ANALYSIS OF RHEOLOGICAL BEHAVIOR OF SS 316L - CNT FEED STOCKS FORMULATED BY METAL INJECTION MOLDING PROCESS

Thota Siva Prasad[1*], Deepak Kumar[2]

Abstract: - Binder selection and formulation play a crucial role in the metal injection moulding process. They are essential for controlling the rheological properties of the feedstock and determining its suitability for successful injection moulding, debinding, and sintering without defects. To achieve this, a four-step process was employed, involving the blending of SS 316L and Carbon Nanotube powders with a binder system based on High-Density Polyethylene (HDPE). The rheological properties of the resulting homogeneous feedstock, such as flow behavior index, flow activation energy, fluidity, and melt flow index, were evaluated using a capillary rheometer. All feedstock formulations exhibited a shear thinning flow behavior. The optimal feedstock composition, consisting of 60 vol.% powder content, 32 vol.% HDPE, 6 vol.% Paraffin wax, and 2 vol.% stearic acid, proved suitable for metal injection moulding of SS316L-CNTcomposite materials.

Keywords: -SS 316L & CNT; HDPE; Metal Injection Moulding; Rheological Properties; Fluidity.

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1. INTRODUCTION

SS 316L-CNT composites possess several remarkable properties, including high specific strengths and excellent corrosion resistance. However, their utilization has been largely limited to specific sectors such as the automotive and domestic industries, where their strength and lightweight nature can be fully justified. Metal Injection Molding (MIM) presents a promising solution for reducing the cost of manufacturing SS 316L composite parts, thereby making them more affordable [1]. This innovative molding technique enables the production of intricately shaped components using a feedstock consisting of metal powders mixed with thermosetting or thermoplastic binders. These binders provide the necessary fluidity required for successful injection molding [2].

MIM opens up opportunities for the cost-effective production of complex SS 316L-CNT composite parts, thereby expanding their applications beyond the automotive and domestic sectors. By leveraging the advantages of MIM, these composites can be manufactured in a more efficient and economically viable manner.

The binder system plays a crucial role in achieving feedstock with desirable rheological properties and ensuring good mechanical properties in the final products. Typically, a binder system consists of at least three components: a backbone polymer that retains the shape of the molded part during debinding and sintering, a low viscosity polymer that provides suitable viscosity to the feedstock and can be easily removed during solvent debinding, and an additive that enhances the wetting ability between powder particles and binder [3].

An effective binder system should possess favorable flow characteristics, be cost-effective, exhibit good interactions with metal powders, facilitate easy debinding, allow for convenient disposal, and be environmentally safe [4].

In a multi-component binder system, the removal of binders is carried out sequentially to prevent the collapse of debound parts during the debinding and sintering processes. Typically, the low-melting-point polymer is eliminated either through solvent debinding or low-temperature thermal debinding. Once most of the low-melting-point polymer has been removed, the high-melting-point polymer can still maintain the shape and geometry of the molded part. The open pores formed during the initial stage of debinding, whether through solvent debinding or low-temperature thermal debinding, provide pathways for extracting the backbone polymer (i.e., the high-melting-point polymer) [5]. The decomposition mechanisms of the polymers depend on the specific nature of the polymers used and the temperature or medium to which they are exposed.

To achieve a homogeneous feedstock for Metal Injection Molding (MIM), it is essential for the powder and binder to be miscible and possess the desired rheological properties. Therefore, identifying appropriate mixing conditions is crucial. In one study [6], a typical feedstock formulation was developed using high-density polyethylene (HDPE), Paraffin Wax (PW), and stearic acid (SA). These ingredients were kneaded for 5 minutes at 180 °C and then for an additional 10 minutes at 160 °C. In another report [7], the MIM feedstock was prepared by dry mixing SS 316L powder with a binder system consisting of HDPE, PW, SA, and an antioxidant. The mixing process was conducted at room temperature for 15 minutes using a Type R02 intensive mixer, followed by extrusion using a twin-screw extruder at temperatures ranging from 150 °C to 181 °C. The powder contents in this study ranged from 40 to 50 vol.% [7]. However, it should be noted that while the authors claimed that two extrusion passes were sufficient for achieving feedstock homogeneity, no direct evidence supporting this claim was provided [7]. The homogeneity of the feedstock is a critical aspect in MIM processing, and it is essential to ensure that the chosen mixing conditions and process steps result in a truly homogeneous feedstock to achieve optimal results in the subsequent molding and sintering stages.

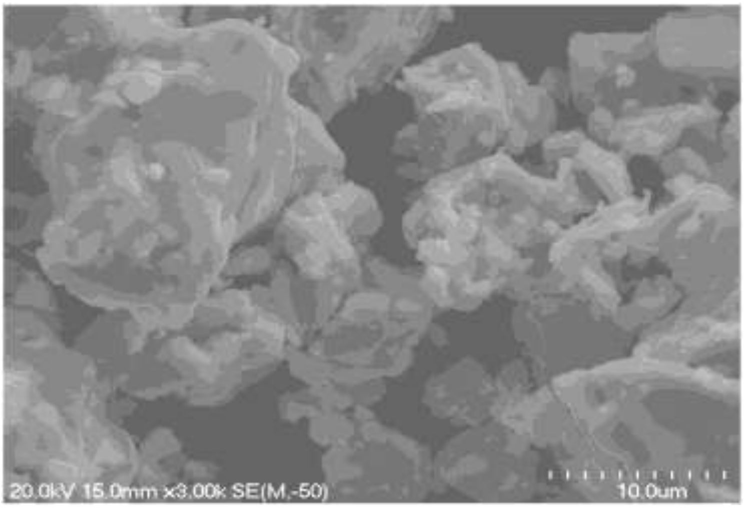

FIGURE 1. Particle morphology of SS 316 L powder.

Indeed, a significant portion of research in Metal Injection Molding (MIM) has focused on achieving feedstocks with low to moderate powder contents. However, there are also studies that have successfully achieved higher powder contents in the feedstock, thereby expanding the possibilities for MIM applications. For example, Krauss et al. [8] obtained a homogeneous feedstock with a powder content of 55 vol.% by mixing alumina powder with a binder system comprising PEG, PVB, and SA. The mixing process involved a sigma-type blade mixer and consisted of 30 minutes at 180 °C, followed by an additional 30 minutes at 160 °C. Weil et al. [9] achieved a homogeneous feedstock with a powder content of 65 vol.% for reactive metal-based MIM by mixing Ti-6Al-4V powder with an aromatic-based binder system (naphthalene, ethylene vinyl acetate, and stearic acid) at 90 °C in a Hake Record 90 mixer (the specific mixing time was not specified). Amin et al. [10] obtained a homogeneous feedstock with a powder content of 64 vol.% by mixing stainless steel powder with a binder system composed of HDPE, PW, and SA. The mixing was performed in a Z-blade type mixer for 30 minutes at room temperature, followed by 60 minutes at 70 °C [10]. Furthermore, there have been numerous other reports exploring the formulation of feed stocks using various binders, mixing conditions, and powder contents. Recently, Wen et al. [11] published a comprehensive overview specifically focusing on the development of binder systems used for SS 316L-CNT injection molding. These studies highlight the ongoing efforts and advancements in developing feedstock formulations with higher powder contents and improved rheological properties, opening up new possibilities for MIM processes.

The rheological properties of a feedstock serve as a direct indicator of its quality. A feedstock with low viscosity, low activation energy, and a low flow behavior index exhibits favorable rheological properties for effective injection molding [12]. In Metal Injection Molding (MIM), the temperature of the feedstock undergoes changes throughout the molding process, transitioning from the feed section (medium temperature, 60 °C–100 °C) to the intermediate section (high temperature, 120 °C–200 °C), and finally to the end mold (low temperature, 25 °C–50 °C). The viscosity of the feedstock can significantly vary with temperature and plays a crucial role in the analysis of its rheological properties.

Flow activation energy is commonly utilized to assess the temperature dependency of viscosity and is influenced by the composition of the binder and the feedstock [2]. A high flow activation energy signifies a strong sensitivity of viscosity to temperature variations. Consequently, even a small change in temperature during the Metal Injection Molding process can lead to a significant alteration in the viscosity of the feedstock. This highlights the importance of understanding the temperature dependence of viscosity and the role it plays in ensuring the successful processing of feed stocks in MIM.

TABLE 1. Feedstock formulations

Feedstock no.	**Powder content (vol.%)**	**HDPE (vol.%)**	**PW (vol.%)**	**SA (vol.%)**	**Binder ratio (vol.%) (HDPE:PW:SA)**
F1	55	33.8	9.0	2.3	75:20:5
F2	60	30.0	8.0	2.0	75:20:5
F3	55	36.0	6.8	2.3	80:15:5
F4	60	32.0	6.0	2.0	80:15:5

In this research, the feed stocks were prepared by blending hydride dehydride (HDH) SS 316L-CNT powders with a binder system based on high-density polyethylene (HDPE), which is water soluble. In general, when formulating SS 316L-CNT feedstock, spherical gas atomized SS 316L powder is the preferred choice. This type of powder offers higher purity and spherical particles, which are desirable for achieving optimal feedstock properties. On the other hand, SS 316L powder is more affordable and readily accessible commercially. It provides a range of options in terms of particle sizes and purity levels, making it a suitable alternative for formulating SS 316L-CNT feedstock in situations where the preferred spherical gas atomized powder is not available or cost-effective. By utilizing commercially available SS 316L powder, researchers can still achieve desirable feedstock properties while considering practical and economical factors.

2. EXPERIMENTAL PROCEDURES

2.1Materials

For the research, different feedstock compositions were prepared using a composite powder of SS 316L and CNT, along with a binder system that was water soluble. The binder system consisted of HDPE, PW, and SA. The materials utilized in this study included SS 316L and CNT powders, HDPE with a molecular weight of 8000 g/mol and a melting point of 65 °C, PW with a molecular weight of 50,000 and a melting point of 185 °C, and SA with a molecular weight of 285 g/mol and a melting point of 74 °C. Analysis of scanning electron micrographs revealed that the SS 316L powder exhibited irregularly shaped particles (refer to Fig. 1). Additionally, the average particle size, as depicted in Fig. 2, was measured to be 70 µm.

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2.2 METHODS

2.2.1Mixing and blending

The homogeneous feedstock was produced through a four-step mixing process. Firstly, a blend of SS 316L and CNT composite powder, along with the binder components listed in Table 1, was subjected to dry mixing. This mixing step was conducted at room temperature (25 °C) for a duration of 30 minutes, using a planetary mixer (Kenwood) operated at a speed of 20 rpm.

Following the initial dry mixing stage, the mixture was transferred to a roller mixer. It underwent further mixing for duration of 16 hours at room temperature, with the roller mixer set to operate at 100 rpm. Subsequently, the mixture was introduced into the mixing chamber of a compounder. Prior to this step, the compounder had been preheated to 130 °C. The mixture was mixed in the compounder for 40 minutes, with a rotation speed of 55 rpm. The resulting feedstock was then subjected to mixing in a twin-screw extruder. The extruder operated at a screw speed of 150 rpm, while the barrel temperature followed a specific profile: 110 °C, 120 °C, 130 °C, 130 °C, and 140 °C (from feed to nozzle). This temperature profile was employed to improve the homogeneity of the feedstock. To assess the homogeneity of the feedstock, burn-out tests were conducted using TGA/DTA (Thermogravimetric Analysis/Differential Thermal Analysis) methods. Additionally, density analysis using a pycnometer was performed on samples collected from each of the four mixing stages.

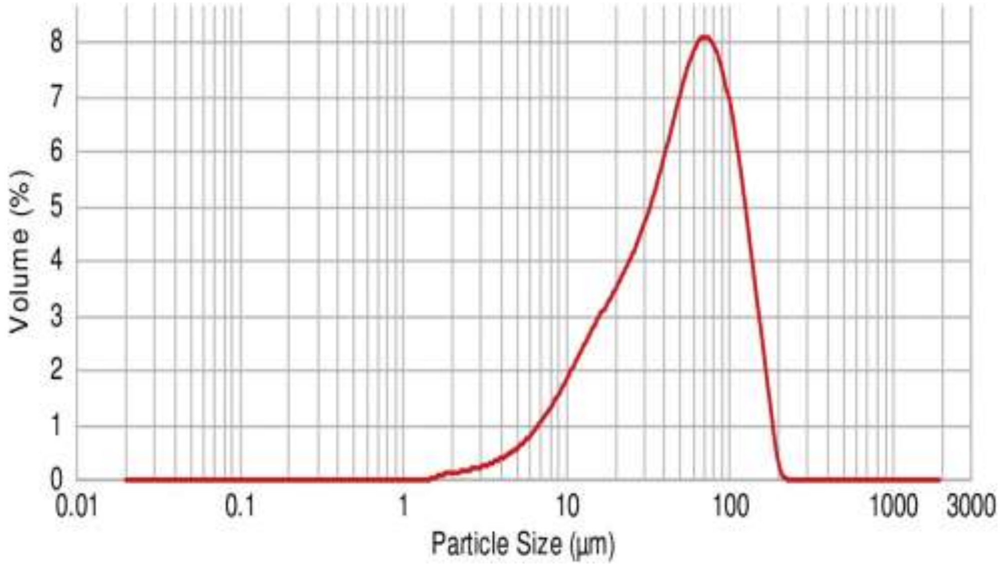

FIGURE 2. *Particle size distribution of SS 316L powder.*

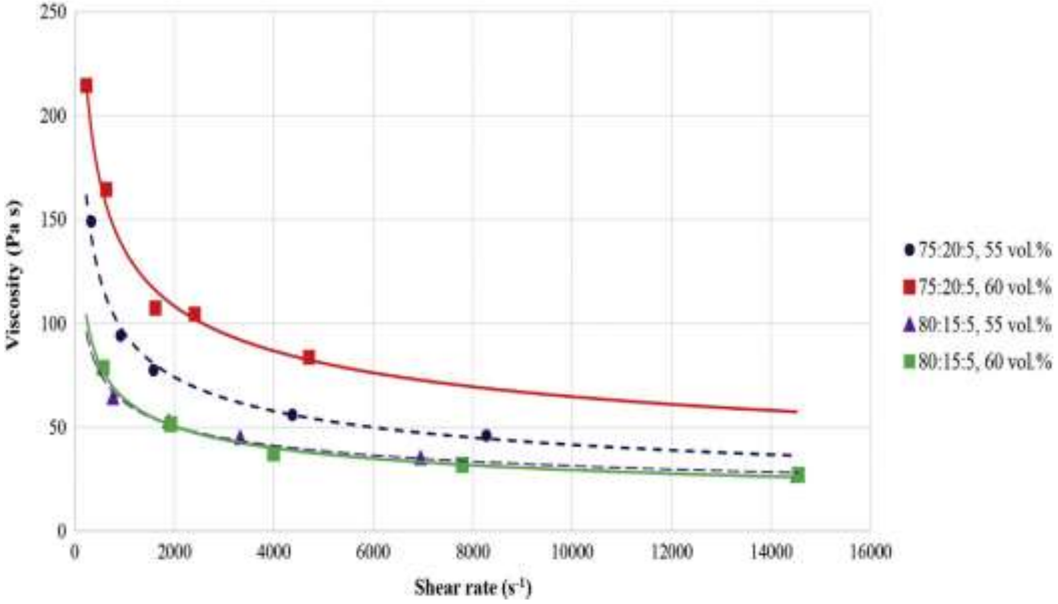

FIGURE 3. *The graph of viscosity versus shear rate showing data fits to the power regression lines.*

2.2.2 Rheological analysis

The rheological properties of the feedstock formulations were investigated using a Shimadzu CFT 500D capillary rheometer equipped with a 1-mm diameter, 10-mm long die. Triplicate 3-gram samples of each feedstock formulation were utilized for the analysis. The capillary rheometer was operated at three different temperatures: 125 °C, 140 °C, and 165 °C. The Bagley correction, an automatic correction method, was applied during the measurements. To cover a wide range of shear stresses and shear rates, the rheometer was loaded with various forces: 20 N, 40 N, 60 N, 100 N, and 160 N. The lower loads (20 N, 40 N, and 60 N) were chosen to obtain rheological properties at lower shear stresses and shear rates, while the higher loads (100 N and 160 N) were used to measure rheological properties at higher shear stresses and shear rates. For each measurement, a random sample was introduced into the preheated capillary barrel, which was preheated for 5 minutes. The rheological data reported were the average of three random samples, ensuring accuracy and reliability. Furthermore, the flow activation energy obtained from the different temperatures was analyzed to evaluate the influence of temperature on the viscosity of the feedstock.

3.RESULTS AND DISCUSSION

3.1Flow behaviour index

The viscosity of all feedstock formulations exhibited a decrease as the shear rate increased, as depicted in Figure 3. This behavior indicates a time-independent, non-Newtonian fluid characteristic known as shear thinning or pseudo plasticity. Shear thinning behavior implies that an increased shear force facilitates a more uniform distribution of particles, allowing smaller particles to fit into the gaps between larger particles [13].

At lower shear rates, a stable network structure is formed by the metallic particles and polymeric binders within the feedstock. However, at higher shear rates, this structure is disrupted. The metallic particles and polymeric binders rotate and re-arrange themselves along the flow direction, enabling inter-particle motion, and leading to the observed shear thinning effect. The viscosity of the feedstock is primarily influenced by hydrodynamic interactions [14]. Furthermore, the application of higher shear rates causes the agglomerates of metal powder particles to break apart, enhancing the packing of particles and improving the overall homogeneity of the feed stock.

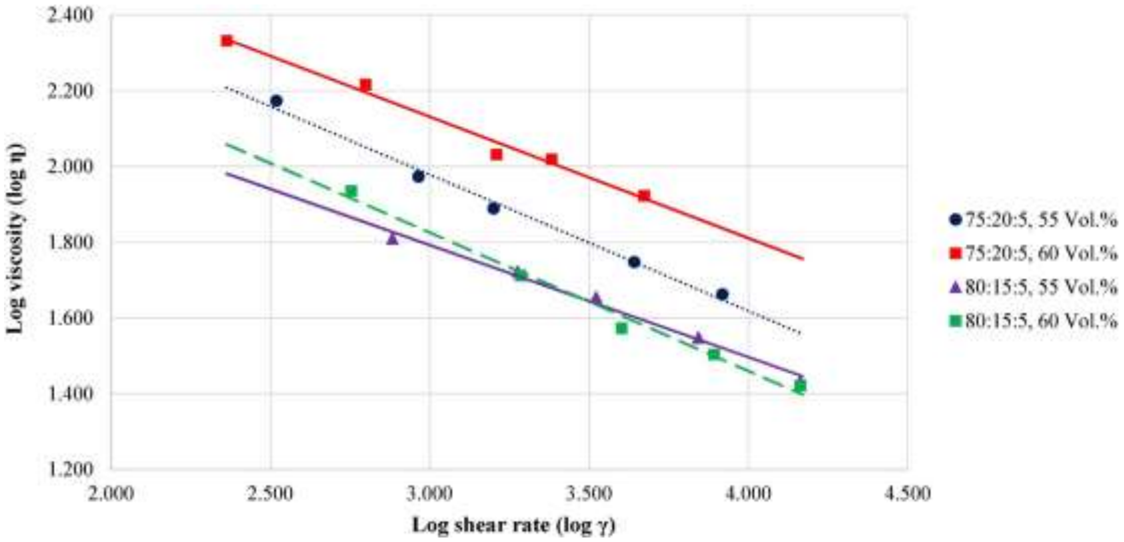

FIGURE 4. *The graph of log viscosity versus log shear rate.*

TABLE 2. *Flow behaviour index of feedstock formulations.*

HDPE:PW:SA	Powder Content 55 Vol.%	Powder Content 60 vol.%
75:20:5	0.64	0.68
80:15:5	0.70	0.63

The data fitting showed a good fit (R2 of between 0.98 and 1.00) to the power law or Ostwald de Waele model, τ=mγn. Viscosity for a power law fluid is given by:

$$\eta = \frac{\tau}{\gamma} m\gamma^{n-1}$$

The value of n is obtained by re-arranging the equation:

$$log\,\eta = \log m + (n-1) log\gamma$$

Flow behaviors of a power-law fluid depend on the value of n [15]:

For

n < 1; the fluid shows shear thinning flow behaviour

n =1; the fluid shows Newtonian flow properties

n >1; the fluid shows shear thickening flow behaviour:

Feedstocks that exhibit shear thinning behavior (n < 1) are considered suitable for Powder Injection Molding (PIM) processes. On the other hand, feedstocks with dilatant flow behavior (n > 1) are not recommended since they can experience powder and binder separation under high shear rates. It's important to note that some feedstocks may exhibit both shear thinning and dilatant flow behaviors, depending on the applied shear rate. Therefore, it is necessary to assess the rheological properties of feedstocks over a wide range of shear rates to fully understand their behavior. In the case of the capillary rheometer used in this study, the applied loads (ranging from 20 N to 160 N) allowed for the investigation of a wide range of shear rates. The flow behavior indices (n) for all the feedstocks were determined by analyzing the gradients of the flow curves, as shown in Figure 4. The values of the flow behavior indices for all the feedstocks, provided in Table 2, were found to be less than unity, indicating shear thinning behavior. Among the feedstocks, feedstock F4 exhibited the lowest flow behavior index (n = 0.63), suggesting the highest degree of shear thinning behavior among the tested formulations.

3.2 Fluidity

Among the range of shear rates utilized in this study, the highest viscosity recorded for the feedstocks at the molding temperature (considered the worst-case scenario) was 1000 Pa•s [16]. The viscosities and shear rates for all the feedstocks produced in this research fell within the following ranges: 26 Pa•s to 214 Pa•s at 230 s−1 and 14,800 s−1, respectively. Furthermore, the fluidity of the feedstocks at 140 °C was observed to increase with the HDPE content, as indicated in Table 3. Feedstocks F3 and F4 exhibited similar levels of fluidity, which were both higher than the fluidity values of F1 and F2.

3.3 Metal Flow Index (MFI)

The Melt Flow Index (MFI) provides an indication of how easily the molten feedstock flows through a capillary die when pressure is applied at a specific temperature. In this study, the MFI of the feedstocks was evaluated under a wide range of shear stresses. It was observed that as the powder content in the feedstock increased from 55 vol.% to 60 vol.% (at a constant load for a specific binder ratio), the MFI values decreased, indicating a decrease in flowability. Conversely, significant increases in MFI values were observed when the PEG vol.% increased from 75 vol.% to 85 vol.% (at a constant powder content and load) or when the applied load was increased. Comparing the feedstocks, F3 and F4 exhibited similar MFI values, which were higher than those of F1 and F2, as shown in Figure 5. These results align with the trend observed for fluidity, as discussed in Section 3.2.

TABLE 3. *Fluidity of feedstock formulations at shear rate of 800 s−1.*

Feedstock	Fluidity (× 10−3 Pa−1 s−1)
F1	9.7
F2	6.9
F3	15.1
F4	14.6

TABLE 4. *Melt flow index of various feedstock formulations at 140 °C.*

Formulatior	content (vol.%)	HDPE:PW:SA (vol.%)	MFI (g/10 min)				
			20 N	40 N	60 N	100 N	160 N
F1	55	75:20:5	19.5	54.2	93.3	225.6	484.9
F2	60	75:20:5	13.6	37.0	85.3	141.9	277.4
F3	55	80:15:5	45.0	111.1	195.8	409.5	855.1
F4	60	80:15:5	33.4	110.6	195.6	409.1	855.0

4. Flow activation energy (Ea)

Mobility of liquid molecules is a temperature-activated process so temperature dependency of viscosity is important when analyzing rheological properties of a feedstock. Temperature dependency of feedstock viscosity can be expressed using the Arrhenius equation

$$\eta=\eta_0 \exp(E_a/RT)$$

Which can be written as:

$$\ln \eta= \ln \eta_0 +(E_a/R)(1/T)$$

where ηo is the viscosity at a reference temperature, Ea is the flow activation energy, R is the universal gas constant and T is the absolute temperature [12]. The value for Ea can be obtained from the gradient of ln η versus 1/T. Fig. 6 shows the relationship between viscosity and temperature of feedstock F2 under various shear stresses (σ = 49.03 to 392.26 kPa). Data were an excellent fit to the Arrhenius equation (R2 of between 0.99 and 1.00). The derived activation energy data of feedstocks F2 and F4 were summarized in Table 5.

TABLE 5. *Flow activation energy of feedstock (KJ/mol).*

Feed Formulations	Shear Stress (Pa)				
F2	39.8	35.7	42.5	39.7	36.8
F4	27.8	29.7	27.2	26.8	14.8

Feedstocks F2 and F4 were specifically chosen due to their superior flow properties and higher powder content compared to F1 and F3. The flow activation energies of F2 and F4 fell within the ranges of 35.7 to 42.5 kJ/mol and 14.8 to 29.7 kJ/mol, respectively. Notably, the flow activation energies of F4 consistently remained lower than those of F2. This observation can be attributed to the higher PEG content in F4. A high flow activation energy suggests that the viscosity of the feedstock is significantly influenced by temperature. As a result, even a slight variation in process temperature during the injection molding process could result in a substantial change in the feedstock viscosity, potentially leading to defects in the final molded product [10]. Based on these findings, it was determined that F4, with its lower flow activation energy and higher HDPE content, is the most suitable feedstock for Metal Injection Molding (MIM) applications.

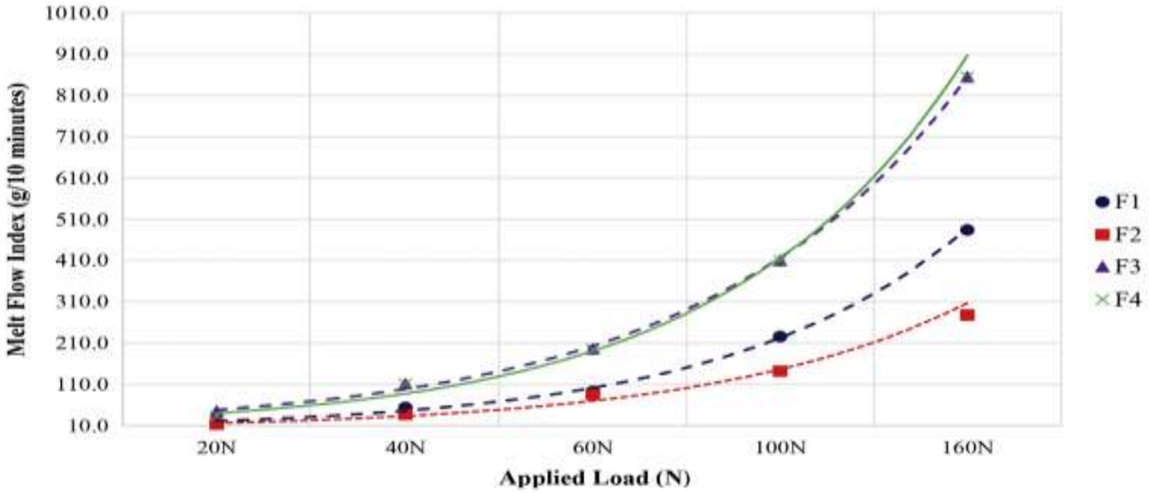

FIGURE 5. *The graph of melt flow index versus applied load.*

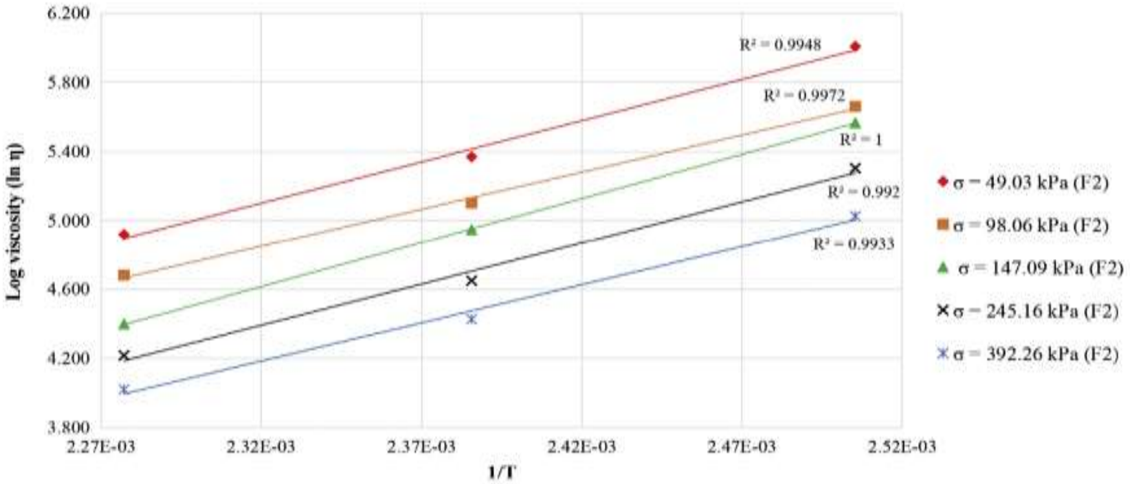

FIGURE 6. *Correlation between viscosity and temperature for the feedstocks F2 and F4.*

4.CONCLUSIONS

All of the MIM (Metal Injection Molding) feedstock formulations developed in this study exhibited the desired shear thinning behavior, which is crucial for successful MIM processes. The viscosity of the feed stocks decreased as the shear rate increased, indicating a non-Newtonian pseudo plastic flow characteristic.

Based on the results obtained, an optimized feedstock formulation was identified. This formulation comprised 60 vol.% SS 316L-CNT composite powder, 32 vol.% HDPE, 6 vol.% PW, and 2 vol.% SA. This particular feedstock demonstrated favorable rheological properties, including a low activation energy, low viscosity, high shear thinning behavior, high fluidity, and a high melt flow rate. Moreover, it had a high powder content, which further enhances its suitability for MIM applications.

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