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Composite material for additive manufacturing

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ABSTRACT: *Composite materials are strategically deployed in the multifaceted landscape of Additive Manufacturing, ushering in a paradigm shift in the qualitative aspects of the manufactured components. The selection of an appropriate composite material within the expansive domain of additive manufacturing is intricately linked to the specific nuances of the adopted additive manufacturing technology. This exploration delves deeply into the intricate realm of Fused Deposition Modeling (FDM) technology, a sophisticated process that pivots on the meticulous extrusion of polymer fibers. This extrusion occurs layer by layer, a meticulous orchestration resulting in the precise construction of the envisaged shape of the manufactured component. The technological nuances of FDM necessitate a discerning consideration of composite materials, with an emphasis on those rooted in polymeric substrates, particularly the versatile realm of thermoplastics. In essence, our focal point centers on composite materials intricately interwoven with thermoplastics, serving as the foundational matrix in this additive manufacturing milieu. The exploration of these composite materials within the purview of FDM not only illuminates the technical intricacies involved but also underscores the pivotal role played by thermoplastics as the elemental backbone of this composite paradigm.*

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I. INTRODUCTION

If we want to print a dimensionally accurate part on a 3D printer, it is necessary to reduce deformations caused by high residual stress. This residual stress arises during the melting and solidification processes of the material. The formation of these stresses greatly affects the rate of expansion and contraction of the material, or the rapid heating of the material by the laser above its melting temperature, after which a relatively high cooling occurs. Geometric deviations often occur during production due to this stress. This is a significant disadvantage, but despite this, these parts compete with conventional production processes in terms of price, mechanical properties or even surface treatment. In their study, Mercelis and Kruth found that the exposure strategy used to melt the powder layers has a significant effect on the level of residual stress within the part. It was found that changing the scanning strategy leads to different defects, geometric deviations and anisotropy of mechanical properties. [1] [2] [3]

For optimizing the dispersion of additive particles within the composite printing filament, it is recommended to address the crushing and subsequent re-extrusion of the material through a purpose-designed extruder apparatus during the formulation of such a filament. However, a pertinent inquiry arises regarding the mechanical properties that the recycled material might retain. Consequently, a closer examination of polymer degradation becomes imperative.

The initial stages of plastic decomposition primarily occur on the surface of the polymer, where it is exposed and susceptible to chemical or enzymatic actions. As a result, microplastics exhibit a faster degradation rate compared to mesoplastics and macroplastics, owing to their elevated surface-to-volume ratio. Observable signs of polymer degradation commence with color alterations and surface cracking. These surface fissures lay bare the interior of the plastic material to further deterioration, ultimately leading to brittleness and disintegration.

The processing of polymers often triggers material degradation, exerting an influence on the properties and lifespan of the manufactured products. Polymer degradation typically manifests as changes in molecular weight due to exposure to high processing temperatures and associated mechanical stress. According to the findings of C. Capone et al., materials processed at the highest extruder speeds demonstrated the least reduction in molecular weight. This is attributed to the shorter residence time in the extruder and the potential for improved material flow along the extruder walls, likely mitigating actual shear stress and viscous dissipation under the conditions of Rapid Prototyping (RP) technology.

Polymer degradation denotes the uncontrolled reduction of molecular weight or a structural alteration within the polymer. In a technological context, any undesirable transformation in polymer properties resulting from exposure to degrading factors is referred to as polymer degradation. This process can occur during two primary phases in the life cycle of a polymer—firstly, during its manufacturing process, and secondly, throughout its routine utilization. Degradation factors encompass heat, mechanical stress, sunlight, atmospheric oxygen, moisture, and various other phenomena.

The degradation of polymers is typically categorized into two types:

- Random degradation
- Degradation at the end of the chain

Random degradation transpires at arbitrary points along the polymer chain and stands in contrast to polycondensation. During random degradation, the polymer undergoes fragmentation, resulting in a lower molecular weight, yet there is no partial release of the monomer.
Conversely, degradation at the end of the chain initiates at the terminus of the polymer chain, leading to the gradual liberation of monomer units. This phenomenon essentially mirrors the inverse process of propagation within the polymerization chain and is consequently termed depolymerization. Throughout chain-end degradation, the polymer's molecular weight diminishes slowly, accompanied by the simultaneous release of a substantial quantity of monomer.
Polymer degradation can be caused by:

1. physical factors:
    a) heat,
    b) mechanical stress,
    c) ultrasonic waves,
    d) light,
    e) high-energy radiation.
2. chemical agents:
    a) by oxidation/Corrosion,
    b) hydrolysis (decomposition of a substance by the action of water),
    c) alcohol,
    d) acid.
3. biological agents (through the action of enzymes and bacteria)

The thermal degradation of polymers constitutes a multifaceted process encompassing random cleavage, depolymerization, and the elimination of side groups. This intricate sequence of events leads to alterations in polymer molecular weight and the consequential loss of valuable properties, including color, mechanical strength, and impact resistance. The velocity and scope of degradation, occurring through radical, ionic pathways, or a combination thereof, can be scrutinized by observing variations in sample weight, alterations in molecular weight, detecting and quantifying changes in reaction enthalpy, and qualitatively analyzing volatile side products.

Comprehending the mechanisms underlying the degradation of polymeric materials is further compounded by factors such as complex morphology, diffusion processes, and interactions between additives. A profound understanding of the thermal degradation mechanisms in polymers is pivotal for their stabilization, with the aim of prolonging their lifespan. Conversely, this knowledge is leveraged to expedite decomposition in thermal recycling processes, illustrating its significance in both enhancing the durability of polymers and facilitating their efficient utilization in recycling endeavors.

Mechanical Degradation - Simple compounds like water and benzene resist degradation under mechanical stress, making methods like high-speed mixing or grinding ineffective in altering their molecular structures. In contrast, polymers such as polystyrene, when dissolved in a solvent and exposed to vigorous mixing or grinding, experience substantial molecular degradation or fragmentation. This process is termed mechanical degradation. For instance, in the rubber industry, rubber undergoes compression between two rotating cylinders to lower its molecular weight, enhancing its processability. Through this pressing procedure, the initially hard and tough rubber transforms into a flexible, and sometimes even semi-solid, substance.

Degradation through light exposure, commonly known as photodegradation, refers to the molecular weight breakdown triggered by ultraviolet light. The yellowing observed in transparent plastics or colored rubber components results from their interaction with ultraviolet light. Polymers are often shielded from the deteriorating impact of light by photostabilizers. The primary role of photostabilizers is to absorb ultraviolet radiation and subsequently disperse the absorbed energy harmlessly into the surroundings. This absorbed energy is then released as heat or radiation with a longer wavelength. The stabilizer functions as a buffer, preventing the radiation energy from directly affecting the polymer molecules.

II. EXPERIMENTAL SECTION

The experimental phase involves conducting tests to investigate the material properties of samples fabricated from composite materials using FDM 3D printing technology. Material characteristics undergo changes based on specific print parameters, including layer height, nozzle diameter, and printing temperature. Each experiment distinctly outlines factors and their corresponding levels, presented in tables for clarity.

Building upon the theoretical research highlighted in the thesis, it is posited that the filler density significantly influences mechanical properties. Consequently, a decision was made to utilize 100% filling density for all samples in the experiment. Other parameters, such as temperature, printing speed, and more, were selected within the range recommended by the material manufacturer.

Experiment planning is a crucial step in this process. It involves naming a set of experiments (measurements), determining the number of repetitions, and establishing the sequence of measurements. The goal is to devise effective, efficient, and cost-effective methods for drawing relevant conclusions from the measurements.

To design an experiment effectively, the goal must be clearly defined, outlining the parameters to be investigated—referred to as experiment factors—and their respective levels. Interactions between factors should also be considered. Post-experiment evaluation may lead to the exclusion of certain factors or interactions if they prove to have no impact on the evaluated quantity, or conversely, the addition of significant factors not initially included.

The experiment employed various devices, with a prominent role played by a 3D printer from the Czech manufacturer Prusa (Figure 1). Utilizing FDM technology, this printer comprises essential components like the frame, print head, extruder, heated pad, magnetic plate, guide and threaded rods, stepper motors, control panel with an LCD display, control unit, and power supply. The print nozzle can be manually changed to accommodate the required diameter for specific applications, and the printer is compatible with a 1.75 mm diameter print string.

Fig - 1: FDM 3D printer

Universal Testing Apparatus - For conducting tensile strength measurements on manufactured test samples, the Inspekt 5 Desk universal testing apparatus (Figure 2) was available. The name implies that the maximum applied force of this device is 5kN. The versatility of the machine lies in its capability to conduct not only tensile tests but also bending tests. The apparatus is connected to a computer to enable real-time data recording during the experiment. The test sample is clamped into the device's grips, and a new test is initiated through the software. The upper grips begin to move upward, and the program starts plotting the stress-strain deformation curve. Upon surpassing the yield strength and the sample failure, the test concludes. The measured data from the experiment is exported for further statistical analysis and evaluation.

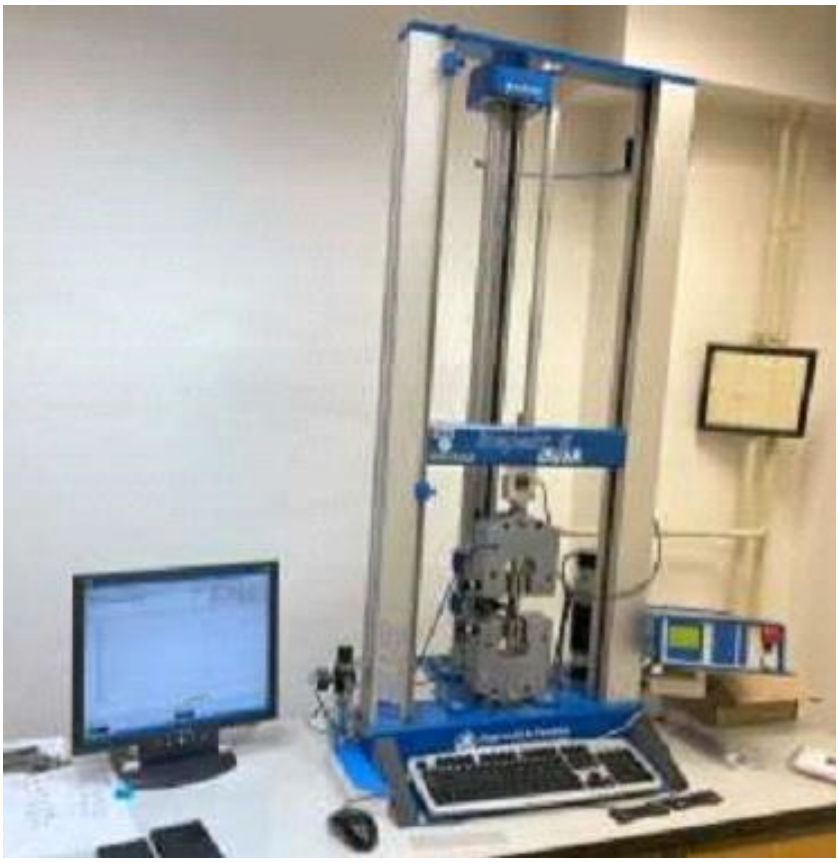

Fig - 2: Universal testing device

Utilizing the available Inspekt 5 Desk apparatus at the faculty for conducting tensile tests, with a maximum permissible derived force of 5 kN, necessitated adjustments to the test sample. The sample, adhering to the dimensions outlined in the STN ISO 527-2 standard, underwent dimensional modifications to ensure proper placement on the testing device. Primarily, changes were made to the cross-sectional area of the sample. The sample underwent modeling in the CATIA CAD program and was subsequently exported to an STL file. Following this, printing parameters were defined using the PrusaSlicer program. The sample was then sectioned into appropriate layers and a print file (.gcode) was generated for the subsequent 3D printing process.

III. PLA/WOOD Composite Printing Filaments

Wood-based materials offer significant potential as raw materials in 3D printing applications, owing to their cost-effectiveness and ample availability. The incorporation of wood powders presents a partial solution to cost, environmental, and sustainability concerns in production. Furthermore, employing bio-adhesives as binders alongside wood powders can enhance environmental benefits. However, as highlighted in the theoretical section, challenges arise when printing composites containing wood particles. Oversized wood particle dimensions and an improper choice of nozzle diameter can lead to nozzle clogging.

One notable issue observed during printing is the failure of the printer to halt its operation, even when the material ceases to flow through the nozzle. If the printer operator is not present or fails to notice the lack of material flow, the print head continues to ascend during the layering process. Subsequently, after resolving the clogged nozzle issue, it becomes impossible to resume continuous material application at the point where the

flow stopped. Such procedural errors significantly escalate the production time of the part. Thus, proactive consideration of the nozzle diameter and layer height is crucial. The layer height should be selected in accordance with the nozzle diameter and should not exceed 80% of the nozzle diameter.

The primary objectives of the experiment are to observe the behavior of the composite material during printing, compare the strength properties of the composite through static tensile testing, and measure and evaluate the Ra surface characteristic. All these assessments will be conducted with a focus on varying printing parameters.

IV. Material Selection

For the experimental endeavor, a composite material combining PLA with wood particles was chosen. Two distinct materials were employed, one from an older batch. Despite being appropriately sealed and stored under recommended conditions, this older batch experienced degradation over time, rendering it unsuitable for printing samples of adequate quality.

The composite printing filaments are PLA-based and include 40% pine wood particles. The specific sizes of these wood particles are undisclosed, as the manufacturer keeps this information confidential. The coloring of each material type is achieved through the addition of dye, with the type of wood particles remaining consistent. Table 1 outlines the recommended printing parameters for the chosen composite materials.

While the PLA/Wood-2 material was available at the faculty and had undergone degradation over time, it still allowed for the printing of four samples for all experiment combinations. Consequently, I opted to include a comparison of the properties between PLA/Drevo-2-degra. and PLA/Wood-2-new. Although not the primary goal of the experiment, this comparison yields interesting insights into the natural degradation of the composite material.

Fig - 3: Printed specimens for tensile testing

Prepared samples made of composite material are prepared in this way for investigation of tensile strength and determination of material properties on the basis of an experiment. Experimental measurements will then be evaluated and conclusions prepared.

V. CONCLUSION

Monitoring the material properties of composite materials is important for construction work in this area. It is important if we want to use such types of materials in practice. Designers should know the strength of the materials they use in their designs and which are used for the production of functional parts.

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