THERMAL ANALYSIS OF 3D PRINTED CONTINUOUS FIBER REINFORCED THERMOPLASTIC POLYMERS FOR AUTOMOTIVE APPLICATIONS

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Abstract

Continuous fiber reinforced additive manufacturing (CFRAM) is a five-year old manufacturing technology with a wide range of potential applications. CFRAM benefits from the advantages of Fused Filament Fabrication as fast and low cost production of complicated structures, while fiber reinforcement improves thermomechanical properties. CFRAM provides wide range of potential applications in auto industry, aerospace, sport goods and medical tools to replace metals and conventional composites with CFRAM parts. The notable attention toward CFRAM technology justifies the need for investigation of thermomechanical properties of printed components. In this study, CFRAM components were manufactured using Markforged 3D-printer. Nylon was used as thermoplastic polymer matrix and carbon fiber (CF), fiber glass (FG), and Kevlar as reinforcing agents. Thermo-Gravimetric Analysis (TGA), and Dynamic Mechanical Analysis (DMA) measurements were conducted to investigate thermomechanical properties. The results of this study will be a milestone for applications of CFRAM components for automotive industry.

Keywords: Additive Manufacturing, Fiber Reinforcement, Mechanical Properties

Introduction

Currently, one of the main challenges of Additive Manufacturing (AM) is low mechanical and thermal properties of fabricated parts compared to metals and traditional composites [1]. Fiber reinforcement by CFRAM technology is considered as a solution to improve mechanical and thermal properties of printed parts to compete with metals [2, 3]. In CFRAM, polymer part improves process ability, fibers improve thermomechanical properties, and 3D printing provides possibility of easy and precise production of components. Polymer composite with desired fiber orientation and percentage is manufactured using a layer by layer deposition of polymer matrix and reinforcing fiber. CFRAM provides advantages such as low cost, easy and fast process of complex parts, flexibility in design of composite by changing fiber volume and orientation, low waste of materials, and recyclability [4, 5]. Produced components have light weight, high strength to weight ratio, short manufacturing time, and flexibility in design. So, they have potential applications in aerospace and automotive industries.

The parts for automotive application need to have acceptable mechanical properties, withstand against constant vibration, thermal stability at high and low temperatures, chemical resistance in contact with chemicals and moisture [6]. For this reason, metals have been used for car parts production for many years. The main drawback of metals is their high density. Besides, their price is higher, their production method is more difficult and more time consuming compared with polymers. Nowadays, reinforced polymers are replacing metals for automotive parts [7]. Polymers due to light weight, ease of production, lower price, corrosion resistance, and sound damping reduce vehicle weight and improve fuel efficiency. On the other hand, reinforcing agents such as nanoparticles and fibers are solutions to improve mechanical, thermal, and other properties of polymers. So, polymer composites are the best candidates for automakers to reduce weight, price, and production time of car parts without sacrificing mechanical strength [8].

Nylon is the most practical thermoplastic used in auto industry [9]. Nylon is semi-crystalline thermoplastic polymer with an excellent balance of properties. Its temperature resistance, mechanical strength, chemical resistance, and reasonable price makes it a good candidate for engineering applications. Properties of nylon can be improved by different strategies. Using reinforcing nanomaterials, compounding and fiber reinforcement (both short and continuous fibers) are technologies to improve material properties and production of nylon used in car industry [9].

Nowadays, more complicated parts are needed in car industry. Subsequently, more precise manufacturing methods are needed for production of these parts. 3D printing is considered as a leading manufacturing technology for production of complicated parts from metals, polymers and reinforced polymer composites. CFRAM components have the potential to be used for the production of automotive parts. Parts with complex geometries can be designed using computer design programs, while fiber type, fiber volume, fiber orientation, and other details can be controlled for different functions.

In recent years, with the advancement of 3D printing technologies, researchers have conducted experimental and computational researches on thermal [10-12] and mechanical [13-15] properties of these materials. Thermal analysis is considered as an important test to evaluate properties of polymer composites. Several researchers have studied thermal properties of conventional polymer composites, but there is a shortage of research in the case of thermal properties of 3D printed composites. Due to the wide range of potential applications of CFRAM components, studying thermomechanical properties of these materials is highly significant. In this research, thermal analysis of CFRAM components for car part applications is investigated. Nylon is used as polymer matrix and CF, FG and Kevlar as reinforcing fibers. TGA test was conducted to measure thermal stability and degradation behavior of printed specimens. The DMA analysis was conducted to study dynamic-mechanical properties of components at different temperatures.

Materials and Methods

Nylon, carbon fiber, fiberglass, and Kevlar were purchased from Markforged Company, USA. Markforged Mark-Two was used as 3D printer. Nylon and fiber filaments are laid down layer by layer to complete the specimen. Nylon matrix was printed with rectilinear arrangement and rectangular infill. Reinforcing fibers were printed with horizontal orientation and isotropic filling. Fiber percentage for CF, FG and Kevlar was %58, %43 and %43 respectively. Isotropic filling pattern means fibers are distributed evenly in the part. Nozzle temperature and bed temperatures were set on 265°C and 40°C respectively. Figure 1 shows SEM image from cross section of CFRAM component of nylon reinforced with carbon fiber. Layer by layer structure of polymer and fiber are clearly visible.



Figure 1 SEM image of CFRAM component of nylon reinforced with CF

Thermogravimetric analysis (TGA) was used to characterize thermal behavior of specimens according to the standard ASTM E1131 and using TA instrument Q600 machine. TGA of pure 3D printed nylon was measured as reference. 5.00 mg of sample was loaded into the machine and Nitrogen with flow rates of 20 mL/min was used as purged gas. Samples were ramped from room temperature to 900°C at a scanning rate of 10°C/min and mass weight of samples was measured continuously as the temperature increased with controlled rate.

The DMA test was conducted using TA Instrument analyzer model Q800. The temperature range was set from 30 °C to 120 °C at a heating rate of 10 °C/min and frequency of 1 Hz. Storage and loss modulus of samples were measured.

Results and Discussion

TGA method was used to characterize thermal properties of nylon reinforced with different fibers. The weight loss at different temperatures and decomposition rate of specimens under nitrogen purged gas are shown in figures 2 and 3 respectively. As shown, with increasing temperature from room temperature, a few percentages of weight loss occur due to the removal of moisture from specimens. The first main weight loss is due to the thermal decomposition of nylon polymer and other organic contents in the temperature range of 350-500°C. The second stage of weight loss of CFRAM components is associated with the fiber degradation due to breaking of chemical bonds at temperatures higher than 500°C.

Results from TGA graphs clearly demonstrated that use of fiber reinforcement enhance the thermal stability of nylon. Results obtained by Essabir for fiber reinforced Polyethylene confirms obtained results [16]. Nylon sample shows a two-stage decomposition process; a weight loss of about 1% until 100°C, due to moisture removal, and a two-step weigh loss of about 99% until

650°C due to decomposition process. Nylon-CF and Nylon-Kevlar show weight loss of 1% until 100°C due to moisture and volatile gases removal, following a weight loss of 5% until 400°C, and a weight loss of 60% in the range of 400-500°C. Nylon-CF shows a steady decrease of 30% in the temperature range of 500-900°C while nylon-Kevlar specimen shows a plateau in temperature range of 500-600°C, weight loss of 10% at 600°C, and weight will not change much in temperature range of 600-900°C. For nylon-FG, there is a 1% weight loss until 100°C due to moisture removal and a weight loss of 73% because of degradation until 500°C. After that, no more weight loss is observed for Nylon-FG until 900°C.

Figures 4 represents the rate of thermal decomposition of components at different temperatures, under nitrogen purged gas. As shown, the rate of decomposition for nylon-CF and nylon-FG is slower than other samples and after that nylon-Kevlar and pure nylon have higher decomposition rates. The peaks of graphs in figures 4 represent the temperature in which samples have the maximum weight loss. As seen, nylon has highest thermal decomposition rate of 1.78%/°C. Nylon-Kevlar with 1.35%/°C, and after that nylon-Fg and nylon-CF with 1.14 %/°C have lower thermal composition rates respectively.



Figure 2 TGA results for CFRAM components under nitrogen purged gas



Figure 3 Rate of decomposition of CFRAM components under nitrogen purged gas

Dynamic mechanical analysis was conducted to study viscoelastic behavior of specimens. A cyclic load is applied on specimens and the strain is measured at different temperatures. The storage and loss modulus were recorded in temperature range of 25-150 °C. The storage modulus shows the energy stored in specimen and represents the elastic behavior of the material, while loss modulus shows the lost energy as heat, which represents the viscous behavior of material. For automotive applications, the part should have high storage modulus to withstand against applied loads. Also, energy dissipation mechanism makes it possible for the materials to damp applied forces.

Storage modulus of CFRAM components in the temperature range of 30-150°C is shown in figure 4. As can be seen, inclusion of carbon fiber, fiber glass and Kevlar improves storage modulus of nylon matrix 47 times, 12 times, and 13 times respectively at room temperature. For other temperatures enhancement is observed too. This means reinforced composites have higher energy storage capacity compared with pure polymer specimens. As can be seen in figure 4, for all specimens, storage modulus reduces as the temperature increase. This can be due to the effect of temperature on loosening both chemical bonding of polymer matrix, and interface between fiber and matrix. As temperature increase, material passes glass transition temperature (Tg). Tg is a temperature that behavior of polymer changes from glassy to rubbery, and polymer chains can move freely [17, 18].

Loss modulus of CFRAM components is shown in figure 5. Specimens with the addition of reinforcing fibers show higher loss modulus value, which means more energy is dissipated when fiber is added to nylon. As can be seen, carbon fiber, fiber glass and Kevlar improve loss modulus of nylon matrix 44 times, 4 times, and 14 times respectively at room temperature. For other temperatures the enhancement is observed too. Increasing the temperature reduces loss modulus for all specimens, (figure 5). This is because of loosening chemical bonds in the polymer structure, and interface between nylon and reinforcing fibers.



Figure 4 Storage Modulus of nylon and fiber reinforced components



Figure 5 Loss modulus of nylon and fiber reinforced components

Case study on automobile parts

Polymers have many applications in automotive industry to replace metals. Polymers because of low density, process ability, lower cost, and sound damping are replacing metals to reduce vehicle weight and fuel consumption. Nylon due to the great balance of properties has many applications for auto industry [6]. Nylon is semi-crystalline polymer with an excellent balance of properties. Fiber reinforcement can improve nylon properties for industrial applications.

With the development of auto industry parts with complicated geometry, light weight and high thermomechanical properties are needed. Production of complicated parts with conventional methods has been a challenge for car industry due to the need to sophisticated equipment, mold, high temperatures, and high expenses [19]. CFRAM is considered as precise manufacturing methods for production of automotive parts.

Air-take manifold is one of the parts that formerly made of metals and currently is made from reinforced polymers. Manifold has a complicated geometry which needs a complicated mold. As a substitute method, manifold can be produced from polymer composite and using CFRAM technology. This technology reduces weight, and improves performance by optimizing the airflow and reducing turbulence.

Car manifold built with the CFRAM technology was produced using nylon as polymer matrix, and carbon fiber (CF) as reinforcing agent. The product is a manifold used for Porsche model 924. Sample was printed using Markforged Mark-Two 3D printer in 11 hours and 41 min. The fiber layers, orientations, and other printing conditions was controlled to optimize properties.

Conclusion

In this study, thermomechanical analysis of CFRAM components of nylon reinforced with CF, FG and Kevlar was conducted using TGA and DMA analyses. Fiber inclusion improves thermal stability by reducing thermal decomposition rate. Samples showed high percentage of degradation more than 80% weight loss until 900°C except FG which showed 18% residue until at 900°C. DMA analysis showed fiber inclusion improves thermal properties of CFRAM components. Results show that CF reinforced nylon shows highest improvement of properties compared with other specimens at the temperatures lower than 150°C. Air-intake manifold and connecting rod were printed as two parts representative of CFRAM applications for automotive applications.

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