

A Critical Review on of 3D Printing Materials and Details of Materials used in FDM

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ABSTRACT

3D printing technology can produce complex objects directly from computer aided digital designs. The technology has traditionally been used by large companies to produce. In recent years however there has been a move to adopt the technology as full-scale manufacturing solution. The advent of 3D printing materials has meant a wider user base are now able to the manufacturing platforms enabling them to produce highly customised products for personal use and sale. This uptake in usage has been coupled with a demand for printing technology and materials able to print functional elements. Here we present classification of 3D printing materials and details of materials specially used in FDM method .we explain the use and properties of particular materials used in FDM formulation of a simple conductive thermoplastic composite we term ‘carbomorph’ and demonstrate how it can be used in an unmodified low-cost 3D printer to print electronic sensors able to sense mechanical flexing and capacitance changes. We show how this capability can be used to produce custom sensing devices and user interface devices along with printed objects with embedded sensing capability. This advance in low-cost 3D printing with offer a new paradigm in the 3D printing field with printed sensors and electronics embedded inside 3D printed objects in a single build process without requiring complex or expensive materials incorporating additives such as carbon nanotubes.

Keywords : 3DP-3d printing, FDM-fused deposition method, PLA-polylactic acid,ABS- Acrylonitrile butadiene styrene

I. INTRODUCTION

3D printing (3DP) is a term to describe technology used for the rapid production of 3D objects directly from digital computer aided design (CAD) files [1] The 3D printing process allows 3D objects to be fabricated in a bottom-up, additive fashion directly from digital designs, with no milling or molding.[1] It can be likened to clicking on the print button on a computer and sending a digital file, such as a letter, to a printer sitting on an office desk. The difference is that in a 3D printer the material or ink is deposited in successive, thin layers on top of each other to build-up a solid 3D object.[2] The layers are defined by software that takes a series of digital cross-sections through a computer-aided design. Descriptions of the slices are then sent to the 3D printer to construct the respective layers. The layers can be constructed in a number of ways depending on the 3D

printer being used. Powder can be spread onto a tray and then solidified in the required pattern with an amount of a liquid binder [3] or by sintering with a laser or an electron beam. Some machines carry out 3D lithographic processes using light and photosensitive resins and others deposit filaments of molten plastic. However each layer is constructed, after the layer is complete the build surface is moved by a fraction of a millimetre and the next layer of material is added. The most prolific technology used in low-cost 3D printers such as the RepRap is Fused Deposition Modeling (FDM) or Fused Filament Modeling (FFM). FFM machines work on the simple principle of extruding a thin (sub 1 mm) filament of molten thermoplastic (normally from a feedstock of larger filament or powder) through a heated nozzle onto a room temperature or heated build platform. The printed filament network cools and adheres to the previously

deposited layers to build up a solid 3D object. The technology is providing a low-cost, low-volume and low-risk route to market for entrepreneurs with novel products leading to a reduction in time to market for new innovations.[4]

Here we present Classification of 3d printing materials and details of materials used in FDM method. The materials available for 3D printing have come a long way since the early days of the technology. There is now a wide variety of different material types, that are supplied in different states (powder, filament, pellets, granules, resin etc). Specific materials are now generally developed for specific platforms performing dedicated applications (an example would be the dental sector) with material properties that more precisely suit the application. However, there are too many proprietary materials from the many different 3D printer to cover them all here. Instead, this article will look at the most popular types of material in a more generic way. And also a couple of materials that stand out.[5]

II. METHODS AND MATERIAL

1. Type of Materials Used In 3D Printing

- **Plastics/Polymers:** PLA- Poly lactic acid, ABS- Acrylonitrile butadiene styrene, HDPE-High density polyethylene, PPSU-Polyphenylsulfone and HIPS-High impact polystyrene
- **Metals:** Aluminium, Brass, copper, bronze, sterling silver, Gold, Platinum and Titanium
- **Ceramics:** Models made out of ceramics are constructed from alumina silica ceramic powder, then sealed with porcelain and silica and glazed.
- **Others:** Papers, plasters, wood, organic (tissue/cells), nylon, food, and concrete.

2. FDM Method

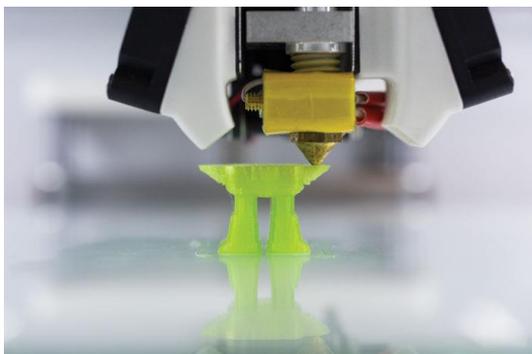


Figure 1: PLA material extruding from the nozzle

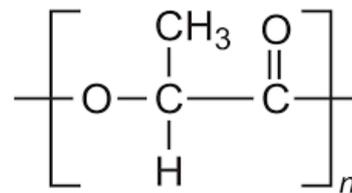
FDM builds parts by depositing a stream of hot viscous materials onto a base plate or previously deposited material.

FDM is a process in which thin thermo plastic filaments or granules are melted by heating and guided by a robotic device. The material leaves the extruder in a liquid form and hardens immediately. The previously formed layers are base for the next layers is kept a temperature below the solidification point of the thermoplastic material. In this method we use polymers like PLA & ABS filaments. We will see the details in elapsed way[6]

3.1 PLA

3.1.1. Introduction

poly (lactic acid) is a biodegradable and bioactive thermoplastic aliphatic polyester derived from renewable resources, such as corn starch, tapioca roots, chips or starch, or sugarcane. In 2010, PLA had the second highest consumption in the world of any other bioplastic of the world. The name "polylactic acid" does not comply with IUPAC standard nomenclature, and is potentially ambiguous or confusing, because PLA is not a lactic acid (polyelectrolyte), but rather a polyester.[4]



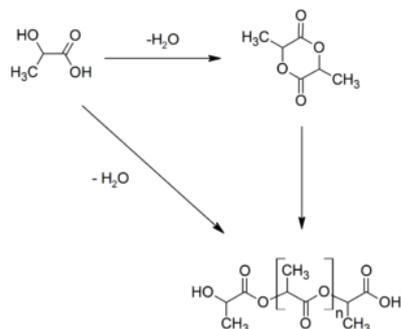
poly(2-hydroxypropanoic acid)
poly(lactic acid), PLA

Figure 2: Chemical formula of PL

3.1.2 Production:

Producers have several industrial routes to usable (i.e. high molecular weight) PLA. Two main monomers are used: lactic acid, and the cyclic di-ester, lactide. The most common route to PLA is the ring-opening polymerization of lactide with various metal catalysts (typically tin octoate) in solution, in the melt, or as a suspension. The metal-catalyzed reaction tends to cause racemization of the PLA, reducing its stereo regularity compared to the starting

material (usually corn starch). [7] Another route to PLA is the direct condensation of lactic acid monomers. This process needs to be carried out at less than 200 °C; above that temperature, the entropically favored lactide monomer is generated. This reaction generates one equivalent of water for every condensation (esterification) step, and that is undesirable because water causes chain-transfer leading to low molecular weight material. The direct condensation is thus performed in a stepwise fashion, where lactic acid is first oligomerized to PLA oligomers. [8] Thereafter, polycondensation is done in the melt or as a solution, where short oligomeric units are combined to give a high molecular weight polymer strand. Water removal by application of a vacuum or by azeotropic distillation is crucial to favor polycondensation over transesterification. Molecular weights of 130 kDa can be obtained this way. Even higher molecular weights can be attained by carefully crystallizing the crude polymer from the melt. Carboxylic acid and alcohol end groups are thus concentrated in the amorphous region of the solid polymer, and so they can react. Molecular weights of 128–152 kDa are obtainable thus.



Polymerization of a racemic mixture of L- and D-lactides usually leads to the synthesis of poly-DL-lactide (PDLLA), which is amorphous. Use of stereospecific catalysts can lead to heterotactic PLA which has been found to show crystallinity. The degree of crystallinity, and hence many important properties, is largely controlled by the ratio of D to L enantiomers used, and to a lesser extent on the type of catalyst used. Apart from lactic acid and lactide, lactic acid O-carboxyanhydride ("lac-OCA"), a five-membered cyclic compound has been used academically as well.[9] This compound is more reactive than lactide, because its polymerization is driven by the loss of one equivalent of carbon dioxide per equivalent of lactic acid. Water is not a co-product. The direct biosynthesis of PLA similar to the poly (hydroxyalkanoate)s has been reported as well.[10]

3.1.3 Manufacturers

As of June 2010, NatureWorks was the primary producer of PLA (bioplastic) in the United States. The second biggest producer of PLA in the world is the weforyou Group with an annual capacity of pure PLA and compounds of 50,000 MT.[11] Other companies involved in PLA manufacturing are Evonik Industries (Germany), Corbion PURAC Biomaterials (The Netherlands) who have announced a new 75,000 ton PLA plant in Thailand by 2018, and several Chinese manufacturers. The primary producer of PDLA is Evonik Industries and Corbion PURAC. Evonik Industries is a specialty chemical company that is industry leading in approximately 80% of the markets they participate. The Resomer brand of PDLA is produced in the Health and Nutrition business segment. Corbion PURAC is a listed company in the Netherlands, and operating plants worldwide, and the only producer of PDLA, produced from the D-isomer of lactic acid. Galactic and Total Petrochemicals operate a joint venture, Futero, which is developing a second generation polylactic acid product. This project includes the building of a PLA pilot plant in Belgium capable of producing 1,500 tonnes/year.

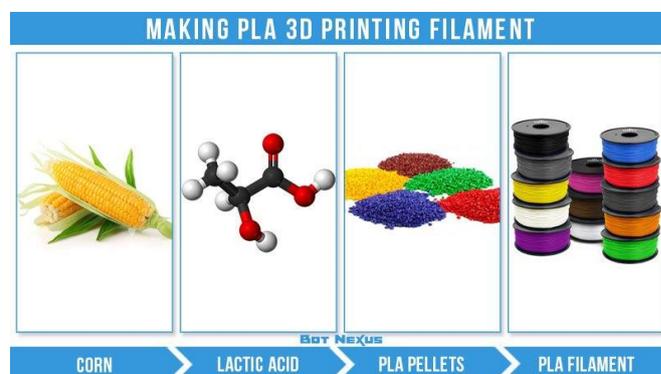


Figure 3: Production cycle of PLA

3.1.4 Chemical and physical properties:

Property	Value
Technical Name	Polylactic Acid (PLA)
Chemical Formula	(C ₃ H ₄ O ₂) _n
Melt Temperature	PLLA: 157 - 170 °C (315 - 338 °F) **
Typical Injection Moulding	PLLA: 178 - 240 °C (353 - 464 °F) **

Temperature	
Heat Deflection Temperature (HDT)	49 - 52 °C (121 - 126 °F) at 0.46 MPa (66 PSI) ****
Tensile Strength	PLLA: 61 - 66 MPa (8840 - 9500 PSI) ***
Flexural Strength	PLLA: 48 - 110 MPa (6,950 - 16,000 PSI) ***
Specific Gravity	PLLA: 1.24 *****
Shrink Rate	PLLA: 0.37 - 0.41% (0.0037 - 0.0041 in/in)*****

Table 1. Chemical and Physical Properties of PLA

3.1.5 Mechanical properties

The mechanical properties described the behavior of the material under the effect of different loading modes, such as tensile, impact, shear, and pressure. PLA had good mechanical properties particularly tensile young's modulus, tensile strength, flexural strength compared to traditional polymers, such as polypropylene (pp), polystyrene (PS) and polyethylene (PE). However, the elongation at a break and the impact strength of PLA were lower than those of PP, PE, PET, PA. Although the tensile strength and Young's modulus (good stiffness) of PLA were comparable to PET, the poor toughness limited its use in applications requiring plastic deformation at higher stress levels, which has motivated the considerable interest toward the toughening of PLA over last five years [12]

3.1.6 Thermal properties

PLA is a semi-crystalline or amorphous with a glass transition temperature and melting temperature of approximately 55°C and 180°C, respectively. The thermal properties of PLA could be affected by different structural parameters, such as molecular weight and composition. The transition temperature was related to the molecular weight of the polymer, and the relation between transition temperature and molecular weight

3.1.7 Biodegradation properties

Biodegradation had a range of definitions but most definitions were based on the same concept. The action of microorganisms on the material and its conversion into carbon dioxide or methane and water. In addition,

according to Japanese Biodegradable polymer society (JBPS), the biodegradation was a process in which the polymer was decomposed to water and carbon dioxide through the action of micro-organisms commonly existing in the natural environment, and the JBPS called this type of polymer (bio degradable polymers) Green plastic. Two types of biodegradation were known, and the biodegradation products were aerobic or anaerobic. No residue mean complete biodegradation and complete mineralization was established when the original substrate was converted completely to the gaseous products. The rate of degradation was affected by a range of factors, such as the medium of biodegradation including temperature and humidity, and the chemical parameters of PLA including molecular weights and composition. Many methods were used to measure the biodegradation rate. Some of them depended on measuring the gaseous products (CO₂ or CH₄) as a function of time. In addition, the structural, thermal, and morphological properties of the sample were monitored during the biodegradation test. Unlike weight loss, which reflected the structural changes in the polymer, CO₂ and CH₄ measurements provided an indicator of the ultimate biodegradability (i.e. mineralization) of the polymer. In these two cases, real or simulated (controlled) composting conditions were used (outdoor or indoor, respectively). PLA degradation was studied in animal and human bodies for medical applications like implants, surgical sutures, and drug delivery materials. In these environments, PLA is initially degraded by hydrolysis and the soluble oligomers formed are metabolized by cells. On the other hand, PLA degradation upon disposal in the environment is more challenging because PLA is largely resistant to attack by microorganisms in soil or sewage under ambient conditions. The polymer must first be hydrolyzed at elevated temperatures (about 58°C) to reduce the molecular weight before biodegradation can commence. The hydrolysis reaction followed first order kinetics, as demonstrated previously and fitted to the Equation

$$MW = aebt$$

Where a and b are constants and equal to 230kDa and 0.18s⁻¹, respectively, and t is the time in days. Recently, the biodegradation behavior of PLA films buried in real soil environments for several months was investigated by measuring thermal and morphological properties of the residual degraded samples [13]. The analyses

showed that the PLA sample surface had many corrosive holes after four months degradation, clearly showing that the PLA was degraded. Kale and coworkers [14] reported the biodegradation performance PLA bottles in real composting conditions (~58°C and ~60% relative humidity (RH)) by measuring the variations in the molecular weight of the degraded polymer with the time. The results showed that the molecular weight increased slightly on the first day, which was attributed to cross-linking or recombination reactions. Major fragmentation which produced decomposition of the polymer chain to shorter oligomer chains and monomers was observed from the fourth day onwards. Figure 13 shows the variation in the molecular weight and polydispersity index (PDI) of the PLA bottles as a function of the degradation time. Molecular weight values below 5 kDa could be obtained after 57 days of the degradation, which was consistent with the values calculated from Equation. However, the biodegradability rate of PLA polymers in soil under real conditions was lower than the rate of waste accumulation. Therefore, several works reported the mixing of PLA with natural materials such as starch and cellulose in order to improve its biodegradability. For instance, in a work reported by Ohkita and Lee [66], PLA/corn starch (CS) composites were investigated in applications where fast bio-degradable was required. The results of biodegradation tests of the composites performed in soil under real composting conditions (~30°C and ~80%RH) are presented in It is clearly seen from Figure 14 that the biodegradation rate increased with increasing corn starch content in the prepared composites due to the high biodegradability of starch materials [15]

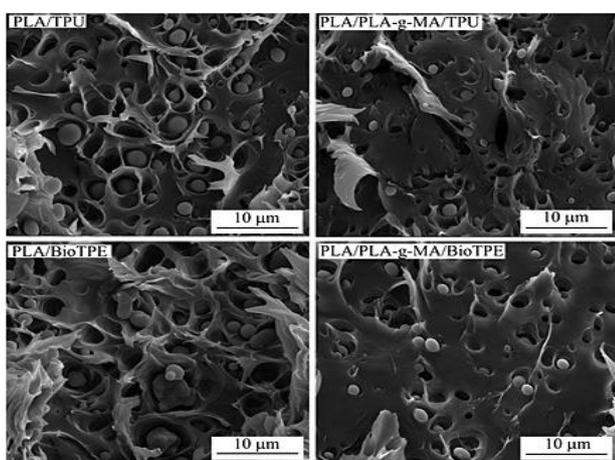


Figure 4 : Micro-structure of PLA

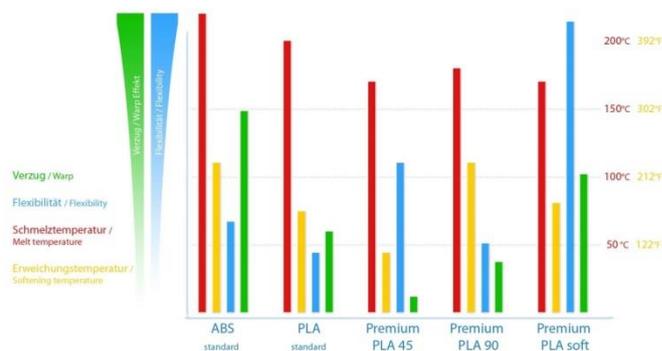


Figure 5 : Graph indication for warp, flexibility, melting temperature, softening temperature for PLA

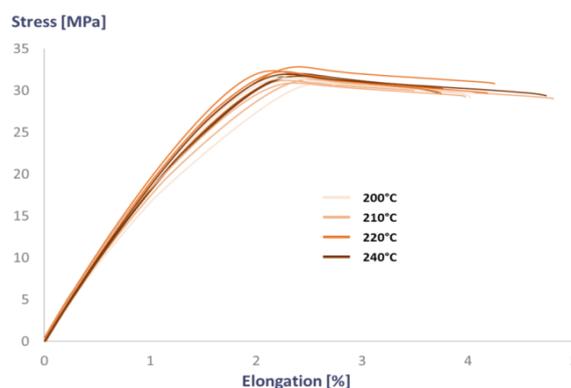


Figure 6 : Stress and strain curve for PLA at different temperature

3.2 ABS

3.2.1. Introduction

Acrylonitrile butadiene styrene (ABS) (chemical formula $(C_3H_3)_x \cdot (C_4H_6)_y \cdot (C_3H_3N)_z$) is a common thermoplastic polymer. Its glass transition temperature is approximately 105 °C (221 °F). ABS is amorphous and therefore has no true melting point.

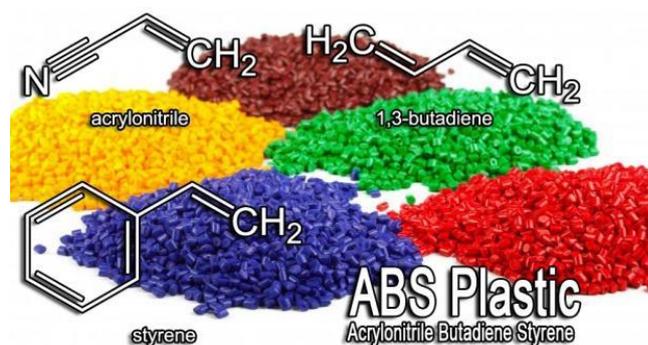


Figure 7: Chemical formula for ABS

ABS is a terpolymer made by polymerizing styrene and acrylonitrile in the presence of polybutadiene. The proportions can vary from 15 to 35% acrylonitrile, 5 to 30% butadiene and 40 to 60% styrene. The result is a long chain of polybutadiene criss-crossed with shorter chains of poly(styrene-co-acrylonitrile).[16] The nitrile groups from neighboring chains, being polar, attract each other and bind the chains together, making ABS stronger than pure polystyrene. The styrene gives the plastic a shiny, impervious surface. The polybutadiene, a rubbery substance, provides toughness even at low temperatures. For the majority of applications, ABS can be used between -20 and $80\text{ }^{\circ}\text{C}$ (-4 and $176\text{ }^{\circ}\text{F}$) as its mechanical properties vary with temperature.[3] The properties are created by rubber toughening, where fine particles of elastomer are distributed throughout the rigid matrix

3.2.2 Production

ABS is derived from acrylonitrile, butadiene, and styrene. Acrylonitrile is a synthetic monomer produced from propylene and ammonia; butadiene is a petroleum hydrocarbon obtained from the C4 fraction of steam cracking;[17] styrene monomer is made by dehydrogenation of ethyl benzene — a hydrocarbon obtained in the reaction of ethylene and benzene. ABS combines the strength and rigidity of acrylonitrile and styrene polymers with the toughness of polybutadiene rubber. While the cost of producing ABS is roughly twice the cost of producing polystyrene, it is considered superior for its hardness, gloss, toughness, and electrical insulation properties. According to the European plastic trade association PlasticsEurope, industrial production of 1 kg (2.2 lb) of ABS resin in Europe uses an average of 95.34 MJ (26.48 kW·h) and is derived from natural gas and petroleum.

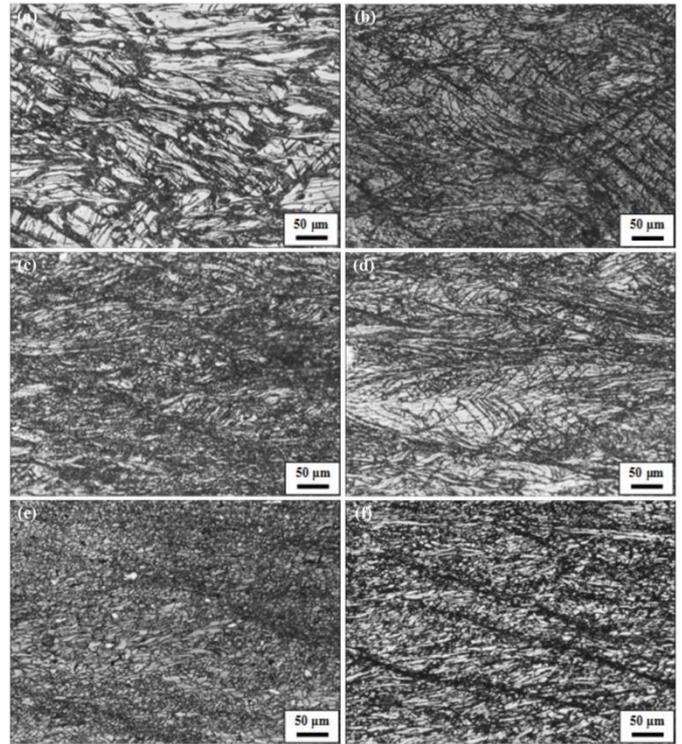


Figure 8 : Micro-Structure of ABS

3.2.3 Properties

The most important mechanical properties of ABS are impact resistance and toughness. A variety of modifications can be made to improve impact resistance, toughness, and heat resistance. The impact resistance can be amplified by increasing the proportions of polybutadiene in relation to styrene and also acrylonitrile, although this causes changes in other properties. Impact resistance does not fall off rapidly at lower temperatures. Stability under load is excellent with limited loads. Thus, by changing the proportions of its components, ABS can be prepared in different grades. Two major categories could be ABS for extrusion and ABS for injection moulding, then high and medium impact resistance. Generally ABS would have useful characteristics within a temperature range from -20 to $80\text{ }^{\circ}\text{C}$ (-4 to $176\text{ }^{\circ}\text{F}$). [18]

The final properties will be influenced to some extent by the conditions under which the material is processed to the final product. For example, molding at a high temperature improves the gloss and heat resistance of the product whereas the highest impact resistance and strength are obtained by molding at low temperature. Fibers (usually glass fibers) and additives can be mixed in the resin pellets to make the final product strong and raise the operating range to as high as $80\text{ }^{\circ}\text{C}$ ($176\text{ }^{\circ}\text{F}$). Pigments can also be added, as the raw material original color is translucent ivory to white. The aging

characteristics of the polymers are largely influenced by the polybutadiene content, and it is normal to include antioxidants in the composition. Other factors include exposure to ultraviolet radiation, for which additives are also available to protect against.

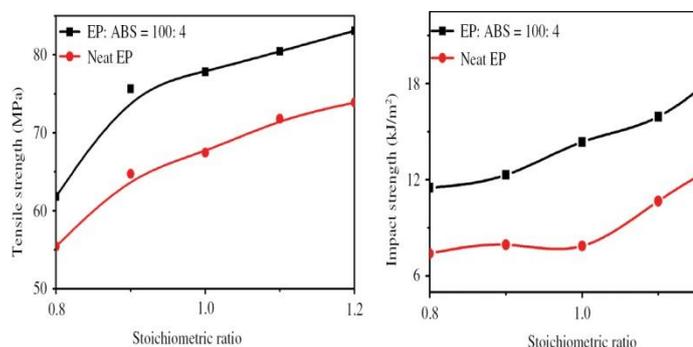


Figure 9: Graphs for tensile and impact strengths

ABS polymers are resistant to aqueous acids, alkalis, concentrated hydrochloric and phosphoric acids, alcohols and animal, vegetable and mineral oils, but they are swollen by glacial acetic acid, carbon tetrachloride and aromatic hydrocarbons and are attacked by concentrated sulfuric and nitric acids. They are soluble in esters, ketones, ethylene dichloride and acetone. Even though ABS plastics are used largely for mechanical purposes, they also have electrical properties that are fairly constant over a wide range of frequencies. These properties are little affected by temperature and atmospheric humidity in the acceptable operating range of temperatures. ABS is flammable when it is exposed to high temperatures, such as those of a wood fire. It will melt and then boil, at which point the vapors burst into intense, hot flames. Since pure ABS contains no halogens, its combustion does not typically produce any persistent organic pollutants, and the most toxic products of its combustion or pyrolysis are carbon monoxide and hydrogen cyanide. ABS is also damaged by sunlight. This caused one of the most widespread and expensive automobile recalls in US history due to the degradation of the seatbelt release buttons. ABS can be recycled, although it is not accepted by all recycling facilities[19]

Acrylonitrile butadiene styrene	
Physical Properties	
Density (ρ)	0.9 g/cm ³ – 1.53 g/cm ³ : median 1.07 g/cm ³

Flammability	1.00
Thermal Properties	
Thermal conductivity (k)	0.1 W/(mK)
Chemical Resistance	
Acids—concentrated	Good
Acids—dilute	Excellent
Alcohols	Poor
Alkalis	Excellent
Aromatic hydrocarbons	Poor
Halogenated Hydrocarbons	Poor

Table 2. Physical, Thermal and chemical properties of ABS material

3.2.4 Physical Properties

Metric	English	Comments
Density	1.04 g/cc	0.0376 lb/in ³
Melt Flow	18 - 23 g/10 min	18 - 23 g/10 min
Mechanical Properties		
Hardness, Rockwell R	103 - 112	
Tensile Strength, Yield	42.5 - 44.8 MPa	6160 - 6500 psi
Elongation at Break	23 - 25 %	23
Flexural Modulus	2.25 - 2.28 GPa	326 - 331 ksi
Flexural Yield Strength	60.6 - 73.1/ MPa	8790 - 10600 psi
Izod Impact, Notched	2.46 - 2.94 J/cm	4.61 - 5.51 ft-lb/in
Electrical Properties		
Arc Resistance	120 sec	120 sec
Comparative Tracking Index	600 V	600 V
Hot Wire Ignition, HWI	15 sec	15 sec
High Amp Arc Ignition, HAI	120 arcs	120 arcs
High Voltage Arc-Tracking Rate, HVTR	25 mm/min	0.984 in/min

3.2.5 Thermal Properties

Maximum Service Temperature, Air 88 - 89 °C 190 - 192 °F

Deflection Temperature at 1.8 MPa (264 psi) 88 - 89 °C 190 - 192 °F

Vicat Softening Point 100 °C 212 °F

Flammability, UL94 HB HB

Tensile test, hardness, flexural test, impact test

Measure Multipurpose Hounsfield H10KT tensile machine with the sensor head measuring power up to 10 (kN) was used to perform measurement of tensile and flexural properties of test samples. The measurement procedure for tensile properties was in accordance with standard ČSN EN ISO 527-1, 2 and for flexural properties was in accordance with standard ČSN EN ISO 178. Measurements were taken to the point of test specimen breakage. The loading speed for tensile test was 50 (mm/min) and for flexural test was (10mm/min).

Shore test was used for evaluation the hardness. The value is subtracted from the scale of hardness after 15 seconds. Measurements were carried on the Shore D hardness test machine. The measurement procedure was carried out according to standard ČSN EN ISO 868. The tip has a cone shape, type D for harder type of materials.

Izod method has been chosen to determine the impact properties of test samples. Measurements were carried on impact test machine CEAST Resil impactor 6967.000. The measurement procedure was in accordance with standard ČSN EN ISO 180/A. Nominal energy of hammer was 2.75 (J).

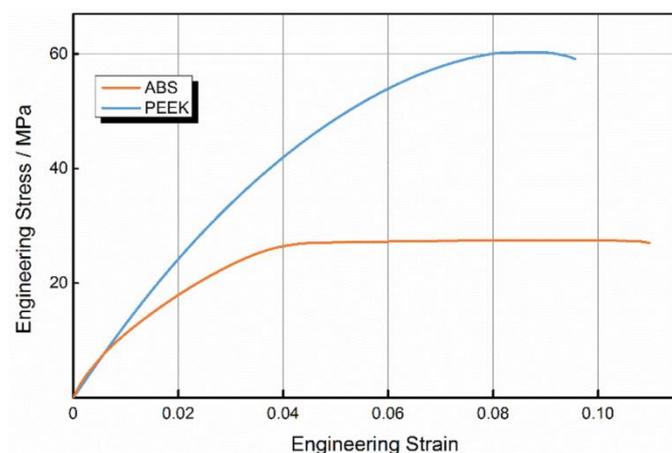


Figure 10: Graphs between engg. stress and strain

III. CONCLUSION

PLA & ABS are the most commonly used polymers in the form of filaments in 3D printing technology .each material has its own properties .they are been used accordingly in the real time both the materials have their own significance , there are many other polymers, but this are more commonly used and easily available in market for general needs .PLA is the best material for the starters.

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