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Research Article

Tensile Strength and Thermal Properties of Polypropylene/Nano-Bentonite Composites with Maleic Anhydride Coupling Agent

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ABTRACT

Polypropylene is the most widely used polymer material in the automotive industry due to its properties such as good rigidity, high melting point, chemical resistance, and easy processability. Polypropylene is usually added with a filler, namely bentonite, to make polypropylene which has better mechanical and thermal properties. The coupling agent is added to improve the adhesion of the matrix with the surface so that the composite component has better durability. To improve the ability of the filler material, bentonite is converted into nanoparticles. Bentonite nanoparticles are expected to have better mechanical, thermal, electrical, and optical properties than particles with micro or macro sizes due to their large surface area. Based on the description above, it is necessary to study the effect of using bentonite nanoparticles with a coupling agent in the form of Maleic Anhydride-g-PP (MAPP) on the tensile strength and thermal properties of polypropylene composites. The variables of this study are the composition variation (weight %) of polypropylene, coupling agent (MAPP), and bentonite nanoparticles of 100:0:0, 95:0:5, 90:5:5, 85:5:10, 92:3:5, and 87:3:10. The method used in this study uses a twin-screw extruder tool with a temperature of 190°C and then tested regarding its tensile strength and thermal properties. The results showed that the addition of nano-bentonite tends to cause an increase in the decomposition temperature of the sample but does not increase the tensile strength of the composite, so it only functions as a polymer composite filler. While based on Differential Scanning Calorimetry (DSC) testing, the enthalpy value decreases with increasing concentration of coupling agent.

INTRODUCTION

Polypropylene is the most widely used polymer material in the automotive industry due to its properties such as good rigidity, anti-corrosion, chemical resistance, and easy processability (Karian, 2003). However, the hardness level of polypropylene is insufficient for use as an engineering plastic. To improve this property, polypropylene is added with fillers and binders to form better composite materials(Ao et al., 2007). Polypropylene polymer-based composites are widely processed using extruders. Some products that use polypropylene materials include food containers, drink containers, toys, household appliances, and automotive products (Aryanti & Pasya, 2021). Talc, mica, chalk, and bentonite are fillers that can be added to polymer compounds. Polypropylene is usually added with a filler, namely bentonite, to make polypropylene a polymer material that has better mechanical and thermal properties(Astutiningsih et al., 2010).

To make a composite material, the matrix is filled with reinforcing materials to have properties superior to those of a single material. Binders are added to improve the quality of composite products, aiming to increase the adhesion of the matrix with its surface so that the composite composition becomes stronger(Wang et al., 2003). To improve the ability of the filler material, bentonite was converted into nanoparticles. Bentonite nanoparticles are expected to have better mechanical, thermal, electrical, and optical properties than particles with micro or macro sizes due to their large surface area.

The research of (Julinawati et al., 2020) tested the morphology and thermal properties of polypropylene nanocomposites using (Montmorillonite) MMT from Bener Meriah Aceh and polypropylene-graft-maleic anhydride (PP-g-Ma) as a coupling agent. The variation used was the weight % ratio of PP, PP-g-Ma, and MMT using a Haake Rheomix 3000 mixer with an operating temperature of 180°C and a rotation speed of 65 rpm. From the study, it was found that the thermal stability increased in the variation of PP/PP-g-Ma/MMT nanocomposite of 85/10/5.

Another study investigated the effect of adding Montmorillonite to make polypropylene nanocomposites on tensile strength and hardness, from which it was found that the optimum tensile strength was obtained at a Montmorillonite composition of 2.4% and the optimum hardness was obtained when the Montmorillonite composition was 3.6% (Barleany Dhena Ria et al., 2011).

Based on research that has been carried out combining polypropylene, MAPP, and bentonite using a Haake Rheomix mixer and from other studies the addition of nanoparticle size of bentonite can increase tensile strength so that in this study several variations were tried using polypropylene, bentonite nanoparticles, and coupling agent in the form of Maleic Anhydride-g- PP (MAPP) using a twin-screw extruder with an operating temperature of 190 ° C and a rotation speed of 100 rpm and tested for tensile strength and thermal properties. The use of a twin-screw extruder and the addition of bentonite nanoparticles is expected to increase the tensile strength and thermal stability of the nanocomposite.

METHOD

Research Procedure

The equipment used in this study are Teach-line Collin Compounder ZK 25×24 D twin-screw extruder, analytical balance, scissors, watch glass, beaker, tweezers, Cometech Manual Forming Machine (MFM) model QC 601-A, Pneumatic Specimen Punch, Universal Testing Machine (UTM), Thermogravimetric Analysis (TGA) TGA55 TA Instrument, Differential Scanning Calorimetry (DSC) type Netzsch 214 Polyma Instrument, and Thermoscientific Mini Injection Molding.

The materials used are Polypropylene (copolymer) from PT Chandra Asri Petrochemical, Maleic Anhydride-g-polypropylene (MAPP) (pellet form), and Nano-Bentonite from Sigma-Aldrich. Polypropylene, MAPP, and bentonite nanoparticles were weighed as much as 6 variations with the weight of each material according to Table 1. After that, all materials were mixed manually before being processed with an extruder machine. The polypropylene nanocomposite pelletizing process used a Teach- line Collin Compounder ZK 25×24 D extruder machine. The heating temperature was set at 190°C, approximately 30°C above the melting temperature of polypropylene. The screw rotation rate, temperature at all zones, and pelletizer rotation rate speed were checked at all times. The resulting nanocomposites were then tested for tensile strength and thermal properties.

Table 1. Research Variations

PP:MAPP:Nano-Bentonite (%weight)	Component			Total
	PP	MAPP	Nano-Bentonite	
100 : 0 : 0	200	-	-	200
95 : 0 : 5	190	-	10	200
90 : 5 : 5	180	10	10	200
85 : 5 : 10	170	10	20	200
92 : 3: 5	184	6	10	200
87 : 3 : 10	174	6	20	200

Tensile strength testing using Ibertest 5kN Universal Testing Machine (UTM) ASTM D882 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 Thermogravimetric Analysis (TGA) brand TA Instrument type TGA55. Samples were tested according to ASTM E 1131-08 standard with 10-30 mg mass samples placed on a pan and then heated to a temperature range of about 50-500ºC. The nitrogen gas rate was set at 50 ml/min. The test ended when the sample was decomposed and obtained thermograms and data on mass and temperature changes.

Another test of thermal properties is using a Differential Scanning Calorimetry (DSC) tool type 214 Polyma at the Polymer Chemical Engineering Instrumentation Laboratory of STMI Polytechnic Jakarta. The sample used was ±6 mg put into a crucible container 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 heating was carried out to a temperature of 220 ° C with a heating rate of 10 ° C / min for the second heating.

RESULT AND DISCUSSION

Acquisition of Compound Result

Based on Table 2, it can be seen that the composition of PP: MAPP: nano bentonite = 95:0:5 has the lowest yield. This is due to the extrudate coming out of the die that clumps so much that it does not enter the pelletizer.

Table 2. Acquisition of Compound Result

PP:MAPP:Nano-Bentonite (%weight)	initial mass (g)	product(g)	Persentage of Compound Result
95 : 0 : 5	250	175.25	70.10

90 : 5 : 5	250	176.15	70.46
85 : 5 : 10	250	198.56	79.42
92 : 3 : 5	250	184.33	73.73
87 : 3 : 10	250	225.50	90.2

Tensile Strength of Nanocomposite

In the tensile strength test carried out for each variation, there are five samples tested for tensile strength, the data presented below is the average value of the five samples that have been tested. The results of the polypropylene/nano-bentonite tensile strength test can be seen in Fig. 1 and Table 3.

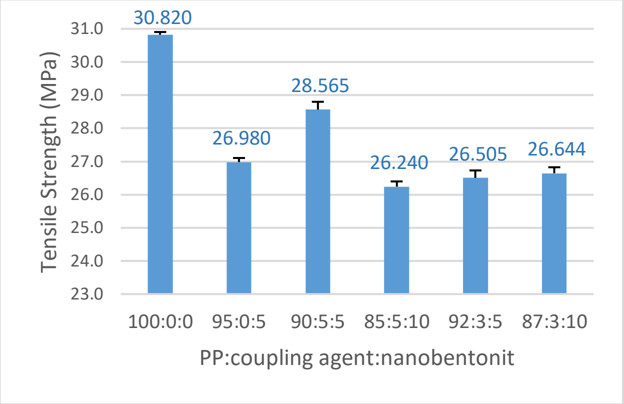

Fig. 1. Tensile strength graph

Table 3. Tensile strength test results

PP : *coupling agent* : bahan pengisi (%weight)	**Tensile Strength (MPa)**	**Modulus of Elasticity (MPa)**
100 : 0 : 0	30.82	3,833.25
95 : 0 : 5	26.98	4,255.77
90 : 5 : 5	28.57	4,222.36
85 : 5 : 10	26.24	4,145.70
92 : 3 : 5	26.51	4,122.28
87 : 3 : 10	26.64	4,148.98

In Fig. 1, it can be seen that the PP/nano-bentonite composite obtained the largest tensile strength of 30.82 MPa at a matrix: coupling agent: filler composition of 100:0:0. This shows that nano-bentonite has not been able to increase the tensile strength of the composite, so it may only function as a polymer composite filler. The addition of a coupling agent is less effective in increasing the tensile strength of the composite. This is due to the possibility that the performance of maleic anhydride can be further enhanced by the addition of an initiator that triggers the formation of free radicals. The reaction that occurs is when the alkene group on maleic anhydride which has non-polar properties binds to polypropylene and the polar anhydride group binds to the filler. Polypropylene that binds to maleic anhydride causes a decrease in the tensile strength value of polypropylene because polypropylene which has a linear polymer chain becomes branched when it binds to maleic anhydride so that the tensile strength of the composite decreases. The elastic modulus in Table 3 is a number that indicates the resistance of the material to elastic deformation when force is applied to the sample. If the elastic modulus value is higher, the tensile strength will be lower, because the more elastic a material is, the lower its tensile strength will be.

Thermal Properties of Composites Using DSC

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. Fig. 2- Fig. 6 shows the results of testing the composite using DSC.

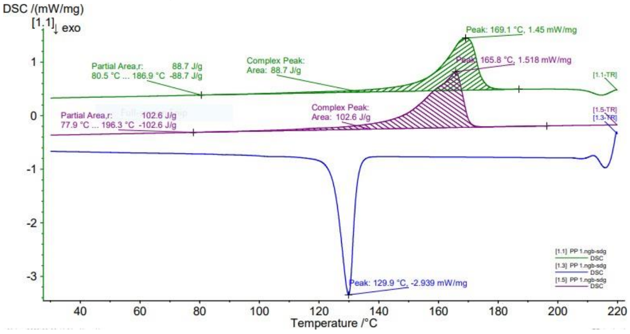

Fig. 2. DSC result of PP : MAPP : *nano-bentonite* = 100 : 0 : 0

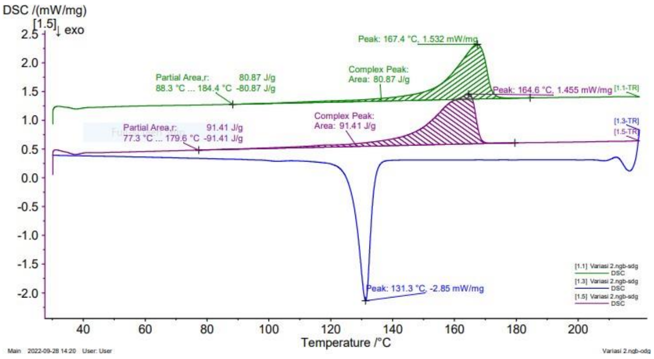

Fig. 3.DSC result PP : MAPP : *nano-bentonite* = 95 : 0 : 5

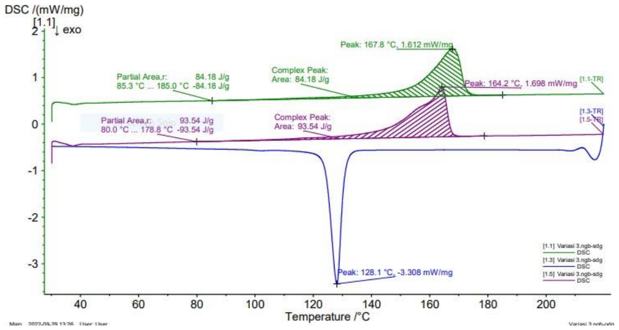

Fig. 4.DSC result PP : MAPP : *nano-bentonite* = 90 : 5 : 5

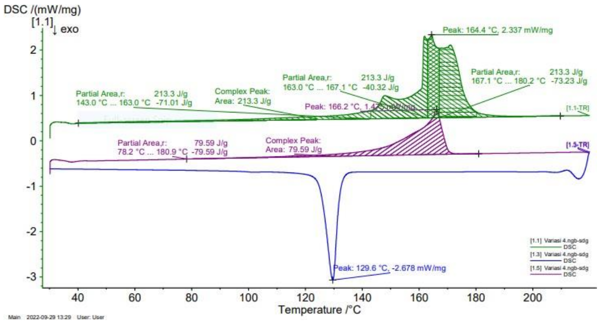

Fig. 5. DSC result PP : MAPP : *nano-bentonite* = 85 : 5 : 10

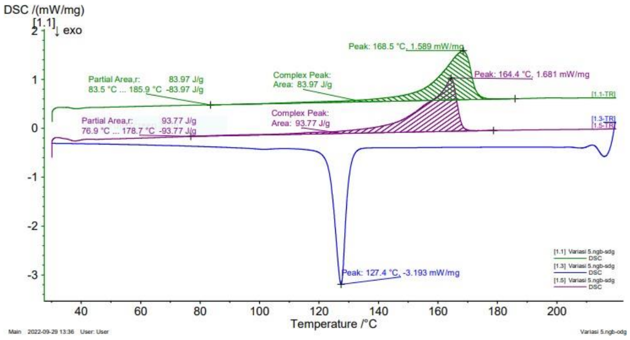

Fig. 6. DSC result PP : MAPP : *nano-bentonite* = 92 : 3 : 5

Composite Testing Results Using DSC

Table 4. Composite Testing Results Using DSC

PP: MAPP:Nano-Bentonite (%weight)	Crystallization Temp. (°C)	Melt. Temp. (°C)	Enthalpy of melting (J/g)	degree of crystalinity (%)
100 : 0 : 0	129.9	165.8	102.6	50.04
95 : 0 : 5	131.3	164.6	91.41	44.58
90 : 5 : 5	128.1	164.2	93.54	45.62
85 : 5 : 10	129.6	166.2	79.59	38.82
92 : 3 : 5	127.4	164.4	93.77	45.78
87 : 3 : 10	131.2	164.3	92.26	45.00

Based on Table 4 of the test results with DSC, calculations can be made to determine the % degree of crystallinity using the formula: (Soy et al., 2017).

$$\mathrm{Xc}(\%) = \frac{\Delta \mathrm{Hm}}{\mathrm{W_{polymer}} \times \Delta \mathrm{H°m}} \times 100\% \qquad (1)$$

Where ΔHm is the enthalpy of melting (Joule/gram), ΔH°m is the enthalpy of melting 100% crystalline PP (207.1 Joule/gram), and Wpolymer is the weight ratio of the polymer. The table shows that the addition of coupling agents to polypropylene/nano bentonite composites tends to decrease the degree of crystallization. In general, the amount of enthalpy decreases with increasing concentration of the coupling agent. The reduction in enthalpy is due to the higher amount of coupling agent, causing the polymer to become elastic. The addition of a coupling agent (MAPP) has the purpose of increasing the adhesion between the matrix and nano bentonite, MAPP is a binder formed from the modification of polypropylene and maleic anhydrous by grafting process (Karian, 2003), maleic anhydride (MA) has a melting point of 50 °C so that with the addition of MA, the polypropylene matrix is reduced causing the enthalpy of melting to be greater. A positive enthalpy change (ΔHm) indicates that in the change there is heat absorption or heat release. Chemical reactions that release or emit heat are called exotherm reactions, while chemical reactions that absorb heat are called endotherm reactions. The exotherm peak indicates the decomposition process of the matrix and filler. When viewed between Table 3 and Table 4, a general conclusion can be drawn that increasing the tensile strength of a polymer will also affect the increase in the degree of crystallinity of the polymer.

Thermal Properties of Composites Using TGA

TGA testing is used to determine the decomposition temperature and percentage of polypropylene/nano-bentonite composite residue. The TGA test results are shown in Table 5.

Table 5. TGA Testing Results

PP: MAPP:Nano-Bentonite (%weight)	Crystallization Temp. (°C)	Melt. Temp. (°C)	Enthalpy of melting (J/g)	degree of crystalinity (%)
100 : 0 : 0	129.9	165.8	102.6	50.04
95 : 0 : 5	131.3	164.6	91.41	44.58
90 : 5 : 5	128.1	164.2	93.54	45.62
85 : 5 : 10	129.6	166.2	79.59	38.82
92 : 3 : 5	127.4	164.4	93.77	45.78
87 : 3 : 10	131.2	164.3	92.26	45.00

PP: MAPP:Nano-Bentonite (%weight)	T onset (°C)	T end (°C)	Initial mass (mg)	Product (mg)	% Residue
100 : 0 : 0	282.83	374.04	16.969	0.046	0.271
95 : 0 : 5	404.11	445.29	15.853	0.615	3.879
90 : 5 : 5	420.06	453.22	16.005	0.583	3.643
85 : 5 : 10	412.09	443.80	11.271	1.085	9.626
92 : 3 : 5	414.59	450.97	15.513	0.424	2.733
87 : 3 : 10	406.42	436.14	11.236	1.138	10.128

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Table 5 shows the difference in maximum decomposition temperatures for each sample. It can be observed that there has been a tendency to increase the decomposition temperature of polypropylene samples with the addition of nano-bentonite. The decomposition temperature of a matrix: coupling agent: filler 90:5:5 produces a higher thermal stability value compared to other variations, namely 450.04°C.

The use of nano-bentonite can also increase the decomposition temperature. The decomposition temperature of the matrix: coupling agent: 90:5:5 filler material produces a higher thermal stability value than the other variations, namely 453.22 ° C. Research by (Arunachalam et al., 2015) produced polypropylene nanocomposites with fillers of four types of nanoclay as much as 5% and 10% in the form of natural montmorillonite, organically modified montmorillonite, and two other types of clay minerals. Testing with TGA produced Tmax in the range of 412-450°C which is higher than pure polypropylene which is only 405°C.

Research by Ma et al., 2001 also showed a significant increase in the thermal stability of nanocomposites characterized by an increase in the maximum decomposition temperature by 44°C (from 416°C to 460°C) of pure polypropylene with the addition of about 10% by weight of clay with a size in the nanometer scale of montmorillonite type. Increasing the percentage of montmorillonite from 2.5% to 10.4% was followed by an increase in the decomposition temperature of the nanocomposite. The greater percent residue shows a value that is almost the same as the size of the addition of nano-bentonite, this is because nano-bentonite has a high melting point (650 °C) so the greater the nano-bentonite, the greater the residue that remains.

CONCLUSION

The addition of nano-bentonite has not been able to increase the tensile strength of the composite, so it only functions as a filler in the resulting composite. The greatest tensile strength was obtained in the composition of polypropylene/maleic anhydride/nano-bentonite 100: 0: 0 which amounted to 30.82 MPa. This result occurs because in this variation polypropylene only undergoes one stage of processing (processing with a hot press) while for other variations it undergoes two stages of processing (extrusion with a twin-screw extruder and also a hot press). The use of a coupling agent in the resulting composite is less effective in increasing the tensile strength of the composite. This is due to the possibility that free radicals have not been formed in maleic anhydride. The performance of maleic anhydride can be further improved by the addition of initiators that trigger the formation of free radicals.

The enthalpy value decreases with increasing concentration of the coupling agent. The reduction in enthalpy is due to the higher amount of coupling agent, causing the polymer to become elastic. The addition of nano-bentonite tends to cause an increase in sample decomposition temperature. The largest temperature change was obtained in the composition of polypropylene/maleic anhydride/nano-bentonite 95/0/5.

Author Contribution: All authors contributed equally to the main contributor to this paper. All authors read and approved the final paper.

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Conflicts of Interest: “The authors declare no conflict of interest.”

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NOMENCLATUR

DSC	Differential Scanning Calorimeter
MAPP	Maleat Anhydride Polypropylene
PP	Polypropylene
TGA	Thermal Gravimetry Analysis
Tc	Crystallization Temperature
Tm	Melting Temperature
Xc	Degree of Crystallization
ΔHm	Enthalpy of melting
J/g	Joule/gram

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