

# Mechanical Properties of functionalized Electrochemical Exfoliated Graphene in Polypropylene

NANOCOMPOSITES

Marc Hove Hansen

19/12-2018

Marc Hove Hansen Mechanical Properties of Functionalized Electrochemical Exfoliated Graphene in Polypropylene

# Title

Title	Mechanical Properties of Functionalized Electrochemical Exfoliated Graphene in Polypropylene
Theme	Master's Thesis
Project period	03/09-2018 to 19/12-2018
Supervisor	Raino Mikael Larsen
Co-Supervisor	Catalina-Gabriela Sanporean
Page number	45

Marchan

# Abstract

This study is elaborate with Aalborg university, to find a way to improve the dispersion and mechanical properties of nanocomposite PP-Graphene. The graphene is produced by electrochemical exfoliation of graphite, with three different concentration of electrolyte 0.1M, 0.5M and 1M H2SO4 see figure 1.



Figur 1: In this setup, the solution is with  $H_2SO_4$  and demistralized water with a graphite rod on the right side and platin(Pt) wire on the left side.

From the Hansen Solubility Parameters(HSP) it was possible to observe a change from the increase in concentration, where the observation was a change in hydrogen boding force. Also, with an increase in concentration defects in graphene structure where more common. From the HSP and a little experiment of dispersion of graphene in a mixture of octadecylamine (ODA). The graphene will be functionalized with ODA.

The functionalized graphene experience better dispersion in polypropylene than pure graphene in polypropylene. The mechanical properties creep resistance and max stress is slightly increased, however the nanofiller has a negative effect on Young's modulus. The graphene in polypropylene is acting as nucleation aid which increasing the degree of crystallinity and crystallization temperature.

# Table of contents

PREFACE
Abbreviations and Units6
INTRODUCTION
LITERATURE REVIEW
Electrochemical exfoliation of graphite8
Dispersion of graphene in polypropylene9
Mechnical properties of funtionalized graphene in polypropylene
THE ELECTROCHEMICAL EXFOLIATION OF GRAPHITE PROCESSES WILL BE DESCRIBED IN THIS SECTION12
CHARACTERIZATION OF ELECROCHEMICAL EXFOLIATION OF GRAPHENE
XRD 15
Hansen SOLUBILITY parameter (HSP)16
Raman spectroscopy
FUNCTIONALIZATION OF GRAPHENE21
Functionalize procedure of graphene22
COMPOUNDING, EXTRUDING AND INJECTION MOULDING PROCESS23
DESCRIPTION OF CHARACTERIZATION METHODS FOR TESTING24
Light optical microscope (LOM) analysis)24
Tensile test
Creep Test

Marc Hove Hansen Mechanical Properties of Functionalized Electrochemical Exfoliated Graphene in Polypropylene

RESULTS AND DISCUSSION2	27
Light optical microscope (LOM) analysis)	27
Tensile test	30
Creep Test	33
Differential Scanning Calorimetry (DSC)	38
CONCLUSION	<b>1</b> 1
REFERENCE	12
APPENDIX	15
Appendix A	45
Appendix B	45

# PREFACE

This report is made as an internal project at Aalborg University at the Department of Mechanical and Manufacturing Engineering. The project is performed as a fourth semester project at the master's programme in Materials Technology under the theme master's thesis.

All references in the report are stated in the end of a sentence as follows: [] containing a reference number. The references list can be found in the end of the report.

During the project many people have been helpful, providing good advices and sparring. A special thanks to:

- R. Mikael. Larsen and Catalina-Gabriela Sanporean for being supervisor on the project.
- The workshop and laboratory at the Department of Mechanical and Manufacturing Engineering for production materials and help to analyse the welds.

### ABBREVIATIONS AND UNITS

### Abbreviations:

AAU	Aalborg University
LOM	Light optical microscope
PP	Polypropylene
XRD	X-ray diffraction
DSC	Differential scanning calorimetry
ODA	
HSP	

### Units:

mm	Millimetre
bar	Bar
N	Newton
S	Seconds
Hr	Hour
Wt-%	Weight percent
MPa	Mega pascal
°C	Celsius

Marc Hove Hansen

## INTRODUCTION

In this master thesis, there will be investigated on, how to improve the dispersion and mechanical properties of electrochemical exfoliated graphene in polypropylene. As graphene has excellent mechanical, electro, thermal properties [1], mass production for graphene is required, to get from lab-scale to application. One method is electrochemical exfoliation see figure 3, which has low cost, environment friendly, safer, fast production and high quality. [12][23][27][6]



Figure 1:Setup of an electrochemical exfoliation of graphite

A problem for improving dispersion of graphene in PP, is the large difference in interfacial energy between them, would lead to aggregation of the nanofiller in polypropylene. By melt blending is most common way to large batches, unfortunately, graphene are easy to aggregate during the process. Therefore, should the graphene surface modifies to overcome the van der Walls forces[4]

Marc Hove Hansen

# LITERATURE REVIEW

## ELECTROCHEMICAL EXFOLIATION OF GRAPHITE

There are many studies, which has experimented with electrochemical exfoliation of graphite. The graphite electrode can be charged either positive or negative, which allows intercalation of anions or cations see figure 2. The electrochemical process can be grouped into first anodic exfoliation in a mixture of water and acids, ionic liquids or aqueous solution. And seconded cathodic exfoliation in organic solvents (propylene carbonate, dimethyl sulfoxide) containing lithium or alkylammonium salts. The intercalation cause gas release because of the electrolyte, which overcome the van der Walls interaction. The exfoliation process is relative fast, it can take from serval minutes to hours. [20] [12] [23]



Figure 2: Electrochemical exfoliation of graphite: anodic and cathodic. [20]

Many studies have got good results by using H2SO4 as electrolyte, but at different concentrations. 0.1M 0.5M 1.0M H2SO4, 5.0M H2SO4 and pure H2SO4 the efficiency of the exfoliation was lower, at higher H2SO4 the concentration. By using pure H2SO4 no exfoliation happened, which indicate that water is crucial for generation of oxygen or hydroxyl for initial stage. [10][12]

Ching-Yuan Su, Adriano Ambrosi and Martin Pumera investigated three different electrolytes for the exfoliation of graphite which are: H2SO4 Na2SO4 and LiClO4. They evaluated structural and chemical, which results in that LiClO4 was highly oxidized, and the electrolytes showed defects in structure, most defects for H2SO4. [12] By wetting the graphite rod with a static bias of a voltage, it causes the SO4 likely to start intercalation gentle. By wetting the graphite rod, higher quality graphene is obtained. [11]

### **DISPERSION OF GRAPHENE IN POLYPROPYLENE**

Covalent functionalization of graphene is the most used functional method widely, graphene edges and defects sites are highly reactive. The graphene oxide prepared by chemical oxidation, can contain numbers of carboxyl groups, hydroxyl groups and other active groups. [25]

Mungse et al. utilized ODA to modify graphene oxide through the reaction between the amino of the ODA and the carboxyl of graphene oxide. The functionalized graphene was stable for a long term in lube oils.

Non-covalent bonding methods.

Melt-blending is the most cost and efficient, way to achieve dispersion of graphene in a polymer matrix. Many researchers have used a melt-blending method to prepare graphene/polymer composite with good dispersibility, and they have found that the combination of graphene and some polymers occurs mainly through the  $\pi$ - $\pi$  interactions [27]

For single-walled carbon nanotubes with HNO3 treated and ODA modification have improved the interfacial strength for a Polymeric composite. [28]

Yuan reported good dispersion by functionalized the graphene with pphenylenediamine(PPD) and Maleic anhydride grafted polypropylene (MAPP) with a long procedure to get functionalized graphene see figure 3.[23]



Figure 3: Yuan reported method for functionalize graphene.[23]

R.Mikael Larsen reported that by octadecylamine(ODA) functionalized reduced graphite in polypropylene by melt mixing, reduced graphite produced by modified hummers method. Got a quite homogenous dispersion but the graphene or graphite flaks are large. [16]

## MECHNICAL PROPERTIES OF FUNTIONALIZED GRAPHENE IN POLYPROPYLENE.

R.Mikael Larsen investigated the mechanical properties of functionalized graphite oxide in PP, and found out by functionalize the graphite oxide with ODA an increase in mechanical properties, with creep resistance improved most.

Yuan reported with a 1wt% functionalized graphene oxide(fGO) in polypropylene. The fGO is acting as nucleation aid for PP to increase the

Marc Hove Hansen Mechanical Properties of Functionalized Electrochemical Exfoliated Graphene in Polypropylene

degree of crystallinity. With only an increase of 0.5wt% fGO storage modulus increased by 15.4%. Tensile strength has no change with increasing loading of nanofiller, however elongation break is decreasing.[23]

Electrochemically exfoliated few layer graphene with two different diameters (5  $\mu$ m and 20  $\mu$ m) and similar thicknesses were incorporated in a PP matrix by melt mixing of 0 to 20 wt% of graphene flaks. Also an increase in crystallization temperature and degree of crystallinity with the flaks acting as a nucleation site for polymer. Mechanical testing showed that the 5  $\mu$ m flakes behaved as short fibres and poorly reinforced the PP matrix compared to the 20 $\mu$ m flakes, These larger flakes gave a linear increase in the modulus even at high wt% [6]

# THE ELECTROCHEMICAL EXFOLIATION OF GRAPHITE PROCESSES WILL BE DESCRIBED IN THIS SECTION

The graphene, used in the nanocomposite is produced by electrochemical exfoliation of graphite. The graphene was obtained by subjecting the graphite bars to three different electrolytes: 0.1[M], 0.5 [M] and 1[M] solutions of sulfuric acid (H2SO4). The solutions were prepared using demineralized water. The setup seen in figure 4 consists by:

- Stand
- Platin Wire
- Power supply
- 2 clamps
- 150 ml breaker
- 96% Sulfuric acid H<sub>2</sub>SO<sub>4</sub>
- Graphite rods, 3,7[gr]

The graphite rod is set to positive voltage and platin wire to negative. The process starts by wetting the graphite rod when applying a voltage on 2[V] for 2[min]. After wetting the volt is increased until 10[V] to the graphite rod is exfoliated completely.



Figure 4: In this setup, the solution is with  $H_2SO_4$  and demistralized water with a graphite rod on the right side and platin(Pt) wire on the left side.

The exfoliation with 1M solution made the platinum wire to become red and hot at 10 [V], therefore the voltage was decreased to 6.9 [V], but the amp [A] was 3.52 [A] similar with 0.5 M solution.



Figure 5: Electrochemical exfoliation of the graphite rod, graphene is exfoliated from the rod.

After the exfoliation of the graphite rod. The suspension with graphene was filtered and washed with demistralized water. So, the pH of the solutions was increased to 5. After filtration, the graphene was dried in a vacuum oven at 40°C for 24hr.

Weight of graphene					
0,1M H <sub>2</sub> SO <sub>4</sub>	2,84 [gr]				
0,5M H <sub>2</sub> SO <sub>4</sub>	2,69 [gr]				
1M H <sub>2</sub> SO <sub>4</sub>	2,79 [gr]				

The left-over graphite rods were weighted and there was a loss between 0,2[gr] to 0,4[gr] for the 3 different solutions.

# CHARACTERIZATION OF ELECROCHEMICAL EXFOLIATION OF GRAPHENE

### XRD

XRD analysis was performed on a PANalytical Empyrean XRD using Cu Ka. Five samples: graphene 0.1MH2SO4, graphene 0.5MH2SO4, graphene 1MH2SO4, graphite and graphene HNO3 were analysed with XRD. The XRD can see how the crystalline structure and possible to characterize the samples.



Figure 6: XRD curves

XRD patterns for the graphite sample, shows high sharp peak at 26.6°, This peak corresponds to the diffraction (002), which indicates high crystallinity. The graphene samples have a much lower and a little boarder peak at 26°. That corresponds to multi-layered graphene, which have layers 10 and over. Few layered graphene and graphene have a lower degree (20) around 22°-25°. [17]

### HANSEN SOLUBILITY PARAMETER (HSP)

Hansen solubility parameters(HSP) is used to calculate the surface attraction between particles. A way to predict to optimize the dispersion of fillers in a polymer matrix, HSP has been used for time to do predict. HSP represent the dispersion ( $\delta_D$ ), polar ( $\delta_P$ ) and hydrogen bonding force parameters ( $\delta_H$ ). The normal procedure for the experimental HSP is based on observation, between the interaction of different sets of solvents with known HSP values. Each solvent is observed and evaluated as a good or bad dispersion, which is indicated 1 for good and 0 for bad. [18]

HSP experiments were conducted for three samples: 0.1MH2SO4 graphene, 1MH2SO4 graphene and 1MH2SO4-HNO3-ODA graphene. 10mg each sample is added into 15 solvents. the solvents have known HSP. There after solvents were ultrasonicated for 1 hr to disperse the graphene even in the solvents. Then the solvents are set to rest for 24hr, afterwards they are evaluated seen in table 1.

		HSB					
	Suspension	δ <sub>D</sub>	$\delta_{p}$	$\delta_{H}$	0,1M	1M	1MODA
1	Acetonitrile	15.3	18	6.1	0	1	0
2	Methanol	15.1	12.3	22.3	1	0	0
3	tetrachloroethylene	18.3	5.7	0	0	0	1
4	dimethyl formamide	17.4	13.7	11.3	1	1	0
5	o-xylene	17.8	1	3.1	0	0	1
6	2-propanol	15.8	6.1	16.4	1	0	0
7	Hexane	14.9	0	0	0	0	0
8	Benzene	18.4	0	2	0	0	0
9	ethyl acetat	15.8	5.3	7.2	1	1	1
10	cis-decahydronaphtalene	18.8	0	0	0	0	0
11	Chloroform	17.8	3.1	5.7	0	0	0
12	cyclohexanone	17.8	6.3	5.1	1	1	0
13	tetrahydrofuran	16.8	5.6	8	0	1	1
14	Acetone	15.5	10.4	7	1	1	0
15	Ethanol	15.8	8.8	19.4	1	0	0

Table 1: Solubility of Graphene 0.1MH2SO4, 1MH2SO4 and 1MH2SO4-HNO3-ODA in various solvents.

After the observations the HSP spheres are calculated to find the position and sphere size with the good solvents enclosed and the bad solvents excluded. The program to calculate them are provided by supervisor.



Figure 7:Calculated HSP for 0.1MH2SO4 graphene in polypropylene.



Figure 8: Calculated HSP for 1MH2SO4 graphene in polypropylene.



Figure 9: Calculated HSP for 1MH2SO4-HNO3-ODA graphene in polypropylene.

It can be seen on figure 7 and 8, that an increase in strength of H2SO4 as electrolyte will decrease the hydrogen bonding and will have a little over lapping with polypropylene, which can indicate oxygen groups on graphene sheets. By threating the 1MH2SO4 Graphene with HNO3 and ODA for method see section functionalization of graphene. It can be seen in figure 9 that 1MH2SO4-HNO3-ODA HSP sphere has been smaller and more concentrated, further the overlapping with polypropylene sphere has increased in polar direction.

## RAMAN SPECTROSCOPY

Raman spectroscopy laser was operating 532 nm. The three graphene samples made by electrochemical exfoliation: 0.1MH2SO4, 0.5MH2SO4, 1MH2SO4 and graphite rod, were analysed. Raman spectra were obtained from the samples are seen in figures 10, 11, 12 and 13 respectively. The Raman spectra for 0,1M, 0.5M and 1M graphene, are very similarly in wave length of the peaks, but not the intensity of the peaks. D band at a wave length of ~1350 cm<sup>-1</sup> corresponding to sp<sup>2</sup> defects. while the peak with a wave length of ~1550 cm<sup>-1</sup> corresponds to in plane vibrations of sp<sup>2</sup> carbon atoms. The shoulder D' band on figure 11 and 12 correspond with the presence of disorders or defects. 2D band at a wave length of ~2700 cm<sup>-1</sup> correspond to multi layered graphene structures, as it is weaker and small shift of the 2D band. [21]



Figure 10:Raman spectroscopy of 0.1MH2SO4 graphene



Figure 11: Raman spectroscopy of 0.5MH2SO4 graphene



Figure 12: Raman spectroscopy of 1MH2SO4 graphene



Figure 13: Raman spectroscopy of graphite.

D/G ratio could be used to evaluate the extent of defects in the graphene samples D/G:  $0.1M=1.07 \ 0.5M=1.09 \ 1M=1.14$ . From the D/G ratio 1M H2SO4 have more defects than the others as expected. [21]

Marc Hove Hansen

# FUNCTIONALIZATION OF GRAPHENE

To improve the dispersion of graphene in polypropylene, graphene should be functionalized after the HSP results. It has been chosen to functionalize graphene by a method supervisor Mikael tried on single-wall carbon nanotubes with octadecylamine (ODA), after a little experiment, where the three different graphene: 0.1M, and 1M H2SO4, 0.1M treated with HNO3 (nitric acid) refluxing for 1 hr, and 0.1M treated with HNO3 ultrasonicated for 1 hr. after that the graphene powders are melted with ODA at 125°C in a furnace. Only a small amount of the three exfoliated graphene will be used for the experiment to see how the dispersion in ODA.



Marc Hove Hansen Mechanical Properties of Functionalized Electrochemical Exfoliated Graphene in Polypropylene

Figure 14: A) 0.1MH2SO4 graphene in ODA B) 1MH2SO4 I ODA C) 0.1M treated with HNO3 refluxing for 1 hr. D) 0.1M treated HNO3 ultrasonicated for 1 hr.

As the suspension with graphene threated with HNO3 ultrasonicated for 1 hr, have the best dispersion of graphene in the melted ODA. There is some large agglomeration, as the powder didn't get mill properly.

### FUNCTIONALIZE PROCEDURE OF GRAPHENE

1.1 gr of each exfoliated graphene were ultrasonicated in 100 mL 5M HNO3 for 1 hr, after it were washed and filtrated. The HNO3 treated graphene's were dried for 24 hr at 40°C. 8.7 gr of ODA was mix with HNO3 treated graphene in a breaker, the three breakers were put in a furnace at 125°C to melt ODA and wet the graphene. The mixtures were left for 6 days. Mixture with 0.1M and 0.5M H2SO4 graphene has absorb and dried with the ODA, and 1m H2SO4 can still have absorb ODA, but didn't dry out.



Figure 15: left)0.1MH2SO4-HNO3-ODA. mid) 0.5MH2SO4-HNO3-ODA. right) 0.1MH2SO4-HNO3-ODA.

After 6 days, 600 mL ethanol was added to dissolve the additional ODA, the mixtures were sonicated and heated before filtration, to be sure that the remaining ODA was removed the graphene suspensions were though filtration process 2 times again. The graphene powders were dried for 24 hr at 40°C.

# COMPOUNDING, EXTRUDING AND INJECTION MOULDING PROCESS.

Six different masterbatches were produced with graphene:

- 0.1M H2SO4 graphene
- 0.5M H2SO4 graphene
- 1M H2SO4 graphene
- 0.1M H2SO4-HNO3-ODA graphene
- 0.5M H2SO4-HNO3-ODA graphene
- 1M H2SO4-HNO3-ODA graphene

The masterbatch is made of 10 wt-% graphene and 90% polypropylene in a micro-compounder (MC 15 cc, Xplore Instruments) with a temperature set on 185°C, screw speed 75[rpm] and a process time on 20min.

The nanocomposites are made from a mix of 10 wt-% masterbatch and 90 wt-% polypropylene. The nanocomposites are feed though an extruder (Prism Eurolab16 Twin Screw Extruder from Thermo Science) two times, to even dispersion of masterbatch in the polypropylene. Extruder temperature set to 200 °C and screw speed 300rpm.

The nanocomposite granulates, and polypropylene were dried for 1hr at 80°C to ensure that excess water is removed. After that tensile test samples and 3-point bending test samples were made by injection mould (Haake MiniJet II from Thermo Scientific) with a cylinder temperature set on 220 °C and mould temperature 70°C. Tensile test samples injection pressure was set to 600bar. For 3-point bending test samples the injection pressure was set to 100bar.

At the analyses of the different nanocomposite and polypropylene will be called

- PP-1%graphene-0.1M H2SO4
- PP-1%graphene-0.5M H2SO4
- PP-1%graphene-1M H2SO4
- PP-1%graphene-0.1M H2SO4-ODA or PP-1%graphene-0.1M H2SO4-HNO3-ODA
- PP-1%graphene-0.1M H2SO4-ODA or PP-1%graphene-0.5M H2SO4-HNO3-ODA
- PP-1%graphene-0.1M H2SO4-ODA or PP-1%graphene-1M H2SO4-HNO3-ODA

To identify what graphene that is used in the different results.

# DESCRIPTION OF CHARACTERIZATION METHODS FOR TESTING

For the description of characterization methods for testing will be conducted as early project mechanical properties of electrochemical exfoliated graphene in polypropylene [19]

## LIGHT OPTICAL MICROSCOPE (LOM) ANALYSIS)

To insure to get optimal analysis with equal flow. Therefore, is the middle of tensile test samples for each compound used to analyse the dispersion. From a starting thickness of 2mm, to a thickness on 0.1mm. To hit that thickness, the samples is grinded with grain size of 800 and a grain size of 1200. In figure16 the samples are placed with double sided tape to a holder. The holder has 0.1mm indicator on the side all around it, that helps to insured that the samples got a thickness on 0.1mm measured with a micrometre.



Figure 16:Sample holder for grinding.

After the samples was taking out of the holder, glue from the tape is on one of the sides. To remove the glue, acetone is used careful, with a white cloth to inspect if any graphene is removed from the samples.[19]

Marc Hove Hansen

### **TENSILE TEST**

The tensile test had been done on Instron 5944 with a weight shell on kN2 and equipped with a clip-on extensometer. Extensometer is careful placed on the test sample. Otherwise little notch could be made in the sample. Then would necking start just under the extensometer. The setup is seen in figure 17.



Figure 17: Setup of tensile specimen, the red circles are indicating where the extensometer is clipped on.

The tensile tests were carried in a room with constant temperature at 20[°C]. The tests ran with a strain rate on 5[mm/min] according with ISO 527-1. The tensile tests are stopped at 50% strain and will be evaluated. As that is in the plastic zone, and only would provide elongation break. [19]

### CREEP TEST

The creep test had been done on an Instron 5944 with a 2kN weight shell on and a clip-on extensometer see figure 18. The creep was evaluated over a time on 1[hr] with a constant stress on 21.1MPa, which is reduced from the yield stress of the polypropylene. The stress on 21.1MPa is chosen so it is possible to compare results from two other nanocomposites. The room temperature was on 20°C. [19]



Figure 18: Creep test setup.

## DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The analyses were carried out on a TA-Q2000. Three samples were made by cutting a little piece under 1[mm] in thickness off, from a cut off that has not been unused in DMA. It was important that the cut is even flat for the samples to have full contact with the bottom of the pan. The pans were Tzero Aluminum pans.

The DSC analyses carried out as heat/cool/heat from 40-200-40-200°C with a ramp on 10°C/min. The first heat phase is to rest the material history. [19]

# RESULTS AND DISCUSSION

## LIGHT OPTICAL MICROSCOPE (LOM) ANALYSIS)

The LOM analysis is made on the 5 specimens, unfortunately one got lost as it could easily fly away on the glass with no time to make a new.

It was possible to grind the specimens to a thickness on 0.1mm  $\pm$ 0.02mm in tolerance.



Figure 19:5 samples for LOM analysis, PP-1%graphene-0.1MH2SO4 disappeared.

From figure 19 it is possible to see, that the functionalization has helped with the dispersion of graphene in PP, this is also in according to HSP combability for 1MH2SO4 and 1MH2SO4-HNO3-ODA, where the 1MH2SO4-HNO3-ODA is overlapping more in polypropylene.



Figure 20: Left) PP-1%graphene-0.1M H2SO4-HNO3-ODA x5. Right) PP-1%graphene-0.1M H2SO4-HNO3-ODA x50.



Figure 21:Left) 0.5M H2SO4 graphene x5 Right) 0.5M H2SO4 graphene x50



Figure 22: Left) PP-1%graphene-0.5M H2SO4-HNO3-ODA x5. Right) PP-1%graphene-0.5M H2SO4-HNO3-ODA x50.



Figure 23: Left) 1M H2SO4 graphene x5 Right) 1M H2SO4 graphene x50



Figure 24: Left) PP-1%graphene-1M H2SO4-HNO3-ODA x5. Right) PP-1%graphene-1M H2SO4-HNO3-ODA x50.

For figure 20, 21, 22, 23 and 24. It is possible to see that the functionalization has help to optimize the dispersion of the graphene in PP, which also HSP combability had a good indication on, unfortunately it was not possible to a homogeneous nanocomposite with ODA as functionalization. But it has helped with the size of agglomerates.

### **TENSILE TEST**

It is possible to calculate the theoretical Young's-modulus with equation:

$$E_1 = V_f \cdot E_f + V_m \cdot E_m$$

E<sub>f</sub> = 1.04TPa [24] V<sub>f</sub> =0.01 E<sub>m</sub> =1350MPa Appendix A V<sub>m</sub> =0.99

 $E_1 = 2376.5$  MPa, is the theoretical Young's modulus if the graphene is fully dispersed in HP400R PP. The Young's modulus has decreased from the pure PP samples, which can indicate no or bad interaction between ODA and PP, or graphene and ODA functionalization, which contradicts the LOM analysis with better dispersion when functionalized with ODA. But sometimes functionalization can have a negative effect on some properties. The standard deviation is good for the specimens, which mean the production of nanocomposite is good to get similarly specimens.



Figure 25: Mean values for Young's modulus for the specimens with standard deviation.

The maximum stress from the tensile curves underneath are taking  $\sim$ 0.1mm/mm where yield stress according to ISO 527-1, -2.

One specimen broke before 0.5mm/mm, PP-1%graphene-0.5MH2SO4-HNO3-ODA-1. Otherwise necking is moved slightly higher in strain and holding ~20MPa to 0.5mm/mm.



Figure 26: Left) PP-1%graphene-0.1M H2SO4 Right) PP-1%graphene-0.1MH2SO4-HNO3-ODA



Figure 27: Left) PP-1%graphene-0.5M H2SO4 Right) PP-1%graphene-0.5MH2SO4-HNO3-ODA



Figure 28: Left PP-1%graphene-1M H2SO4) Right) PP-1%graphene-1MH2SO4-HNO3-ODA



Max stress has increased slightly for all nanocomposites, that corresponding with a dispersion of graphene in polypropylene. The functionalization has helped with a small increase over non-functionalized specimens, but with standard deviation all the specimens overlapping each other. Furthermore, the functionalized specimens have higher standard deviation.



Figure 30: Mean values of max stress with standard deviation.

### CREEP TEST

A small improvement of creep resistance for the samples. Which are a little surprised as the previous knowledge of nanocomposites with graphene and carbon nanotube, creep resistance has always improved most. But from previous report, maleic anhydride grafted PP(MAgPP) was used in the nanocomposite, that could give an effect on creep resistance will be a possibility. More test needs to be conducted. [19] but from R.Mikael got good creep resistance improvements that only corresponds with PP-1%graphene-1MH2SO4-HNO3-ODA. [16] The standard deviation is a little higher for non-functionalized specimens. So the standard deviation shifts between max stress, creep, and is almost even at Young's modulus.



Figure 31:



Specimen 1 to 3



Figure 32: HP 400R pure



Specimen 1 to 3



Specimen 1 to 3



Figure 34: PP-1%graphene-0.5M H2SO4

1 2 3



Specimen 1 to 3



Specimen 1 to 3



Figure 36: PP-1%graphene-0.1M H2SO4-HNO3-ODA

1 2 3





Figure 37: PP-1%graphene-0.5M H2SO4-HNO3-ODA

Specimen 1 to 3



Figure 38: PP-1%graphene-1M H2SO4-HNO3-ODA

### DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The crystallinity is calculated for cold phase and second heat phase, as first heat phase is to rest the history for the nanocomposite.

The Crystallinity was calculated by equation.

$$X_c = \frac{\Delta H}{\Delta H_0} \cdot 100$$

 $\Delta H_0=207[J/g]$ . [15]  $\Delta H$  = Enthalpy for crystallinity [J/g].

DSC calculation of crystallinity								
Polypropyle	ΔH0							
ne	[J/g]	207						
					PP-	PP-	PP-	
		PP-	PP-		1%Graphen	1%Graphen	1%Graphen	
		1%Graphen	1%Graphen	PP-	e-	e-	e-	
	HP400	e-	e-	1%Graphen	0.1MH2SO4	0.5MH2SO4	1MH2SO4-	
Samples	R Pure	0.1MH2SO4	0.5MH2SO4	e-1MH2SO4	-HNO3-ODA	-HNO3-ODA	HNO3-ODA	
Crystaline								
temperature								
[°C] Tc	119,76	127,97	127,3	128,14	125,85	126,44	128,18	
Enthalpy								
[J/g] ∆Hc	89,5	93,46	92,23	92,3	92,35	91,99	94,46	
Crystallinity								
[%]	43%	45%	45%	45%	45%	44%	46%	
Melting								
temperature	159,53	163,27	163,2	163,13	162,62	163,13	162,22	
Enthalpy								
[J/g] ∆Hm	85,26	91,89	89,09	89,78	88,36	89,51	90,88	
Crystallinity								
[%]	41%	44%	43%	43%	43%	43%	44%	

Table 2: DSC calculation of crystallinity

It is possible to a slightly increase in degree of crystallinity as expected as the graphene helps nucleation this can have influence on the improvement in max stress and not the graphene. The melting temperature improved by 3-4 degree Celsius.





## CONCLUSION

Electrochemical exfoliation of graphite with H2SO4 as electrolyte, is a fast way to produce multi-layered graphene. Higher concentration of H2SO4 faster exfoliation process happens, with water present. With higher concentration of electrolyte H2SO4, higher defects are presents in the graphene structure.

The dispersion of graphene seen easily in figure 43 that functionalization method with ODA gave a better dispersion of graphene in polypropylene. As HSP combability, gave a good indication on the dispersion with the HSP 1MH2SO4-HNO3-ODA and polypropylene HSP spheres overlapping.



Figure 43: 5 samples for LOM analysis, PP-1%graphene-0.1MH2SO4 disappeared.

The mechanical properties for nanocomposites have only improved in two areas max stress and creep resistance, where max stress can have increased as the degree of crystallinity is increased. The Young's modulus had got a negative effect on the filler. It could be if the graphene structure has to many defects, which lowers the graphene properties.

From the standard deviation, no sample have stood out from each group. So it is good to be careful when making the nanocomposite and take time to do the characterizing test.

# REFERENCE

[1] A roadmap for graphene K.S. Novoseloc V. I. Fal'ko, L. Colombo, P. R. Gellert, M. G. Schwab & K. Kim. 10 oct. 2012.
https://www-nature-com.zorac.aub.aau.dk/articles/nature11458

[2] Electrochemical exfoliation of graphite and production of functional graphene. Pei Yu, Sean E. Lowe, George P. Simon, Yu Lin Zhong. 4 November 201.

[4] Mechanical and dielectric properties of graphene incorporated polypropylene nanocomposites using polypropylene-graft-maleic anhydride as a compatibilizer. Chao-QunLi<sup>,</sup> Jun-WeiZha Hua-QianLong<sup>,</sup> Si-JiaoWang<sup>,</sup> Dong-LiZhang<sup>,</sup> Zhi-MinDang composites science and Technology

[5] Electrochemical Exfoliation Synthesis of Graphene Chapter 2 Liu, Jilei

[6] Few layer graphene-polypropylene nanocomposites: the role of flake diameter. Cristina Valles. Amr M. Abdelkader, Robert J. Young and Ian A. Kinloch. 1 July 2014

http://pubs.rsc.org/en/content/articlepdf/2014/fd/c4fd00112e

[7] The Device Application of Electrochemical Exfoliated Graphene. Chee Kiat Tan, Khi Poay Beh, Faris Hidayat Ahmad Suhaimi, Yu Zhang Ng, Fong Kwong Yam, Hwee San Lim, Mohd. Zubir Mat Jafri.

https://aip.scitation.org/doi/pdf/10.1063/1.4998360

[10] Electrochemically Exfoliated Graphene as Solution-Processable, Highly Conductive Electrodes for Organic Electronics. Khaled Parvezt, Rongjin Li, Sreenivasa Reddy Puniredt, Yenny Hernandez, Felix Hinkel, Suhao Wang, Xinliang Feng, and Klaus Müllen 26. March 2013

https://pubs-acs-org.zorac.aub.aau.dk/doi/10.1021/nn400576v

[11] Electrochemically Exfoliated Graphene and Graphene Oxide for Energy Storage and Electrochemistry Applications. Adriano Ambrosi and Martin Pumera. 2016. chemPubSoc EUROPE

[12] High-quality Thin Graphene Films from Fast Electrochemical exfoliation. Ching-Yuan Su, Ang-Yu Lu, Yanping Xu, Fu-Rong Chen, Andrei N. Khlobystov, and Lain-Jong Li. 3 jan 2011 ACS NANO [15] Roger L. Blaine. Ta Polymer Heats of fusion http://www.tainstruments.com/pdf/literature/TN048.pdf

### [16]

R. Mikael Larsen. MECHANICAL PROPERTIES OF FUNCTIONALIZED GRAPHITE OXIDE PP NANOCOMPOSITES 21 st International Conference on Composite Materials Xi'an, 20-25 th August 2017.

[17] Simple and cost-effective synthesis of graphene by electrochemical exfoliation of graphite rods. Maria Coros, Florina Pogacean, Marcela-Corina Rosu, Crina Socaci, Gheorghe Borodi, Lidia Magerusan, Alexandru R. Biris, and Stela Pruneanu. RSC. 2016 https://pubs.rsc.org/en/content/articlepdf/2016/ra/c5ra19277c

[18] Comparative Study on Dispersion and Interfacial Properties of Single Walled Carbon Nanotube/Polymer Composites Using Hansen Solubility Parameters Jing Ma and Raino Mikael Larsen. ACSAMI.

[19] Mechanical Properties of Electrochemical Exfoliated Graphene in Polypropylene. AAU master Thesis made by Marc Hove Hansen

[20] Exfoliation of Conductive Layered Materials in Solutions. Johannes Gutenberg-Universität Mainz. https://pure.mpg.de/rest/items/item\_2575057\_1/component/file\_2575056/content

[21] Raman spectroscopy as a versatile tool for studying the properties of graphene. Andrea C. Ferrari & Denis M. Basko Nature Nanotechnology.

[22] Graphene-based Composites for Electrochemical Energy Storage. Liu, Jilei Springer Theses

[23] Preparation of functionalized graphene oxide/polypropylene nanocomposite with significantly improved thermal stability and studies on the crystallization behavior and mechanical properties BiheYuan ChenluBao LeiSong NingningHong Kim MeowLiew, YuanHu Chemical Engineering Journal Volume 237, 1 February 2014, Pages 411-420

[24] Effective mechanical properties of multilayer nano-heterostructures T. Mukhopadhyay, A. Mahata,<sup>2</sup> S. Adhikari, and M. Asle Zaeem. Sci Rep 2017. <u>https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5693924/</u> [25] Synthesis and exfoliation of isocyanate-treated graphene oxide nanoplatelets SashaStankovich, Richard D.Piner, SonBinh T.Nguyen, Rodney S.Ruoff, Carbon volume 44 issue 15

[26] Synthesis, dispersion and lubrication potential of basal plane functionalized alkylated graphene nanosheets Harshal P. Mungse, Niranjan Kumarb and Om P. Khatri. RSC advances 2015.

[27] Enhanced interfacial interaction between polycarbonate and thermally reduced graphene induced by melt blending. BinShen, WentaoZhai, mim iTao Dingding Lu, WengeZheng. Composites science and technology

[28] Modification of single-walled carbon nanotubes and its influence on the interfacial strength in polymeric composites R. Mikael Larsen. Springer science+business

# APPENDIX

## APPENDIX A

Data Sheet PP-HP400R - PDF.

## APPENDIX B

Mean Data with DSC Calculations - Excel file.