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of Graphene-, Graphene Oxide- and Reduced Graphene Oxide-Doped Microfibrillated Cellulose Nanocomposites

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Abstract

Micro- nanofibrillated cellulose (MFC/NFC) and graphene-based materials are interesting materials due to their complementary functional properties, opening up potential in a variety of applications. Graphene, graphene oxide (GO) and reduced graphene oxide (RGO) were used in this comparative study as reinforcement functional fillers for the fabrication of multifunctional MFC nanocomposites using a simple aqueous dispersion based mixing method. The MFC composites showed different properties depending on the type of filler used. Graphene was seen to agglomerate and was poorly dispersed in the MFC matrix, whilst GO and RGO were homogeneously dispersed due to the presence of functional groups that promoted a strong interfacial molecular interaction between the filler and the MFC matrix. At 0.6 wt% filler loading, the tensile strength for MFC/GO and MFC/RGO increased by 17% and 22%, respectively, whilst the Young's modulus increased from 18 GPa to 21 GPa and 25 GPa, respectively. Compared to the neat MFC, addition of 5 wt% of graphene enhanced the thermal stability by 5% and whilst with the addition of GO and RGO stability increased by 2 and 3%, respectively. Graphene/MFC and RGO/MFC showed a high electrical conductivity of 1.7 S/m and 0.5 S/m, respectively while the GO reinforced composites were insulators.

Keywords: Micro and nanofibrillated cellulose; graphene; graphene oxide; reduced graphene oxide; nanocomposites; electrical conductivity

1. Introduction

Cellulose is the most abundant and sustainable natural biopolymer on the planet. It is comparatively inexpensive, biodegradable, renewable and non-toxic. Cellulose originates from renewable materials such as wood, cotton, hemp etc. Cellulose can easily be processed into different forms such as micro nanofibrillated cellulose (MNFC), dissolved polymers, macro and nanofibres by enzymatic, chemical and mechanical processes [1-4]. MNFC exhibits unique properties, such as high oxygen barrier, high tensile strength and stiffness, lightweight, transparency, biocompatibility and biodegradability [5-7]. As such, MNFC has huge potential to be utilised in various applications, including nanocomposites, functional nanopapers, hydrogels in biomedicine, aerogels and foams for structural insulating materials and barrier membranes for packaging [1,3,8] just to name a few. The use of MNFC, particularly in nanocomposite materials has also gained some interest. This is because the surface of MNFC contains an abundance of hydroxyl groups, which in turn might be used to promote strong binding interaction and a homogeneous dispersion of MNFC with various reinforcement fillers or polymers *via* grafting, for example. The strong interfacial interaction of the filler and polymer matrix enhances the overall properties of the nanocomposite material. However, high moisture absorption, low processing temperature and poor wet strength are the main challenges for using MNFC for reinforcement applications [9].

Graphene is a 2-dimensional single layer of carbon atoms with exceptional properties. Defect free graphene possesses an extremely high electron mobility, more than $200\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ at room temperature at electron densities of over $2 \times 10^{11}\text{ cm}^{-2}$ [10,11], which is much greater than the values that can be observed in semiconductors or metals [12]. Graphene also poses a high theoretical surface area of $2\,630\text{ m}^2\text{ g}^{-1}$ [13], excellent thermal conductivity ($5\,000\text{ W m}^{-1}\text{ K}^{-1}$) [14], very high light transmittance $\sim 98\%$ [15] and is one of the strongest materials known, with a Young's modulus reaching $1\,100\text{ GPa}$ (~ 200 times stronger than steel) and fracture strength of about 125 GPa [16]. Due

to these excellent properties, graphene and its derivatives, in particular graphene oxide (GO) and reduced graphene oxide (RGO), have found interesting applications in nanocomposites, energy storage devices, transparent films, printable electronics, catalysts, sensors etc. [17-21]

The 2D platelet structure of graphene, particularly due to its high aspect ratio (platelet diameter to thickness ratio), makes it an ideal filler option to enhance the mechanical, electrical and thermal properties of nanocomposite materials at much lower loading than is used for typical mineral-based fillers. The control of the surface chemistry of graphene is vital for achieving a homogeneous incorporation of graphene into the polymer or suspension matrix. Pristine graphene, produced by liquid phase exfoliation from natural graphite flakes, for example, does not contain active reactive sites. Therefore, in theory, it is not the best option in its pure form to be used as a filler especially in natural polymer composites because of the challenges in achieving a homogeneous nano-dispersion in the polymer matrix [22].

GO and RGO have been widely considered as good reinforcements for nanocomposite materials [22,23]. GO is produced by exfoliation of graphite oxide and RGO by reduction of GO. The fabrication of graphite oxide is achieved mainly by the Hummer's, Brodie's or Staudenmaier's method [24-26]. These methods involve intercalation of graphite with an oxidant, which introduces functional oxygen groups, hydroxyl or epoxide groups in the basal plane and carbonyl and carboxylic moieties on the edges [27]. After oxidation, graphite oxide is dispersed in water and subjected to sonication or shearing, resulting in individual dispersed graphene oxide sheets that are homogeneously dispersed in water. The functional groups that are introduced by oxidation of graphite help to disperse and stabilise graphene oxide in water [28]. RGO is produced by reduction of GO using various methods including reducing agents. However, some of the functional oxygen groups remain on the surface and edges of graphene even after reduction [29]. Therefore, due to these functionalities, GO and RGO are widely utilised in nanocomposite fabrication due to their high compatibility with various polymer matrices.

However, harsh oxidation conditions introduce irreversible deformation in the filler that modifies the mechanical and electrical properties, and thus GO and RGO do not possess the same high-level properties exhibited by pristine graphene.

Fabrication of functional graphene nanocomposite materials based on renewable and natural polymers is of importance, and is desirable for a variety of applications, not only for economical or ecological reasons but also for high efficiency and productivity. To derive the best properties, compatibility between the filler and polymer matrix, namely the filler dispersibility in the polymer (aqueous suspension of cellulose polymer fibrils in the current case), filler and matrix bonding, ratio of filler to matrix and the quality of graphene filler and polymer matrix, is very important. These parameters are thoroughly investigated in this study by using three different graphene based fillers, which, in principle, could provide different properties to the composites and can be tailored for specific applications, and combining the two materials in composite fabrication can lead to enhanced functional properties that, subsequently, can be used in potentially wide-ranging applications.

The objective of this study is to make a comprehensive comparative study of pristine graphene, GO and RGO in MFC forming composites using a simple dispersion mixing technique that is viable for large scale application, and investigate how they affect the mechanical reinforcement, electrical and thermal properties.

2. Experimental

2.1. Materials

Natural graphite flakes, sodium cholate (NaC), hydrochloric acid (36 wt%), sulphuric acid (95-97 %), ascorbic acid (≥ 99 %), sodium hydroxide (1 M) were purchased from Sigma Aldrich. Potassium permanganate (99 %) was supplied by J.T. Baker, and hydrogen peroxide (30 %) by VWR Chemicals.

MFC (derived from hardwood Kraft pulp 5 %) was provided by Suzano Pulp and Paper and used as received. Some measured basic MFC properties are shown in Table 1.

2.2. Characterisation of MFC

The shear viscosity of diluted MFC suspension was measured by a Brookfield viscometer, model DV2TRV Extra, using a V-72 vane spindle at 1.5 % solids (consistency). Spectroscopic transmittance was measured using a Shimadzu UV-Vis spectrophotometer 2550 at wavelengths 200 – 900 nm at 0.1 % MFC consistency. The experiments were conducted according to the procedures given by Kangas *et al.* [30].

Zeta-potential was measured using a Zetasizer Nano ZS Instrument (Malvern Instruments Ltd) at 0.1 % MFC consistency. To measure the water retention value (WRV), MFC was mixed with pulp and adjusted to 10 % consistency. The full experimental details for WRV measurements can be found in the study reported by Maloney [31]. All the chemicals were used without modification. Deionised (DI) water was used throughout the experiments.

2.3. Preparation of graphene, GO and RGO dispersions

Pristine graphene was prepared by shear exfoliation using an IKA Magic Lab (1-l module micro-plant equipped with a single-walled open 1 dm³ vessel). A detailed experimental description was reported in our earlier study [32]. Briefly, natural graphite flakes were dispersed in sodium cholate (NaC) aqueous solution ($C_{\text{NaC}} = 1 \text{ mg cm}^{-3}$) at a concentration of 40 mg cm⁻³. The graphite dispersion was then subjected to shear exfoliation for 1 h followed by centrifugation for 60 min at a rotation speed of 4 700 min⁻¹ (rpm) in a Thermo Scientific centrifuge SL40FR to remove all unexfoliated graphite flakes. The supernatant was carefully collected and used for further study.

GO and RGO were prepared using a modified Hummers method. Concentrated sulphuric acid (200 cm^3) was added to a $1\,000\text{ cm}^3$ flask immersed in an ice bath. Then, 10 g of graphite flakes were added with continuous stirring. After 5 min of mixing, 30 g of potassium permanganate was slowly added to the mixture to keep the temperature around $15\text{ }^\circ\text{C}$. The ice bath was then removed and stirring continued for 30 min. The mixture was then heated to around $40\text{ }^\circ\text{C}$ in a water bath and kept for 2 h. Next, the mixture was cooled down to room temperature followed by the additional of 200 cm^3 DI water that led to an exothermic reaction and the rise of temperature to about $80\text{ }^\circ\text{C}$. The mixture was again transferred to a water bath at $95\text{ }^\circ\text{C}$ and kept for 90 min. After cooling down to room temperature, the mixture was divided into two batches for the preparation of GO and RGO, respectively.

To prepare GO, 25 cm^3 of hydrogen peroxide (30 %) was injected into the batch followed by the addition of 250 cm^3 DI water. The product was filtered and washed with 10 % HCl followed by DI water until neutral pH was reached. Graphite oxide powder was obtained after vacuum freeze-drying. To prepare RGO, excess sulphuric acid from the second batch was filtered off and the pH of the mixture was adjusted to 7-8 using sodium hydroxide. Then, 40 g of ascorbic acid was dissolved in 200 cm^3 DI water and subsequently added to the mixture. The mixture was transferred to a water bath and heated at $95\text{--}98\text{ }^\circ\text{C}$ for 2 h to reduce GO to RGO. The mixture, still immersed in a water bath was left overnight to cool down. The mixture was then vacuum filtered, washed with hydrochloric acid followed by DI water until neutral pH was reached. To obtain RGO powder, the filtered mixture was dried by vacuum freeze-drying. GO and RGO dispersions were prepared in DI water using the same method described above for pristine graphene.

2.4. Preparation of composite sheets

The respective dispersions of graphene, GO and RGO were mixed with MFC suspensions in various proportions to yield a solid filler content of 0.3, 0.6, 1, 3, 5, 7 and 9 wt% with respect to that of

solid MFC. The composite sheets were prepared using a modified laboratory hand-sheet former with a pressurised top chamber. The final consistency of the suspensions prior to composite sheet forming was about 0.7 wt%. This ensured that the suspensions could be spread easily over the dewatering screen. A nylon membrane with 1 μm mesh openings was placed on top of the conventional steel wire to prevent excessive loss of material. Enough suspension was added to the forming device to reach a final basis weight of 80-85 g m^{-2} . To ensure complete drainage of water from the sheets, the dewatering time was set to be 12 min using a 50 kPa overpressure. To prevent shrinkage during drying, the sheets were removed from the hand sheet former and put between two steel mesh wires. Two blotting papers were then placed on the outside of the sandwich structure. The sheets were subsequently dried in a hot press at 120 °C for 10 min applying a pressure of about 50 kPa. The composites were then stored in a controlled atmosphere before mechanical testing.

2.5. Characterisation methods

2.5.1. UV-Vis spectroscopy

UV-Vis measurements were carried out using a Shimadzu UV-Vis spectrophotometer 2550 at wavelengths 200 – 800 nm. The dispersions were controllably diluted before the measurements.

2.5.2. Scanning electron microscopy (SEM)

The structure, and morphology, of the composite sheets was recorded using a Zeiss Sigma VP scanning electron microscope at 2 kV acceleration voltage. The films were first sputtered with a platinum film before SEM measurements.

2.5.3. Paper formation index measurements

The local grammage variation of the composite sheets was measured by a SCAN-test method based on beta ray absorption using a Beta Formation Tester (Ambertec, Finland). For each sample, 400 points with a step of 1 mm in both x and y -directions on the sheet, covering an area of $19 \times 19 \text{ mm}^2$,

were measured. A lower number of formation indicates greater uniformity. Specific formation F_{1g} ($= \frac{F_{1g}}{\sqrt{w}}$), in $\sqrt{g} \text{ m}^{-1}$, is derived from the formation number F_{1g} , in g m^{-2} , normalised with respect to the square root of the sheet grammage w , in g m^{-2} .

2.5.4. Attenuated total reflectance infrared spectroscopy (ATR-FTIR)

The chemical structure of the sheets was observed using a Unicam Mattson 3000 FTIR spectrometer equipped with PIKE Technologies GladiATR (with diamond crystal plate). All spectra were scanned within the range $400 - 4\,000 \text{ cm}^{-1}$, with 16 scans and a resolution of 32 cm^{-1} .

2.5.5. Raman analysis

Raman spectra were measured using a WITec alpha300 R Raman microscope (alpha 300, WITec, Ulm, Germany) equipped with a piezoelectric scanner using a 532 nm linear polarised excitation laser. The samples were prepared by vacuum filtering of the graphene, GO and RGO colloidal suspensions onto filter membranes then washed with water to remove impurities and dried at 40°C in a vacuum for 24 h.

2.5.6. X-ray photoelectron spectroscopy (XPS)

The surface chemical composition of graphite, GO and RGO sheets as well as the 9 wt% filler loaded MFC composites were analysed with XPS, using an AXIS Ultra spectrometer with monochromatic Al K α irradiation at 100 W, under neutralisation. Pure cellulose filter paper (Whatman) was measured with every sample batch as an in-situ reference for XPS experiments; in this study, it was also used as a reference for neat cellulose. Before the measurements, the samples were pre-evacuated overnight. Survey scans as well as C 1s and O 1s high-resolution regions were acquired from 2-3 locations; the area of analysis area was less than 1 mm^2 while the analysis depth is necessarily typically less than 10 nm. CasaXPS software was utilised in data analysis, in which the carbon and oxygen contents were each determined from survey scans, while carbon high-resolution data were utilised in further chemical analysis; for the fitting parameters, see reference [33].

2.5.7. Thermogravimetric and differential analysis (TGA)

The thermal stability of the composites was characterised by thermogravimetric analysis (TA Instruments Q500). All measurements were conducted under a nitrogen flow rate of $60 \text{ cm}^3 \text{ min}^{-1}$ over a temperature range of $25\text{--}800 \text{ }^\circ\text{C}$ with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$.

2.5.8. Mechanical properties

The mechanical properties of the composite sheets were measured with an MTS-400/M testing system equipped with a 200 N cell load. The gap length was set to 5 cm and elongation rate to 12 mm min^{-1} . Eight strips with dimensions $70 \times 15 \text{ mm}^2$ were cut from the sheet and used for measurements for each test point. Prior to the measurements, the samples were stored in a controlled atmosphere ($23 \text{ }^\circ\text{C}$; 50 % RH) for 48 h.

2.5.9. Electrical conductivity

Electrical conductivity of the composite sheets was measured with a four-point probe method (Jandel RM3000: Jandel Engineering Ltd.). The measured resistance was converted to sheet resistance, $R_s \text{ } \Omega \text{ sq.}^{-1}$, and the specific resistance, ρ , was then calculated from $\rho = R_s \times t$, where t is the film thickness in cm, and subsequently the corresponding electrical conductivity, $\sigma = 1/\rho \text{ (S cm}^{-1}\text{)}$ was calculated.

3. Results and discussion

The dispersions of graphene, GO and RGO were prepared *via* shear exfoliation. We showed in our earlier study [32] that shear exfoliation is an effective method for fabrication of high quality and high concentration graphene colloidal dispersions. Successful exfoliation of graphene, GO and RGO was characterised by UV-vis and Raman spectroscopy, Figure 1. The UV-Vis spectra of the studied materials are shown in Figure 1A. These are typical and distinct spectra for quasi two-dimensional materials, and are consistent with exfoliation of graphite to graphene. As expected, the spectra for all systems are featureless and flat in the visible region and a maximum absorption is only observed at around 269 nm for graphene and RGO. The maximum absorption peak for graphene is attributed to the $\pi \rightarrow \pi^*$ transitions of aromatic C–C bonds [34]. In GO, this peak is observed at ~ 231 nm and another at ~ 310 nm due to the $n \rightarrow \pi^*$ transition of the C=O bonds [35]. The red shift at 269 nm for RGO is due to the restoration of sp^2 hybridisation of carbon atoms and increased concentration of π -electrons [36] which confirms the successful reduction of GO to RGO.

The Raman spectra of graphene, GO and RGO are presented in Figure 1B. Raman spectroscopy can be used to analyse crystal structure and disorder of carbon based materials. Analysis of the spectra of GO and RGO shows that the D and G bands of graphene, which were observed at around $1\,338.5\text{ cm}^{-1}$ (D) and $1\,570.9\text{ cm}^{-1}$ (G) for graphene shifted to $1\,345.9\text{ cm}^{-1}$ (D) and $1\,594.7\text{ cm}^{-1}$ (G) for GO, and $1\,336.1\text{ cm}^{-1}$ (D) and $1\,573.3\text{ cm}^{-1}$ (G) for RGO. Unsurprisingly, the intensity ratio of the D band and G band, I_D/I_G , shows that the quantity of defects is higher for both GO and RGO when compared to graphene. The defects introduced by oxidation of graphite are both basal and edge defects, which is evident by the high intensity of the D-band as well as the broadening and shifting of the G-band, while in graphene only edge defects are found [32]. The intensity of the D-band is related to the size of sp^2 domains, and the observed increase in the D-band for RGO after reduction of GO is indicative of

formation of more sp^2 graphitic domains [37]. This is also conclusive evidence of successful reduction of GO to RGO. Similar results were also observed in this study [38].

To develop the best properties of the nanocomposites, the filler must be homogeneously dispersed in the polymer suspension matrix. This distribution can be correlated with the sheet formation. A beta ray absorption device from Ambertec was used to measure the formation of the sheets. The results in Figure 2 show that the best formation or mass distribution in MFC was achieved by GO and RGO. The homogeneous mass distribution of hydrophilic GO in the MFC matrix is attributed to the initial wettability and subsequent hydrogen bonding that occurs between the oxygen functionalities of GO and MFC. RGO still retains many oxygen functionalities even after reduction [22,39], which also promote better distribution in the MFC matrix. However, the pristine graphene distribution in the MFC matrix is poor, as is to be expected due to its hydrophobic nature that leads to hydrophobic association and aggregation in the aqueous system. Clumping and inhomogeneous dispersion of graphene is clearly visible in the photographs in Figure 2A, especially at 1 wt% graphene loading.

The FTIR analysis (Figure 2C) also confirms the presence of oxygen functionalities that promote homogeneous dispersion for GO and RGO in the MFC matrix. The broad bands observed at 3 349 cm^{-1} and 1 402 cm^{-1} correspond to the O-H stretching and deformation vibration mode of intercalated water. The peak at 1 716 cm^{-1} is related to the C=O stretching vibration of carboxylic moieties at the edges of GO [40], while the peak at 1 618 cm^{-1} corresponds to the carbonyl moieties. The stretching vibration peaks of C–O (epoxy) and C–O (alkoxy) are observed at 1 036 and 965 cm^{-1} , respectively. For RGO, however, the reduction process either eliminated or significantly reduced the intensity of the groups, thus additionally confirming successful reduction of GO [41]. No significant peaks relevant to any functional groups are observed in pristine graphene, as has been reported also by others [42,43].

XPS was also employed to analyse the structure of graphene, GO and RGO with their respective composites with MFC. Figure 3A and B show the XPS spectra together with high resolution C1s ratio of graphene, GO and RGO (Figure 3A), with their corresponding MFC composites at 9 wt% filler loading (Figure 3B). In the case of neat graphitic films, successful oxidation is shown in terms of the significant increase in the surface oxygen content (from 8 to 24 at%) and the appearance of oxidised carbon species in the C 1s high resolution region (Figure 3A and 3A insert). Reduction of the GO is seen also clearly as oxygen content is decreased down to 17 at%, and the high resolution carbon spectra loses almost all features from the oxidised carbon species.

In the case of composite materials, differences between samples with non-oxidised and oxidised graphene at 9 wt% loadings vanish, and all composites show predominantly cellulosic features, see Figure 3B. However, when compared to neat cellulose, the CC component, i.e. photoelectrons coming from carbon atoms without oxygen neighbors is significantly increased for all the composites, indicating a strong presence of non-cellulosic carbon at the film surface even at only 9 wt% loading of either graphene, GO or RGO.

Figure 4 shows the tensile stress against strain curves for the MFC nanocomposite films doped with different concentrations of RGO (Figure 4A), GO (Figure 4B) and graphene (Figure 4C). The neat MFC films can withstand a stress of ~100 MPa with a 2.8 % elongation, while with an additional of 9 wt% of graphene, GO and RGO, 55 MPa (2 %), 98 MPa (3.2 %) and 130 MPa (3.9 %), respectively (in brackets, elongation at break). Incorporation of graphene, GO and RGO into the MFC matrix plays a significant role in the mechanical performance of the composite films. It is clear from Figure 5A that, there is a general overall increase of the tensile strain at break and tensile strength with the addition of RGO and GO into the composite materials, and decreases with the addition of graphene. For example, at 0.6 wt% filler loading, tensile strength increased by 16 % (graphene/MFC), 17 % (MFC/GO) and 22 % (MFC/RGO), while at 9 wt% a significant decrease was observed for graphene (- 43 %) and a steady

increase for MFC/RGO (+30 %) and MFC/GO (+5%). The decrease in the tensile strength of the composites with graphene loading is not surprising. Although pristine graphene has excellent mechanical properties, the binding properties with other polymer materials, for example, is limited to hydrophobic and π - π interactions, as well as weak van der Waals forces. These interactions are normally not strong enough to act as the primary bonding mechanism between filler and the MFC constituent polymer matrix to enhance the overall composite properties. The deterioration of the mechanical properties is also attributed to the poor distribution of graphene in the MFC matrix, as already shown in Figure 2B, and aggregation of graphene, especially at high loadings. The latter tendency toward inhomogeneous aggregation of the graphene is seen more markedly at higher loadings due to strong clumping of the particles caused by hydrophobic attraction and resulting aggregation that disrupts the homogeneity of the fibre packing, and, hence, reduces the mechanical strength properties.

Enhancement of the tensile strength observed with the addition of RGO and GO is attributed to the homogeneous distribution and interaction of RGO and GO with the MFC matrix. The oxygen functional groups on the surface and edges of RGO and GO interact with MFC molecular chains to form strong hydrogen bonds, which act as interfacial load transfer regions between the MFC matrix and GO or RGO. It is still not very clear why the reinforcement behaviour of RGO is much stronger, than that of GO but this is probably attributed to the restoration of defects in the carbon network and reduction of interlayer spacing between RGO sheets and MFC after the reduction of GO. Similar results were reported by Li *et al.* [44], who also observed greater enhancement for RGO reinforced poly(vinyl alcohol) composites than those containing GO.

There was also a strong change of Young's modulus with the addition of graphene, GO and RGO into the MFC composites, as shown in Figure 5B. The neat MFC exhibited a Young's modulus of 18 GPa, and with an addition of 0.6 wt% it changed to 16 GPa, 21 GPa and 25 GPa for MFC/graphene, MFC/GO and MFC/RGO composites, respectively. When the loading was increased to 9 wt%, the

composites showed a modulus of 11 GPa, 21 GPa and 24 GPa for MFC/graphene, MFC/GO and MFC/RGO, respectively. The presence of well-dispersed RGO sheets in the MFC matrix provides a strong resistance pillar for the displacement or movement of the MFC chains and thus leads to an increase in Young's modulus of the composites. The Young's modulus for graphene/MFC composites showed, therefore, a similar trend as that for the tensile strength. A significant decrease was observed with graphene loading due to the aggregation and inhomogeneous dispersion of graphene in the MFC matrix as well as interruption of cellulose-cellulose hydrogen bonds. Additionally, with the incorporation of RGO and GO a high increase in tensile stiffness (Figure 5C) was observed for the MFC composites. This is attributed to the strong interfacial adhesion between the MFC polymer chains with the sheets of GO and RGO. However, poor tensile stiffness was observed for MFC/graphene due to lack of interaction between graphene and the MFC matrix and the associated flocculation of graphene within the MFC matrix.

A significant decrease of break elongation was observed for all the composites, as shown in Figure 5D. This is due to the high aspect ratio of the sheets and interaction of the filler and the MFC matrix, which provides high resistance to the movement of the MFC chains. The decrease is also attributed to the brittle nature of GO and RGO versus graphene sheets, which are highly flexible though brittle in extension.

The top and fractured surface of the composite films after tensile testing was examined by SEM, shown in Figure 7 and Figure 8, respectively. The cross-sectional views of the neat MFC and with different loadings of graphene, GO and RGO are shown in Figure 7. A slightly different morphology was obtained with the different type of filler loading distribution as shown in the schematic in Figure 6. The neat MFC composites showed a randomly distributed fibrous structure. The graphene based composites showed an inhomogeneous kind of morphology with large voids between the layers (Figure 7) and the layers were not distinct due to aggregation of graphene. However, the

structure for both GO and RGO based composites showed a more even and surface-similar morphology, not surprisingly given that XPS analysis showed that RGO also retains a good number of functional groups. Both GO and RGO based composites showed a very distinct compact multilayered structure, as shown in Figure 7, indicating good dispersion in the MFC matrix. The top surface analysis of the composites in Figure 8 also indicates the differences in the dispersion of the fillers. More MFC fibres are seen on the surface of graphene/MFC composites indicating aggregation and poor graphene interaction with MFC. For MFC/GO and MFC/RGO, however, a more uniform surface is observed similar to that of pristine MFC, indicating good dispersions in the matrix.

The SEM images go some way to support the interpretations above. Pristine graphene is a carbon-based material without any functional groups present on the surface or edges. Graphene is naturally hydrophobic and disperses in the polymer matrix through $\pi - \pi$ stacking. The hydrophobic nature of graphene causes aggregation in the hydrophilic MFC matrix due to the $\pi - \pi$ stacking effect of graphene sheets that prevents even distribution, and subsequently gives rise to poor mechanical properties as already seen in the earlier discussion. The weak interaction of graphene and the MFC matrix leads to poor stress transfer, and the aggregation of graphene disrupts the continuous network of MFC fibres, which results in lower tensile strength and elongation. In contrast, both GO and RGO contain oxygen functional groups on the surface and edges as shown from XPS and FTIR analysis earlier. These functional groups promote a particulate dispersion of GO and RGO sheets in the MFC matrix due to the interaction with the hydrophilic MFC chains. Additionally, there is also a hydrogen bonding between functionalised GO and RGO and the MFC matrix that leads to enhanced interfacial binding and, thus, higher mechanical properties of the composites [45].

Thermal stability of the produced nanocomposite films was investigated by TGA in a nitrogen atmosphere to determine the effect of graphene, GO and RGO, respectively, on the thermal degradation properties of MFC. The comparative TGA and differential thermogravimetry data for the

MFC/Graphene, MFC/RGO and MFC/GO composites at 5wt% filler loading are shown in Figure 9A. It is clearly seen that, with the addition of 5 wt% of graphene, GO and RGO, the thermal stability of the pure MFC films was enhanced. The films show a large weight loss at about 260 and 350 °C due to thermal decomposition of MFC. At 800 °C, the residual weights for MFC, MFC/GO, MFC/RGO and MFC/graphene were 13.0, 18.5, 20.0 and 23.0 wt%, respectively. If, for example, we investigate decomposition temperature at two weight losses, T_{10} % and T_{65} %, representing 10 wt% and 60 wt%, respectively, we can see from Table 2 that at only 5 wt% loading all the composites showed an increase in the thermal decomposition temperature. Higher weight loss observed for GO and RGO based composites is due to the decomposition of oxygen functionalities, and the loss is lower for RGO based composites due to the lower amount of oxygen moieties present after reduction. These results are in agreement with earlier studies, which showed that incorporation of graphene in the MFC matrix increases the thermal stability even at much lower loading [46,47]. The amount of residual weight 'char' at 800 °C, as shown in Table 2, is also a good indicator of the thermal stability property of the materials. During combustion, a network of char layers is formed and thus prevents or constrains the escape diffusion process of gaseous decomposition products [48,49]. Therefore, pristine graphene is the better choice for enhancement of thermal stability of MFC composite films due to lack of oxygen functional groups that decompose at much lower temperature, thus contributing to the overall reduction of thermal performance of the composites.

The electrical conductivity of the composites was measured by a four-point probe technique, shown in Figure 9B. As expected, GO was an insulator because of the many oxygen containing functional groups attached to it. The highest electrical conductivity was achieved by MFC/graphene and reduced MFC/RGO composite films, reporting 1.66 S m^{-1} and 0.57 S m^{-1} , respectively. For MFC/graphene films, electrical conductivity was observed only after at least 1 wt% loading. At the lower graphene loadings of 0.3 and 0.5 wt%, the MFC/graphene composites did not show any electrical

conductivity. This is due to the inhomogeneous distribution of graphene in the MFC matrix as earlier discussed (Figure 2B). Electrical conductivity in nanocomposites is achieved by the formation of a continuous network of the conductive particles. Clumping and aggregation prevents the completion of an intimate contacting network of graphene in the MFC matrix. However, as more and more of the filler is added, the network percolates and starts to form continuous contact, which occurs at around 1 wt%, and a resulting low electrical conductivity is observed. The conductivity continues to increase with the increase in filler content, due to an improvement in the graphene-sheet-to-sheet contact [50] that eventually promotes the formation of a continuous conductive 3D network. However, for MFC/RGO composites, electrical conductivity was observed at the lowest loading of 0.3 wt%. This is attributed to the more homogeneous distribution of the RGO sheets in the MFC matrix as opposed to graphene. Therefore, even at much lower loading, a complete infinitely extending conductive RGO network is formed. The low percolation threshold is achieved due to the high aspect ratio of the graphene morphology and a homogeneous dispersion of RGO in the MFC matrix.

4. Conclusions

A comparative study on the reinforcement properties of graphene, GO and RGO in MFC composites was conducted. A significant decrease of the mechanical properties was observed with the addition of graphene in the MFC matrix due to poor compatibility between graphene and MFC. Poor dispersion of graphene in the MFC matrix is considered to have led to the decrease in the mechanical strength properties. On the other hand, the functional groups present on the surfaces of GO and RGO provided for a homogeneous dispersion of the fillers in the MFC matrix and thus higher mechanical strength properties including the strong interaction of GO and RGO with the MFC matrix leading to a strong bonding effect.

Although pristine graphene has theoretically by far the best mechanical properties amongst the potential reinforcement fillers, graphene is generally unreactive, and, thus, the binding capabilities with the polymer matrix are achieved only via the weak van der Waals forces, hydrophobic and $\pi - \pi$ interactions. Due to the long-range weakness of these interactions they do not contribute to the enhancement of the mechanical properties, but rather weakening resulting from the poor bonding between the filler and the matrix. Functionalised GO and RGO on the other hand are rich with oxygen functional groups that promote a molecular interaction between the filler and MFC matrix. This strong interfacial binding, including hydrogen or covalent bonding, enables a connective structure to be formed providing an excellent means of stress transfer between the two materials together with an even distribution in the matrix leading to enhanced mechanical properties.

Pristine graphene is more suitable for enhancement of thermal and electrical properties. Lack of functional groups, which are otherwise present in the GO and RGO, means that the graphene based composites do not degrade at such lower temperatures as seen for GO and RGO containing composites related to the oxidation potential of the surface groups, and thus graphene containing composites display greater thermal stability. In terms of electrical conductivity, GO is an insulator due the abundance of the oxygen containing groups, whilst RGO retains many of these groups even after reduction, and, thus, it does not show the same excellent properties exhibited by pristine graphene.

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COMPLIANCE WITH ETHICAL STANDARDS

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

References

1. Kalia S, Boufi S, Celli A, Kango S. Nanofibrillated cellulose: Surface modification and potential applications. *Colloid Polym Sci* 2014;292(1):5-31.
2. Zhang Y, Nypelö T, Salas C, Arboleda J, Hoeger IC, Rojas OJ. Cellulose nanofibrils: From strong materials to bioactive surfaces. *J Renew Mater* 2013;1(3):195-211.
3. Abdul Khalil HPS, Davoudpour Y, Islam MN, Mustapha A, Sudesh K, Dungani R, Jawaaid M. Production and modification of nanofibrillated cellulose using various mechanical processes: A review. *Carbohydr Polym* 2014;99(0):649-665.
4. Siddiqui N, Mills RH, Gardner DJ, Bousfield D. Production and Characterization of Cellulose Nanofibers from Wood Pulp. *J Adhes Sci Technol* 2011;25(6-7):709-721.
5. Siro I, Plackett D. Microfibrillated cellulose and new nanocomposite materials: a review. *Cellulose* 2010;17(3):459-494.
6. Fukuzumi H, Saito T, Iwata T, Kumamoto Y, Isogai A. Transparent and High Gas Barrier Films of Cellulose Nanofibers Prepared by TEMPO-Mediated Oxidation. *Biomacromolecules* 2009;10(1):162-165.
7. Syverud K, Stenius P. Strength and barrier properties of MFC films. *Cellulose* 2008;16(1):75.
8. Jorfi M, Foster EJ. Recent advances in nanocellulose for biomedical applications. *J Appl Polym Sci* 2015;132(14).
9. Azizi Samir M, Ahmed Said, Alloin F, Dufresne A. Review of Recent Research into Cellulosic Whiskers, Their Properties and Their Application in Nanocomposite Field. *Biomacromolecules* 2005;6(2):612-626.
10. Bolotin KI, Sikes KJ, Jiang Z, Klima M, Fudenberg G, Hone J, Kim P, Stormer HL. Ultrahigh electron mobility in suspended graphene. *Solid State Commun* 2008;146(9-10):351-355.
11. Morozov SV, Novoselov KS, Katsnelson MI, Schedin F, Elias DC, Jaszczak JA, Geim AK. Giant Intrinsic Carrier Mobilities in Graphene and Its Bilayer. *Phys Rev Lett* 2008;100(1).

12. Dürkop T, Getty SA, Cobas E, Fuhrer MS. Extraordinary Mobility in Semiconducting Carbon Nanotubes. *Nano Lett* 2004;4(1):35-39.
13. Zhu Y, Murali S, Cai W, Li X, Suk JW, Potts JR, Ruoff RS. Graphene and Graphene Oxide: Synthesis, Properties, and Applications. *Adv Mater* 2010;22(35):3906-3924.
14. Balandin AA, Ghosh S, Bao W, Calizo I, Teweldebrhan D, Miao F, Lau CN. Superior Thermal Conductivity of Single-Layer Graphene. *Nano Lett* 2008;8(3):902-907.
15. Nair RR, Blake P, Grigorenko AN, Novoselov KS, Booth TJ, Stauber T, Peres NMR, Geim AK. Fine Structure Constant Defines Visual Transparency of Graphene. *Science* 2008;320(5881):1308-1308.
16. Lee C, Wei X, Kysar JW, Hone J. Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. *Science* 2008;321(5887):385-388.
17. Yoo E, Kim J, Hosono E, Zhou HS, Kudo T, Honma I. Large reversible Li storage of graphene nanosheet families for use in rechargeable lithium ion batteries. *Nano Lett* 2008;8(8):2277-2282.
18. Tung VC, Allen MJ, Yang Y, Kaner RB. High-throughput solution processing of large-scale graphene. *Nat Nanotechnol* 2009;4(1):25-29.
19. Li X, Wang X, Zhang L, Lee S, Dai H. Chemically derived, ultrasmooth graphene nanoribbon semiconductors. *Science* 2008;319(5867):1229-1232.
20. Schedin F, Geim AK, Morozov SV, Hill EW, Blake P, Katsnelson MI, Novoselov KS. Detection of individual gas molecules adsorbed on graphene. *Nature Materials* 2007;6(9):652-655.
21. Hu K, Kulkarni DD, Choi I, Tsukruk VV. Graphene-polymer nanocomposites for structural and functional applications. *Prog Polym Sci* 2014;39(11):1934-1972.
22. Phiri J, Gane P, Maloney TC. General overview of graphene: Production, properties and application in polymer composites. *Mater Sci Eng , B* 2017;215:9-28.
23. Dhand V, Rhee KY, Ju Kim H, Ho Jung D. A Comprehensive Review of Graphene Nanocomposites: Research Status and Trends. *J Nanomater* 2013;2013:14.
24. Hummers WS, Offeman RE. Preparation of Graphitic Oxide. *J Am Chem Soc* 1958;80(6):1339.
25. Brodie BC. On the Atomic Weight of Graphite. *Philosophical Transactions of the Royal Society of London* 1859;149:249-259.
26. Staudenmaier L. Verfahren zur Darstellung der Graphitsäure. *Berichte der deutschen chemischen Gesellschaft* 1898;31(2):1481-1487.

27. Bonaccorso F, Lombardo A, Hasan T, Sun Z, Colombo L, Ferrari AC. Production and processing of graphene and 2d crystals. *Mater Today* 2012;15(12):564-589.
28. Singh V, Joung D, Zhai L, Das S, Khondaker SI, Seal S. Graphene based materials: Past, present and future. *Progress in Materials Science* 2011;56(8):1178-1271.
29. Pei S, Cheng H. The reduction of graphene oxide. *Carbon* 2012;50(9):3210-3228.
30. Kangas H, Lahtinen P, Sneek A, Saariaho A, Laitinen O, Hellen E. Characterization of fibrillated celluloses. A short review and evaluation of characteristics with a combination of methods. *NORD PULP PAP RES J* 2014;29(1):129-143.
31. Maloney TC. Network swelling of TEMPO-oxidized nanocellulose. *Holzforschung* 2015;69(2):207.
32. Phiri J, Gane P, Maloney TC. High-concentration shear-exfoliated colloidal dispersion of surfactant-polymer-stabilized few-layer graphene sheets. *J Mater Sci* 2017;52(13):8321-8337.
33. Johansson L, Campbell JM. Reproducible XPS on biopolymers: cellulose studies. *Surf Interface Anal* 2004;36(8):1018-1022.
34. Wang X, Zhi L, Tsao N, Tomović Ž, Li J, Müllen K. Transparent Carbon Films as Electrodes in Organic Solar Cells. *Angew Chem Int Ed Engl* 2008;47(16):2990-2992.
35. Chua CK, Pumera M. Chemical reduction of graphene oxide: a synthetic chemistry viewpoint. *Chem Soc Rev* 2014;43(1):291-312.
36. Eda G, Chhowalla M. Chemically Derived Graphene Oxide: Towards Large-Area Thin-Film Electronics and Optoelectronics. *Adv Mater* 2010;22(22):2392-2415.
37. Guo Y, Sun X, Liu Y, Wang W, Qiu H, Gao J. One pot preparation of reduced graphene oxide (RGO) or Au (Ag) nanoparticle-RGO hybrids using chitosan as a reducing and stabilizing agent and their use in methanol electrooxidation. *Carbon* 2012;50(7):2513-2523.
38. Sobon G, Sotor J, Jagiello J, Kozinski R, Zdrojek M, Holdynski M, Paletko P, Boguslawski J, Lipinska L, Abramski KM. Graphene Oxide vs. Reduced Graphene Oxide as saturable absorbers for Er-doped passively mode-locked fiber laser. *Opt Express* 2012;20(17):19463-19473.
39. Becerril HA, Mao J, Liu Z, Stoltenberg RM, Bao Z, Chen Y. Evaluation of solution-processed reduced graphene oxide films as transparent conductors. *ACS Nano* 2008;2(3):463-470.
40. Szabó T, Berkesi O, Dékány I. DRIFT study of deuterium-exchanged graphite oxide. *Carbon* 2005;43(15):3186-3189.

41. Stankovich S, Piner RD, Nguyen ST, Ruoff RS. Synthesis and exfoliation of isocyanate-treated graphene oxide nanoplatelets. *Carbon* 2006;44(15):3342-3347.
42. Singh K, Ohlan A, Dhawan SK. Polymer-Graphene Nanocomposites: Preparation, Characterization, Properties, and Applications. In: Ebrahimi F, editor. *Nanocomposites - New Trends and Developments*. Rijeka: InTech, 2012.
43. Patole AS, Patole SP, Kang H, Yoo J, Kim T, Ahn J. A facile approach to the fabrication of graphene/polystyrene nanocomposite by in situ microemulsion polymerization. *J Colloid Interface Sci* 2010;350(2):530-537.
44. Li Y, Yu T, Yang T, Zheng L, Liao K. Bio-Inspired Nacre-like Composite Films Based on Graphene with Superior Mechanical, Electrical, and Biocompatible Properties. *Adv Mater* 2012;24(25):3426-3431.
45. Liu L, Barber AH, Nuriel S, Wagner HD. Mechanical Properties of Functionalized Single-Walled Carbon-Nanotube/Poly(vinyl alcohol) Nanocomposites. *Advanced Functional Materials* 2005;15(6):975-980.
46. Mahmoudian S, Wahit MU, Imran M, Ismail AF, Balakrishnan H. A Facile Approach to Prepare Regenerated Cellulose/Graphene Nanoplatelets Nanocomposite Using Room-Temperature Ionic Liquid. *Journal of Nanoscience and Nanotechnology* 2012;12(7):5233-5239.
47. Zhang X, Liu X, Zheng W, Zhu J. Regenerated cellulose/graphene nanocomposite films prepared in DMAC/LiCl solution. *Carbohydr Polym* 2012;88(1):26-30.
48. Kashiwagi T, Du F, Douglas JF, Winey KI, Harris RH, Shields JR. Nanoparticle networks reduce the flammability of polymer nanocomposites. *Nat Mater* 2005;4(12):928-933.
49. Kim H, Abdala AA, Macosko CW. Graphene/Polymer Nanocomposites. *Macromolecules* 2010;43(16):6515-6530.
50. Stankovich S, Dikin DA, Dommett GHB, Kohlhaas KM, Zimney EJ, Stach EA, Piner RD, Nguyen ST, Ruoff RS. Graphene-based composite materials. *Nature* 2006;442(7100):282-286.

Figure captions

Figure 1 (A) UV-Vis absorption spectra of graphene, GO and RGO dispersions, and (B) Raman spectra at 532 nm for graphene, GO and RGO

Figure 2 (A) Photographs of flexible MFC/Graphene, MFC/GO and MFC/RGO films with filler loadings of 1 and 9 wt%. Poor distribution of graphene in MFC is clearly visible, especially at 1 wt% loading; (B) specific formation number of MFC/Graphene, MFC/GO and MFC/RGO composite films as a function of filler loading; (C) FTIR spectra of graphene, GO and RGO.

Figure 3 XPS analysis for graphene, GO and RGO: (A) with corresponding composites at filler loading of 9 wt%, (B) the inserts show XPS high resolution C 1s data.

Figure 4 Tensile stress-strain curves with different loading for (A) MFC/graphene, (B) MFC/GO, and (C) MFC/RGO composites.

Figure 5 Mechanical properties of the composites as a function of different filler loading of graphene, GO and RGO: (A) tensile strength, (B) Young's modulus, (C) tensile stiffness, and (D) break elongation. *Error bars* indicate standard deviation of 8 measurements (a colour version of this figure can be viewed online.)

Figure 6 Schematic descriptions of the microstructure of (A) neat MFC, (B) MFC/graphene, (C) MFC/GO and (D) MFC/RGO composites at lower filler loadings. At lower graphene loading, due to poor distribution of graphene in the MFC matrix, there is no continuous connection of graphene sheets thus making the composite an insulator.

Figure 7 SEM images of fractured cross sections of the MFC composites incorporated with graphene, GO and RGO, respectively, at loadings of 0, 0.3, 5, and 9 wt%.

Figure 8 SEM images of the top surfaces of (A) neat MFC, and with a loading of 9 wt% (B) GO, (C) RGO, and (D) graphene

Figure 9 (A) Comparison of TGA and DTG curves of neat MFC and MFC nanocomposites with the additional of 5 wt% of graphene, GO and RGO, and (B) Electrical conductivity of MFC/graphene, MFC/RGO and MFC/GO composite films with a range of concentrations of filler loading. The MFC/GO composites did not show any electrical conductivity.

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Table 1 Basic measured properties of MFC

Shear viscosity /mPa.s (10 min ⁻¹ (rpm), 1.5 % consistency)	13 283
Transmittance /% (800 nm, 0.1 % consistency)	23.88 ± 0.58
Fines content /%	32.8
Water retention value /cm ³ g ⁻¹	4.49 ± 0.05
Zeta potential /mV (0.1 % consistency)	-31.6 ± 0.84

Table 2 TGA results of pure MFC films and composites of MFC with the addition of 5 wt% GO, RGO and graphene, respectively.

Sample	$T_{10\%}$ °C	$T_{65\%}$ °C	Residue / wt% at 800 °C
MFC	298.4	360.9	13.0
MFC/GO	305.3	368.7	18.5
MFC/RGO	308.6	371.3	20.0
MFC/graphene	312.6	378.4	23.0