toxic and sometimes expensive chemicals, longer reaction time, critical control of reaction conditions and disposal of chemicals, etc.

Since current research trend is moving towards a ‘green’ era, the eco-friendly or green alternatives to disperse CNMs must come into focus. In the following sections, the novel mechanical/physical approaches to disperse CNMs are discussed in detail.

4 Physical-aided dispersion of CNMs

The chemical treatments are very useful to increase the interfacial compatibility between matrix (especially hydrophobic) and CNMs. In most of the cases, there is a significant increase in thermal stability and tensile properties of the composites. But there is no proper visual or quantitative evidence of the improvement of dispersion state of CNMs. Besides facilitating interfacial interaction, well-aligned and oriented CNMs help to enhance the physical properties of the composites. Moreover, in most of the cases, the chemicals used in the surface treatments of

CNMs are toxic in nature and some are very expensive. Also, these chemical reactions are very sensitive to the reaction conditions such as temperature, pH, moisture, pressure, etc. Thus, finding a green alternative is critical.

Besides forming covalent bonding via chemical modifications, the dispersion state of CNMs can also be improved by physical means such as plasma, electric discharge, magnetic attraction, ultrasonication, drawing, etc.

4.1 Plasma-induced surface modification

Plasma-induced surface modification is a simple, replicable, and efficient method in which a nanometric layer is deposited on the surface of nanoparticles, thus significantly tuning their surface chemistry [38]. Plasma treatment is widely studied to improve surface properties of cellulose films or sheets [39–43]. The plasma treatment of cellulose powders or fibres is a difficult task because of suction, spreading, or limited contact. But submerged liquid plasma (SLP) is a promising route to modify powder or nanomaterials when they are dispersed in liquid [44]. In plasma-induced polymerization, free radicals are generated through electric discharge. Though this technique was previously used for the polymer surface modification, recently this is applied to modify surface chemistry of nanoparticles [45].

Alanis et al. proposed a green alternative to functionalize CNC by means of plasma surface modification utilizing monomers of different nature – caprolactone, styrene, and farnesene [46]. The TEM images exhibited the typical rod-like structure of the modified CNCs, which confirmed that the modification did not affect the natural anisotropic behaviour of the crystals. Moreover, the coating of polycaprolactone (CNC_{Ca}) provided a lower C/O ratio than the other monomers, due to the polyester structure of polycaprolactone [46]. Vizireanu et al. used a combination of SLP and ultrasonication treatment to modify

micro crystalline cellulose (MCC) [47]. SEM images (Figure 5) showed an enhanced defibrillation, with a small increase in aspect ratio (3–7) of MCC compared to pristine MCC. SEM images of fractured composites emphasized better polymer/cellulose interface in case of the plasma-treated MCC containing composites resulting in more effective stress transfer [47]. A study by Panaitescu et al. demonstrated application of plasma torch and filamentary jet plasma, which helped surface chemistry modification of the nanocellulose fibres dispersed in a liquid phase [48]. The plasma treatment was able to remove bonded water and low molecular weight impurities in NC. The plasma treatment facilitated a more homogeneous dispersion of CNCs due to formation of small length nanofibres in higher proportion. Both oxygen and nitrogen functionalization improved adhesion of components in nanocomposites [48]. In another study of Panaitescu et al., poly(3-hydroxybutyrate) was modified by bacterial nanocellulose fibres (BC) using melt compounding and plasma treatment or zinc oxide (ZnO) nanoparticle plasma coating for antibacterial activities [49].

All types of plasma treatments showed an increase in thermal stability of the modified CNCs. In case of ABS matrix nanocomposites, the TGA thermographs showed a decrease in weight loss (%) of the modified CNC at 250°C (onset degradation temperature of cellulose), because of a substantial polymer coating on the surface of nanocrystals [46]. For PHB/MCC composites also, TGA studies confirmed that after 1 h plasma exposure, both the maximum degradation temperature ($T_{\max}$) and onset temperature of

thermal degradation (T_{on}) were decreased [47]. Irrespective of the amount of BC nanofibres, plasma treatment preserved the thermal stability, crystallinity, and melting behaviour of PHB–BC nanocomposites [49]. The viscoelasticity of the materials was also analysed by DMA which exhibited a decrease in the integral area of the loss factor (tan delta), indicating more elastic behaviour of ABS/CNC composites compared to ABS. On the other hand, the storage modulus exhibited an increasing trend compared to the reference material, suggesting an enhanced stiffness of the composite material [46]. The storage modulus of PHB containing 2 wt% BC increased by 19% at room temperature and 43% at 100°C [49]. The higher aspect ratio and the increased surface area of the plasma-treated CNMs could be beneficial to improve mechanical properties of the polymer composites reinforced with nanoparticles. Incorporation of CNC_{Ca} in ABS matrix showed an increment of 114% in the impact strength of composites compared to only 34% increase of the unmodified CNC loaded composites [46]. The PHB/MCC composites exhibited 40% increase in Young's modulus values compared to the composites with untreated MCC [47]. Small amount of plasma functionalized NC increased the tensile strength of the composites up to 10–15% compared to the composites formed with untreated NC [48]. In case of PHB–BC composites, the tensile strength also increased by 21%. In addition, the plasma treatment inhibited the growth of bacteria (*Staphylococcus aureus*, *Escherichia coli*) by 44 and 63%, respectively. In case of ZnO plasma coating, a strong chemical bond was formed between PHB surface and metal oxide nanoparticles [49].

Plasma-induced surface modification techniques significantly contributed towards novel dispersion methods of CNMs. It is a quick, easy, safe, reliable, and replicable method to surface functionalize CNMs and thereby improve dispersion in the polymer matrices. To date, there are many researches on the modification of the surface properties of polymer matrices, but there are very few efforts attributed to the modification of nanoparticles by plasma treatment. Recently, plasma has gained significant attention for the surface functionalization of CNMs. The extent of dispersion of plasma-modified CNMs in polymer matrices and subsequent increase in mechanical properties of composites must be studied more elaborately.

Figure 5: SEM images of fractured samples (a) PHB-MCC Ar, (b) PHB-MCC Ar/N₂, (c) PHB-MCC Ar/O₂, (d) PHB-MCC Ar/CAN. Adapted from ref. [47].

4.2 Ultrasonication

Ultrasonication is another reliable mechanical method to disperse CNCs in liquids. Ultrasonication improves CNCs'

dispersion state in the aqueous suspensions by breaking agglomerates. Efficiency of the ultrasonication is strongly dependent on the power level of the probe, which must be higher than the total energy to favour the dispersion.

Beugel et al. observed a decrease in the average hydrodynamic diameter for CNCs, to a limiting value of ~ 75 nm [50]. The CNC aqueous suspensions showed a decrease in intrinsic viscosity after strong ultrasonication and an increase in maximum packing concentration. This phenomena indicated an increased agglomerate break-up, releasing both ions and water in suspension. The ionic strength increase can produce a thinner electrostatic double layer surrounding the CNC, reducing their apparent concentration [50]. Cao et al. studied the relationship between the CNC dispersion and strength [51]. They examined whether the ultrasonication reduced agglomeration and improved mechanical performance. For the CNCs in DI water, the critical concentration above which the agglomeration started was 1.35 vol%. When the CNCs were placed in a simulated cement pore solution, the critical concentration reduced to 0.18 vol%. After ultrasonication, the dispersion of CNCs improved the strength of the cement pastes by 50%, compared to cement pastes with raw CNCs (only 20–30% increase). It indicated that the dispersion of CNCs is the key to improve the flexural strength of cement pastes with higher CNC concentration [51]. In an article of Li et al., aqueous NCF water suspension was mixed with an aqueous PVA solution (10 wt%) and dispersed via ultrasonication treatment [52]. The mixtures were degassed in a dessicator for film formation. The composite films were fabricated using variable NCF content (0, 2, 4, 8, 12 wt%). The films became increasingly opaque with the increase in NCF content. The SEM cross-sectional image of the PVA/NCF (4 wt%) composite film showed uniform dispersion of NCF in the PVA matrix. At 8 wt% of NCF in the composite, the transmittance was considerably reduced from 92 to 50%, indicating poor dispersion and increased agglomeration of NCFs. The tensile strength and Young's modulus values of the composites increased by 1.86 and 1.63 times compared to the neat PVA, at 4 wt% NCF content. However, both tensile strength and Young's modulus values were decreased, when the NCF content was increased beyond 4 wt%. This is attributed to the increased aggregation of NCFs in PVA, which triggered local concentration of stress, leading to tensile failure [52]. Sinclair et al. extracted cellulose nanofibrils (CNF) from biomass residue [53]. A clear change in transparency was observed (Figure 6) in the aqueous suspension of CNF after ultrasonication [53]. Szymańska-Chargot et al. reported the effect of ultrasonication on the physicochemical

Figure 6: Change in transparency of CNF samples (a) before and (b) after ultrasonication. Adapted from ref. [53].

properties of apple-based nanocellulose fibrils (ACNF)/calcium carbonate (PCC) nanocomposites [54]. The effects of different ultrasonication conditions were studied to evaluate time (0–60 min) and power's (0–400 W) influence on the composite properties. The samples were found to be pseudoplastic fluids, in all cases, with low viscosity. After 60 min of ultrasonication, the mean hydrodynamic diameter of particle dispersions decreased the most and the dispersion was also most homogeneous (Figure 7) [54]. Syafri et al. fabricated a biocomposite comprising the nanocellulose from water hyacinth (*Eichhornia crassipes*) and bengkuang starch using solution casting method [55]. The biocomposite gel ultrasonicated for 60 min showed highest thermal stability and low moisture absorption. The soil burial test proved that this biocomposite sample's biodegradation rate is much slower than the other ones. The morphological evaluation showed that the 60 min vibrated samples had a coarse surface and low porosity [55].

Septevari et al. enhanced the thermal insulation and mechanical properties of a rigid polyurethane foam (RPUF) by incorporating CNC through an optimized solvent-free ultrasonication method [56]. The lowest initial thermal conductivity and best retention of thermal conductivity with ageing were obtained at 0.4 wt% of CNC, with an ultrasonication period of 40 min at an amplitude of 80%. There was a 5% reduction in the initial thermal conductivity of the resultant RPUF, surpassing the effect of the other unmodified nano-nucleating agents (almost double). This happened due to the enhanced compatibility of CNC with the polymer foam matrix [56]. Shojaeiarani et al. studied the effect of ultrasonication amplitude and time on CNC morphology and the dispersion in a water-soluble polymer [57]. The results showed that the measured particle size of CNCs sonicated for longer time (10 min) and higher amplitude

Figure 7: SEM images of ACNF/PCC nanopapers before (top row) and after (middle and bottom row) ultrasonication. The images (middle and bottom row) represent images of composites after use of 80% ultrasonicator power and 30 and 60 min treatment, respectively. Adapted from ref. [54].

(90 μm) was significantly lower than the other samples. Additionally, higher amplitude (90 μm) helped to reduce the length of CNCs by 17% in comparison to lower amplitude (60 μm) samples sonicated for equal time. With the increase of sonication time and amplitude, the crystallinity index of CNC was decreased by 12% as the ultrasound energy destroyed the crystalline structure of CNCs [57].

Ultrasonication is highly effective for low concentration of CNMs. But in case of higher concentration, ultrasonication may fail to improve the CNM dispersion state. Ultrasonication must be studied in further detail to improve its efficiency for the higher concentration of CNMs.

4.3 Magnetic force-induced alignment

CNCs exhibit lyotropic liquid crystalline phase behaviour; i.e. they self-assemble into a cholesteric phase in aqueous medium above the critical concentration. This cholesteric polydomain structure of CNC can be preserved during drying in the presence of a magnetic field [58]. The

diamagnetic susceptibility of CNMs in the direction of the CNM axis is higher than that in the perpendicular axis. In the presence of a magnetic field, the CNMs align perpendicular to the field. Unlike the other methods, an externally applied magnetic field may render itself suitable for industrial-scale production [59].

Li et al. fabricated a unidirectional reinforced nanocomposite paper from CNWs and wood pulp under an externally applied magnetic field [59]. In this article, a 1.2 T magnetic field was applied in order to align the nanowhiskers. Under the influence of a magnetic field, the slender nanowhiskers became aligned perpendicular to the magnetic field due to their anisotropic diamagnetic susceptibility. As a result, the storage modulus along the perpendicular direction became much higher than that parallel to the field. The storage modulus increased from 652 MPa to 4.88 GPa [59]. De France et al. investigated the effects of comparatively weak magnetic fields (0–1.2 T) and CNC concentration (1.65–8.25 wt%) on the kinetics and degree of CNC ordering [60]. CNCs form chiral nematic liquid crystals above a critical concentration (C^*). In a 1.2 T magnetic field for CNC suspensions

Figure 8: Polarized light microscopy images of (a) 5 v/v% CNW-reinforced composite within the magnetic field, (b) 5 v/v% CNW-reinforced composite rotated by 45° to the polarization axis. Adapted from ref. [61].

above C^* , partial alignment was achieved in 2 min and nearly perfect alignment in under 200 min. At 0.56 T, the ordering rate was 36% slower. Outside the magnetic field, the order parameter came down to 52% after 5 h, indicating significant effects of weak magnetic field on CNC alignment. Under C^* , no magnetic alignment was seen [60]. Pullawan et al. investigated the effect of magnetic field on the alignment of CNWs all-cellulose nanocomposites. Tunicate-derived CNWs were incorporated in a cellulose matrix system and magnetic field (1.2 T) was applied during solvent casting to improve their alignment.

CNWs were found to orient themselves in the direction of the magnetic field and eventually increased stiffness and strength of the composites (Figure 8). Low volume fraction of CNWs permitted more degree of freedom and also increased the mechanical properties of the composites. Polarized light microscopy proved that the composites had a domain structure, with some domains showing pronounced orientation [61].

Tatsumi et al. produced anisotropic polymer composites synthesized by immobilized cellulose nanocrystal suspension (CNC) oriented under a magnetic field [62]. CNC suspensions (–6 wt%) in 2-hydroxyethyl methacrylate (HEMA) were separated into an upper isotropic phase and a lower anisotropic (chiral nematic) phase. A static or rotational magnetic field was applied to the system. The structural characterizations (X-ray, optical and scanning electron microscopy) indicated that CNCs of anisotropic

phase were oriented distinctively along the applied magnetic field (Figure 9), while the isotropic ones did not show any specific orientation. In dynamic mechanical experiments (tensile or compressive mode), a clear mechanical anisotropy of polymer composites was observed. A higher modulus (in compression) was also detected for the composites [62].

Magnetic force is an age old method to disperse CNMs. It is a safe, reliable, and industrially scalable technique to disperse CNMs in polymer matrix. The only drawback of this method is that it is only effective at low concentration of CNMs. To make it operative at higher concentration, the behaviour of CNMs under magnetic force must be studied in further details.

4.4 Electric discharge

Although electric field application was widely used to orient nanoscale particles, only a few studies were dedicated to cellulose nanoparticles dispersion. Alignment induced by an electric field is a well-known phenomenon in the cases of liquid crystalline materials, crystalline phases in polymer blends and gels, particles in suspensions, and colloids. Recently, there are some investigations on the influence of an external electric field to align cellulose at macroscopic and colloidal levels. Cellulose must be dispersed in an organic apolar solvent during the application of the electric field [63].

Kadimi et al. studied the effect of electric field on the alignment of nanofibrillated cellulose (NFC) in silicone oil [63]. The magnitude, frequency, and duration of an AC electric field affected the orientation of NFCs of different surface charge density and aspect ratio. Electric field alignment occurred in two steps. First, NFC made a gyratory motion influenced by the dielectrophoretic force (DEP). Second, NFCs interacted with itself to form chains parallel to the electric field lines. When the duration of the electric field was increased, NFC chains

Figure 9: FESEM micrographs of fracture surfaces of polymer nanocomposites (a) lower magnification image, (b) enlarged view and (c) higher magnification image under the influence of an external magnetic field. Adapted from ref. [62].

became thicker and longer. The optimal parameters of alignment were found to be 5,000 Vpp/mm and 10 kHz for the duration of 20 min [63]. Habibi et al. demonstrated that when an alternating voltage is applied to a cellulose nanocrystal suspension (CNC), a highly homogeneous orientation of CNCs is obtained [64]. The parameters of applied electric field such as strength and frequency and CNC aspect ratios affect the orientation and CNC assembly. The orientation of CNCs (Figure 10) becomes more homogeneous with electric field higher than 2,000 V/cm with a frequency range of 10^4 – 10^6 Hz [64]. Ten et al. explained how CNWs in a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) matrix were aligned by an external electric field [65]. During solvent evaporation, a DC electric field of 56.25 kV/m was applied. Dynamic mechanical analysis results showed that CNW concentration had a strong influence on the degree of CNW alignment. The electric field remained effective up to 4 wt% CNW concentration. Samples with higher concentration of CNW showed virtually isotropic behaviour. This indicated significant restraints on CNW mobility attributed to CNW/CNW or CNW/polymer interaction [65].

Electric discharge is an established technique to disperse inorganic nanoparticles, but recently it is applied to align CNMs. The electric field parameters and nature of the field significantly influence the alignment of CNMs in a polymer matrix. Also, CNM aspect ratios and concentration affect their orientation behaviour under the electric field. These aforesaid parameters must be studied elaborately to make this method more effective and industrially scalable.

4.5 Electrospinning

Electrospinning is one of the most powerful methods to produce fibres from micro to nano range and fabricate

Figure 10: AFM image of electric field-oriented CNC films. Adapted from ref. [64].

polymer nanocomposites. This method has advantages such as high quality, low cost, wide material suitability, and consistent nanofibre quality. Lee et al. described the reaction mechanism of a classic electrospinning setup. A charged droplet of polymer solution is held at the tip of a fine capillary [66]. During jet initiation, an electric field is applied to the polymer droplet which helps to overcome the surface tension and elongate the polymer droplet to form a conical shape named Taylor cone. When a critical electric field intensity is achieved, the electric forces overcome the surface tension and result in a forcible ejection of polymer jet. Therefore, there are complex electrohydrodynamic and rheological interactions acting on each other [66].

Cai et al. fabricated uniaxially aligned cellulose nanofibres (CNFs) by electrospinning of the cellulose acetate derived from bamboo cellulose (B-CA) and used those CNFs as reinforcements to make optically transparent composite films [67]. The B-CA concentration and electrospinning parameters (e.g. spinning distance and collection speed) were investigated for their effects on the fibre morphology and orientation (Figure 11). The improvement in interfacial interactions facilitated the effective stress transfer from polymer matrix to fibres, which in turn enhanced the overall stiffness and mechanical strength of the composite films. The resultant composite films also showed high visible light transmittance even with a high fibre content [67]. He et al. fabricated electrospun nanocomposite nanofibres using uniaxially aligned cellulose nanofibres with CNC as a reinforcement (CNF/CNC) [68].

The micrographs showed (Figure 12) that most CNFs were uniaxially aligned and CNCs were well-dispersed in the non-wovens and achieved considerable orientation in the long axis direction. This unique hierarchical microstructure of the produced nanocomposites gave rise to remarkable enhancement of the physical properties of the composites. By incorporating 20% (w/w) CNCs, the tensile strength and elastic modulus along the fibre axis direction increased by 101.7 and 171.6%, respectively [68]. Liao et al. fabricated optically transparent epoxy resin nanocomposite films reinforced with electrospun cellulose nanofibrous mats by solution impregnation method [69]. SEM micrographs showed indistinct epoxy/fibre interfaces, epoxy beads adhered on the fibre surfaces,

Figure 11: SEM images of (a) aligned B-CA nanofibres and (b) CNFs after regeneration. Adapted from ref. [67].

Figure 12: SEM images of CNF/CNC nanocomposite nanofibres: (a) 0% CNC, (b) 5% CNC, (c) 12.5% CNC, and (d) 20% CNC. Adapted from ref. [68].

and torn fibre remnants were on the fractured composite film surfaces. So, the epoxy resin and cellulose fibres formed good interfacial adherence through hydrogen bonding. The mechanical strength and Young's modulus also increased by 71 and 61%, respectively [69]. Song et al. investigated the effect of electrospinning on the liquid crystal orientation of CNCs and fibre alignment under high voltage electric field [70]. The composite nanofibres selectively reflected frequent and continuous birefringence, regarded as nematic phases of CNCs, induced by uniaxial stretching under the high voltage electric field. The synergistic effect of the rigidity of the nanocrystals and stretching orientation of the nematic phases provided higher tensile strength and strain to the aligned nanofibrous mats compared to the randomly oriented or core-sheath nanofibrous mats at the same loading of CNC [70].

The uniaxial stretching under high voltage electric field of CNMs during electrospinning facilitates their orientation and thereby enhances the physical properties of the resultant composites. There are several studies on uniaxial alignment of nanofibrous polymer mats during electrospinning, but little attention is attributed to the alignment of reinforcements (CNMs). Therefore, there is a great scope to investigate the effect of electrospinning process parameters on the CNM alignment and the overall effect on nanocomposite properties.

4.6 Drawing

Drawing is an established technique to align the fibres or nanoparticles in the drawing axis direction. There are different types of drawing (hot/cold) depending on the material and process conditions. In a drawing method, there exists a difference in speed which produces sufficient shear force to forcibly align the fibres or nanoparticles along the drawing direction.

Lee et al. fabricated high-performance CNC/PVOH composite fibres via coaxial coagulation spinning, followed

by hot-drawing [71]. Drawing condensed the fibre and increased the alignment of both CNC and polymer in the fibre direction as indicated by the X-ray diffraction patterns. The individual CNCs remained well-dispersed in the composite at loadings up to 40 wt%. At 40 wt% CNC loading, the tensile strength and stiffness reached up to 880 MPa and 29.9 GPa, respectively [71]. Wang et al. established an effective drawing procedure that induced a high degree of orientation of CNCs in a matrix of carboxymethyl-cellulose at a high level of reinforcement (50 vol%) [72]. Scanning electron microscopy (SEM) and two-dimensional X-ray diffraction (Figure 13) quantify the alignment of CNCs. The improvement in alignment showed a synergistic increase in the stiffness, strength, and toughness at the same composition. The composites showed stiffness greater than 10 GPa and tensile strength of 125 MPa at 90% R.H. [72]. Singh et al. studied the effects of drawing

Figure 13: SEM images of a fractured cross section of a drawn and strongly aligned film, DR = 2.5, acquired (a) perpendicular to and (b) within the drawing direction (scale bars are 500 nm), 2D WAXD data to characterize the extent of alignment, (c) DR = 2.5. (d) Orientation index, π , and order parameter, S , as a function of DR, establishing a direct link between drawing and orientation of the reinforcements. Adapted from ref. [72].

conditions (temperature, speed, and draw ratio) on the composite tapes of plasticized polylactic acid (PLA)/CNF (1 wt%) prepared using uniaxial solid-state drawing [73]. Microscopy studies confirmed the orientation of the macromolecular chains perpendicular to the draw direction, indicating the formation of ‘shish-kebab’ morphology. Improved mechanical properties and toughness up to 60 times compared to the undrawn composites were observed. The drawing also improved thermomechanical properties. The storage modulus increased and the tan delta peak shifted towards higher temperature, broadened, and decreased in height with increasing draw ratio and drawing speed [73]. Wang et al. established an effective fabrication method for producing high-performance macrofibres from ultralong bacterial nanocellulose fibres (BC fibres) via wet-drawing and wet-twisting process [74]. The as-prepared BC fibres without wet-drawing showed rough and undulated surfaces, which was composed of randomly oriented nanofibre bundles. But, the surface roughness was significantly reduced in case of 30% wet-drawing strain fibres. The glossy surface was attributed to the closely packed nanofibres with reduced porosity and orientation along the fibre axis direction. The resulting macrofibres yielded tensile strength as high as 826 MPa and Young’s modulus of 65.7 GPa. The specific tensile strength of the macrofibres ($598 \text{ MPa g}^{-1} \text{ cm}^3$) was even higher than novel lightweight steel ($227 \text{ MPa g}^{-1} \text{ cm}^3$) [74]. Sehaqui et al. reported a preparation route of nanocomposite made of nanofibrillated cellulose (TEMPO-NFC)/hydroxyethyl cellulose (HEC) by cold drawing [75]. The AFM images (Figure 14) clearly showed the preferential orientation of fibrils parallel to the direction of drawing. At high draw ratio, the degree of orientation became as high as 82 and 89% in the plane and cross-sectional planes, respectively. The mechanical properties improved and tensile strength increased to 430 MPa and modulus to 33 GPa [75].

Figure 14: AFM micrographs of surfaces of (a) a reference undrawn TEMPO-NFC nanopaper sample ($DR = 1$), (b) a drawn TEMPO-NFC nanopaper at $DR = 1.4$. Adapted from ref. [75].

Drawing can significantly improve alignment of CNMs in polymer matrices and thereby enhance the overall physical properties of the composites. The drawing parameters (temperature, speed, draw ratio) affect the extent of drawing and eventually the resultant physical properties of the composites. There are several articles on drawing of CNMs as building blocks, but lesser effort is attributed to the drawing of the CNMs as reinforcements. Therefore, there is a great opportunity to investigate the effects of drawing on the CNMs as reinforcement materials of the polymer composites.

4.7 Quantum dot (QD) treatment

Enzymes, mainly composed of proteins or catalytic RNA molecules, are powerful biocatalysts and have been widely used in industrial, medical, and biological fields. However, because of significant drawbacks of natural enzymes for practical purposes (high cost for preparation and purification, low operational stability, sensitivity to environmental conditions, difficulties in recycling and reusing), researchers now shifted their focus to alternatives. Nanozymes are emerging as a new class of nanomaterials with nanoscale sizes (1–100 nm) and enzymatic catalytic properties. The nanoparticles (NPs) have garnered special attention because of their facile synthesis process, simple biofunctionalization, wide range of temperature stability, and dimensional and morphological tunability. The decrease in dimensions of NPs increases their enzymatic activities because of the larger surface area available. QDs are member of an extremely small class of nanomaterials (typically 2–10 nm diameter) and used for conventional fluorescence-based applications. But their enzymatic activity is yet to be explored and can facilitate significant improvement of sensing applications [76,77]. For the last two decades, researchers presented facile approaches to construct hybrid nanomaterials composed of CNMs/metal quantum dots. There are several research papers on the application of these hybrid nanomaterials (CNC-CdSe/ZnS, CNF/CdTe, CNF/CdS) in bioimaging, biosensing, tissue engineering, etc. [78–80]. Compared to traditional metal-based QDs, carbon quantum dots (CQDs) and graphene quantum dots (GQDs) (Figure 15) have distinct advantages such as low toxicity, biocompatibility, renewability, low cost, and better chemical resistance [77].

GQDs possess one or few layers of graphene and connected chemical groups on edges. They are anisotropic in nature having lateral dimensions larger than their height [81]. Sekiya et al. explained the structural characteristics

Figure 15: (a) AFM image of GQDs, (b) AFM image of CQDs. Adapted from ref. [83] and ref. [85], respectively.

of GQDs [82]. GQDs are amphiphilic in nature, having hydrophobic character in their basal plane and hydrophilic on the edges as a result of the presence of carboxylic acid groups [82]. CQDs are always spherical and have an obvious crystal lattice. In the article of Zhu et al., many approaches to fabricate GQDs and CQDs are elaborated, most popular of which are ‘top down’ cutting from different carbon sources and ‘bottom up’ synthesis from organic molecules or polymers [81]. Khabibullin et al. fabricated an injectable shear-thinning hydrogel from CNC and GQDs [83]. CNCs and GQDs can exhibit hydrophobic interactions and form hydrogen bonds between the surface hydroxyl groups present in CNC and carboxylic acid groups of GQDs. Moreover, CNCs carry a negative charge on their surface because of the carboxylic groups [83]. Thus, GQDs and CNCs exhibit mutual electrostatic repulsion, which in turn can improve dispersion of CNCs in polymer matrix. Guo et al. [84] and Junka et al. [85] explained the reaction mechanism of CQDs with CNMs. In case of CQDs, there is an electrostatic attraction between the two oppositely charged nanoparticles: positively charged CQDs and negatively charged CNMs. Generally, the covalent coupling reaction between the CQDs and CNMs is assisted by EDC/NHS chemistry. This reaction is affected by change in pH. At neutral and acidic pH, CQDs are positively charged. But, at alkaline conditions, CQDs become uncharged and result in a reduced electrostatic interaction [84,85]. Therefore, surface functionalization of CNMs by CQDs/GQDs can be the future path to effectively disperse CNMs in the polymer matrices and eventually improve the physical properties of the polymer nanocomposites.

5 Conclusion and future direction

There exist many challenges in the production of CNM/thermoplastic polymer composites. For example, agglomeration

of CNMs during drying, insufficient interfacial compatibility between CNMs and the matrices, and degradation of CNMs during processing. Physical form of CNMs also plays a very significant role in their dispersion. Achieving optimum dispersion of CNMs is very difficult and success depends on multiple efforts attributed to the complexity of the entire process. Both chemical and physical surface treatments have been demonstrated to assist in the dispersion of CNMs in polymer matrix. In case of chemical-aided dispersion techniques, polymer grafting, silylation, acid and isocyanate treatment, and acetylation or esterification methods improve mechanical performance of the composites. All these are expected to be industrially scalable techniques. Moreover, silylation is a water/alcohol-based system and esterification can be done in a solvent-free reaction medium, which makes them eco-friendly. But there is no visual evidence of improvement in CNM dispersion in any of the aforesaid methods, except polymer grafting. Use of organic solvents makes polymer grafting non-eco-friendly. Silanes are expensive chemicals and acid and isocyanate treatments involve use of highly corrosive and toxic chemicals. In case of physical-aided dispersion techniques, plasma-induced surface modification, ultrasonication, magnetic force, electric discharge, electrospinning, and drawing can visibly improve dispersion or orientation of CNMs in the polymer matrix. Also, mechanical properties of the composites are enhanced in these techniques. Plasma, magnetic force, and electric discharge are very quick methods. Electrospinning provides acute control over process parameters which in turn gives consistent product quality. However, ultrasonication and magnetic force are only effective in low concentration of CNMs, till now. Electric discharge and ultrasonication both are energy-consuming methods and ultrasonication is a time-consuming one. Plasma involves expensive equipment. Electrospinning requires trained personnel for setup. This method also involves use of organic solvents in some cases. In drawing, drawing parameters (draw ratio, speed) and environmental conditions (humidity, temperature) may affect the efficiency of the method. All these physical dispersion techniques are not fully explored to make them industrially scalable. It appears that a combination of chemical and physical treatment can solve this problem at lab scale and at industrial scale. The quantum dots (QDs) are an emerging class of materials which can fine-tune the surface properties of CNMs by complex electrostatic interaction and surface chemistry. The comparatively new (discovered in 2004) CQDs and GQDs can be the flagship of the quantum dots treatment, avoiding the toxicity and other limitations of the conventional metal QDs. As CQDs/GQDs are compatible with both CNMs and polymer matrix

(hydrophobic and hydrophilic), they can prove to be a successful path to improve both the interfacial interaction between CNMs and polymer and the dispersion state of CNMs.

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