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THE INFLUENCE OF NANO FILLER ON THE THERMAL AND MECHANICAL PROPERTIES OF POLYPROPYLENE

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ABSTRACT

In order to obtain specific properties in the commercial and engineering applications, PP materials are often combined with additives. Filler is one of solid additive type that made of inorganic materials and is generally distinguished by its influence on the mechanical properties of the resulting mixture with the plastic matrix. Filler dimension less than 100 nm is often categorized as a nano filler and added to plastics with the range of percentage from 1% up to 10%. Various studies have been conducted to know the influence of filler on mechanical properties, but this study is also conducted to investigate the effect of nanofillers on thermal properties of PP material. Thermal properties are very important to know from the stage of design, processing until the end use final product. Most plastic products are made in soft or liquid condition, the melting temperature (melting temperature, Tm) becomes the basis of the processing parameter adjustment. Investigations done by comparing the thermal properties of commercial copolymer PP material (virgin material and injection molding specimen) and PP materials containing nano filler (virgin material and injection molding specimen) by using Differential Scanning Calorimetry (DSC), while data of mechanical properties was obtained by the tensile test. Both 1^{st} heating and 2^{nd} heating DSC Experiment showed that nano filled PP need the highest endhothermic effect (2.63 W/g and 1.79 W/g), but nano filler gave no effect on melting temperature to all type of specimens (in the range of 164.3 – 166.3 °C). The elastic modulus of nano filled PP was around 1486 Mpa, higher than non filled PP (999 Mpa).

Keywords: DSC, mechanical properties, nanofiller, Polypropylene, thermal properties.

1. INTRODUCTION

Recently, nano filled polymer has been used increasingly because their capability to improve mechanical and thermal properties over the unfilled plastic. Various fillers have been used to design the desired properties in the polymer matrix. It has been found that the addition of a few percent by weight of these nanoparticles can result in significant improvement in physical and chemical properties (S. Karamipour et.al,. 2011). It has also been investigated that the addition of CaCO3 nanoparticles could improve the thermal and mechanical properties of polypropylene (PP) (Z. Zhang, C et.al,. 2012). An increase of nanofiller content in the composite results in higher tensile strenght, higher thermal degradation temperatures, higher hydrophilicity, and higher thermal conductivity (Elif Bahar et.al., 2011).

The objective of this research was to investigate the properties different of unfilled Polypropylene and nano filled Polypropylene (commercial product), focusing on thermal and mechanical properties. The dumbell specimens were made by injection molding machine, variation on temperature, pressure and injection speed were applied to the specimen which affected those two properties. The possibility of filler orientation caused by injection process were ignored in this research.

2. METHODOLOGY/ EXPERIMENTAL

2.1. Material

Two type of PP material are investigated. The first type is commercial PP product namely BormodTM BF970MO produced by Borealis. BormodTM BF970MO is heterophasic copolymer (block copolymer) which has optimum combination of high stiffness and impact strenght. The application field of this material is in the area where a thickness reduction needed, for example: bottle crate, boxes, houseware and any other engineering tools.

The second type of material is a non commercial PP that containing Bormod BF970MO, 5.5 % Nanofill 948 and 2.6 % Scona TPPP compatibilizer made by Kometra. Nanofill 948 has suitability intercalation with organics and it is possible to achieve a very fine and homogeneous dispersion in polymer systems. The very low particle size of Nanofill 948 (diameter: 100 – 500 nm, at layer thickness 1 nm) and the high aspect ratio (more than 100) yield an improvement of the polymer. Normally the recommended polymer to be combined with Nanofill 948 is Grafted Polypropylene, but in this case a block copolymer PP was used.

2.2. Injection Molding Machine

A 70 tons Injection molding machine is used to produce the dumbell specimen which has geometry as follow:

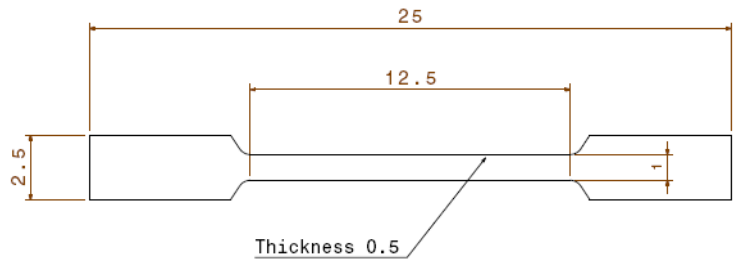

Figure 1. Specimen

The processing parameter are described below:

- Melting temperature : 210 – 260 °C
- Injection speed : 300 mm/s
- Injection pressure : 900 bar
- Holding pressure : 500 bar
- Holding time : 1.1 s
- Cooling time : 3 s
- Cycle time : 7 – 8 s
- *Back pressure* : 20 bar
- Switch over point : 1.3 cm^3
- *Dosing stroke* : 2 cm^3
- Clamping force : 15 KN
- Mold temperature : 30 – 80 °C

Trial on PP Bormod BF970MO were done by using two set of parameter, the main different of both parameter is on the mold tempereture. Firstly, the mold temperature was set at 30 °C, after having few sample, the temperature was changed into 80 °. The same setting parameter were used on both unfilled PP and nanofilled PP (i.e. 2nd setting parameter).

Table 1. Temperature setting

Suhu [°C] Trial Ke	Hopper	Zona 1	Zona 2	Zona 3	Zona 4	Suhu Mold
1	45	200	210	215	215	30
2	45	200	210	215	215	80
3	45	200	210	215	215	80

2.3. Differential Scanning Calorimetry (DSC)

DSC is a measuring device that used to measure the energy required to produce near-zero temperature difference between a substance / sample with an inert reference material. This method provides qualitative and quantitative information of endothermic or exothermic

processes or changes in heat capacity using minimal sample quantities. Samples and reference will be heated and then cooled, both temperature difference or energy required to reach equilibrium was observed and monitored.
By using DSC the following information can be obtained: Temperature Glass Transitions, melting temperature, crystallization temperature and time, the percentage of crystals, specific heat, heat capacity, thermal stability, etc.
The measuring method consist of 4 segments. A 5 mg sample was put into 40 µ crucible, the measurement were performed in nitrogen atmosphere. The setting parameters are described below:

- Initial temperature: 30°C
- Final temperature : 30 °C
- Time Interval : 1 s
- Temperature adjusment: automatic
- 1st Segment :
  Temperature : 30 °C
  Duration : 2 minutes
  Gas: N2, 60 ml/min
- 2nd Segment :
  Initial temperature: 30 °C
  Final temperature : 230 °C
  Heating rate : 20 °C/min
  Gas : N2, 60 ml/min
- 3rd Segment :
  Temperature : 230°C
  Duration : 2 min
  Gas : N2, 60 ml/min
- 4th Segment :
  Initial temperature: 230 °C
  Final temperature : 30 °C
  Heating rate : -20 °C/min
  Gas : N2, 60 ml/min

2.3. Universal Testing Machine (UTM)

This instrument is used to obtain mechanical properties data of the samples, namely: E-modulus, stress and strain limit, and strain at break. According to ASTM D 638, 10 times test were performed for each sample.

3. RESULTS AND DISCUSSION

3.1. Thermal Properties

DSC first heating method (1st heating) was done by melting both sample of PP Bormod BF970MO and PP with nanofiller which taken from a small part of dumbbell specimen and granulat raw material. Melting is an endothermic process requiring heat absorption.
The results show that the dumbell specimen had a double peak curve, while the curve of granulat plastic has only one peak. Double peaks curve is an indication of the thermal history of the dumbell specimen because it has undergone the heating process (injection

molding process). The peak curve of nanofilled specimens and unfilled specimens are higher than the peak curve of granulat PP, it may indicate that the with a thermal history requires a higher endothermic effect. The molded specimen at mold tempereture 80 ° C has the lowest melting temperature compared to other samples, whereas Bormod PP plastic pellets have the highest temperatures. But in general, it can be stated that in this case nanofiller does not give effect to the melting point of the material.

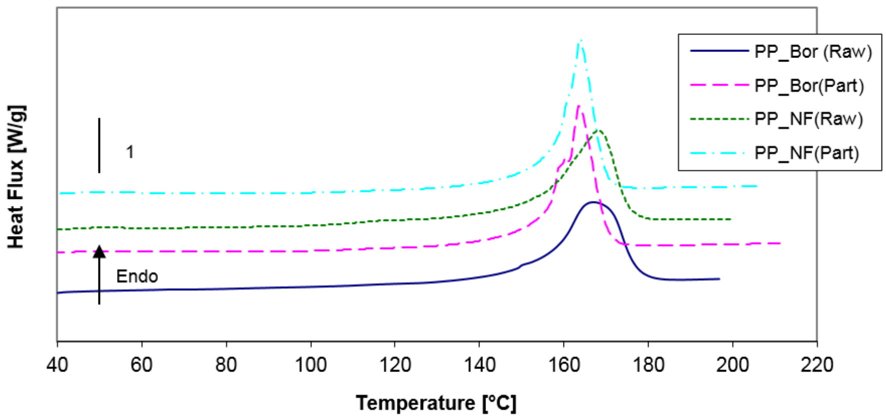

Figure 2. Measurement result from 1st heating

Where:

——— Granulat Unfilled PP (a)

– – – Dumbell Speciment unfilled PP (b)

········ Granulat nanofilled PP (c)

– · – · Dumbell Speciment nanofilled PP (d)

Table 2. DSC *1st heating results*

Hasil	**Sampel**			
	a	b	c	d
Onset [°C]	154,89	158,27	155,29	157,86
Peak height [W/g]	1,41	2,5	1,585	2,68
Extrapol. peak [°C]	168,54	163,79	169,42	164,08
Melting point [°C]	167,33	163,46	168,665	163,74
Endset [°C]	177,35	170,34	175,715	169,78
Peak Width [°C]	14,83	9,03	12,59	6,95

From the curve and table above it can be seen some temperature characteristics. Onset (beginning of melting) is a temperature at the top and intersection with a baseline. In order to determine the melting point, a line extrapolation of baseline with peaks temperature offending curve should be done.

To obtain a complete result interpretation, the experiment to was continued by a process called 1st cooling. As PP is in the group of semicrystalline materials, it will reach the crystallisation point characterized by a curve toward the exothermic process in which heat released.

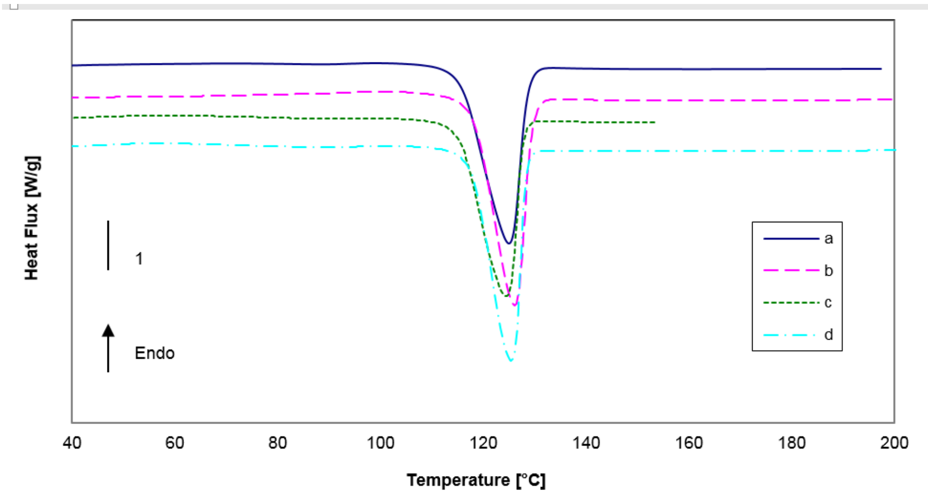

Figure 3. 1st cooling curve

Di mana:

a) Unfilled granulat PP Bormod
b) Unfilled dumbell speciment PP Bormod
c) Nanofilled granulat PP
d) Nanofilled dumbell speciment PP

All of the curve have identical shape, so it can be stated that the crystal in all samples are evenly distributed. However, the peak of molded specimen is slightly higher, this means that it has a larger crystal size. Crystallization point in all samples approaching the same value in the range of 123-126 °C.

Table 3. DSC results of the *1st cooling*

Results	**Sample**			
	a	b	c	d
Onset [°C]	128,82	129,69	127,59	128,45
Peak height [W/g]	3,5	4,12	3,5	4,19
Extrapol. Peak [°C]	125,10	126,22	123,745	125,52
Crystallization point [°C]	124	126,05	123,665	125,4
Endset [°C]	115,40	118,00	174,345	117,76
Peak width [°C]	7,72	6,66	15,185	6,38

Next step is second heating process (2nd heating). The 2nd heating process is used to evaluate inherent properties of the material, because of the possibility of such material to have a thermal history from the previous process. So, by doing 1st heating all thermal history is removed and then the 2nd heating can produce better thermal response.

In the 2nd heating curve, the double peak is no longer visible, the height of both nanofilled PP higher than the unfilled PP. This condition is different from the 1st heating curve. Nano filler give effect on the endothermic reaction of melting samples.

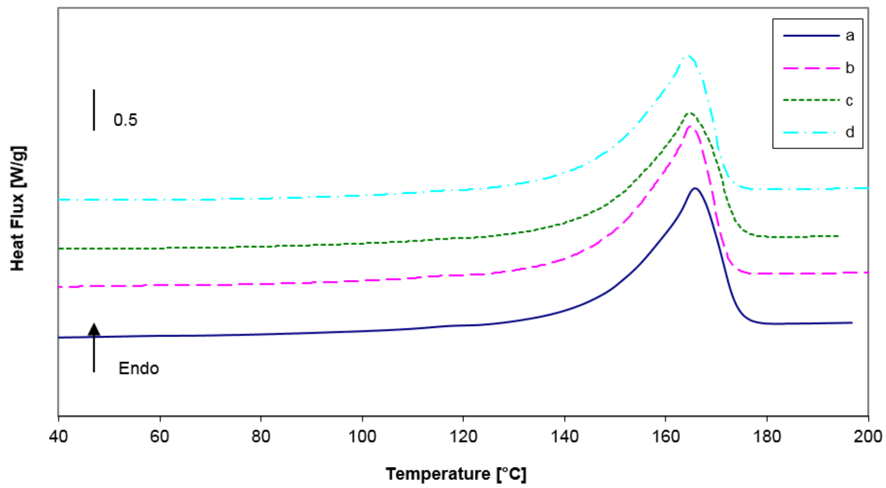

Figure 4. *2nd heating curve*

Where:


Unfilled PP Bormod
Dumbell speciment PP Bormod
Nanofilled granulat PP
Nanofilled dumbell speciment PP

Table 4. DSC result from *2nd heating*

Results	Sample			
	a	b	c	d
Onset [°C]	152,04	150,88	150,8	148,88
Peak height [W/g]	1,64	1,79	1,475	1,63
Extrapol. Peak [°C]	166,78	165,92	167,13	165,80
Melting point [°C]	166,33	164,95	165,33	164,32
Endset [°C]	174,41	172,35	174,345	172,16
Peak width [°C]	14,75	13,92	15,185	14,73

3.1. Mechanical Properties

Following are the results of tensile test using UTM. The mechanical properties taken from the test are E - modulus, elongation limit, elongation and strain at break.

Table 5. Tensile test results of PP Bormod BF970MO (mold temperature: 30°C)

Test Nr	E-Modulus (N/mm2)	Yield strenght (N/mm2)	Elongation at yield (%)	Elongation at break (%)
1	1012.38	36.76	275.10	282.54
2	716.67	38.49	268.45	275.17
3	1174.12	38.39	268.44	276.55
4	1216.21	37.22	268.44	275.28
5	973.99	38.68	259.51	271.12
6	1064.65	37.21	270.64	289.87
7	1107.92	38.61	279.62	295.40
8	1538.57	38.84	272.89	282.45
9	982.69	38.73	259.52	269.135
10	819.06	37.18	266.30	284.05
Avg	1060.63	38.01	268.90	280.15
Std Dev	226.16	0.811	6.297	8.29

Table 6. Tensile test results of PP Bormod BF970MO (mold temperature 80°C)

Test Nr	E-Modulus (N/mm2)	Yield strenght (N/mm2)	Elongation at yield (%)	Elongation at break (%)
1	847.27	36.59	6.56	296.69
2	967.26	35.77	5.976	309.99
3	1062.33	35.50	5.99	262.16
4	1353.57	35.937	6.50	223.35
5	1149.77	35.36	6.51	215.90
6	1262.33	35.93	6.54	311.32
7	782.84	37.24	6.07	276.15
8	858.09	36.16	6.54	314.13
9	782.93	37.13	6.59	228.44
10	927.70	37.20	6.57	339.52
Avg	999.41	36.27	6.38	277.77
Std Dev	201.16	0.71	0.26	43.62

Table 7. Tensile test results of nanofilled PP (mold temperature 80°C)

Test Nr	E-Modulus (N/mm2)	Yield strenght (N/mm2)	Elongation at yield (%)	Elongation at break (%)
1	2207.85	37.72	4.35	162.35
2	1841.86	36.73	4.74	177.97
3	1675.26	37.96	4.78	159.08
4	1056.54	37.31	5.45	185.28
5	1903.03	37.54	4.77	72.99
6	1738.68	37.95	4.87	198.41

7	1603.67	38.71	4.84	161.48
8	900.70	38.82	4.95	135.66
9	947.87	38.11	5.26	177.76
10	992.23	41.15	5.35	75.57
Avg	1486.77	38.20	4.94	150.65
Std Dev	470.88	1.21	0.33	43.69

The comparison of mechanical properties are clearly described on the following figures:

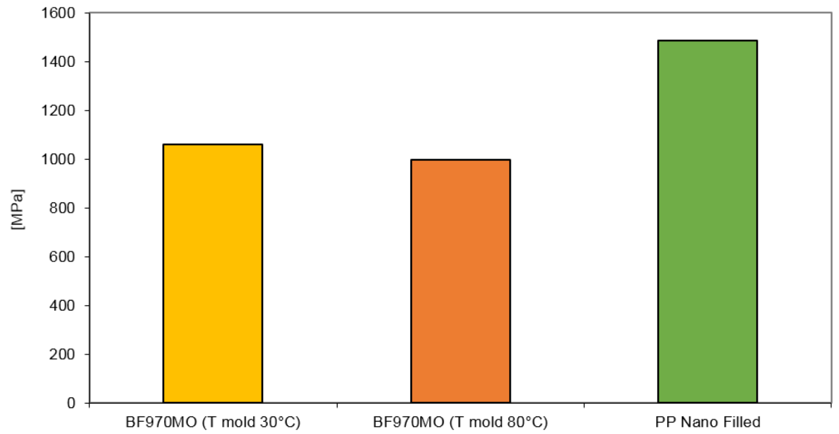

Figure 5. E-modulus comparison

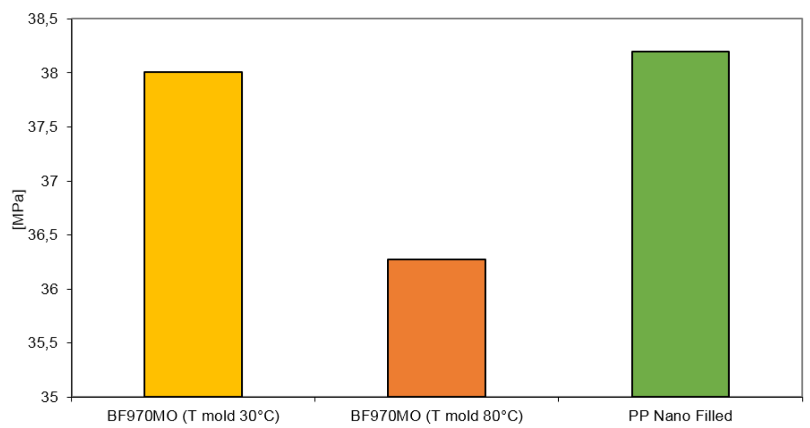

Figure 6. Yield strenght comparison

Where:

- Unfilled Speciment PP Bormod (mold temperature 30° C)
- Unfilled Speciment PP Bormod (mold temperature 80° C)
- Nanofilled Speciment PP (mold temperature 80° C)

To obtain comparable results, parameter adjustment on tensile testing machine is set by using the setting value of PP Bormod BF970MO (mold temperature 80° C). Elongation speed of 1 N / mm2 is used to provide pre tension to the samples.

According to ASTM D 638, 10 experiments were performed for each type of samples. In general there were significant difference of E modulus of PP Bormod BF970MO (mold temperature 80° C) and unfilled PP (487.36 Mpa), while the modulus difference between PP Bormod BF970MO (mold temperature 80° C) and PP Bormod BF970MO (mold temperature 30° C) was only amounted 20.63 MPa. Nanofilled PP had the highest E-modulus (1486 Mpa in average) but showed the lowest value in elongation. Nanofiller interfere the polymer chain movement that decreases the molecular mobility leading to an increase in the composite strength, moreover the nanofiller have ability to carry the load and transfer the stress more than the polymer matrix.

At the time of break, the lowest average strain values is 150.65% shown by the nanofilled PP, while the other two samples showed no significant difference with the average strain in the range of 270-280%.

Interestingly the strain value of PP Bormod BF970MO (mold temperature 30° C) in elastic region is not so much difference to the strain value at break, this situation was not visible on the PP Bormod BF970MO (mold temperature 80° C) and nanofilled PP with nano filler.

4. CONCLUSION

The comparison of thermal and mechanical properties of materials Bormod PP with PP noncommercial BF970MO containing nano filler has been done. From the thermal properties point of view, it can be concluded that:

- Crystal portion in all samples were evenly distributed.
- There were no differences in crystallization point.
- The crystal size was controlled by thermal condition of the sample, the higher temperature made the crystal size larger.
- Nano filler gives the effect of increasing the melting endothermic reaction of the sample.

While from the mechanical propertiesside, it can be concluded that:

- Nano filler increases the value of E - modulus
- Nano filler makes the strain at break value become lower
- Low mold temperature minimized the difference between yield strain and strain at break
- The testing results of the test specimen prepared by micro-injection is strongly influenced by the molecular orientation and process parameter variation

5. ACKNOWLEDGEMENT

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