



NOVEL POLYMER- COMPOSITE ARTIFICIAL MUSCLES

designing, production & testing



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*'It does not matter how slowly you go as
long as you do not stop'
Confucius 555 – 479 b.c.*

Novel polymer-composite artificial muscles: designing, production & testing.



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Summary

This thesis project ‘‘Novel polymer-composite artificial muscles: designing, production & testing’’ has been conducted to fulfill the graduation requirements for the Bachelor of Science in Process & Food Technology (PFT). The project is a continuation of the research done by Haines et al (21 Feb 2014, Vol 343, Issue 6178 pp 868-872). In cooperation with the robotics lab at the TU Delft, the 3ME department and the applied research department of the The Hague University of Applied Science. The main goal for this project is to identify the possibility of improving nylon through producing (novel) polymer-composites with better thermal and electrical conduction properties. In order to answer this question several sub questions were formulated, including the following; Which are formulated in the introduction. This research project has been conducted between November 2016 and June 2017. Dr. M. Leemhuis has served as my primary supervisor for this thesis. While Dr. C. van de Kamp has served as the _____ company _____ supervisor.

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I am pleased to share that I have been awarded an academic scholarship through the VSBfonds and have been accepted to continue my education at the postgraduate level in both the Schools of Engineering and Social and Political Science of the University of Edinburgh, Scotland. I am fully convinced this would not have been possible without the mentorship of Dr. Leemhuis. Whom I consider as much a friend as a mentor, teacher and role model.

This thesis is dedicated to my family, my parents whom have worked extremely hard through personal illness for years while raising a child with both ADHD and ASD, as well as other physical impairments, and have somehow managed to raise me into a successful young adult while facing almost impossible to overcome odds. They never stopped supporting me or my interests even though that has not always been easy. I thank them from the bottom of my heart, and hope I can make them proud by contributing positively to the world.

List of Symbols and Abbreviations

DNA = Deoxyribonucleic Acid
ROP = Ring-Opening Polymerization
PA6 = Polyamide 6
G = Graphene
GO = Graphene-Oxide
PFT = Process and Food Technology
THUAS = The Hague University of Applied Sciences
H₂O = Water
OH = Diol
(CH₂)₅C(O)NH = Caprolactam
C-N = Carbon-Nitrogen bond
T_m = Melting temperature
PTAM = Polymer Twisted Artificial Muscles
T_g = Glass-transition temperature
N = number of twists
ΔT = Change in number of twists
ΔL = Change in contraction length
λ = Thermal conductivity
HDPE = Highly Dense PolyEthylene
PE = Polyethylene
DSC = Differential Scanning Calimotery
2D = Two-Dimensional
CNT = Carbon Nano Tube
SG = Sulphonated Graphene
Ω = Ohm/ Resistivity
3D = Three Dimensional
ABS = Acrylonitrile-Butadiene-Styrene
NMR = Nuclear Magnetic Resonance
FTIR = Fourier Transform InfraRed Spectroscopy
HPLC = High-Performance Liquid Chromatography
GPC = Gel Permeation Chromatography

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Introduction

The first chapter serves as an introduction chapter to the production of nylon 6 and the production of artificial muscles from nylon. This chapter will include a detailed process description of how nylon 6 is produced, the chemical and physical properties that make it an advantageous material for the intended use and a detailed examination of the molecular structure of polymers. The second chapter will also link those properties to the structure in order to help identify improvement areas or alternative materials with similar or even better characteristics. The third chapter will discuss previous literature about thermal conductivity and nylon-6 composites and acts as a projective chapter to establish result expectations. The fourth chapter will discuss the construction of the extruder used and initial tests. This chapter will answer the first research question (1) The fifth chapter will discuss how polymer composites have been made. The sixth chapter will discuss the results from chapters 4 and 5 and there by attempt to answer the sub-questions (2)(3)(4) The last chapter will discuss next steps for this project and provide recommendations for continuation.

Research questions:

- (1) *:How can custom wires be produced on a lab-scale?*
- (2) *:Can enough pulling force to produce structural alignment adequate for artificial muscle contraction be reached in a lab-scale production of nylon 6?*
- (3) *:Does improving the energy conductive properties of nylon 6 by producing nylon 6 – carbon derivative composites improve the muscle contraction, and if yes, by how much?*
- (4) *:What is the optimal composition of nylon 6, graphene (G) and graphene-oxide (GO) in relation to muscular contraction?*

This project is part of the research work for the betafactory led research group into biomaterials, including biorobotics. It is especially important because soft compliance robot actuators such as polymer artificial muscles can lead the way to increased dexterity and safety for next generation robotics. Allowing robots to perform even more human-like movement and being able to adjust to ‘soft’ impacts in cases of emergency such as when a robotic arm would swing against a human worker. Soft compliant artificial muscles or actuator could with the help of sensors stop movement when flesh is detected much more easily and effectively than current mechanical actuators.

Student Background

My specialization in the Process and Food Technology program has been functional food. My previous internship was conducted in the field of cleaning and disinfection for Unilever Supply Chain in Rotterdam, The Netherlands. After the successful completion of my internship I have continued to work as a process engineer for Unilever on a part-time basis till the start of this graduation project. Because I have an interest in human movement, Dr. Leemhuis presented this project opportunity to me. This research project is a challenging endeavor for me because I have focused on the practical application of process engineering for most of my studies. The focus on the theoretical aspects and the R&D aspects of this project is what attracted me to this research opportunity. Allowing me to work on the ‘researching’ competency of the DAS, something that I found extremely valuable.

1. Production of Nylon 6

This chapter will discuss the production process of nylon 6 on the industry scale. The chemical structure of nylon 6 and how that influences its chemical-physical properties will be discussed in depth, this knowledge will be used in other chapters to identify improvement areas or alternative opportunities.

1.1 What are Polymers?

A polymer is a macromolecule that is composed of many repeating, in different combinations, subunits. They are created through a process called polymerization from monomers (single molecules), examples include nylon (polyamides) and biopolymers such as DNA and proteins [1][2]. Because 'polymers' is such a broad term, several terms are used to subdivide polymers into groups. This can be done by the polymerization reaction required to produce the polymer, which can be divided in condensation and addition polymerization. The main difference is that in condensation polymerization not the entire monomer ends up in the formed polymer while in addition polymerization monomers are added together without losing any parts. Polymers can also be subdivided by properties including thermoplasticity, flexibility and crystallinity [3]. Another subdivision method is by dividing in natural and synthetic polymers. Polymers can either be formed according to step growth polymerization or chain growth polymerization. Typically ring-opening polymerization (ROP) leads to chain growth polymerization and condensation polymerization leads to step growth polymerization. The main difference is that chain growth polymerization leads to ABAB configured polymer chains and can thus create very long chains of the monomer to form long chained polymers [4]. While condensation polymerization leads to more random configurations of monomers with more variation in polymer chain length, and generally leads to lower crystallinity.

1.2 How is Nylon 6 formed?

Nylon 6 is the trivial name for polycaprolactam, which is also known as polyamide 6, which is a semi-crystalline polyamide of the monomer caprolactam ((CH₂)₅C(O)NH). The chemical structure of caprolactam can be seen in figure 1.1, it is a chain growth ROP polymer, which was developed as an alternative to nylon 6,6 without breaking patent rights. It is the only nylon that is produced by ROP. Below in figure 1.1 & 1.2 the molecular structures of nylon 6 and caprolactam are shown [5][6].

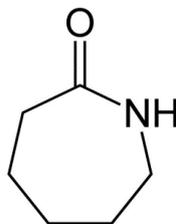


Figure 1.1:
Molecular structure
of caprolactam
[5][6]

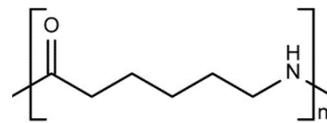


Figure 1.2: Molecular structure
of nylon 6 [5][6]

It is clear from figure 1 that caprolactam is an cyclic amide, with a carbon 6 ring. From figure 1.2 it is clear that nylon 6 has no carbon rings. The process from caprolactam monomers to nylon 6 chains goes as follows: In order to start the ROP, adequate heat is required. 250° C Is typically used, and 80-90% by weight caprolactam monomers are mixed with 10-20% water by weight. What happens next is that the carbonyl oxygen 'sees' the H₂O molecule in its proximity, The carbonyl group is highly reactive and steals a hydrogen atom from the H₂O molecule, in return for the proton the carbonyl oxygen donates a pair of electrons to the remaining H₂O molecule creating a free hydroxyl group and protonated carbonyl, a schematic representation of this process can be seen in figure 1.3.

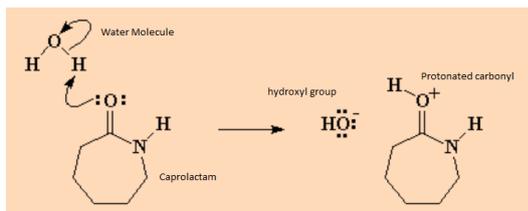


Figure 1.3: The Carbonyl group steals a proton from the water molecule, creating a hydroxyl group and a protonated carbonyl group [5][6].

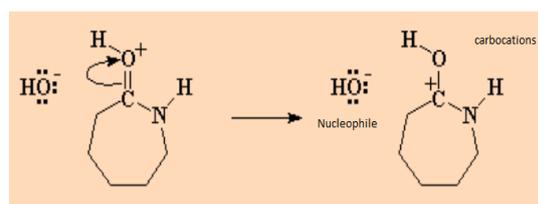


Figure 1.4: The positive charge of the double bond is broken and moved to the oxygen creating a highly reactive carbocation in the carbon ring. [5][6]

The carbonyl now has a positive charge which it doesn't want, in order to get rid of this charge the double bond between the carbon ring and carbonyl is broken, moving the positive charge from the oxygen atom to the carbon in the carbon ring. This forms a carbocation where the carbon has a positive charge. This carbon atom only has 6 electrons in its outer valence shell which doesn't adhere to the octet rule [7], leading this to be extremely reactive, because the carbon wants to restore a neutral charge and adhere to the octet rule, it is left open to react with the hydroxyl group produced in the first step, a schematic representation can be seen in figure 1.4.

The resulting reaction forms an unstable diol (multiple OH groups). The nitrogen atom donates a pair of electrons to a hydrogen atom on one of the hydroxyl groups, stealing it. The electrons that the hydrogen shared with its oxygen shift to form a double bond between the oxygen and carbon atom and lastly, the electrons the carbon and nitrogen shared shift completely to the nitrogen, which severs the nitrogen – carbon bond and opening up the carbon ring. These steps can be seen schematically in figures 1.5 & 1.6.

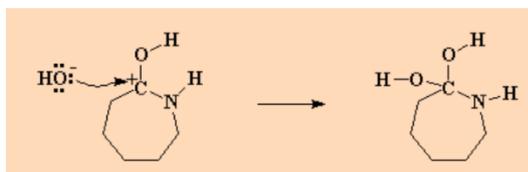


Figure 1.5: Diol formation from nucleophilic reaction From the free hydroxyl group. [5][6]

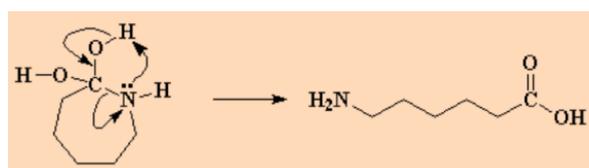


Figure 1.6: Electron shuffling as a result of diol instability, leading to the formation of an amino acid. [5][6]

After this the amino acid alcohol group acts in much the similar way that the H₂O molecule did before, another caprolactam molecule swaps the hydrogen atom from the formed amino acid for an electron and forms the same protonated carbonyl that we saw in figure 1.3. This can be seen schematically in figure 1.6. This protonated carbonyl is open to reactions with nucleophiles however this time the nucleophile available to react with is not the H₂O molecule but the amino acid who just lost its hydrogen atom.

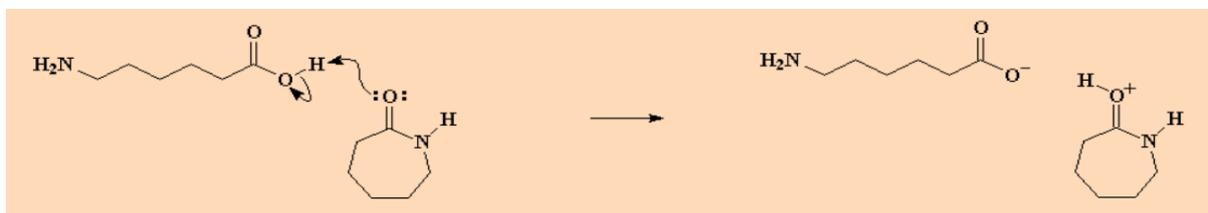


Figure 1.7: The newly formed amino acid has one of its protons stolen by another caprolactam molecule in change for an electron. [5][6]

The resulting reaction leads to a bond between the carbon⁺ from the caprolactam carbon ring and the nitrogen from the linear amino acid. Forming a highly unstable ammonium compound which can be seen in figure 1.7.

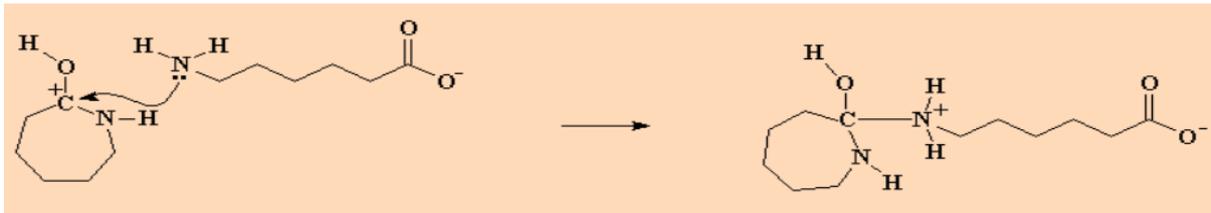


Figure 1.8: Nucleophilic reaction between the caprolactam and formed linear amino acid to form an unstable ammonium [5][6].

The nitrogen in the carbon ring steals an electron from the hydrogen from the ammonium nitrogen, as a result the bond between C-N is severed breaking another caprolactam carbon ring. This can be seen in figure 1.8.

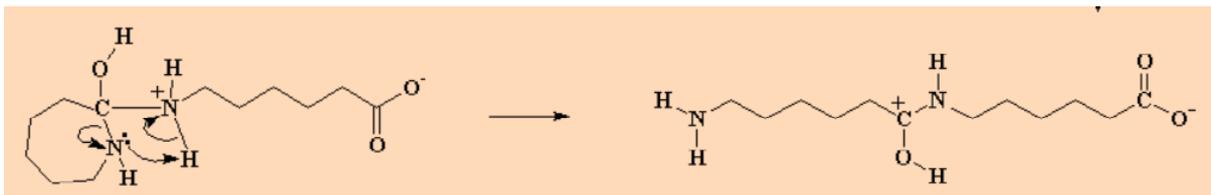


Figure 1.9: Reshuffling of electrons to form a linear molecule. [5][6]

The last step in the process is the carboxylate group at the end stealing the hydrogen from the alcohol group in the middle. The positive charge from the alcohol carbon moves to form a double bond between the carbon and oxygen and this creates a new carbonyl group and regenerates the carboxylic acid at the end of the chain, this can be seen in figure 1.9. This acid will then react with another caprolactam molecule, and the newly formed acid will then react with another caprolactam molecule forming a long chain of nylon 6 until there is no more caprolactam available.

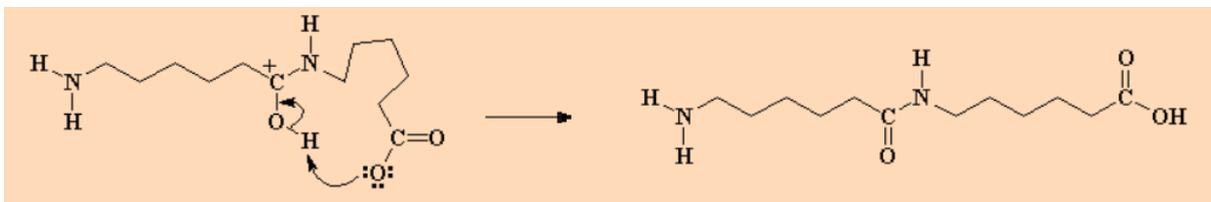


Figure 1.10: Final step in the production reaction of nylon 6. [5][6]

When figure 1.10 and figure 1.2 are compared the nylon 6 structure is clearly identifiable in the polymer chain.

1.3 Production of nylon artificial muscles

In this section the production process of the artificial muscles will be discussed. The original production process used by Haines et al [9] was used as the basis for the TU Delft production process. It is recommended to read the original production method before reading further. The biorobotics lab uses a custom machine that spins the nylon and iron wire into a coil shape. This machine can be seen in figure 1.11. After this the coiled nylon – iron composite wire is spun around a mandrel, this can be seen in figure 1.12. Then this mandrel is placed in an oven at 155C° for an hour before being cooled by the surrounding temperature for 30 minutes. After cooling, the muscle can be removed from the mandrel and used for testing. An example of a completed artificial muscle can be seen in figure 1.13.



Figure 1.11: Machine set up used to twist the nylon around itself and around an iron wire.



Figure 1.12: example of an artificial muscle, the quality of which is poor, however this is first trial with extruded nylon 6.



Figure 1.13 Completed artificial muscle, note: not the same one as in figure 1.12. This one can be seen in chapter 6.

2. The science of polymer muscles

Polymers are semi-crystalline materials consisting of crystalline (highly structured) and amorphous regions (no structure). A schematic representation of polymers semi-crystalline structure can be seen in figure 2.1 The many different polymer strands are held together by cross-linking bridges in between the amorphous regions of the material, these add to the high mechanical and tensile strength that is typical in semi-crystalline polymers [9][10][11]. These amorphous regions also allow movement when the polymer is heated above its glass transition temperature (T_g) which is the leading movement mechanic of polymer twisted artificial muscle (PTAM). The problem is that this structure while allowing for movements the semi-crystalline nature also leads to poor thermal and electrical conductivity, which in turn leads to the poor energy efficiency of PTAM's which is currently the biggest bottleneck for most applications [9][10]. High temperatures ($>150C^\circ$) are currently required to achieve notable contraction, this is dangerous if contact with mammals happens during usage and also leads to deformation due to relaxation of the muscle shape due to the long periods of time in close proximity of melting temperature (T_m). Another problem this provides is very slow cooling speeds of the PTAM and thus slow changes in contraction and relaxation of the muscle on a macroscale.

Haines et al [9][10] reported that regular nylon 6 and nylon 6,6 can contract by 3,9-4,2% [9]. When they changed the geometry to a chiral shape they were able to achieve contractions up to 49% [9][10]. Several mathematical models have been proposed to explain the contracting before. Where Love's equation (1) shows most promise.

$$\Delta L = I^2 \Delta T / N \quad (1)$$

Where N is the number of coils, ΔT is the change in inserted filament twist when heated and ΔL is the change in coil length [10] When heated, the twisted filament wants to untwist, this causes adjacent coils to be pulled closer together and shortens the muscle on macroscale. This remarkable contraction is over two times as much as humanoid muscle and combined with the cheapness and readable availability of the raw material is why polymer artificial muscles are so promising. Work by Li et al [11] hypothesis is that improved energy conductivity of the PTAM's will lead to higher muscle contraction at the same energy input or similar contraction at much lower energy inputs.

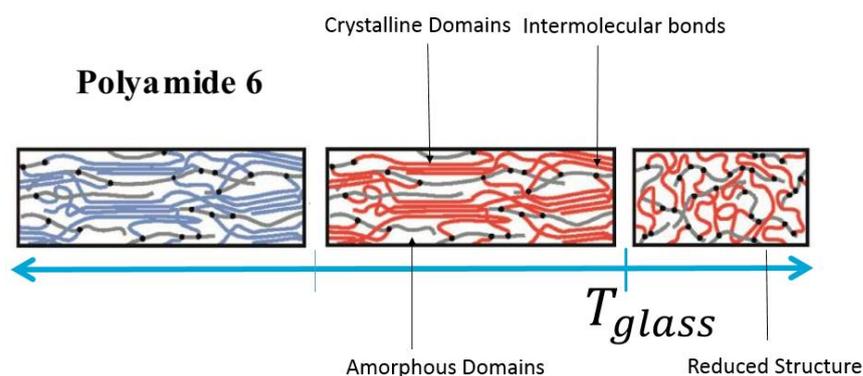


Figure 2.1: Semi-crystalline structure from ambient temperature to above T_g for PA6 this is $43C^\circ$.

2.1 Thermal conductivity and crystallinity

Nylon 6 is a poor thermal conductor (isolator) [12] this is inherent to the semi-crystalline structure that can be seen in figure 2.1. The thermal conductivity (λ) of bulk nylon 6 is around the order of $0.4 \text{ W/m}^{\cdot 1} \cdot \text{K}^{-1}$ [6][13]. The main influencing factor is the crystallinity (the amount of crystals over total volume) which can range between 0.3 and 0.9 for PA6 and HDPE respectively [11]. The amount of crystals in the polymer is important because phonons require repeating structure in close proximity for thermal conduction to be efficient, a notable example of extremely high molecular structure and thus high λ is diamond. Another factor influencing the λ is the inherent anisotropy of polymer structures [10]. The crystal structural direction can be influenced by drawing or extruding the polymer fiber in the direction required for the application it is intended for. For the purpose of this project that is the axial direction. An unfortunate side effect of the hypothesis from Haines et al [9][10] is that the amorphous regions are required to achieve the muscle contraction that makes polymers such an interesting option for use as artificial muscle. This also means however that addition of other materials (and thus a reduction in crystallinity) may have a negative effect on muscle contraction.

The two factors determining thermal conductivity of polymers that can be controlled during production are the draw ratio, which can be controlled by the amount of force applied to drawing during the extrusion step of the polymer production. And the temperature profile of the production, where the cooling rate is of special significance. Crystallization can only occur above the T_g and below the T_m . Above the T_m the temperature is too high for structures to exist and below the T_g the temperature is too low for inter- and intramolecular movement. Differential Scanning Calimotery (DSC) analysis of the polymer used by the TU Delft laboratory has been conducted in the analytical laboratory of THUAS. The results of this analysis can be seen in appendix A. This analysis revealed that peak crystallization temperature was 163°C . When artificial muscles were annealed and tested at $160\text{-}170\text{-}180^{\circ}\text{C}$ the highest contraction was seen at 160°C annealed artificial muscles. Crystallization is a process that requires time to occur. When extremely fast cooling speeds are used, the crystallization process ‘freezes’ in place, leading to lower crystallinity and more disorder [12]. This is the reason that nylon 6 has such low thermal energy efficiency and is caused by the structural properties of the nylon and it’s production process.

It is worth mentioning that crystallinity impacts other factors than just thermal conductivity of the polymer. For instance tensile strength, yield stress and flexibility of the product are properties that are all tied to crystallinity. In this regard an optimal balance between crystallinity and contraction has to be identified.

Highly drawn and dense polymers have been created in the past, with crystallinity’s above 90% [13]. These however were single strands of polyethylene (PE) and are not useable for artificial muscle applications due to extreme production costs and very small fibers. An initial proposed trial for this project was to create a highly drawn nylon 6 fiber near the T_m the purpose of this test is to create nylon 6 (or a composite) with as high as possible crystallinity in the axial direction to improve the thermal conductive properties to maximum. How this would compare to regular nylon 6 in terms of muscle contraction is unknown because the equipment to produce this product is currently not possible. This coupled with the thermal experimentations lead us to a path of improving the λ via addition of highly conductive components.

2.2 Electrical conductivity

For electrical conduction to occur there has to be free valence electrons. In metals there are large amounts of these free electrons present which can then nudge the electrons of atoms in close proximity until large chains of electron energy transfer occurs. In nylon 6 all the electrons are in sp^3 hybridization, this means that they are 'trapped' in a pyramid shape where very little to no free movement occurs [13]. Because of this inability of valence electrons to transfer energy in between atoms in the nylon 6, the electrical conduction is very low [14]. To go back to the diamond example given in section 2.1. The carbons in diamond are structurally in very rigid positions and all in sp^3 hybridization, this explains why diamond is an incredible thermal conductor but an electrical insulator. The reason that electrical conduction is interesting in the context of my thesis. Is because if the polymer would be good electrical conductors, electrical heating could be used more effectively. Because electric heating can be controlled to a great extent allowing for much muscle control with little ambient energy loss, as is the case in thermal conduction.

To improve the electrical (and thermal) conduction of the artificial muscles, graphene and graphene-oxide will be used. Graphene has several advantages for this intended usage, including: lightness, toughness, flexibility, very high thermal, electrical conduction, and it is fairly affordable [14].

The flat 2D crystal structure of graphene, which can be seen in figure 2, consists of a single layer of carbon atoms with sp^2 hybridization [14]. This means that they contain free electrons unlike nylon 6 and have measured electrical conductivity as high as silver. It also boasts thermal conductivity of up to $2500 \text{ W/m}^{-1}\cdot\text{K}^{-1}$ which is over five orders of magnitude higher than nylon 6. For the purpose of improving the contraction experimental materials have been created at the THUAS laboratory in The Hague, The Netherlands. The exact production process and results of which will be discussed in chapter 5 [13][14].

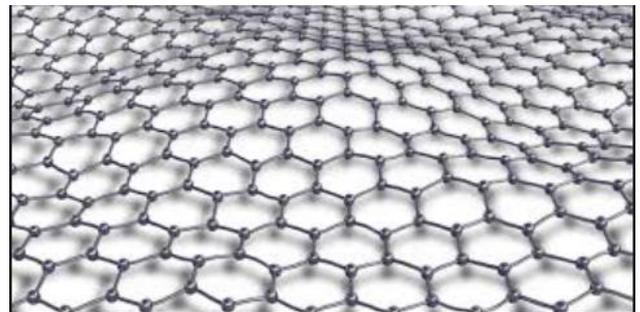


Figure 2.2: Computer generated representation of graphene molecular structure.

3. Previous literature

There has been some nylon – graphene [15] , and nylon graphene-oxide composites [16][17] before. Although the final applications of these composites were different (anti-bacterial, 3D-printing construction or usage as electronic wires) the change in thermal and electrical conductivity can be estimated by using the collective data to produce a projective model. Zang et al [15] showed that PA6 with 10% filler (consisting of carbon nano tubes (CNT's) and sulphonated graphene (SG) increased the electrical conductivity from $1 \log p / (\Omega.cm)$ to $16 \log p (\Omega.cm)$ they showed an electrical conductivity between $6 \Omega.cm$ and $26 \Omega.cm$. The group of Zeng et al [16] focused on creating super high thermal conductive PA6 polymers by using in situ polymerization with PA6, graphene (G) and graphene-oxide (GO) composites. This same procedure will be used to create the super muscles for this project, and will be discussed at length in chapter 6. As discussed in chapter 2, the thermal conductivity of bulk PA6 is $0.4 \text{ Wm}^{-1}\text{K}^{-1}$. By combining PA6, G and GO in different ratios they were able to obtain $2.2 \text{ Wm}^{-1}\text{K}^{-1}$ at 10% filler percentage (filler in this case being G and GO). They do not however specify the exact ratio of GO to G, although they note it is small [16]. In their procedure they use 0.2 g of GO for 1.8 g of G with 18 g of PA6. If we assume that ratio remains the same throughout their experiments the total ratio's would be 90% PA6, 9% G and 1% GO. They also compared their composite to a PA6 with 10% G composite and were only able to obtain a thermal conductivity of $1.37 \text{ Wm}^{-1}\text{K}^{-1}$. The third group of Wang et al [18] only used 3% filler with SG and PA6 (97%) and were able to increase the thermal conductivity from $0.4 \text{ Wm}^{-1}\text{K}^{-1}$ to $0.6 \text{ Wm}^{-1}\text{K}^{-1}$. From the available research it seems that a composite of PA6, G and GO will yield the most optimal results. Although none of the research reached the limit thermal conductivity as visible from their graphs, they all noted that higher than 10% of filler would offset the costs to benefits ratio [15][16][17] and negatively impact mechanical strength, due to a decrease in crystallinity.

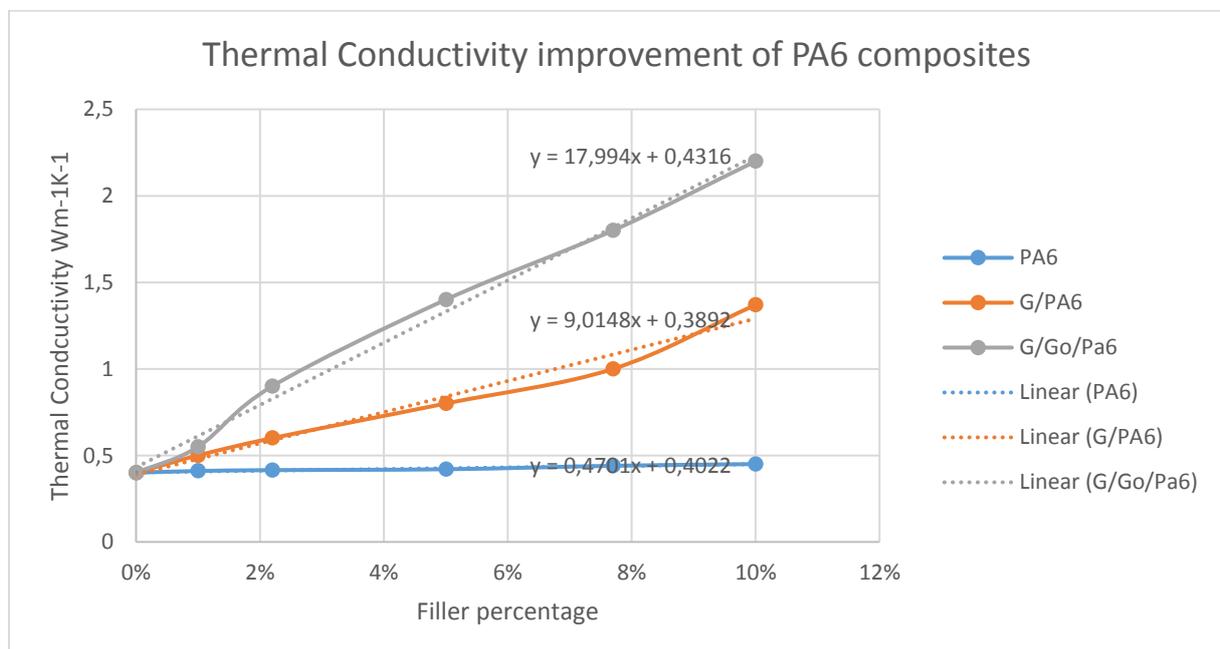


Figure 3.1: Thermal conductivity improvements at different filler percentages with a composition of PA6, Graphene and Graphene-oxide [17].

There is no available literature that analyzed a composite containing PA6, graphene, graphene-oxide and nanosilver. However Kim et al [17] have produced inkt containing nanosilver particles with extremely low resistivity (0.8 Ohm.cm at room temperature). It is expected that the addition of 1% wt nanosilver to the composite will significantly improve conduction, and thus muscle contraction. Using the data available, a reasonable estimation of 7-10 fold improvement in conductive properties can be established.

4. Extruder

For this project the PFT programme ordered a filament extruder [18], in this chapter the construction process and initial testing with PA6 (PA6 pellets from Sigma Aldrich [19]) and testing with the nylon 6 used by the tests at the TU Delft biorobotics lab (midnight moon 0.6 mm clear nylon) [20] will be conducted. These will also be made into artificial muscles as described in section 1.3 and tested for muscle contraction. Answering the first research question (1).

4.1 Materials and parts

The full list of materials and parts can be seen in appendix B. The most important of these will be discussed in more length in this subsection. By far the most important part of material is the extrusion screw, also known as the auger. This screw is approximately 30 cm in length and is paramount to produce filaments. The heating unit and nozzle are two other parts that are vital to the operation of the filastruder.

Besides the filastruder THUAS also ordered the filawinder, a specialized spool that can be used to produce large quantities of custom filament and ensure diameter stays equal throughout the production process. This has not been assembled because of technical issues with our 3D printer. This will be assembled when the newly ordered 3D printer arrives, probably next academic year.

4.2 Production process

The filament extruder assembly procedure has been described extensively in the assembly manual [21]. It consists of a mechanical assembly part and an electrical assembly part. Members of Rheon [22], the student association of the electrical engineering department of THUAS have been kind enough to assist with the electrical assembly component. The filastruder during mechanical assembly can be seen in figures 4.1 & 4.2. The electrical wiring can be seen in figure 4.3 and the finished filastruder can be seen in figure 4.4.



Figure 4.1: Mechanical assembly of the filastruder part 1/2.



Figure 4.2: Mechanical assembly of the filastruder completed, part 2/2.

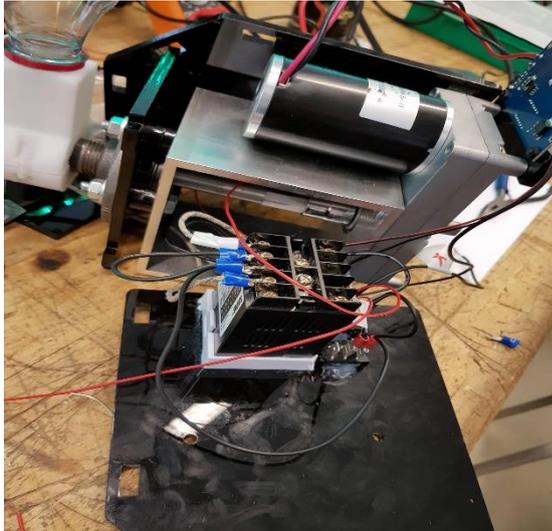


Figure 4.3: Electrical installation of the filastruder, the electrical engineering department of THUAS was kind enough to assist with this.

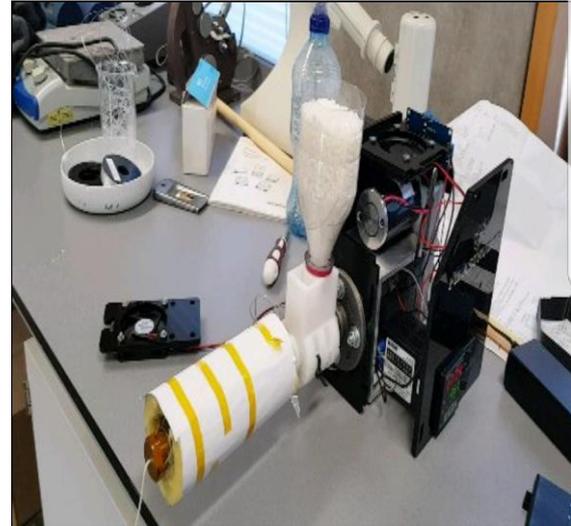


Figure 4.4: Completed filastruder testing with ABS extrusion.

In order to produce filament, suitably small (5 mm in any direction) pieces of plastic are put into the filastruder hopper. The hopper acts as a temporary storage vessel for the production process. The pieces drop into the screw holes of the filastruder auger which, powered by a small motor, moves the plastic particles towards the heating element near the end of the extruder. The heating element is controlled using the control panel on the side of the filament extruder and can reach temperatures of 250°C. The forward rotation of the screw forces the now molten filament through the nozzle via shear force extrusion, the nozzle diameter size coupled with the production speed and temperature of extrusion determine the diameter of the final filament. A schematic representation of the polymer extrusion process can be seen in figure 4.5

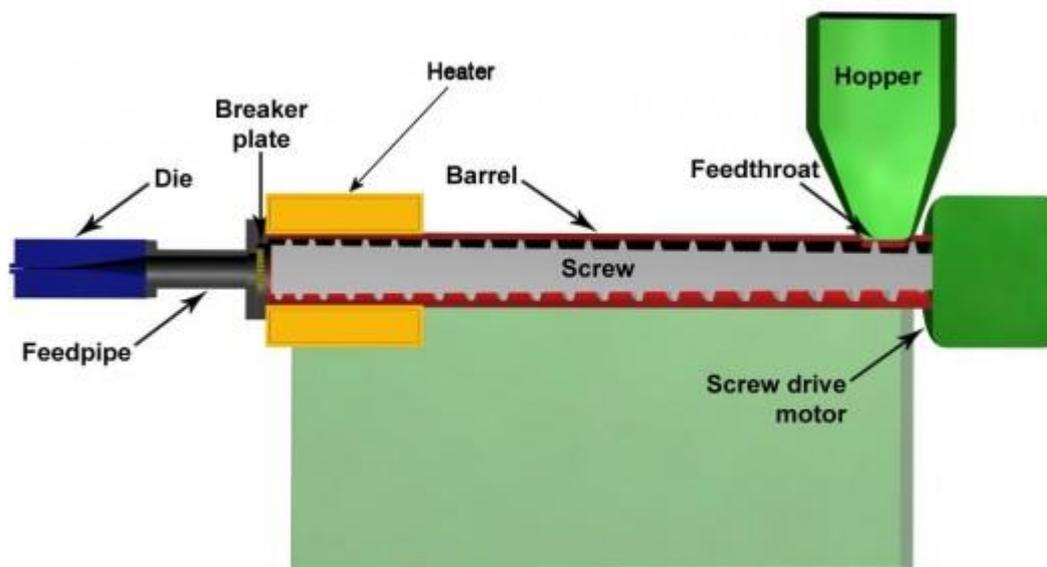


Figure 4.5: Schematic representation of the extrusion process, note that the nozzle referred to in the text is called the Die in this schematic.

4.3 Tests

In these tests PA6 [19] will be extruded and tested as artificial muscle in the TU Delft biorobotics laboratory. The muscle will be produced according to the procedure discussed in subchapter 1.3. The muscle will then be tested for contraction using electrical energy (connected to the iron wire) as energy source. The setup can be seen in appendix C. An overview of failed parameters can be seen in appendix D.

Acrylonitrile butadiene styrene (ABS) filament was produced from the ABS pellets that came with the filastruder. As per the assembly manual this was extruded for 8 hours to clear the assembled filastruder of remaining contaminants such as metals, dust and dirt. [21] After this, PA6 was extruded to remove the ABS from the filastruder to ensure that the produced wires would be high quality nylon 6. After the remaining ABS was removed, the PA6 supplied by Sigma Aldrich has been extruded [19]. These were then tested and compared to the fish wire they normally use, the results of which will be shown and discussed in chapter 6. The ABS was extruded at 185°C, with a 1.75 mm diameter nozzle. The diameter was relatively constant. An example of the extruded ABS can be seen in figure 4.6.

A 0.6 mm diameter nozzle was used to extrude the PA6 because this is the diameter of the fishing wire used by the biorobotics lab for their current polymer twisted artificial muscles, Dr. van der Kamp was kind enough to help with the drilling of the nozzle. The extrusion of PA6 was notably more difficult than ABS and required several tries. Initially the melting temperature of 225°C was used but this proved too hot, as a result the extruded nylon 6 stuck to the side of the nozzle and the diameter was not constant. After this 200°C was used, this showed improvement but the extruded nylon was still too liquid, resulting in failed extrusions, an example of this can be seen in appendix D. Eventually the correct temperature was found through trial-and-error, this temperature is 182.2°C. This has been used to extrude PA6 twice with consistent diameter for up to 10 meter pieces, although constant human attention is required to prevent the nylon from getting stuck, almost glued, to the side of the nozzle. It is my expectation that once the new 3D-printer for the PFT laboratory and the filawinder [23] are up and running, this behavior will diminish or even stop completely. I would highly recommend the filastruder [21] to be mounted on a wall vertically as this would greatly decrease the amount of sideways movement. An example of the extruded nylon 6 can be seen in figure 4.7.



Figure 4.6: First batch of ABS extruded using the filastruder. As can be seen the overall diameter variance is fairly low.



Figure 4.7: First successful batch of extruded PA6, 0.6 mm with a larger variance than the ABS extruded in figure 4.6.

5. Nylon 6 composite production

In this chapter the production process of the nylon – composite muscle will be explained, the test procedures of the nylon muscle will also be discussed. The results compared to regular PA6 will be discussed in chapter 6.

5.1 Experimental procedure

The production process of the novel polymer composite will be discussed here. Two separate production methods for the composites have been utilized and compared. They are both explained in sections 5.1.1 through 5.1.3

5.1.1 Acetic acid-nylon crystals

The PA6 supplied by the biorobotics laboratory has to be reduced in size to below 0.5 mm (plastic pallet size) to be able to be extruded by the filastruder. Experimental methods have been tried to achieve this size reduction (due to physical handicap cutting the wire to size is impossible)[24]. 0.5 grams of the nylon wire have been cut in chunks of 3-4 cm in length. These were put in a two-way flask, to which 10 mL of 16.0M acetic acid has been added. The contents of the flask were continuously mixed with a magnetic stirring bar at 1000 rpm to ensure homogenous mixing of the PA6 once dissolved. It took 38 minutes to dissolve the 0.5 g of PA6 at 70°C.

After the nylon had been dissolved the acetic acid was evaporated (in a fume cupboard) at 135°C. Crystal structures were clearly visible but were solidified against the flask surface. It is currently unknown if the crystal structures were actually the nylon crystals or a combination of the acetic acid and nylon 6 salt.

The experiment was altered for the next attempt where instead of evaporation as separation method, vacuum filtration has been used. In order to ensure quality and as method of comparison the experiment was repeated using not only acetic acid as solvent but also formic acid (99.5% solution in water).

5.1.2 Formic acid dissolving

1 gram of PA6 [19] was dissolved in 20 mL room temperature formic acid. This step took 1 hour, and was done using constant stirring. After which the solution was pipetted into a large excess of non-solvent (demineralized water) with mechanical stirring at 300 rpm. The result was a nice separation of nylon 6 with a very clear white colour. The resulting precipitate can be seen in figure 5.2. To separate the PA6 from the water-formic acid solution, a Buchner funnel was used. An additional liter of demineralized water was used to clean the PA6 from any remaining formic acid to ensure none of the acid could end up in the extruding machine. The sample was then dried at room temperature for 24 hours before DSC analysis was conducted. The same procedure was used for 10 grams of PA6 and dried in an oven at 50°C for 16 hours before extrusion, because water is notoriously bad for nylon 6, weakening it's mechanical strength.

5.1.3 Composite production

Chen et al [15] managed to create nylon 6, G and GO composites using in situ polymerization of caprolactam. The building block of nylon 6. By mixing a dissolved mixture of G and GO with heated (155°C) caprolactam in a Nitrogen environment (the catalyst of the ROP for nylon 6) they created stable polymer composites. In the same paper they used melt compounding to achieve similar stable polymer-carbon composites.

Because no polymer artificial muscles exist in literature that are a composite of nylon 6, G and GO Dr. Leemhuis and myself decided that for this stage of the project it would be more efficient to extrude a wire with only



Figure 5.1 PA6 precipitate after formic acid dissolving.

graphene and graphene-oxide mixed into the nylon. Mostly because the nanosilver is a solution in tetradecane, which can only be used in a pure nitrogen environment, which is hard to setup in the chemical laboratory of THUAS. In the future it may be interesting to set up a Schlenk apparatus to combine nylon 6, G, GO with small quantities of nanosilver (1-3% wt) to improve the energy conduction even further.

Two procedures were used to prepare 5 gram batches of polymer composite. The first batch followed the same formic acid dissolving procedure as described in section 5.1.2, with the added step that after dissolving the graphene (0.498g) and graphene-oxide (0.0403g) were mixed in and allowed to stir for two full hours at 70°C. The resulting polymer before drying can be seen in figure 5.2.

The second production method was to a small scale reproduction of melt compounding. 4.504g Of nylon 6 (Sigma Aldrich) was melted in a 50 mL glass bottle using a conduction heater set up to 300°C, well above the melting point of 225°C as specified by the supplier [19]. Once the nylon was liquefied the graphene (0.587g) and graphene-oxide (0.0483g) were added and manually, and aggressively mixed using a glass-stirring rod. The resulting polymer composite can be seen in figure 5.3. Note: this is the polymer before freezing, which will be used to separate the polymer from the glass walls.

Both polymer composites have been analyzed using DSC, and compared to unaltered nylon 6. An overview of the different DSC results can be seen in appendix E and F

30 Grams, the minimum amount the extruder can produce (while producing enough constant force to extrude quality wire) of polymer composite was produced with a 90% nylon 6, 9% graphene, 1% graphene-oxide composition using the formic acid dissolving technique. The same method was used to make a 95% nylon, 4.5% graphene and 0.5% graphene-oxide composite. This was then grinded into a particle size below 0.4 mm (rough powder) to ensure minimal chance of clogging inside the extruder auger. The extruded composite wire can be seen in chapter 6. The same method was used to produce a 95% nylon, 4.5% graphene and 0.5% graphene-oxide composite

5.2 Tests

The production of the nylon composite muscle will be done in the same way as outlined in subchapter 1.3. The tests will be conducted with the same setup as in subchapter 4.3. This set up can be seen in appendix C. The results will be discussed in chapter 6.



Figure 5.3: Nylon 6 (90%), graphene (9%), and graphene-oxide (1%) polymer composite produced through melt compounding.



Figure 5.2: nylon 6 (90%), graphene (9%) and graphene-oxide (1%) polymer composite produced through the formic acid dissolving production method.

6. Results and discussion

This chapter will describe the results and describe and discuss the results, as well as provide commentary regarding the results and how they were obtained.

6.1 Chemical analyses

In order to ensure a true composite has been produced, instead of a temporary mixture, Fourier Transform InfraRed spectroscopy (FTIR) and DSC analysis has been conducted of both composites and compared to nylon 6 [19]. The FTIR results can be seen in figure 6.1 and the DSC results can be seen in figure 6.2.

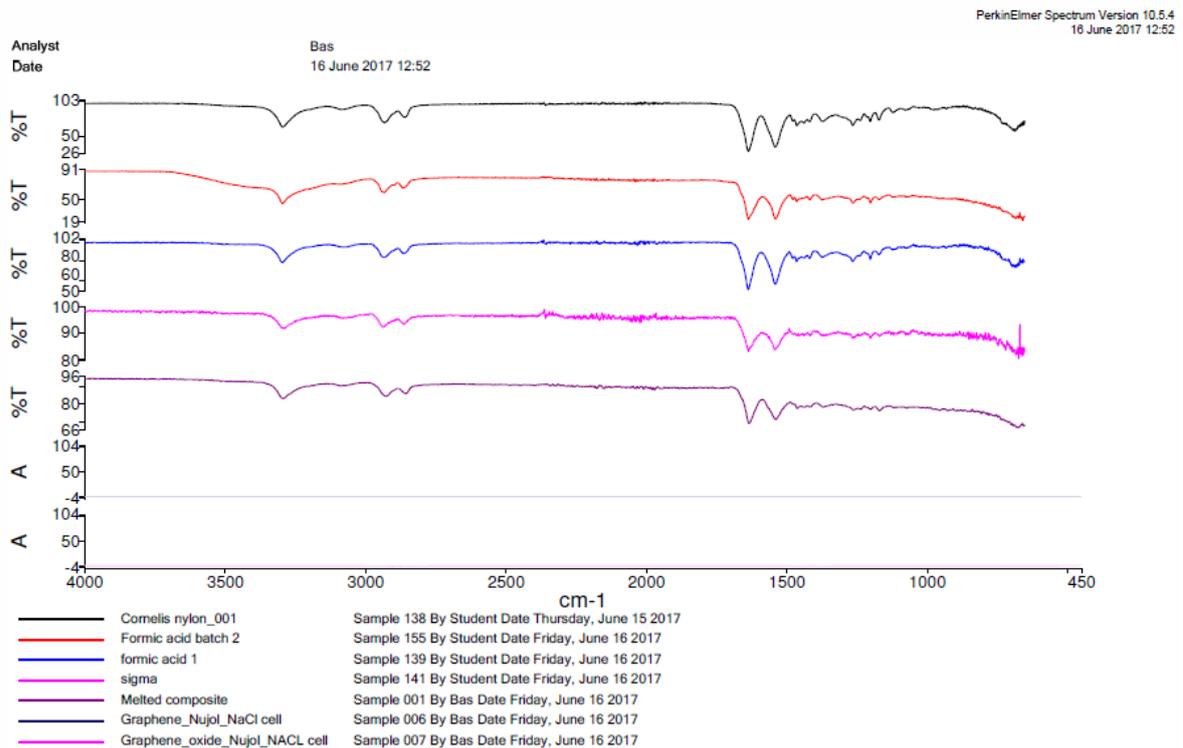


Figure 6.1: FTIR analysis results of the made batches.

The results of the FTIR analysis show that the biggest concentration of chemical bonds present are amide bonds, which is perfectly logical seeing that nylon 6 is a polyamide. In figure 6.2 the FTIR analysis of the formic acid dissolved (9%) graphene-nylon composite can be seen, it is worth noting that the amide bonds (3300 cm^{-1}) and double carbon bonds (2900 cm^{-1}) are the most prevalent bonds, which is to be expected because nylon 6 contains both of those. The formic acid 1 and formic acid batch 2 results were produced using the formic acid dissolving production process (section 5.1.2). The melted composite was produced using melted compounding (section 5.1.3).

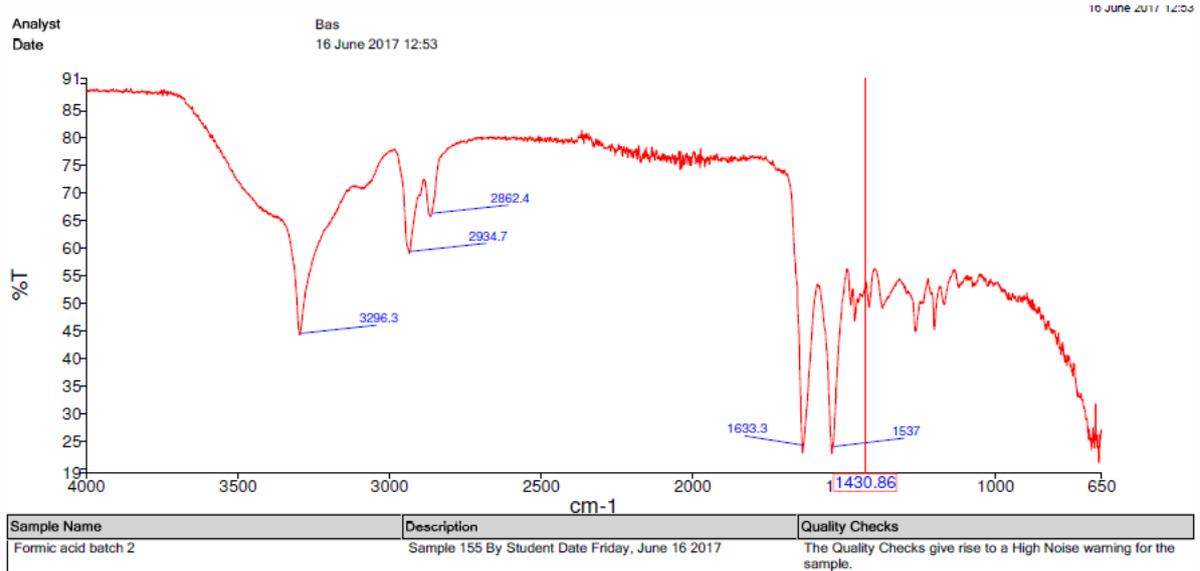


Figure 6.2: FTIR analysis of formic acid dissolved PA6 – graphene (9%) composite.

This composite had the highest amounts of C=C bonds of all the samples tested, the peaks were also sharper overall in general, although the descent after 1500 cm^{-1} was quite steep. For polymer chemistry the range below 2000 cm^{-1} is not typically used.

The DSC results of melted-compounded graphene composite (figure 6.4) and the formic acid dissolved graphene composite (figure 6.5) show a decrease in T_m from 227°C to 223°C and 222°C respectively. The results of the Sigma nylon 6 DSC analyses can be seen in figure 6.3.

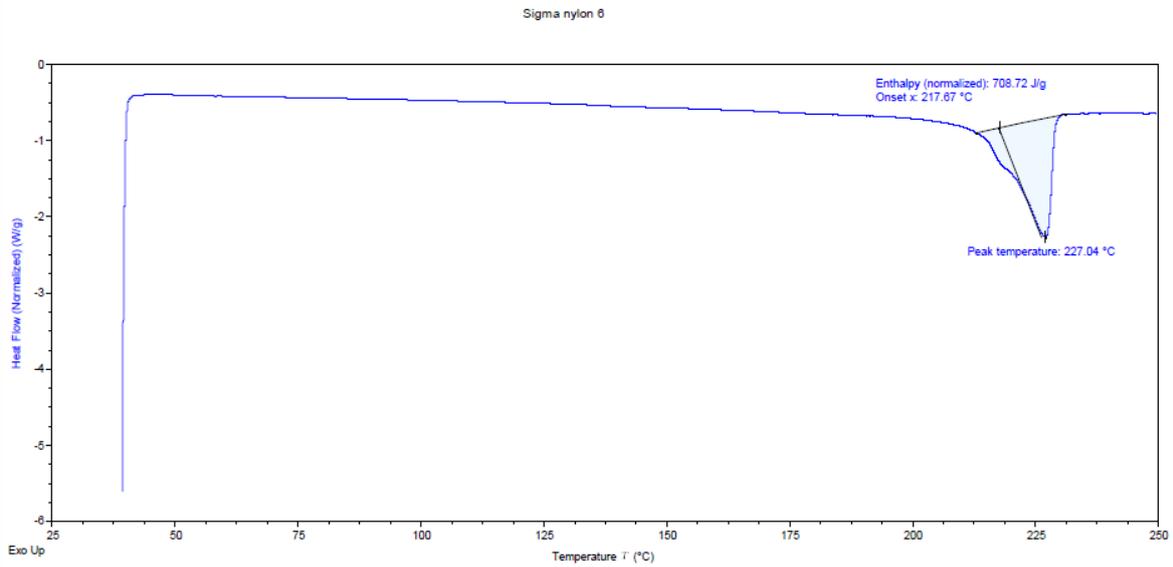


Figure 6.3: DSC analysis results for sigma nylon 6.

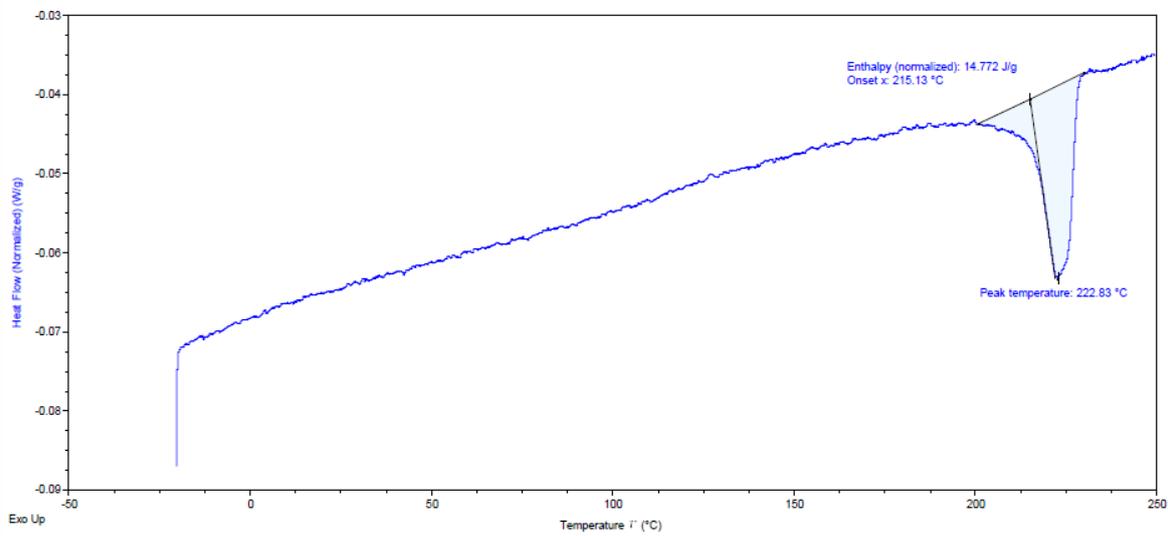


Figure 6.4: DSC analysis results for the melted compounded graphene – nylon composite.

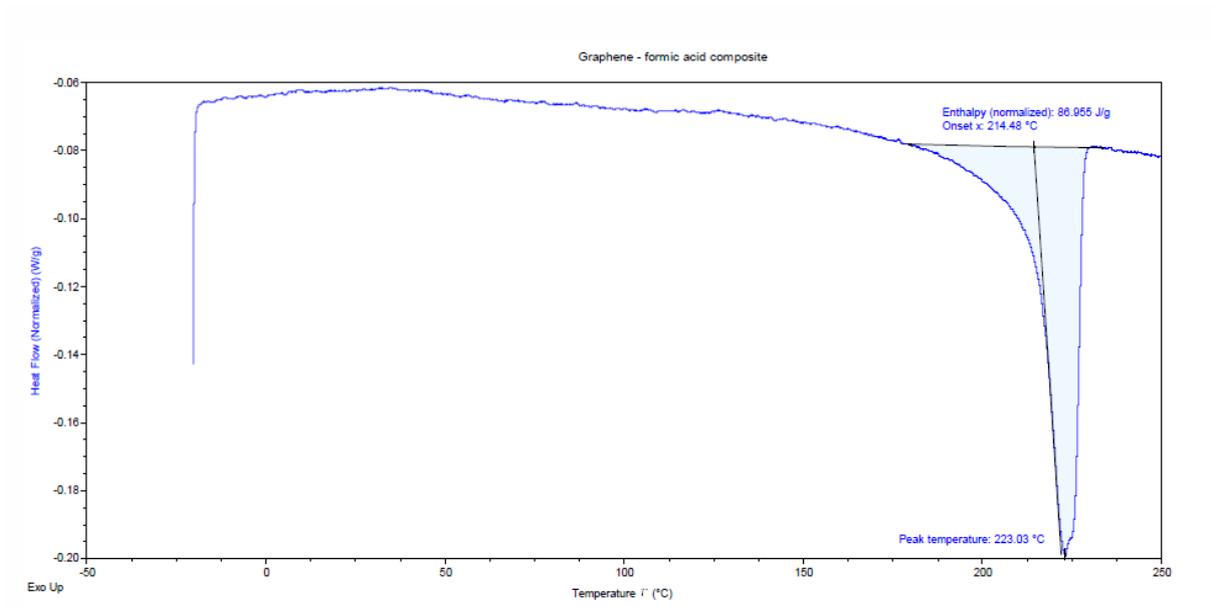


Figure 6.5: DSC results for the formic acid graphene-nylon composite.

It is interesting to note that both the composites required significantly lower amounts of energy to heat up (enthalpy of 708.82 J/g (Sigma), 14.772 J/g (melted compounded) and 86.955 J/g (formic acid))

Which would indicate an improvement in thermal conduction. Extrusion with the melted compounded nylon has not been achieved yet.

6.2 Extruded nylon wires

Several nylon wires have successfully been extruded using the filastruder, including a graphene (9%), graphene-oxide (1%) composite, as well as a composite with graphene (4.5%) and graphene-oxide (0.5%) have been produced. The 9% graphene wire can be seen in figure 6.6. The 4.5% graphene wire looks identical (black wire) so a picture has not been added. These were both wrapped around a laboratory spoon as replacement for a small spool. The regular nylon 6 wire can be seen in figure 4.7.



Figure 6.6: 9% Graphene, 1% graphene-oxide, 90% nylon composite wire on the left, compared to regular nylon 6 wire on the right. It is clear that the wire on the left is black while the regular nylon is a light yellow/white colour.

6.3 Extruded nylon muscle

The extruded nylon 6 [19] has been made into a muscle using the production method described in section 1.3 and tested using the test setup that can be seen in figure 6.7. The results of which can be seen in figure 6.7. The original production method was used as used by Haines et al [9], with the addition of iron wire wrapped around the muscle. A heat gun was used on both the first and second settings, being careful to keep a 5 cm distance as to not melt the nylon artificial muscle.

The muscle was produced using the method described in section 1.3. Unfortunately, when we tested it with a heat gun and 10 grams of weight attached to it, we were unable to achieve a contraction with this muscle. I believe this is because we were unable to achieve proper twist insertion due to excessive elasticity of the nylon. When force was applied to twist, it the lever arm of the machine did not shorten, as it normally does with fishing wire [9][25]. This suggests that the wire lengthens instead of twists around its own axes. Further research is required to find out the root cause of this issue. It is possible that the midnight moon nylon is in fact not nylon 6, or at least not the same grade of nylon 6 as that of Sigma. It is worth noting that the diameter of the extruded nylon (which was extruded with a 0.6 mm nozzle) was notable smaller than the midnight moon nylon, which leads me to believe too much pulling force is applied, or pulling force varies too much during extrusion to create a smooth consistent wire.

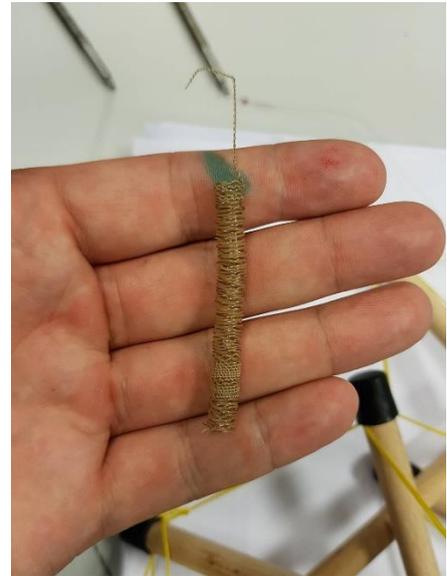


Figure 6.7: Extruded nylon 6 (Sigma) produced into a muscle.

The 9% graphene composite muscle can be seen in figure 6.8 and the 4.5% graphene composite muscle can be seen in figure 6.9. All three muscles were tested using the setup shown in appendix C using a heat gun as well as low electrical current of 12V (separate tests). They unfortunately did not contract on any of the tests. When a multimeter was used to check for conduction we were unable to measure any.



Figure 6.8: 4.5% Graphene composite muscle, unfortunately this did not contract.



Figure 6.9: 9% Graphene composite muscle, unfortunately this did not contract.

6.4 Discussion

The compound melted composite was notably more black after 4 days than the formic acid dissolved composite. I believe this is because not all the nylon melted before mixing so the composition is different. It looked like about half the nylon melted before mixing which would mean that the percentage graphene and graphene oxide was up to 40% compared to just 10% in the formic acid composite. The 4.5% graphene composite looked identical to the 9% graphene composite.

It is my hypothesis that the production methods used did in fact, not lead to a composite of graphene – nylon 6. But to new ways of creating nylon – graphene salts. Alternatively, it is possible that the acid group was able to attract the free proton of the nitrogen in amide (Figure 1.2), which would in turn be auto-catalytic for nucleophilic attack by atmospheric H₂O. This would result in chain fractures along the chain length leading to a graphene-nylon oligomer instead of a polymer, this means that the chain length would be very short, which would significantly impact the mechanical strength and tensile strength of the nylon and could help to explain the elastic properties that were observed during the muscle production stage of the project.

Some papers showed successful composites using graphene-graphene oxide with nylon 6 by performing the mixing of the nylon while producing the nylon from its monomer through polymerization. [10][11] For this stage of the project this was not done due to difficulty in setting up the lab for this. If the acid did in fact cause the polymer production to fail it is worth to try as a next step to polymerize caprolactam, this can be done at 255 K using an inert nitrogen environment. This can be achieved on a lab-scale using a Schlenk apparatus. The nanosilver also requires a nitrogen environment so in that case it would be prudent to also add the nanosilver.

One of the attractive qualities of nylon is the affordability, unfortunately for now making graphene-nylon composites is quite expensive. Thorough testing is required before accurate cost expectations can be made, including economics of scale. Including life-cycle assessment and life cycle cost assessment. Thorough testing of the efficiency and workability of the extruded composite muscles is also required to obtain the optimum between affordability and composition of the artificial muscles.

It is worth mentioning that it is possible that the nylon used by the TU Delft is in fact, not (entirely) nylon 6. It is possible that it is a mixture of several different nylons or a mixture of different grades of nylon. It is notable that that besides the diameter being larger, the wire was also much stronger (unbreakable by hand while the extruded wire were breakable by manual pulling). It is possible that this is only related to the diameter or this is related to potentially being another material. It would be interesting to try to extrude midnight moon, using the formic acid dissolving process, once the filawinder [20] has been installed and optimized. Unfortunately, this will have to wait until the new 3D printer arrives for the PFT laboratory. It would also be interesting to see how nylon 6,6 handles extrusion. It is perhaps also a good idea to use the last undrilled nozzle and cut a slightly larger than 0.6 mm hole in this nozzle, during extrusion the extruded wire diameter was smaller than the nozzle size and became smaller with rising extrusion temperatures.

6.5 Conclusion

Unfortunately I have only been able to answer the first research question (1), we are in fact able to produce nylon wires on a lab scale. However, great strides towards future success of this project have been made. A nylon extruder has been produced, and extruding parameters for both ABS and nylon 6 have been established and have been shown experimentally to work on multiple occasions.

It is currently unknown if the graphene-nylon composite produced is in a fact a polymer, it is likely that it is a oligomer or perhaps even a salt. This would explain some of the negative material properties that were experienced during testing, such as the elasticity and the wetness of the material.

The extruded nylon has been twisted, coiled and wrapped around a mandrel that does keep it's shape, is springy, did support 10 grams of weight but unfortunately did not contract during heating. Besides this, much new knowledge about polymer production and behavior as wire and muscles has been realized which can be strategically used for future research. An overview of the things we have discovered and recommendations on how to continue can be seen in chapter 7.

7. Recommendations

Several very important recommendations have to be made in regards to this project, first of all it should be noted that this project is not only very interesting it is also very current. Therefore, my first recommendation is to continue working on the project of improving the material of artificial muscles, especially working towards solving the other research questions.

DSC analyses of the midnight moon fish wire suggest that the wire is a co-polymer blend instead of pure PA6, which could perhaps be the reason that they have a problem with rapid deformation as experienced by the biorobotics laboratory in Delft. My second recommendation is to analyze pure polymers further to see if the same deformation can be seen when purer polymer wires are used.

The third recommendation is in regards to the filastruder machine, it is a decent machine but there are better machines on the market. My personal recommendation for a machine would be the 3D Devo (<https://3devo.eu/>) produced in Utrecht, The Netherlands. It is more expensive than the filastruder (5000 euro) but has gotten stellar reviews from the aerospace engineering department of the Delft University of Technology. If this is not possible for budgetary reasons I would recommend that the filawinder be constructed as fast as possible and that the filastruder be mounted vertically to reduce sideways motion during the extrusion process, which should hopefully reduce most of the problems experienced during this project.

My fourth recommendation is in relation to the polymer blend, different production methods with variations of graphene and graphene-oxide loading should be tested to find the optimum in terms of performance to costs. I would also recommend to add other materials to the blend (for instance the nanosilver we purchased for this project initially) or try blends without graphene but with other 2D materials such as boron nitride (Thomas sSwan). It is also interesting to look at different types of polymers as the main material, instead of nylon 6. Tests should be conducted using midnight moon nylon as soon as the filawinder has been build.

My fifth recommendation would be to obtain both a Nuclear Magnetic Resonance (NMR) machine and a Gel Permeation Chromatography (GPC) machine, this combined with the FTIR, High-Performance Liquid Chromatography (HPLC) and the DSC analyses would be optimal proof of the polymer composite which is important for any potential publications in (polymer) chemistry journals. However, wait until constant diameters are achieved and a working artificial muscle has been produced. Or they could be used to proof the suspicion that the acid renders the polymer more vulnerable to nucleophilic attack of atmospheric water.

My sixth recommendation is to reach out to a physical chemistry lab that can do tests including but not limiting to: tensile tests, life-cycle analysis, mechanical strength tests. This would greatly increase the knowledge available about the polymer twisted artificial muscles and would also improve the success of further composite attempts.

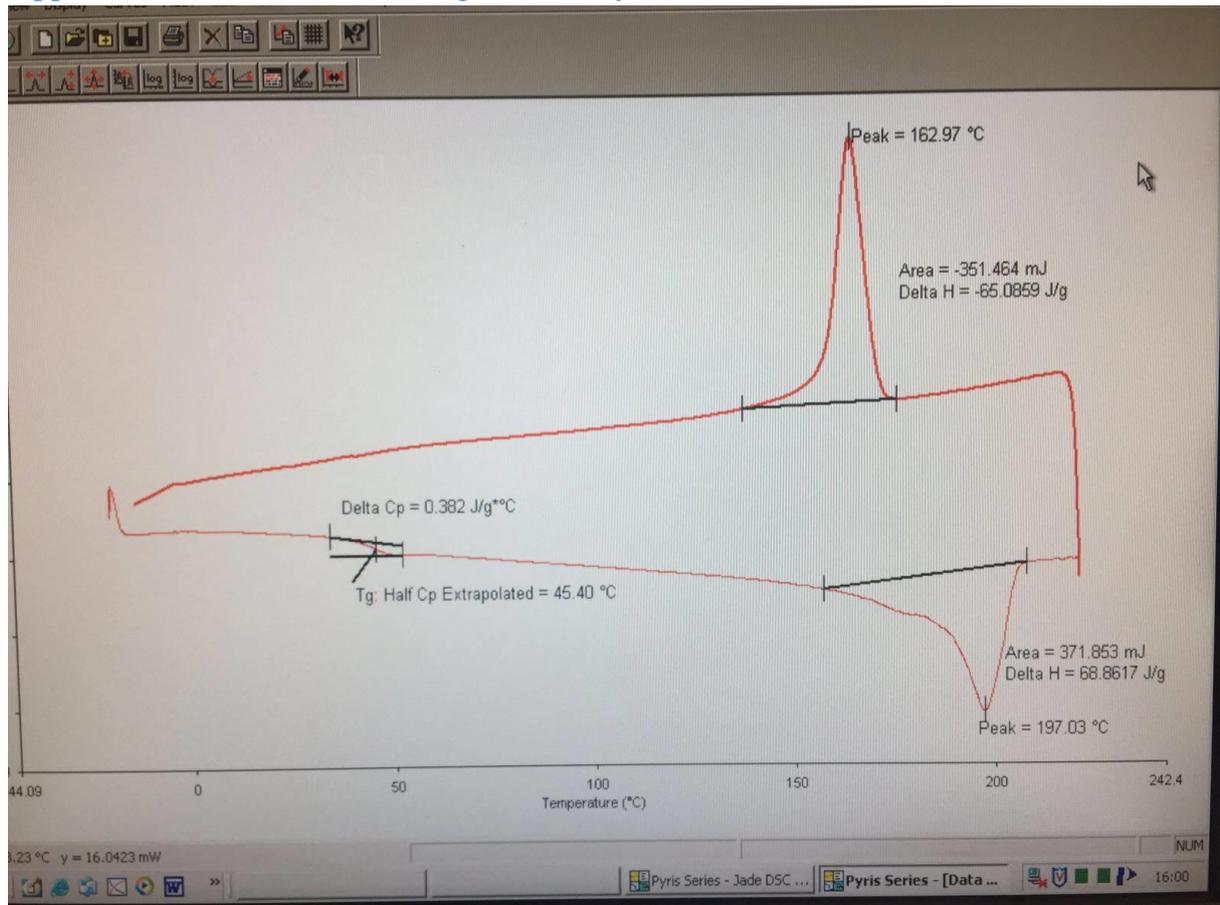
My seventh recommendation is to include a thorough costs to benefit analysis when suitable polymer composites have been identified. This should include economics of scale, variation in ingredient costs, different suppliers, grade of material ingredients used, and the amount of contractions the muscle is good for on average. This will make it easier to upscale and to create a potential business case.

My eight and final recommendation is that the betafactory and Delft University of Technology should apply for all relevant patents on artificial muscle actuators using new polymer blends they produce, this way they will have the certainty that at least for a few years no one will be able to work on their original research and if it ever reaches commercial scale they may benefit financially.

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Appendix A: DSC results midnight moon nylon



Appendix A: DSC results of nylon sample as provided by Dr. C. van de Kamp, DSC analyses performed by Dr. M. Leemhuis revealing peak crystallization temperature at 163C. This was later confirmed by Marloes Roling, a master's graduate student from the TU Delft mechanical engineering program.

Appendix B : Materials and parts of the filastruder

Included Parts - Mechanical: bag

- 8 inch barrel/flange assembly
- Pipe coupling
- Shaft collar
- Thrust bearing
- Hex socket
- Grey PVC washer
- (4) ¼"-20 1.5" bolts
- (4) ¼" hex nuts
- (8) ¼" washers
- (6) M5-.80x40 motor mount bolts
- (4) M5-.80x100 enclosure bolts
- (4) M5 nuts
- (2) M3x10 Stall protection board bolts
- (12) 6-32 7/8" length screws
- (12) 6-32 nuts
- Filament guide (PTFE tube)
- 2 Regular zip ties

Included Parts – Electrical bag:

- Thermocouple (K-type)
- (2) 60mm fans, 12volt
- 5 female spade terminals
- 2 rocker switches
- Heater band
- (2) grommets

Other Items Not Bagged

- Insulation
- Auger/feed screw
- Lasercut enclosure (remove masking tape protection)
- Aluminum chassis
- 12v power supply
- Stall protection board
- 12v gearmotor
- Temperature PID controller

- Brass plug/nozzle

Appendix C : Muscle test set up



Appendix D Failed extrusion parameters

TEMPERATURE	ABS	NYLON 6
160 °C	X	X
165 °C	X	X
170 °C	X	X
182 °C	X	Success
185 °C	Success	X
190 °C		X
200 °C		X
210 °C		X
220 °C		X
230 °C		X