Effect of the method of dispersion on the properties of carbon nano tube and microfibrillar cellulose composites

Ali Naderi

Innventia Report No.: 433
August 2013

Acknowledgements

The Wallenberg Wood Science Centre is gratefully acknowledged for the financial support.

Jonas Sundström at Innventia AB, is thanked for his invaluable assistance.

Table of contents

Page

1 Summary

Homogenization, as a high-shearing blending route, was employed for preparation of microfibrillar cellulose-carbon nanotube composites. It was shown that the employed route gives superior properties with respect to mechanical and conductive properties, as compared to the currently used dispersion process (at Linköping University). It was further shown that increasing the number of homogenization steps does not lead to the improvement of the sought properties; explanations for this observation were proposed.

2 Introduction

Innovative development of bio-based materials with high mechanical, thermal and conducting properties produced by environmentally friendly processes is highly desirable. Such materials are envisaged to become indispensable in for example lightweight electronics in a sustainable society. Organic/inorganic nanocomposites are promising materials that meet the above needs.

Among the inorganic materials in nanocomposite applications, carbon nanotube (CNT) has been widely studied due to the unique[1] structure and combined remarkable mechanical, electrical, optical and thermal properties. Among the bio-based materials, microfibrillar cellulose (also known as nanocellulose or nanofibrillated cellulose, NFC) has attracted increasing attention during the past three decades, because MFC is not only environmentally compatible but also have distinctive[2] characteristics, such as high stiffness, high strength, low thermal expansion and the ability to form highly dense layers, when applied as a coating. The latter is attractive in applications where highly smooth surfaces are required for printing of e.g. micro-/nano-sized electrical circuits.

However, despite the described attractive properties of the materials by their own, the materials have yet to display equally impressive properties as (nano-)composites. Several explanations have been put forward for the poor performance of the composites, two of which are the inefficient de-entanglement processes of highly aggregated nanoparticles (CNT and MFC) upon dilution and equally inefficient processes for the blending of the different systems, which is required for attaining an even distribution of the entities, and the inherent incompatibility of the highly hydrophilic MFC and the highly oleophilic CNT.

The purpose of the studies of this report was to address the dispersion problem. Innventia AB is in possession of high-shearing mixing machinery, known as homogenizers (a.k.a Microfluidizers), which the accumulated in-house experiences have shown to be more efficient for belending processes than other common processes like sonication and Polytron homogenization. Hence, trials were made in which CNT-MFC composites were manufacturing by employing the Microfluidizer of Innventia AB. The mechanical and conductive properties of the composites were thereafter compared with CNT-MFC composites which had been produced at Linköping University, through a standard procedure.

3 Materials and Methods

3.1 Materials

Deionized water was used through-out the experiments. Glycerol (with a stated purity of ≥ 99.5%), CNT (multi-walled, product number 724769 Aldrich) and Triton-X-100 (BioUltra, 10% (w/w) solution) were purchased from Sigma-Aldrich. The microfibrillated cellulose was prepared at Innventia AB, Sweden, from a softwood sulphite-dissolving pulp (Domsjö Dissolving plus, Domsjö Fabriker AB, Sweden), which had subsequently been carboxymethyled; a detailed description of the carboxymethylation process can be found in e.g.[3]. The pre-treated fibres, diluted to about 1.8% (w/w) using deionized water, were homogenized in their sodium form. The homogenization process was conducted at 1700 bars using a high-pressure fluidizer

(Microfluidizer M-110EH, Microfluidics Corp., USA) employing 2 serial coupled z-shaped interaction chambers with the diameters of 200 and 100 μm, respectively. The total charge of the MFC was determined by conductometric titration to be 610 μeq/g.

3.2 Method of preparation of nanocomposites: The Linköping University route

First a 0.3% (w/w) CNT stock solution was prepared, by blending water, CNT and 1% (w/w) Triton-X-100 in the ratio of 99.7:0.3:0.3 on the weight basis. The mixture was homogenized by using an IKA T-10 homogenizer, at 3000 rpm. The blend was thereafter sonicated in an ultrasonic bath (Ecoren BLC 8/3) at 50% power for one hour. Further homogenization was achieved by an ultrasonic probe (Bandelin Sonopuls HD 2070) at 7W, 20 kHz, for 5 minutes.

Microfibrillated cellulose (1.9% (w/w) used as received), CNT (0.3% (w/w)), glycerol (the added amount was calculated as 10% (w/w) on the total amount of CNT and MFC) and water were mixed in 20 ml vials and homogenized with an Ultra Turrax homogenizer for 3 minutes. The vials were thereafter sonicated for 1 hour. The content was diluted with water to a total volume of 30 ml, which was then homogenized for 1 additional minute with the Ultra Turrax.

3.3 Method of preparation of nanocomposites: The Innventia route

First a 0.3% (w/w) MFC suspension containing 10% (w/w) of glycerol calculated on the amount of MFC was prepared. This was achieved by blending about 1427g 1.80% (w/w) MFC with 6073g water, and mixing with a propeller mixer for 10 minutes. The blend was thereafter homogenized at 400 bars (using 400 + 200 μm interaction chambers).

A 0.3% (w/w) CNT suspension, containing 10% (w/w) glycerol calculated on the amount of MFC was prepared. This was obtained by first blending (with a propeller mixer) about 1495g of water with 0.45g of glycerol. 4.5g 1% (w/w) of Triton-X-100 was thereafter added to the mixture and blended for 5 minutes. 4.5g CNT was added to the mixture and blended for 10 minutes using a propeller mixer.

Finally, the mixture was homogenized at 1700 bars (using 200 + 100 μm interaction chambers). The content was thereafter gently poured in polystyrene petri dishes, which were kept in a room with constant humidity and temperature (50% Rh, 25 °C) for about two weeks for the slow evaporation of the water content of the systems.

It is noted that in the manufacturing of the nanocomposites, the amount of MFC and the amount of glycerol (based on the total dry content of MFC+CNT in the system) were kept constant, while the amount of CNT in the system was altered. The total dry content of the nanocomposites was in the end less than 0.3% (w/w).

3.4 Tensile strength studies

The mechanical properties of the composites were investigated by tensile strength studies.

The samples are kept at 50% Rh/25 °C, for at least 3 days, before conducting the measurements. The nanocomposites samples were weighted before strips were cut out by an Arpi Press machine (Type: T 150/S 1, ARNE PIPER ApS). The length and width of the strips were 45 mm and 0.6 cm, respectively. The ribbons were then mounted (with the span width set to 30 mm) into a tensile strength machine and run with a speed of 100%/min.

3.5 Conductivity measurements

To determine the conductivity of the CNT-NFC samples, films were cut into (5x25 mm) stripes. Thereafter, the resistance over the length of the stripes were measured by using a Keithley 2602A instrument with a two-probe setup. It is noted that for reducing the contact resistance, the edges of the samples were coated with silver paint. The conductivity (k) was calculated from the dimensions (L = length, w = width, t = thickness) of the samples and its resistance (R):

$$k = {}^{L}/_{(R * w * t)}$$

4 Results and discussions

In table 1 a list of the theoretical composition of the different samples after drying has been summarized; in the calculations complete drying of the systems has been assumed.

Table 1. Theoretical composition of the different MFC-CNT nanocomposites. * indicates that the sample was homogenized 3 times at 1700 bars (200 + 100 μm interaction chambers).

Sample	CNT/MFC % (w/w)	MFC %(w/w)	CNT %(w/w)	Glycerol %(w/w)
CNT-0	0	91	0	9
CNT-1*	1	90	1	9
CNT-10	10	83	8	9
CNT-20	20	76	15	9
CNT-30	30	70	21	9
CNT-40	40	65	26	9
CNT-50	50	61	30	9
CNT-10-2*	10-2	83	8	9

In Figure 1 pictures of the CNT-40 system prepared through the different routes have been displayed. As can be seen the system that has been prepared through the Innventia route has a more glossy appearance (indicating a smoother surface) and displays less wrinkling.

In table 2 the mechanical properties of the different systems have been summarized. Several observations are emphasized. First, the mechanical properties of the composites made through the Innventia route, show better properties compared to the Linköping University route; this trend becomes more apparent with the content of CNT in the

system. Second, there is little change in the mechanical properties of the composites when compared to the system with pure MFC. And third, the results show that increasing the number of passes through the homogenization does not lead the enhancement of the mechanical properties.

Figure 1. Representative pictures of CNT-40 prepared through a) the Linköping University route; b) the Innventia route.

The conductivity properties of the composites have been presented in figure 2. It is clear that better conductive properties can be obtained when the Innventia route for blending is employed. It is further noted that a dramatic increase in the property is achieved when the CNT concentration in the system exceeds 20% (w/w). The observed effect is aching to be viewed as percolation effect. However, the apparent percolation threshold should be regarded as too high for particles like CNT having very high aspect ratios. The explanation for this is proposed to be the inability of the different employed processes to liberate the CNTs from their aggregated state and/or breakage of the fibrils in the homogenization steps.

Interestingly, in figure 2, no levelling-out tendencies in the conductivity curves are observed. The observation implies that the amount of CNT in the composite can further be increased.

Finally, it is noted but not shown that increasing the number of passes (from 1 to 3) through the homogenizer does not lead to the enhancement of the conductivity properties. This was investigated with the CNT-10 system, and the observation is in accordance with the mechanical properties of the systems (as discussed earlier).

Table 2. The mechanical properties of composites manufactured through the Innventia-route ("Inn") and Linköping university route ("LU").

System	Tensile Strength (kNm/kg)	Tensile Stiffness (kNm/kg)	TEA Index (kNm/kg)	Strain (%)
Pure MFC	142±20	8±1	7±2	7±2
CNT-1-LU	120±21	6±1	7±2	9±1
CNT-1*-Inn	139±17	8±0	7±2	7±2
CNT-10-LU	102±2	6±0	5±0	7±1
CNT-10-Inn	131±17	7±0	6±2	7±1
CNT-20-Lu	96±4	4±0	7±0	11±0
CNT-20-Inn	138±17	6±0	8±2	8±2
CNT-30-LU	93±10	4±0	5±1	8±1
CNT-30-Inn	125±18	6±1	5±2	7±3
CNT-40-LU	80±3	3±0	5±0	9±1
CNT-40-Inn	125±14	6±2	6±2	8±4
CNT-50-LU	69±3	3±0	4±0	9±0
CNT-50-Inn	110±11	5±0	7±1	10±2
CNT-10-2*-Inn	131±15	7±0	5±2	6±1

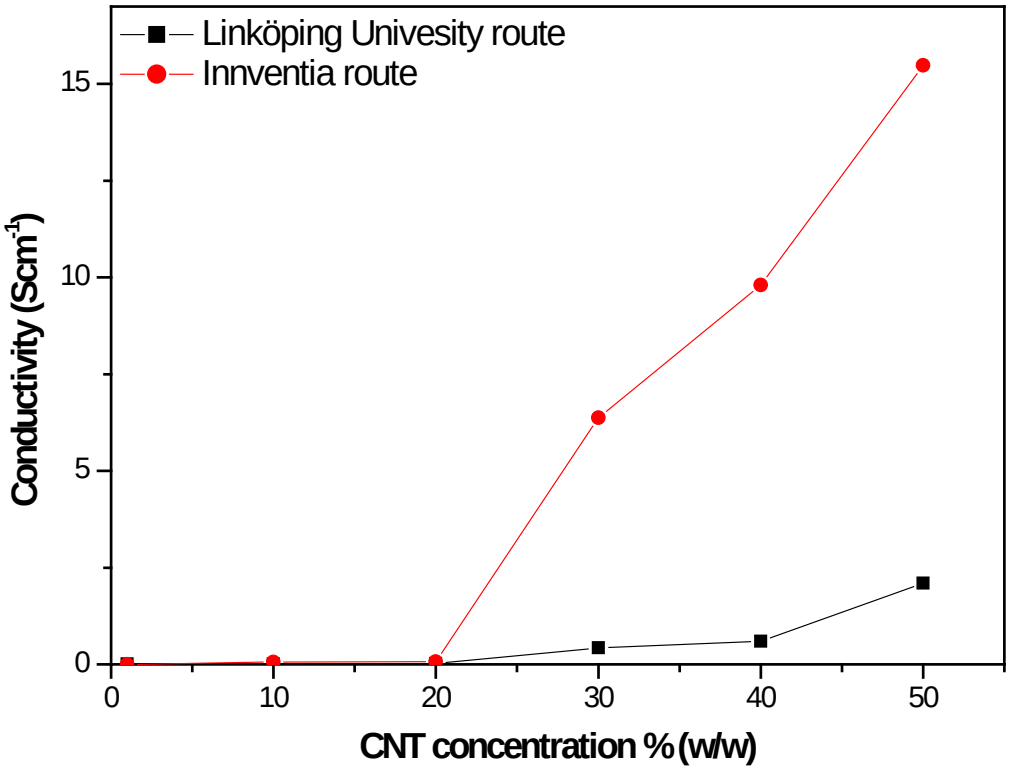

Figure 2. The conductivity of CNT-MFC composites prepared through different routes.

5 Discussions and conclusions

The outcome of the investigations clearly shows the benefit of using homogenizers for dispersing MFC-CNT systems. The benefit is obtained thanks to the severe shearing that occurs in the interaction chambers of the instrument. Interestingly, no enhancement in the mechanical and/or conductivity properties was observed with increasing the amount of shearing (passes through the homogenizer). Several explanations can be envisaged. One (which is currently investigated at Innventia AB) could be that the homogenizer cannot break the aggregates further once a critical size has been reached. And another possible explanation is the breakage of the nanofibrils during the homogenization step, leading to the lowering of e.g. the aspect ratio of the system which has an impact on the percolation property.

The results also showed that it is possible to increase the amount of CNT in the composite beyond 50% (w/w), to achieve increasing conductivity. However, based on the results, the increase in the conductivity property is most likely linear and not exponential.

6 Suggestions of future work

Based on the outcome of this work the following are proposed as a continuation of the studies.

1) Increasing the amount of CNT beyond 50% (w/w) to find the upper critical CNT concentration.
2) Optimization of the preparation protocol:
    a. Dispersion of the CNT with a higher amount of surfactant, or through the employment of a more efficient surfactant.
    b. Changing the homogenization protocol for obtaining better dispersion, with shortest number of steps – which would make the process more attractive from an industrial point of view.
3) Investigate the possibility of enhancing the CNT-MFC compatibility through the modification of the surface properties of MFC through the grafting of aliphatic moieties onto the MFC surface.

7 References

1. Ebbesen, T. W., *Phys. Today* **1996,** *49* (Copyright (C) 2013 American Chemical Society (ACS). All Rights Reserved.), 26-32.
2. Klemm, D.; Kramer, F.; Moritz, S.; Lindström, T.; Ankerfors, M.; Gray, D.; Dorris, A., *Angew. Chem., Int. Ed.* **2011,** *50* (24), 5438-5466.
3. Wågberg, L.; Decher, G.; Norgren, M.; Lindström, T.; Ankerfors, M.; Axnäs, K., *Langmuir* **2008,** *24(3)*, 784-795.

8 Innventia Database information

Title

Effect of the method of dispersion on the properties of Carbon Nano Tube and Microfibrillar Nano Cellulose Composites

Author

Ali Naderi

Abstract

Homogenization, as a high shearing blending route, was employed for preparation of microfibrillar cellulose-carbon nanotube composites. It was shown that the employed route gives superior properties with respect to mechanical and conductive properties, as compared to the currently used dispersion process (at Linköping University). It was further shown that increasing the number of homogenization steps does not lead to the improvement of the sought properties; several explanations for this observation were provided.

Keywords

Nanocellulose, carbon nanotube, homogenization, conductivity, mechanical properties

Classification

1252, 1340

Type of publication

Other

Report number

433

Publication year

July 2013

Language

English

INNVENTIA AB is a world leader in research and development relating to pulp, paper, graphic media, packaging and biorefining. Our unique ability to translate research into innovative products and processes generates enhanced value for our industry partners. We call our approach *boosting business with science.* Innventia is based in Stockholm, Bäckhammar and in Norway and the U.K. through our subsidiaries PFI and Edge respectively.

INNVENTIA AB
Drottning Kristinas väg 61, BOX 5604
SE-114 86 Stockholm Sweden

Tel +46 8 676 7000
Fax +46 8 411 55 18
VATno 556603110901

info@innventia.com
www.innventia.com

INNVENTIA