The Plausibility Of Recycling Used Tennis Strings As 3D Printing Filament

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Tennis is a globally admired sport with a huge fan following. And as all things human, it generates waste. I am an avid tennis player and wanted to explore how the game could be made more sustainable and environmentally friendly. I evaluated a key component of the game, the tennis racquet and its strings. I found that if the seven million racquets produced each year were to be restrung once a year, 84 thousand kilometers of string would be required. This is enough to circumnavigate the planet twice. Burning this can release around 800 tons of carbon-dioxide into the atmosphere.

Through my research, I identified that tennis strings could be recycled and used as 3D printing filaments, thereby extending the lifecycle of the string, and making the sport more environmentally sustainable. I compared tennis strings made from Nylon (Nylon 6,6) and Polyester against literature available for 3D printing filaments for physical and chemical parameters. I focussed my experiments to compare nylon and polyester strings against Poly-lactic Acid (PLA) 3D printing filament for evaluating the temperature range at which extrusion, a key process of 3D printing, is possible. My study shows that Polyester is a potential candidate for replacement of PLA.

Keywords
3D-Printing, Sustainability, Tennis, Polymer and Chemistry

1. Introduction

I am a tennis player with a passion for sustainability. However, tennis isn't the most sustainable sport. I wanted to identify areas to improve this and focussed on researching ways of reusing tennis strings. To identify the scale of this problem, I talked to my local racquet stringer and estimated that he strings close to 400 racquets a month, each using about 12 meters of string. This means that his shop alone generates about 4800 metres of waste string per month. These 12 meters weigh about 17 grams, therefore there is around 81.6 kg of plastic waste created per month in this one shop alone. This is without taking badminton, squash and other racquet sports into consideration. The global annual production of tennis racquets is seven million. If each racquet were to be restrung once every year, 84 thousand kilometers of string would be required, which is enough to circumnavigate the planet twice. Burning this can release around 800 tons of carbon-dioxide into the atmosphere.

The problem I researched is the identification of an alternate use of used tennis strings thereby extending the lifecycle of this material and preventing it from finding its way into landfills and/or incinerators. I hypothesized that I could use these tennis strings as 3D printing filaments. Through the experiment described in this paper, I explored the plausibility of using two types of common strings (nylon and polyester) in 3D printing.

I believe that as 3D printing gains wide acceptance, a critical feedstock for this can be provided by the sporting industry. This will make the sport more sustainable and benefit our planet. While I studied tennis strings, the methods presented are applicable to other racquet sports like squash and badminton.

1.1 Objectives

My research focuses on finding the possibility of replacing Poly-lactic Acid (PLA) 3D printing filament with used Nylon 6,6, or Polyester tennis string. A key objective of the experimentation was to determine the temperature at which the rate of flow of a filament made from a used tennis string is similar to the rate of flow of 3D printing filament, for use in a 3D printer.

2. Literature Review

In order to begin my experimentation, I required a background understanding of the materials I was hoping to reuse as well as the material that I was planning on replacing. My research helped me form a hypothesis, and it was only after comparing the qualities of these materials that I decided to go ahead with my experiments. I looked at the structure of Polyester and Nylon as compared to PLA, as well as their chemical and water resistance. I also researched the tensile strength, durability, and flexibility of all three materials in order to validate that the materials were similar enough that my idea was worth testing.

I discovered that while there has been no research into using tennis string as 3D printing material, a recent NTU study by Panda et. al, titled "Additive manufacturing of geopolymer for sustainable built environment" explores the possibility of using a coal residue to 3D print building. The research "evaluates the potential of fly ash based geopolymer cement for large scale additive manufacturing (AM) of construction elements", and finds that it can be done, and "that the mechanical properties of 3D printed geopolymer are mostly dependent of loading directions due to anisotropic nature of the printing process and retains intrinsic performance of the material." Given that this research was successful, and that it is possible to 3D print with unconventional materials, it seemed plausible to reuse nylon and polyester tennis strings as 3D printing filament.

3D printing filaments are in demand now more than ever as the technology is used to create so many diverse products. Jewellery, prototypes, automobiles, aircraft engines and human body parts all have components that are made by 3D printing. Since the applications of 3D printing are so varied, naturally, so are the properties of the materials used. In today's world, there are many different types of the 3D printing filament, each with different strengths and weaknesses. A good 3D filament depends on what the filament will be used for. Table 1 compares common physical properties of different types of materials. Table 2 compares the uses that the properties listed in table 1. Table 3 compares the chemical compatibility of different materials against common chemicals. Table 4 compares the chemical properties of different materials.

PLA is a material that is normally used to print prototypes or things valued for their aesthetics. PLA is a fairly strong filament, which gets its strength from its semi-crystalline nature. The rigidity and regularity of molecules on a crystalline structure makes PLA strong, however, it is not a very durable material. PLA is an aliphatic material which absorbs moisture quite quickly. This moisture reduces the tensile strength of the filament, which is why it is recommended to store PLA in cool, dry places. Figure 1, from Special chem, Polylactide (PLA): Complete Guide to Accelerate your 'Green' Approach shows a PLA molecule. Some forms of PLA (PPLA) use a plasticizer molecule to make it more pliable, however, PLA 3D printing filament does not contain a plasticizer, instead of getting its plastic-like properties from the fact that it is a long-chain polymer. PLA is a thermoplastic, meaning that it has the ability to soften upon melting, and harden once it is cooled down, without degrading the material in any way.

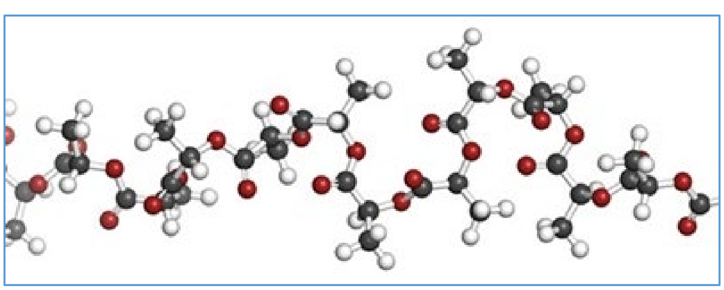


Figure 1: Poly-lactic Acid (PLA) Chemical Structure

Nylon 6,6 is a long-chain polymer, which gets its strength, durability, and heat resistance from its semi-crystalline nature. A crystal is nothing but a rigid, repetitive structure, like the nylon shown in the picture below. This regular structure also forms strong bonds. Due to these strong intermolecular bonds, Nylon 6,6 has high tensile strength and durability. Strong bonds need higher temperatures and greater amounts of energy to be broken, therefore Nylon 6,6 has high heat resistance. Nylon 6,6 is not very water-resistant and absorbs moisture from its surroundings. This is because it is an aliphatic compound. An aliphatic compound is an open chain of monomers, rather than a closed chain that forms an aromatic compound. Nylon absorbs water, and these water molecules ‘wedge’ themselves into the long chain polymer, therefore weakening bonds in the material and causing its degradation. Aliphatic compounds like Nylon 6,6 get saturated by moisture much faster than aromatic, closed chain compounds. The moisture absorbed by the nylon acts as a plasticizer, inserting itself in the long polymer chain and distancing molecules from each other, thereby making the intermolecular forces weaker and the material not as strong. To remove this moisture, and return normal functionality to the material, nylon can be heated at its glass transition temperature. Figure 2, from Ortega, R et al, "Nylon 6,6 Nonwoven Fabric Separates Oil Contaminates from Oil-in-Water Emulsions", depicts a Nylon 6,6 molecule.

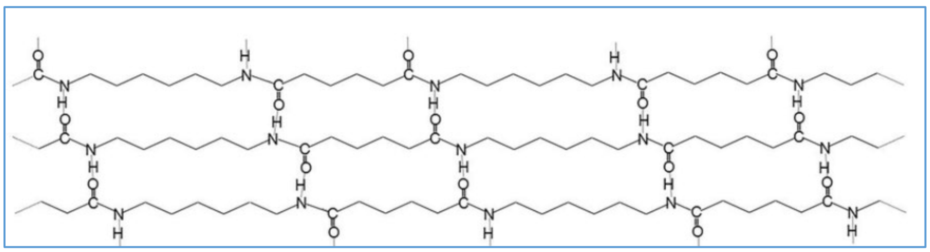


Figure 2: Nylon 6,6 chemical structure

Polyester is also semi-crystalline thermoplastic and long-chain polymer in nature and once again, is strong and flexible due to these properties. Different types of polyester can be either aliphatic or aromatic in nature. Those used in tennis guts are most likely aromatic, given that polyester does not absorb moisture as easily as the aliphatic compounds of Nylon and PLA. Figure 3, from dreamstime.com, depicts the repeating structure of a Polyester molecule.

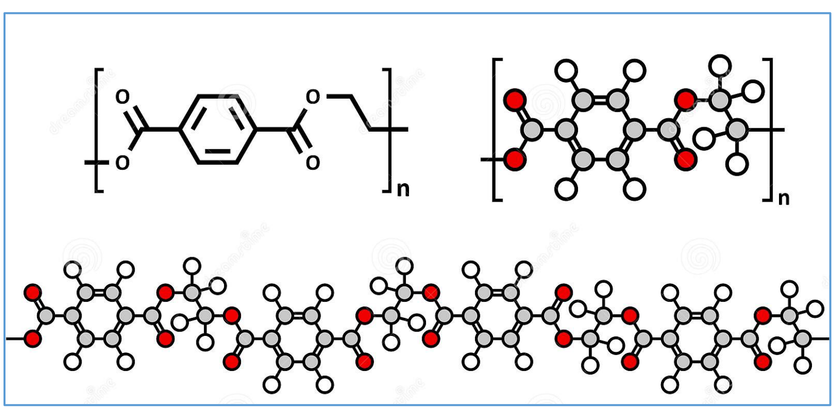


Figure 3: Polyester chemical structure

For my experiment, I used nylon strings (made of Nylon 6,6), Polyester strings, and 3D filament made from Polylactic Acid (PLA). In order to find similarities and differences between these three materials, I researched existing chemical databases and studies and compiled my information in the tables below.

Table 1. Comparison of utility properties of PLA, Polyester and Nylon 6,6

Material	Strength high: ≥40 MPa	Durability	Flexibility	Heat resistance Low:≤210 °C Medium: 210-235°C High : 235-260 °C Very high: ≥260 °C	Chemical resistance high : ≤ 1% change in mass and dimensions Medium: 1%-5% Low: ≥5%	Water resistance high : ≤ 1% change in mass and dimensions Medium: 1%-5% Low: ≥5%
PLA	High	Low	Low	Low	Low	Medium
ABS	High	High	Low	High	High	Medium
PETG	High	High	Low	Medium	High	High
TPU	High	High	Very high	High	Medium	High
PEEK	Very high	High	Low	Very high	Very high	High
Nylon 6,6	High	High	Low	High	High	Medium
Polyester	High	High	Medium	High	High	High

Table 2. Comparison of uses of PLA, Polyester and Nylon 6,6

Material	Uses based on properties listed in Table 1
PLA	Prototyping since prototypes need only give a basic understanding of the product, and don't need to be particularly durable
ABS	Children's toys like Lego are made with ABS since it is strong and durable. So are electronic appliances and consumer goods, and automotive (car) interiors
PETG	Mechanical prints as well as artistic ones like jewellery are printed using PETG since it is both strong as well as durable with reasonable resistance. It is very versatile
TPU	Car tires are amongst the things that can be made with TPU due to its flexibility. Cable, wire, tubes, films and tires for (bicycles only)
PEEK	Due to its high strength and durability, PEEK is used in objects which bear a lot of pressure of weight, like bearings**.** It is a High temp and chemical resistance polymer for aerospace and medical application
Nylon 6,6 Polyester	The nylon and polyester that I aim to use would have already been used and exposed to the environment, potentially lowering its strength, durability and resistance. This means that while the materials in their virgin states could have been used for various things like RC cars or other everyday items, as already used materials, they are better suited to do things where durability is not a big concern, like prototyping. If this can be done, it would mean that they could potentially replace virgin PLA.

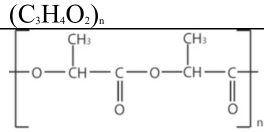
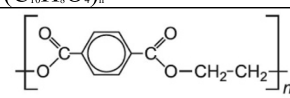
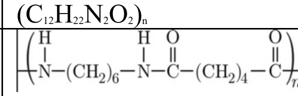
When a material is not compatible with another chemical, it results in the material getting denatured and potentially causes a change in its properties. For example, when Nylon 6,6 reacts with Hydrochloric Acid, it dissolves and partial hydrolysis takes place. This means that the molecule absorbs water and bonds are broken, resulting in a shorter chain of molecules, with different properties than the original Nylon 6,6. To ensure that a material functions in the way that it is intended, one must know which materials to avoid. Table 2 summarizes the chemical compatibility with common chemicals for PLA, Polyester and Nylon 6,6.

Table 3. Chemical compatibility of PLA, Polyester and Nylon 6,6 with common chemicals

Chemical	PLA	POLYESTER	NYLON 6,6
Deionized water	High	High	High
Isopropanol	High	Medium	High
Acetone	Low	Medium	High
Ethanol	Medium	High	High
Hydrochloric acid	High	Medium	Low
Hydrogen peroxide	Medium	High	Low
Nitric acid	Low	Medium	Low
Sulfuric acid	Low	Low	Low
Acetic acid	Low	Low	Low

Notes:
high : ≤ 1% change in mass and dimensions (during one week immersion)
Medium: 1%-5% change in mass and dimensions (during one week immersion)
Low: ≥5% change in mass and dimensions (during one week immersion)

Table 4. Comparison of Chemical Properties of PLA, Polyester and Nylon 6,6

Parameter	PLA	POLYESTER	NYLON 6,6
Chemical formula	$(C_3H_4O_2)_n$	$(C_{10}H_8O_4)_n$	$(C_{12}H_{22}N_2O_2)_n$
Chemical structure			
Melting point	150-160°C	295°C	268.8 °C
Density	1.210-1.430g/cm^3	1.38g/cm^3	1.14g/cm^3
Crystallization ability	Semi-crystalline	Semi-crystalline	Semi-crystalline
Solubility	Insoluble in water, soluble in acetone	Insoluble in water, moderate solubility in acetone	Insoluble in water and acetone
Glass transition temperature	60-65°C	80 °C	70°C
Aromatic or aliphatic	Aliphatic	Aromatic (aliphatic polyesters exist, but tennis strings are made of aromatic polyester)	Aliphatic
Plasticiser needed?	No	No	No

Note:
Semi-crystalline structures have sharp melting points. This means that they do not gradually melt as temperature increases, instead, they melt rapidly as soon as a given quantity of heat is absorbed. This property is useful for 3D printing filament, as it makes the process faster and more efficient.

Plasticisers are often bad for the environment, hence many chemical companies refrain from using them. Furthermore, they are not needed to give Nylon, Polyester, or PLA their properties

3. Methods

The dependent and independent variables under consideration are depicted in table 5 below. Table 6 describes the control variables in this experiment. Details of the apparatus used are described in table 7. Figure 4 provides a picture of the apparatus. Table 8 describes several hazards and the safety precautions taken against these.

The experiment was performed in two stages. Stage 1 is to prepare the used tennis strings by removing their protective coating and any dirt and impurities gather during regular play. The steps followed to perform this are:

1. String is cleaned vigorously with acetone in order to remove protective coating on top of it. Afterwards, the string should feel slightly rougher than before.
2. String is cleaned with rubbing alcohol to rid it of impurities. Alcohol is rubbed one to the string twice in both directions to rid it of as many impurities as possible.
3. String placed on an aluminium lined baking tray and heated in the oven at its glass transition temperature for 3 hours. For Nylon this is ~ 70℃, and for polyester it is ~ 80 ℃.

Stage 2 of the experiment is carried out to determine the melting point of the used tennis strings. The steps to perform this are as follows:

1. The tip of the soldering iron, used as a heat source, is placed at the edge of the aluminium strip to heat it.
2. Soldering iron is used to heat aluminium pieces to certain temperature (190℃, 200℃, 210℃, 220℃, 230℃, 240℃)
3. The temperature of the aluminium foil is taken at several positions to determine a temperature gradient
   - 3.1. the point of contact of the soldering iron with the aluminium foil
   - 3.2. quarter or halfway between the point of contact of the soldering iron and the opposite edge of the foil
   - 3.3. another quarter (refer figure 5 and 6 for more details)
   - 3.4. opposite edge or end of the aluminium foil
4. The strings, PLA, Polyester and Nylon are placed onto the foil and data is recorded on whether or not it melted.
5. Steps 2 through 4 are repeated for a different temperature
6. As a control, melt the 3D filament at the same temperature as used when using a 3D pen (230 ℃) to observe the flow state

Table 5. Variables Studied and Methodology

Variable	Independent / Dependant	Why am I changing it?	How am I changing it?
Temperature (℃)	Independent	In order to find the temperature at which the used tennis string melts, I must test it at different temperatures	By heating a piece of aluminium foil with a soldering iron and measuring its temperature using a thermocouple type temperature probe unit connected to a multimeter.
Material	Independent	Since tennis strings are made of more than one material (there are nylon strings, polyester strings, Kevlar strings) I wanted to test out the heat required to melt more than one of these strings, so as to broaden the impact I could have. I used Nylon and Polyester strings for my	After collecting the string, I identify the material it is made with (be researching the name of the string). This allows me to sort my pile of string based on material. I then choose one polyester string, and one nylon string.

		experiment as they are the most commonly used synthetic guts.	
Melting point of the tennis string	Dependent	-	-

Table 6. Control Variables and the need to control these

Control variables	Why I control them
Type of tennis string	• Different tennis strings are made of different chemical substances and will therefore have different melting points (as seen in the tables above) • Since strings are used, different sets of strings may have come in contact with different environmental factors (rain, humidity levels etc.). Using string from the same racket ensures that each piece of string has been previously exposed to exactly the same environmental factors, therefore reducing the chances of irregular data due to pre-existing conditions.
Type of 3D printing filament	• I used a length of 3D printing filament to test the accuracy of the experiment. As I have used it before, I knew the temperature at which it is supposed to melt. Using it as a part of the experiment as a control test, shows that the experiment is accurate
Length of string used (both tennis string and 3D filament)	• Longer lengths of string would take longer to melt. To conduct a fair experiment, both lengths of string (tennis and 3D) were required to be the same length.
Measurements of the aluminium foil pieces	• Each piece of aluminium foil (on which the string was melted), had the same measurements, and was made of the same material (used the same brand of foil). Therefore, each piece had the same heat transfer characteristics.

Table 7. Apparatus

Item	Quantity	Size/ specifications
Wooden block	1	40 cm X 9 cm X 1 cm
Slender wooden support like toothpicks	6	3 cm length
Aluminium foil pieces	12	5 cm X 3 cm
Yonex ATG 850p nylon tennis string	1	30 cm, gauge 1.32 mm
Head Lynx Edge Polyester string	1	30 cm, gauge 1,25 mm
ANTEX XS25 Soldering Iron	1	-
Rubbing alcohol	50 ml	-
Acetone	50 ml	-
Cotton balls	4	-
Oven	1	Must go up till 100 ℃
Stopwatch	1	-
Tweezers	1	-

TENMA 72-7730 multimeter with thermocouple based Temperature Probe unit	1	-
Pliers	1	-
PLA 3D printing filament	1	1.25 cm
Baking tray	1	33cm X 24 cm
Aluminium foil	1	33 cm X 24 cm

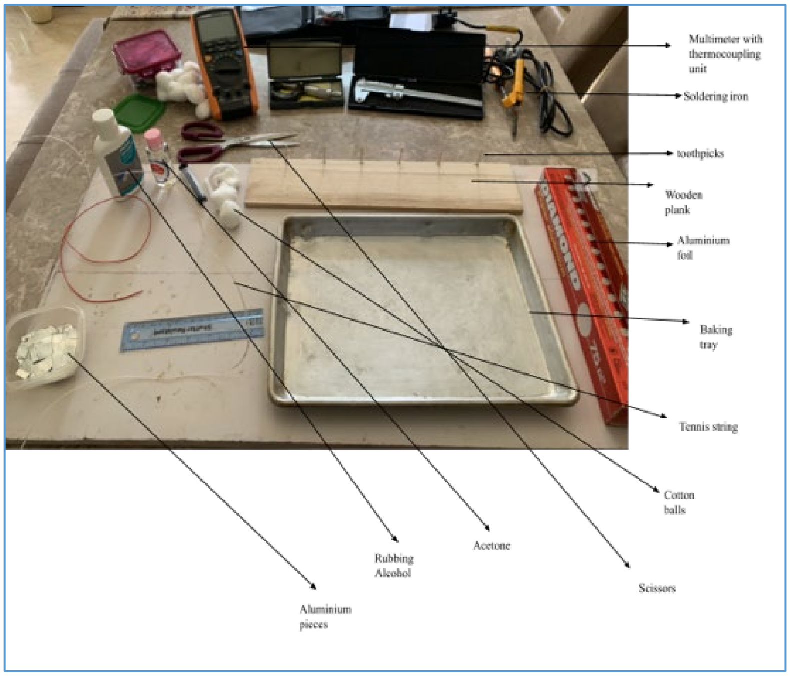


Figure 4: apparatus

Table 8. Hazards and Precautions

Hazard	Preventative measure
Pure acetone can cause irritation in eyes, nose, skin and throat	Handled carefully, in a place without lots of people to mitigate chances of accidents and proper ventilation
Soldering iron can reach temperatures of 500 °C	Pointed away from body and handled with care around few people to reduce chances of accidents

4. Data Collection

The data was collected for comparing the independent variables – Temperature and Material versus the dependent variable of Melting point. This is tabulated in Table 8. For any observation which is not comparable to the control variable, the dependent variable was considered to have not melted. Figure 5 and Figure 6 show the observations of the experiment. The blue filaments in Figure 5 and 6 are PLA, the red filaments are Polyester and the white filaments are Nylon 6,6.

Table 9. Tabulation of Observations

Temperature	Material	Melted – True / False	Additional Observations
200℃	Poly-lactic Acid (PLA)	True	
200℃	Polyester	False	
200℃	Nylon 6,6	False	
230℃	Poly-lactic Acid (PLA)	True	
230℃	Polyester	False	
230℃	Nylon 6,6	False	
290℃	Poly-lactic Acid (PLA)	True	Melts and coils up
290℃	Polyester	True	
290℃	Nylon 6,6	False	Melts and oxidises

NOTE: Since it was hard to control the temperature of the foil, I was unable to test at 10 ℃ intervals and I had to test at the three temperatures detailed in table 8 above.

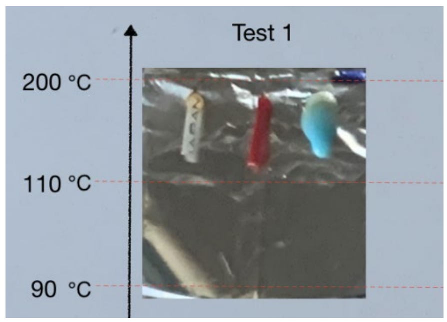


Figure 5: Test 1- Pictorial result

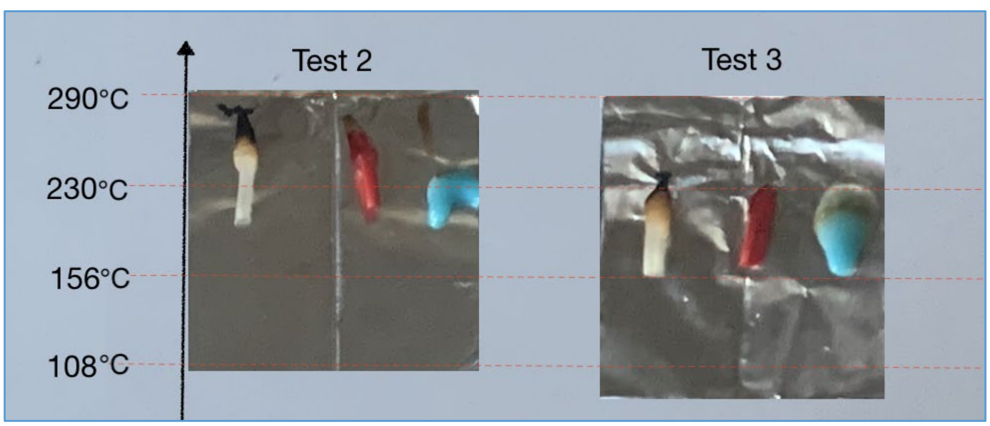


Figure 6. Test 2 and 3 - Pictorial result

5. Results and Discussion

5.1 Numerical Results

Assigning a value of one (1) for true and zero (0) for false to the data in table 8, we can summarize the results as depicted in Table 9.

Table 10. Summary of Results

Temperature	PLA	Polyester	Nylon
200℃	1	0	0
230℃	1	0	0
290℃	1	1	0

As can be seen from this result (Table Polyester reaches a suitable melting point around 290℃. From the preceding discussions in the literature review, we can also see from Tables 1, 2 and 3, that Polyester has similar or better properties to that of PLA as well as ABS. Once can therefore infer from this data, that Polyester is a suitable candidate for use as a 3D printing filament.

5.2 Graphical Results

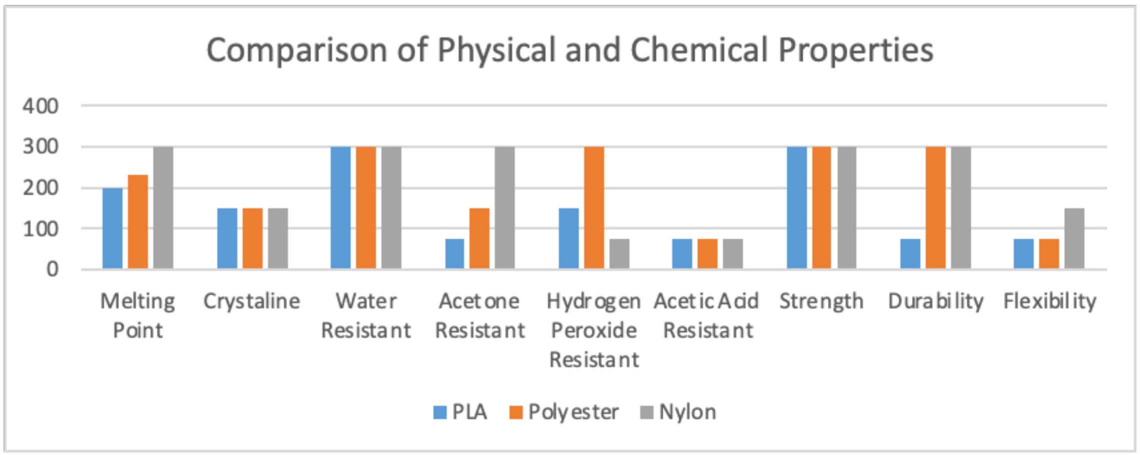


Figure 7. Scaled graphical comparison of properties

Figure 7 depicts the comparison of the three materials I tested. As can be seen, the chemical and physical properties of PLA, Polyester and Nylon are highly comparable. However, closer inspection reveals that Polyester exhibits better properties in comparison to Nylon and is better suited as a replacement for PLA.

5.3 Proposed Improvements

There are several aspects of the experiment that can be improved if access to a proper lab were possible during the COVID lockdown.

1. Controlling the temperature profile
    - The soldering iron that I used could not be set to a specific temperature, meaning that I had to constantly monitor the temperature of the aluminium foil and adjust its position in relation to the soldering iron accordingly. Since the temperature could not be kept constant, there may have been some slight inaccuracy in the data collected (+/- 5°C).

2. Controlling the gauge of the string
    - In my experiment, I tried to keep the strings as similar as possible, so that the material that they were made of would be the only difference between them. However, I was unable to control the gauge of the strings (as they are manufactured differently with different specifications).

5.4 Validation

6. Conclusion

Based on the above experiment, polyester could be suitable as a replacement for 3D printing filament, however Nylon may not be. This is because Nylon filament oxidises, making it useless. Polyester melts completely, without oxidation, by 290 ℃. This is much higher than the melting point of PLA (160 ℃). Unfortunately, this means that printing with polyester filament would be energy inefficient in comparison to PLA. Polycarbonate-ABS (PC-ABS), another type of filament, prints at a comparable temperature to that of polyester. This indicates that polyester could potentially replace PC-ABS. This would need to be tested in a printer which is capable of printing at such temperatures (like the Stratasys F370 3D printer), however I currently do not have access to one. The uses of polyester as a substitute for PC-ABS is the topic of another article.

I believe that as 3D printing gains wide acceptance, a critical feedstock for this can be provided by the sporting industry. This will make the sport more sustainable and benefit our planet. While I studied tennis strings, the methods presented are applicable to other racquet sports like squash and badminton.

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Biography

Anoushka Ghosh is a high school student enrolled in the International Baccalaureate program in United World Colleges, South East Asia (Dover), Singapore. She has a keen interest in chemistry and plans on pursuing a university degree in the subject. She is also very interested in sustainability and has worked on reports and made presentations on sustainable packaging to companies like Proctor and Gamble. She is the head of the Chemistry Club in school and is also a member of the school tennis team.