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CHARACTERIZATION OF MECHANICAL, THERMAL, AND PHYSICAL PROPERTIES OF POLYPROPYLENE COMPOSITES WITH RICE HUSK FILLER USING COUPLING AGENT MALEIC ANHYDRIDE

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Abstract

Polypropylene is a thermoplastic that is widely applied in various automotive industries. Polypropylene is used as a matrix in composite manufacturing because it has the advantages of ease of processing, corrosion resistance, mechanical stiffness, low density, and affordable prices. The advantages of organic fillers (rice husk) are environmentally friendly, low density, and renewable. However, there is a weakness of polypropylene composites using rice husk filler, namely the lack of compatibility between the Polypropylene matrix which is hydrophobic while the filler (rice husk) is hydrophilic, to increase the bond between the matrix and filler can be done by adding a coupling agent. Based on this description, it is necessary to study the effect of the addition of maleic anhydride composition on the manufacture of polypropylene composites with rice husk filler because it can be used as an alternative in reducing agricultural waste. The addition of maleic anhydride in this study is expected to increase the bond compatibility between polypropylene and rice husk to improve the mechanical properties and crystallinity of the resulting polymer composite. The variation of this research is the composition variation (weight %) of polypropylene, rice husk, and maleic anhydride of 80:20:0, 80:18:2, 80:17:3, 80:15:5. The method used in this research is using a twin-screw extruder tool with a temperature of 190℃ and then testing mechanical properties using tensile tests and thermal properties using Differential Scanning Calorimetry (DSC). The results showed that the mechanical properties and thermal properties of the composite increased and decreased along with the variation of maleic anhydride addition, with the highest value obtained in the variation of polypropylene, rice husk, and maleic anhydride = 80:17:3 with a tensile strength value of 10.117 MPa and a crystallinity value of 27.39%..

Keywords: Composite, Polypropylene, filler, rice husk, coupling agent, maleic anhydride

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1. Introduction

Composite or composite material can be defined as a combination of two or more materials that have different characteristics, both in physical form and chemical structure, which then produces a new form that has better characteristics (Aryanti, 2021). The advantages of organic fillers (rice husk) are environmentally friendly, low density, lower energy manufacturing, and renewable. Currently, technological developments, especially in the field of polymer composites, have produced composite products that are a combination of rice husks and polymers (Kim et al., 2007). With the development of this technology, it is possible to maximize the utilization of rice husk and polymer to reduce the amount of waste produced. Research on the effect of the percentage of rice husk with variations of 10%, 20%, 30%, and 40% by weight on the tensile strength and impact strength with polypropylene matrix has been conducted by (Yang et al., 2004) obtained the highest tensile strength test results with the addition of 10% by weight of rice husk with a tensile strength value of 28 MPa, and impact strength of 15 kgf.cm/cm3. The content of rice husk contains 35% cellulose, 20% lignin, and 19% hemicellulose, which can affect the mechanical properties of polymer composites (Ramamoorthy et al., 2015).

Polypropylene is used as a matrix in composite manufacturing because it has the advantages of ease of processing, corrosion resistance, mechanical stiffness, low density, and affordable prices (Toro et al., 2005). However, there is a weakness of polypropylene rice husk composites, namely the lack of compatibility between the matrix (PP) which is hydrophobic while the filler material (rice husk) is hydrophilic (Majeed et al., 2017). According to various literature and existing studies increasing the bond between matrix and filler can be done by adding a coupling agent(Diharjo, 2006). The basic principle of coupling agent performance is due to bifunctional molecules that can interact with the matrix and filler to combine the two materials. The addition of coupling agents provides hydrophilic groups that can bind to the filler material while the polymer groups can link with the polymer matrix.

Maleic anhydride is a coupling agent that can improve the mechanical properties and crystallinity of composites by increasing the adhesion of matrix and filler interfaces. The reactive anhydrous group in MA allows it to react with the matrix and filler in the composite. MA will form crosslinks in the matrix and filler so that the composite will be stronger. MA has a low molecular weight that will increase the wetting of the matrix so that the matrix can spread evenly on the composite. MA is easily available due to its high production and affordable price.

In research conducted by (Fathanah, 2011) the addition of 8% MA can improve the mechanical properties of composites. In the study, the addition of 4% MA did not increase the fracture toughness, but in the addition of 8% MA the fracture toughness increased by 82.5-85.2 kgf.cm-2. MA can increase the density and mechanical properties of composites because of its function which can reduce the interfacial tension of the material so that it is more compatible. Another study conducted by (Yeh et al., 2015) with the addition of 2% MA and alkalization of rice husk using 10% NaOH can increase tensile strength and impact strength on rice husk/polypropylene composites.

Based on this description, researchers are interested in researching the effect of the addition of maleic anhydride composition on the manufacture of polypropylene/rice husk composites because it can be used as an alternative in reducing agricultural waste and further testing and analysis to see how the effect of the addition of maleic anhydride composition on the mechanical properties, thermal properties, and physical propertis of polypropylene composites with rice husk filler.

2. Experimental and Methods

Compounder ZK 25×24 D twin-screw extruder, analytical balance, scissors, watch glass, beaker, tweezers, Manual Forming Machine (MFM) Cometech model QC 601-A, Pneumatic Specimen Punch marto QC-603 A, Universal

Testing Machine (UTM) Ibertest Eurotest, Differential Scanning Calorimetry (DSC) type Netzsch 214 Polyma Instrument, density kits, and analytical balance. The materials used are Polypropylene brand Hanwha Total Energies Petrochemical Co, Rice Husk from the Bekasi City area, Maleic Anhydride brand Sigma-Aldrich, Aquadest, and NaOH brand Merck.

Rice husk preparation begins with preparing the materials to be used in the alkalization process. The stages of the rice husk alkalization process are carried out by grinding with a blender to reduce the size of the husk. The pulverized rice husk is then sieved with a 60-mesh sieve to homogenize the size of the husk. The size of the rice husk affects the alkalization process because the smaller the size of the husk the lignin content decreases because the surface area of the husk will be greater to facilitate direct contact with the alkaline compound, namely NaOH.

The NaOH alkaline compound was weighed as much as 80 grams, then the NaOH compound that had been weighed was dissolved with 1000 ml of distilled water in a container, after which the rice husk was put into the NaOH solution container and then soaked for 4 hours. Every 1 hour stirring of the rice husk is done to ensure that the rice husk is completely submerged, after soaking for 4 hours the rice husk is washed with running water until it reaches normal pH which aims to remove the rest of the NaOH alkaline compound soaking. The next stage is the drying process of rice husk. The rice husk is dried for about 3 days by drying the husk to remove the water content until the weight of the rice husk stabilizes and dries. If the rice husk has dried, it is then stored in zipper plastic to avoid the husk being contaminated with the environment, then the rice husk can be used for making compounds. The compound was made using a Teach-line Collin Compounder ZK 25×24 D twin-screw extruder. The polypropylene, rice husk, and Maleic Anhydride materials were put into a beaker and weighed according to the specified variations and then stirred using a spoon for some time until they were well stirred. The homogenized material is poured into the extruder machine through the hopper with a rotation rate of 20 rpm towards the material melting process and then the melted material comes out through the die. The material is cooled with a water bath until it hardens until it enters the pelletizer and produces output, namely compound pellets. The finished pellets are then weighed and ready to be used for molding and cryogenicity tests on each composite variation.

After the finished compound is then formed into a composite plate using a manual forming machine cometech QC-601A. The size of the molded metal plate is 20cm×20cm×0.2cm. The material is weighed with a weight of 75 grams so that the composite material to be molded meets the mold plate. The temperature of the manual forming machine is set according to the melting temperature of the plastic, for polypropylene using a melting temperature of 180℃. The composite melting and molding time is 20 minutes with a pressure of 300 kgf/cm2. After the composite plate is finished, it is then molded into a dogbone shape test specimen using a pneumatic specimen punch marto QC-603A machine with a pressure of 5 bar. Mechanical properties testing using Ibertest 5kN Universal Testing Machine (UTM) ASTM D638 standard with 5 specimens per sample. The test specimens were first conditioned at 23±2ºC, 50±10% relative humidity for at least 40 hours. Thermal properties testing using a Netzsch 214 Differential Scanning Calorimetry (DSC) machine. The sample used was ±6 mg put into the crucible and then heated from 30°C to 220°C. At a heating rate of 10°C/minute then held for 5 minutes for the first heating. Next, the sample was cooled at a cooling rate of 10°C/minute to a temperature of 30°C and held for 5 minutes. Then it will heat up to 220°C with a heating rate of 10°C/minute for the second heating.

The density testing method is by weighing the specimens with density kits in a dry state in the air and a state dipped in distilled water, then the values obtained are entered into the following formula:

$$\rho = \frac{A}{A-B} \times (\rho_0 - d) + d$$

notes:

ρ = sample density (g/cm^3)

A = sample mass in the air

B = sample mass in the distilled water (gram)

d = density of air (0,001 g/cm3)

ρ_0=liquid densitas (g/cm3)

Table 1. Research Variations

Variation	Composition(%weight)		
	Polypropylene	Rice Husk	Maleic Anhydride
1	80	20	-
2	80	18	2
3	80	17	3
4	80	15	5

3. Results and Discussion

3.1 Mechanical Properties

The results of testing mechanical properties using a Universal Testing Machine tool for all variations can be seen in Table 2.

Table 2. Mechanical Properties (Tensile Strength)

Variation	Tensile Strength (MPa)					Average (MPa)
	Specimen					
	1	2	3	4	5	
1	7,372	6,101	4,312	7,606	5,019	6,082
2	6,304	7,192	7,768	7,297	6,814	7,075
3	9,364	10,173	11,047	9,882	9,939	10,081
4	9,061	7,355	9,371	8,545	6,522	8,171

Table 2 shows the tensile strength of the composite has increased and decreased along with the variation of maleic anhydride (MA) addition. In Polypropylene/rice husk composites without the addition of MA, the tensile strength value is 6.082 MPa. In the Polypropylene/rice husk composite with the addition of 2% MA, it increased with a tensile strength value of 7.075 MPa. In Polypropylene /rice husk composites with the addition of 3% MA, the tensile strength value increased to 10.081 MPa. In Polypropylene/ rice husk composites with the addition of MA 5% decreased with a tensile strength value of 8.171 MPa. From the data, the highest tensile strength value was obtained at the addition of MA 3% of 10.081 MPa. This shows the maximum tensile strength value in the composition of the addition of MA 3%. The increase in tensile strength with the addition of MA occurs due to the success of MA binding to the matrix and filler material. MA has a reactive functional group where the alkene group on MA will bind to PP by addition reaction and the anhydrous group will bind to cellulose contained in rice husk such that the bond formed will affect the increase in tensile strength of the composite. The results of this study are in line with the results of research conducted by(Kim et al., 2007), with the addition of MA 3% in Polypropylene/rice husk composites can increase the tensile strength of composites. In the addition of 3% MA, the tensile strength value is 40 MPa, while without the addition of MA it is 30 MPa.

The decrease in tensile strength with the addition of 5% MA in this study can occur due to excessive MA composition factors so that MA is not effective in increasing the compatibility of PP/rice husk composites. The decrease in tensile strength value can occur because at the time of making the composite plate, there are air bubbles or voids during the process of making the composite sheet using a manual forming machine.

3.2 Thermal Properties

Thermal testing using DSC to determine the value of crystallization temperature (Tc), melting temperature (Tm), enthalpy of melting (ΔHm), and crystallinity (Xc) of the composite. Figures 1-4 show the results of testing the composites using DSC.

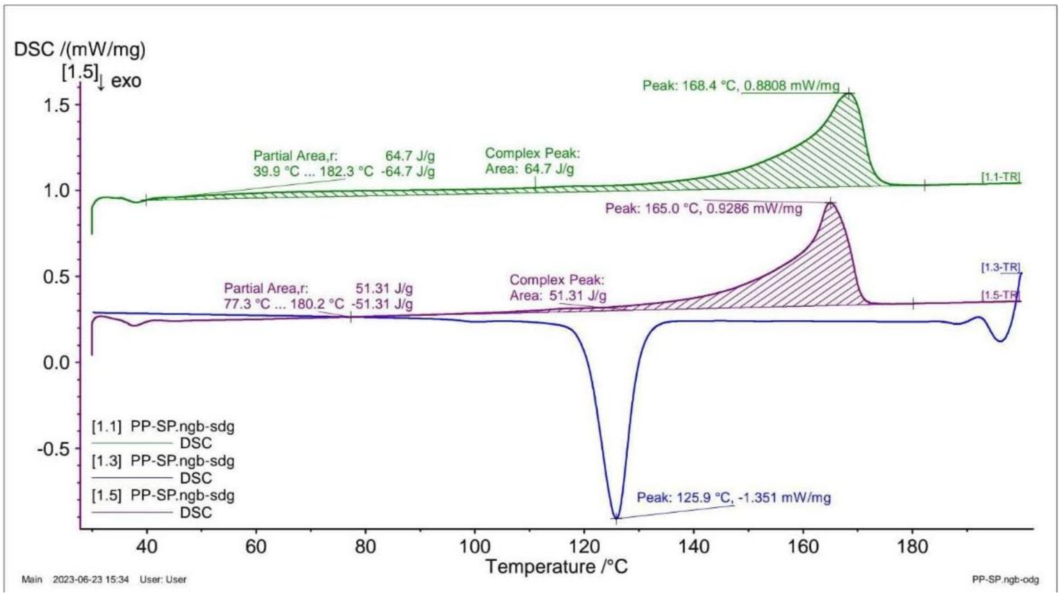

Figure 1. DSC thermogram of Variation 1

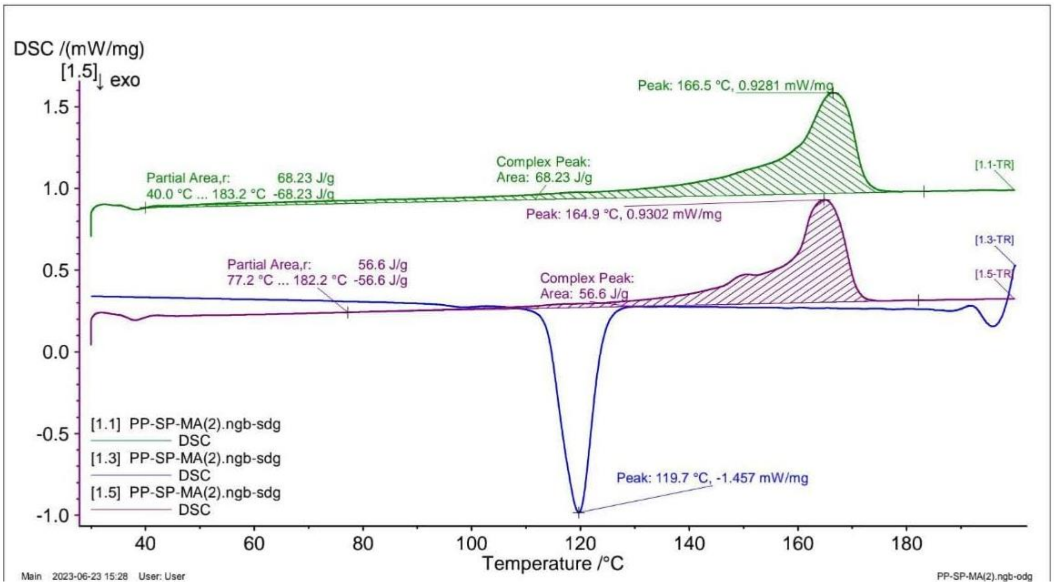

Figure 2. DSC thermogram at Variation 2

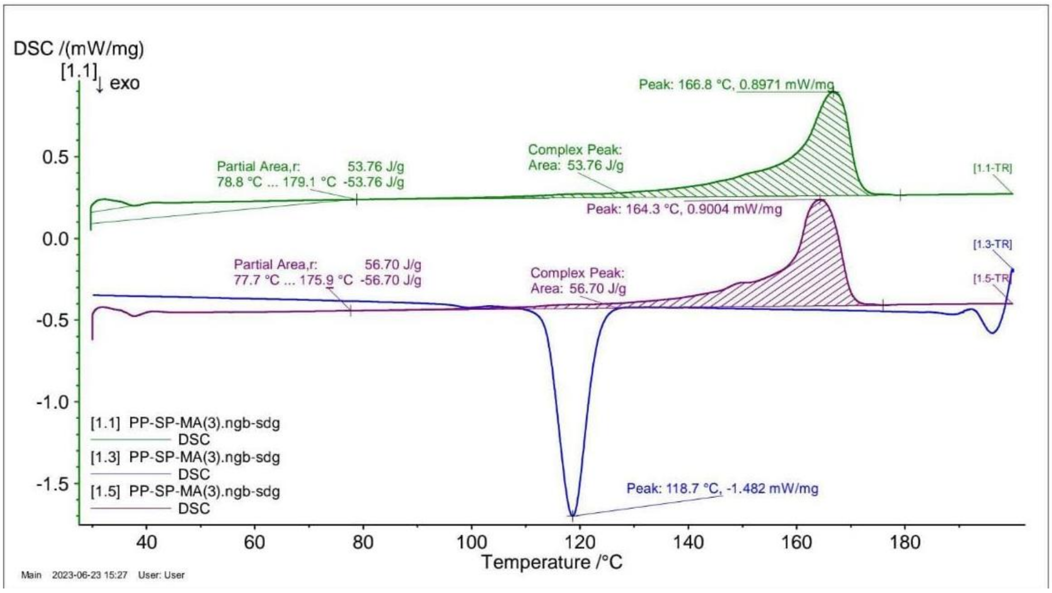

Figure 3. DSC thermogram at Variation 3

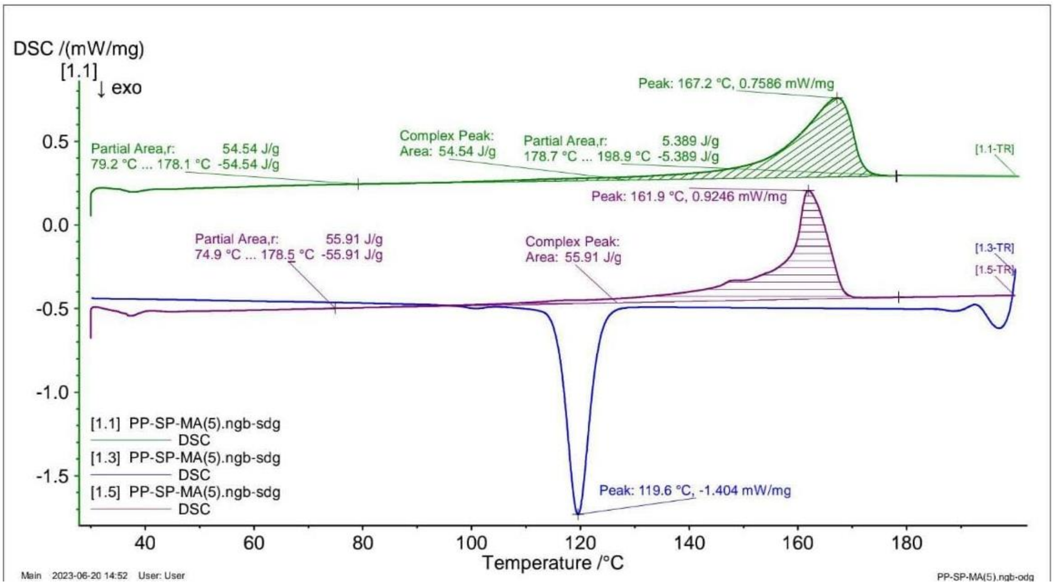

Figure 4. DSC thermogram at Variation 4

The DSC test thermogram on the Polypropylene/rice husk composite shows an endothermic thermogram curve whose peak curve points upwards. The endothermic curve is the melting temperature. The striped curve is the melting process of the material. The melting process is endothermic because the energy released by the crucible contained in the DSC machine is absorbed by the material. The energy released is the enthalpy value of the melt. The enthalpy value is obtained from the area of the melting process. A positive enthalpy value is an endothermic reaction while a negative enthalpy value is an exothermic reaction. The data of melting temperature and crystallinity test results of PP/rice husk composites can be seen in Table 3.

Table 3. DSC Test Data Results

Variation	**ΔH_m (J/g)**	**T_m (°C)**
1	51,31	165,0
2	56,60	164,9
3	56,70	164,3
4	55,91	161,9

The crystallinity of PP/rice husk composites can be calculated using the enthalpy value resulting from the DSC thermogram, the degree of crystallinity (Xc) in PP/rice husk composites can be calculated using the formula: (Chafidz et al., 2016).

$$Xc = \frac{\Delta \mathrm{Hm}}{\Delta \mathrm{H°m}} \times 100\%$$

Notes:

X_c = Crystallinity (%)

ΔHm = enthalpy of melting (J/g)

ΔH°m = enthalpy of melting 100% crystalline polypropylene (J/g) = 207 J/g

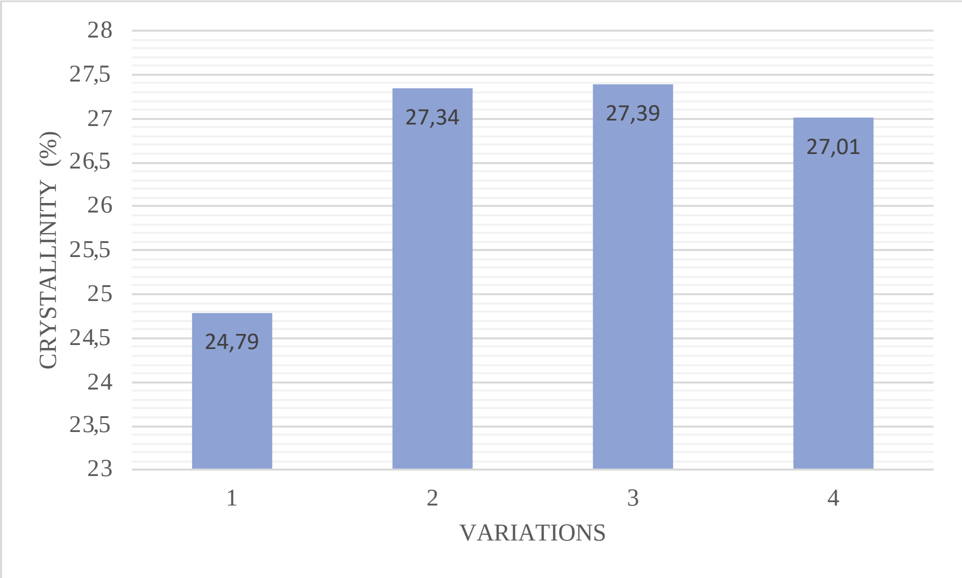

Figure 5. Crystallinity values at various variations

The addition of MA affects the crystallinity of the composite. Crystallinity increases and decreases with the addition of MA in PP/rice husk composites. The crystallinity value of PP/rice husk composite without MA addition is 24.79%. In PP/rice husk composites with the addition of 2% MA, the crystallinity value increased by 27.34%. In PP/rice husk composites with the addition of 3% MA, the crystallinity value increased by 27.39%. In PP/rice husk composites with the addition of MA 5% decreased the crystallinity value by 27.01%. From the test data, the highest crystallinity value was obtained in the PP/rice husk composite with the addition of 3% MA at 27.39%.

The increase in crystallinity occurs when MA can act as a nucleating agent in the composite that helps crystal formation. This is in line with research conducted by (Huang et al., 2018). Research conducted by (Huang et al., 2018) on the effect of MA addition on the crystallinity of PP-matrixed composites with MA variations of 1%, 3%, 5%, and 7% found that the addition of MA 5%, 7% decreased crystallinity, namely 40% and 38% with the highest crystallinity value at the addition of MA 3% at 43%. This can occur because when the composition of MA is at its critical peak, it will increase the crystallinity formed. MA has anhydrous functional groups, and double bonds and can act as a nucleating agent during crystal formation. Upon heating, MA and PP will melt and MA will disperse into PP molecules.

The dispersed MA binds to PP and becomes the starting point in the formation of crystal nuclei. MA affects the displacement of polymer chains and regulates the orientation of the formed crystal chains. The decrease in crystallinity with the addition of 5% MA by weight occurs due to the excessive composition of MA and the structure of PP molecules cannot be reorganized due to interactions with fillers. MA distributed in the matrix will inhibit the strong linear bonding of the PP matrix. This is in line with research conducted by (Huang et al., 2018) when the composition of MA addition is excessive, the crystallinity of the composite formed will decrease. PP is a crystalline polymer when the addition and distribution of MA that is not appropriate has the effect of reducing its crystallinity because the addition of excess MA can interfere with the formation of crystals in the polymer matrix, but if the addition of MA is appropriate it can increase crystallinity.

The crystalline region is composed of regular and tight molecular chains so it has a greater tensile strength than the amorphous region because the amorphous region has an irregular arrangement of molecular chains. The ratio between the crystalline phase and the amorphous phase is called crystallinity. Therefore, PP is a semi-crystalline polymer, adding MA unevenly and inappropriately can reduce the crystallinity of the composite, because MA can interfere with the formation of crystals in the composite when the composition is too much, causing the crystalline phase in PP to decrease.

3.3 Physical Properties

Physical properties testing using density test. From the calculation of the density of the composite, a graph is obtained as below

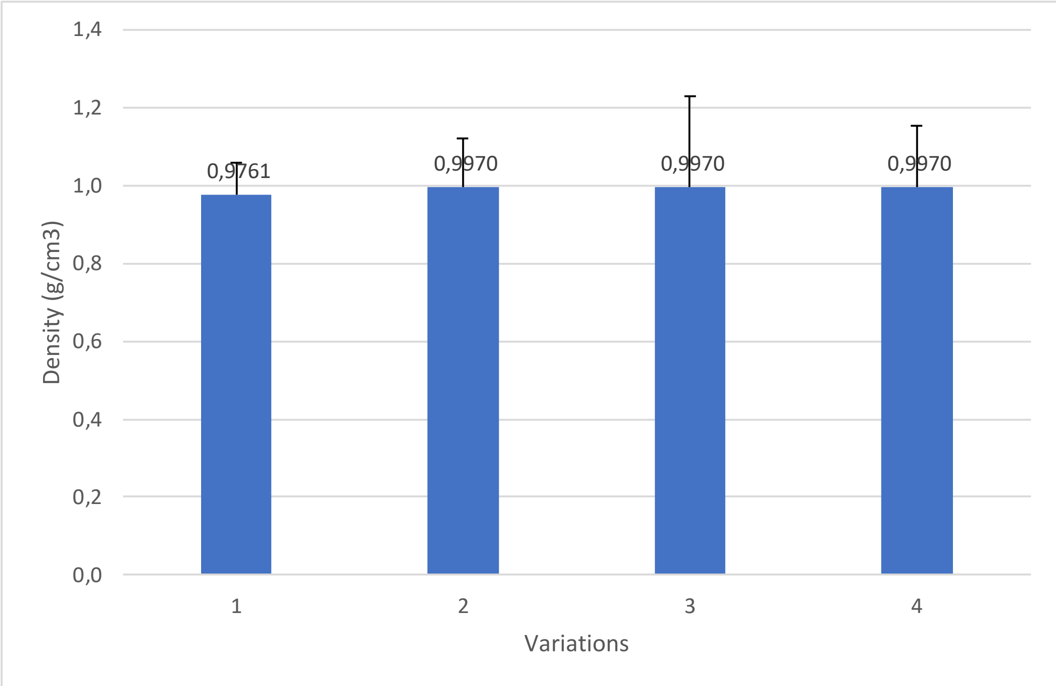

Figure 5. Density results on various composite variations

The density of rice husk is smaller than the density of PP so the same volume of material is obtained. Figure 6 shows that the addition of MA into the PP/rice husk composite increases the density of the composite. This is not by the literature because the distribution of filler and disperse in the test sample at the time of mixing PP with rice husk is not perfect, causing the rice husk to not fill the cavity in the composite so that the density becomes higher (Aryanti & Maghfira, 2022). The average density obtained for all MA additions is 0.9970 g/cm3.

4. Conclusion

Polypropylene composites with rice husk filler and coupling agent using maleic anhydride have been made and tested for mechanical properties and thermal properties. The addition of maleic anhydride for mechanical properties and thermal properties on polypropylene/rice husk/maleic anhydride composites generally increased, the highest peak tensile strength value was in the composition of the addition of maleic anhydride 3% is 10.081 MPa, and also the highest crystallinity value occurred in the composition of maleic amhydride 3% is 27.39%. The average density obtained for all MA additions is 0.9970 g/cm3.

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