

## Experimental Study of Composites Material Based on Thermal Analysis

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### ABSTRACT

One of the most significant current discussions in material properties is the chemical treatment effect on the proposed materials. In this paper, the effects of NaOH and  $\alpha$ -APS silane treatments on the characteristics and thermal analysis of Polypropylene (PP) /Recycled Acrylonitrile Butadiene (NBRr) / Banana Skin Powder (BSP) was studied. The heated two roll mill was used to melt, mix the compositors at a temperature of 180°C to produce six different fibre loading (70/30/5, 70/30/10, 70/30/15, 70/30/20, 70/30/25 and 70/30/30w/w). The effects of NaOH and  $\alpha$ -APS silane treatment on PP/NBRr/BSP composites were analyzed by Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). Based on the results, the  $\alpha$ -APS silane treated PP/NBRr/BSP composites has higher improvement on mechanical properties compared to the NaOH treated PP/NBRr/BSP composites, followed by the weakest mechanical properties of untreated PP/NBRr/BSP composites. These were due to good compatibility and stronger interaction between Si-O-Si moieties with the surface of fiber for  $\alpha$ -APS silane treated BSP. Both  $\alpha$ -APS silane and NaOH treated PP/NBRr/BSP composites have the same improvement of thermal properties and better than untreated PP/NBRr/BSP composites. DSC results also showed  $\alpha$ -APS silane treated composite has a higher crystalline portion than untreated PP/NBRr/BSP composites. The results presented here may facilitate improvements in the material properties, especially Polypropylene (PP) /Recycle Acrylonitrile Butadiene Rubber (NBRr) /Banana Skin Powder (Bsp) Composites with NaOH and A-Aps Silane Treatment.

#### Keywords:

Materials, composites, thermal, polypropylene, NaOH, NBRr

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## 1. Introduction

Polyolefins are the major industrial polymers which are based on low-priced petrochemicals or natural gas and the required monomers are created by cracking or refining crude oil [1,2]. Low cost and good in mechanical and thermal properties are two of the reasons that Polypropylene (PP) is widely used [3,4]. Besides, PP also has high crystalline as well because of the rigid polymer

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structure. These advantages can help in forming and toughness and high mechanical and thermal resistance to composite [5-8].

The Recycle Acrylonitrile Butadiene (NBR) can be seen widely used in industries for oil requirement and chemical resistance such as conveyor belting, hydraulic hose, roll covers, oil field packers and seals for all kinds of plumbing and appliance application [9-11]. The Nitrile rubber glove is one of an example product of NBR. It consists of monomer acrylonitrile, butadiene and carboxylic acid that will form a synthetic polymer together. Plastics which modified by using NBR will have higher tensile strength and flexibility. Thus, nitrile rubber gloves should be recycled and its natural fillers can be added to become cheaper and lighter composite materials [12,13]. Natural fiber such as banana fibers has following advantages: low density, inexpensive, harmless to human and environment, large in quantity, cannot deplete when used, high stiffness and strength properties, and finally, it is easily decomposed by living organisms [14][15]. Banana Skin Powder (BSP) had been chosen to be used on Polypropylene (PP) /Recycled Acrylonitrile Butadiene Rubber (NBRr) composite in order to minimize waste production as well.

There are many studies carried out by researchers on polymer composites to improve their mechanical and thermal properties by reinforcing with natural fibers, such as High Density Polyethylene/ Banana Peel Fibers (HDPE/BP) [12], Banana Fiber/ Polyester, Banana Fiber/ Epoxy [16], and Risk Husk Powder filled Polypropylene/ Recycled Acrylonitrile Butadiene Rubber (PP/NBRr/RHP)[9]. However, due to the hydrophobic effect between the hydrophilic fiber and hydrophobic matrices, many studies on chemical modification or treatment had been carried out to remove the hydroxyl groups from lignin and cellulose of natural fiber to improve strength and fitness of fiber as well as adhesion between matrices and fiber in natural fiber composites [17].

In this paper, a novel experiment based on the effect of NaOH and  $\alpha$ -APS silane treatment in the PP/NBRr/BSP composites was studied. The effects of NaOH and  $\alpha$ -APS silane on the thermal and morphological properties were analyzed. The primary goal of this study is to improve the thermal properties of the proposed material. A few measurement such as Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) was calculated to compare with another treatment process. The rest of the paper is organized as follows: Section 2 explains the methodology of the experiment. Section 3 describes the result and discussion based on TGA and DSC and finally, section 4 concludes this work.

## 2. Experimental Study

### 2.1 Materials

PP Grade 6331 with a density of  $0.9\text{g/cm}^3$  and a melt flow index of  $1.4\text{g/min}$  at  $230^\circ\text{C}$  was obtained from Titan Pro Polymers (M) Sdn. Bhd. Johor, Malaysia. Recycled Acrylonitrile Butadiene Rubber (NBRr) powders with 33% acrylonitrile content was processed from the used nitrile gloves obtained from Juara One Resources Sdn. Bhd. Penang, Malaysia. The nitrile gloves were first masticulated by using two roll mills machine. After that, the NBRr were grinded and sieved to an obtained particle size of  $150\mu\text{m}$ . Coupling agent  $\alpha$ -aminopropyltrimethoxysilane (APS) was provided by Alfa Aesar (M) Sdn Bhd, Malaysia and NaOH pellets were bought from AR Alatan Sains (K) Sdn Bhd, Malaysia. Banana skins were collected from a fried banana hawker stall near Dragon institution, Universiti Malaysia Perlis, Malaysia and the banana type used is *Musa paradisiaca* var. Awak or also known as 'Pisang Awak'[18]. The banana skins were first to cut into smaller pieces with a pair of scissors. Then, they were dried at  $80^\circ\text{C}$  for 24 hours in an oven. The dried banana skins were grinded, followed by sieving the banana skin powder to a particle size of  $150\text{-}300\mu\text{m}$ .

## 2.2 Formulations

The formulations of PP/NBRr/BSP components are presented in Table 1. Table 1 indicates that the PP/NBRr/BSP composites with and without 5 w/w of NaOH and 5 w/w of  $\alpha$ -APS silane treatment.

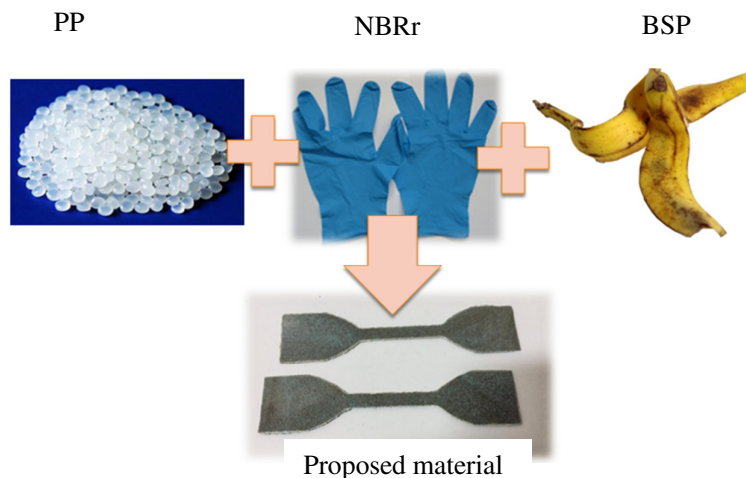
**Table 1**

Formulations of BSP filled PP/NBRr Biocomposite with and without NaOH and  $\alpha$ -APS silane

Material	Amount (w/w)					
PP	70	70	70	70	70	70
NBRr	30	30	30	30	30	30
BSP	5	10	15	20	25	30

## 2.2 Preparation of Composites

Formulations of BSP filled PP/NBRr biocomposites were shown in Table 1. PP granule, NBRr powder, and BSP powder were dried by using a vacuum oven at 80° C for 24 hours before compounding. In order to mix the composite, the heated two roll mills were used with a temperature of 180°C. PP was allowed to melt first for 4 minutes before adding NBRr matrices for another 3 minutes to the mixer. BSP was then added to the mixture for the fabrication of this biocomposite after 7 minutes of mixing. Another 3 minutes were required for the mixing in order to obtain the stabilization torque. The whole mixing process was taken 10 minutes for all samples. 1mm sheet of test samples was created by allowing the composites undergoing a compression-molded process by using Go-Tech compression moulding machine type GT-7014-A30C, manufactured by Go-Tech Testing Machines Inc, Taichung, Taiwan. For producing the test samples, the composites were undergoing preheating for 7 minutes at 180°C, followed by compression at 1000 psi for 3 minutes, and then cooled for another 3 minutes. After moulding, a Wallace die cutter model: S6/1/6.A was used to cut the moulded samples into dumbbell shapes. The proposed material are shows in Figure 1. As shown in the Figure 1, the combination of three waste materials such as PP, NBRr and BSP were used in order to produce the material.



**Fig. 1.** Combination of PP, NBRr and BSP to produce the proposed materials

## 2.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analyses of the composites were conducted with a Perkin-Elmer Pyris 6 TGA analyzer according to ASTM D3171. The samples were weighed around 10-12mg. The samples were scanned under a nitrogen flow of 50 mL/min at a heating rate of 10°C/min from 30°C to 600°C. The sample size was kept nearly the same for all tests.

## 2.3 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) measurements were conducted on 4–5mg samples by using a Perkin-Elmer DSC-7 apparatus according to ASTM D3418. The samples were first heated from 30°C to 220°C by using nitrogen flowing rate of 50mL/min at a heating rate of 10°C/min and held at 220°C for 5 minutes to remove the thermal history. The samples were then cooled from 220°C to 30°C at cooling rate of 10°C/min and then reheated back to 220°C at 10°C/min. The crystalline portion ( $X_{pp}$ ,  $X_{com}$ ) will be calculated using Equation 1:

$$X_{com} = \frac{\Delta H_f}{\Delta H_f^\circ} \times 100\% \quad (1)$$

where  $\Delta H_f^\circ = 209\text{J/g}$  for 100% crystalline PP [19],  $\Delta H_f =$  heat of fusion of sample.

## 3. Results and Discussion

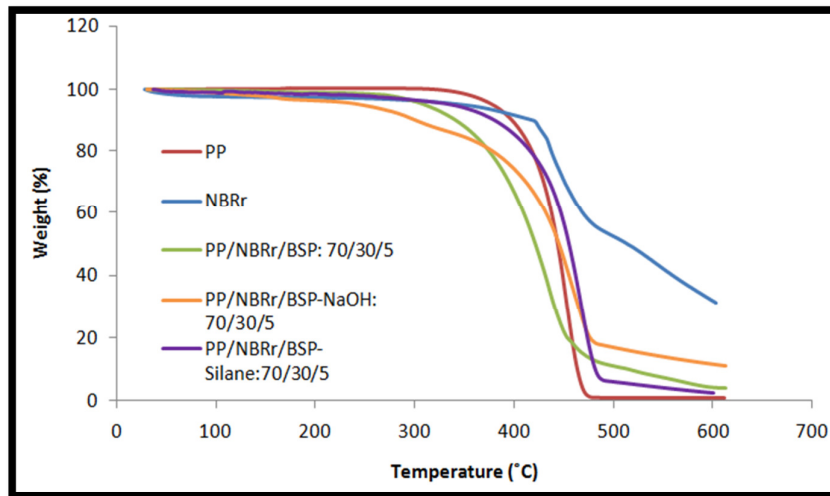
### 3.1 Thermal Analysis

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) had been carried out to determine the thermal stability of materials. The curves of TGA and DTG for pure PP, NBRr, untreated PP/NBRr/BSP composite as well as NaOH treated PP/NBRr/BSP composite and  $\alpha$ -APS silane treated PP/NBRr/BSP composite been plotted and shown in Figure 2 and Figure 3. The onset of degradation, degradation temperature at 70% of materials' weight, residue weight at 600°C and DTG peak degradation temperature had been summarized in Table 2 below.

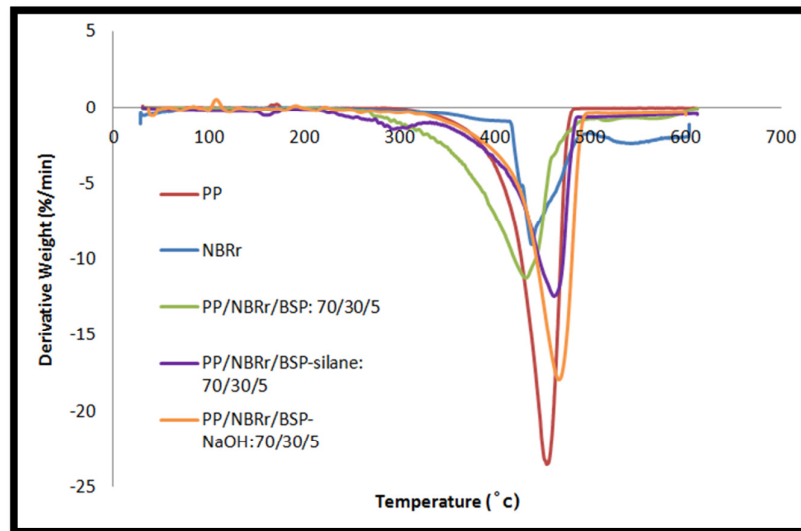
As can be seen in Figure 2, the temperature degradation at 70%, the highest among the five samples was NBRr, 452.1°C, followed by 435.8°C for silane treated composite, 431.2°C for PP, 416.5°C for NaOH treated composite, and untreated composite had the lowest temperature, 395.0°C. The char residue of samples from Figure 2 illustrated that NBRr had the highest percentage of residue which is 56% of its own weight that cannot be further degrade, followed by PP/NBRr/BSP-NaOH composite, 18%, 12% for untreated PP/NBRr/BSP composite, 7% for silane treated PP/NBRr/BSP composite and last but not least, PP which was only 1% left. The NaOH treated composite had higher char percentage than untreated composite because of the better filler-matrix interaction of treated composite result in the formation of char layer.

By comparing the onset temperature in Figure 3 below, the hardest sample to degrade was PP, 335°C, followed by NBRr and silane treated PP/NBRr/BSP composite, both were 220°C, and 215°C for NaOH treated PP/NBRr/BSP and finally the easiest to degrade sample, 200°C for untreated PP/NBRr/BSP composite. This happens because of the presence of banana fiber in the treated and untreated composite decrease the onset temperature of PP or NBRr matrix. PP had greater onset temperature than NBRr because of the structure and isotactic properties of polypropylene which make melting point higher. NaOH and silane treated composites will have higher values due to the enhancement of the interaction between filler and matrix by NaOH and Silane that leads to better dispersion of banana skin fiber particles in the PP/NBRr matrix. Based on Figure 3, NaOH treated

PP/NBRr/BSP composite has the highest peak temperature which was 468.9°C, followed by 462.3°C for silane treated PP/NBRr/BSP, 458.7°C for virgin PP, and 438.2°C for NBRr, and lowest peak temperature, 436.4°C for untreated PP/NBRr/BSP composite. This is because of the reinforcement of composite with NaOH and silane modifications had strengthened and improved thermal resistance of the pure PP and NBRr.



**Fig. 2.** TGA curves of pure PP, pure NBRr as well as untreated, NaOH treated and APS silane treated of PP/NBRr/BSP biocomposites



**Fig. 3.** DTG curves of pure PP, pure NBRr as well as untreated, NaOH treated and APS silane treated of PP/NBRr/BSP biocomposites

**Table 2**

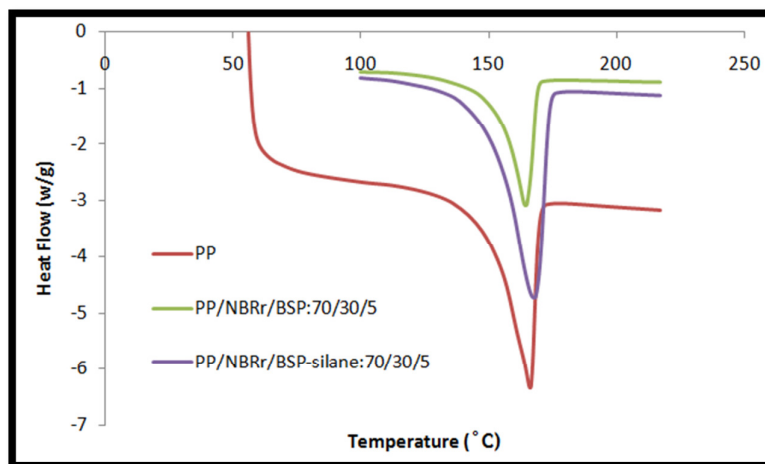
Weight loss and degradation peak for PP, NBRr and their untreated and treated composites

Samples	$T_{\text{onset}}$ (°C)	$T_{\text{degrade}}$ (°C) at 70%	Residual Weight at 600°C (%)	DTG Peak Temperature (°C)
NBRr	220	452.1	56.0	438.2
PP	335	431.2	1.0	458.7
PP/NBRr/BSP : 70/30/5	200	395.0	12.0	436.4
PP/NBRr/BSP-NaOH : 70/30/5-5	215	416.5	18.0	468.9
PP/NBRr/BSP-Silane : 70/30/5-5	220	435.8	7.0	462.3

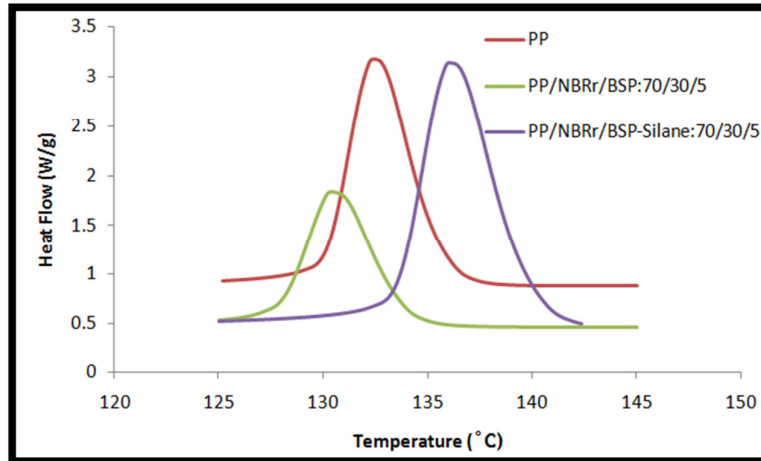
### 3.1 Differential Scanning Calorimetry (DSC)

The melting and crystallization behavior of both silanes treated and untreated PP/NBRr/BSP composites as well as virgin PP was analyzed using Differential scanning calorimetry (DSC) and shown in Figure 4 and Figure 5. The results were tabulated in Table 3 below. According to the Table 3, the highest crystalline temperature and melting temperature was PP/NBRr/BSP composite treated with silane ( $T_c = 136.00^\circ\text{C}$ ,  $T_m = 171.51^\circ\text{C}$ ), followed by pure PP ( $T_c = 132.45^\circ\text{C}$ ,  $T_m = 166.25^\circ\text{C}$ ), and finally, PP/NBRr/BSP composite without any treatment ( $T_c = 130.37^\circ\text{C}$ ,  $T_m = 164.65^\circ\text{C}$ ). This is due to the composite without treatment consists of the hydrophobic effect caused by the existence of fiber which leads to the poor interfacial properties and thus had the lowest melting point and crystalline point. The use of silane treated composite had improved the mixing of the product by becoming coupling agent between fiber and matrices, thus had the highest melting point and crystalline point.

Table 4 shows the crystalline percentage for PP was 27.51%, PP/NBRr/BSP was 18.29%, and PP/NBRr/BSP-silane was 27.83%. Untreated PP/NBRr/BSP composite had the lowest percentage of crystallinity because of the fiber between the polymers block the polymer chain cannot pack together closely to form crystalline. Pure polypropylene without the presence of fiber the polymer chain can pack closely and having a higher degree of crystallinity. As for the silane treated PP/NBRr/BSP composite, it has the highest portion of crystallinity because silane acts as the coupling agent to improve the compatibility between hydrophobic matrices and hydrophilic fibers by forming chemical bonding between them.



**Fig. 4.** DSC of melting temperature of PP, untreated and silane treated PP/NBRr/BSP composites



**Fig. 5.** DSC of crystalline temperature of PP, untreated and silane treated PP/NBRr/BSP composites

**Table 3**

Thermal properties of the temperature of PP, untreated and silane treated PP/NBRr/BSP from DSC

Material	$T_c$ (°C)	$T_m$ (°C)	$\Delta H_{f(M)}$ (J/g)	$\Delta H_{f(C)}$ (J/g)
PP	132.45	166.25	57.51	58.95
PP/NBRr/BSP : 70/30/5	130.37	164.65	38.22	41.13
PP/NBRr/BSP-silane : 70/30/5-5	136.00	171.51	58.16	87.41

**Table 4**

Crystalline portion of samples

Material	Crystalline Portion $X_{com}$ (%)
PP	27.51
PP/NBRr/BSP : 70/30/5	18.29
PP/NBRr/BSP-silane:70/30/5	27.83

#### 4. Conclusion

The present study was designed to determine the effect of comparison between a treatment and untreated BSP. Based on the result evaluation,  $\alpha$ -APS silane treatment have better improvement of mechanical properties than NaOH treatment and both treated PP/NBRr/BSP composites are better than untreated composites. On the other hand, both  $\alpha$ -APS silane and NaOH treated PP/NBRr/BSP composites have the same improvement of thermal properties and better than untreated PP/NBRr/BSP composites. DSC analysis shows  $\alpha$ -APS silane treated composite has higher crystallinity portion than untreated composite might prove  $\alpha$ -APS silane treated composite has better tensile properties as well. Future research should therefore concentrate on the analysis such as water absorption, Scanning Electron Microscope (SEM) and Fourier Transform Infra-Red (FTIR).

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