advances
in Technology

Adv. Technol. **2021**, *1(1), 161-176*

Research Paper

Sustainable Use of Biomass Boiler Ash as a Reinforcement Filler for Polyamide 6 Composite

Maddumage S. Thathsarani,[a] Mahesh J. Dheerasinghe,[b] Suranga M. Rajapaksha,[a] Sisira K. Ranatunga,[c] Shiran Perera,[c] and Chami N. K. Patabendige[b,*]

[a] Department of Materials and Mechanical Technology, Faculty of Technology, University of Sri Jayewardenepura, Pitipana, Homagama 10200, Sri Lanka
[b] Department of Science for Technology, Faculty of Technology, University of Sri Jayewardenepura, Pitipana, Homagama 10200, Sri Lanka
[c] Stellana LK, 51 -54, I.D.B. Industrial Estate, Horana 12400, Sri Lanka

Email correspondence: cpatabendige@sjp.ac.lk (C. N. K. Patabendige)

Received: 30 March 2021; Revised: 27 April 2021; Accepted: 4 May 2021; Published: 31 May 2021

Abstract

The use of biomass combustion ash as a reinforcing filler has taken the attention in recent years to reduce the overall production cost and increase the mechanical properties of plastics. This study evaluates the effect of biomass boilers ash (BBA) as a reinforcing filler on polyamide 6 composites (PA6). The chemical composition and thermal stability of BBA were analyzed by X-ray fluorescence (XRF), Thermogravimetric analysis (TGA), and Differential thermal analysis (DTA) thermographs. Test samples were prepared by varying the ash content (2.5%, 5%, 7.5%, and 10%), and also samples were prepared without adding ash as a control. Moreover, surface modification was carried out by using N-2 (Aminoethyl) 3-aminopropyl triethoxy diamino-silane as a possible coupling agent for BBA and it was tested by varying the coupling agent concentration (0.5%, 1%, and 2%) by dry process and the samples were prepared by extrusion and injection molding processes. Comparative analysis of the degree of crystallinity, mechanical properties including tensile, flexural, and thermal properties were tested. The highest degree of crystallinity was obtained with 7.5% BBA-filled composites. The addition of 2% surface-modified BBA (SBBA) filled composites (PA6 / 10% Ash 2% CA) showed an increase of tensile strength and elongation at break than the 10% unmodified BBA (UBBA) (PA6/ 10% Ash) filled composites. Stress at peak and bending modulus values in the flexural test data were increased up to 10%. But it was significantly reduced with the increasing of modifying agent concentration due to the increment of stiffness of the composite.

Keywords: Biomass boiler ash, composite, silane coupling agent, surface modification

---

https://doi.org/10.31357/ait.v1i1.4884

Introduction

Composite is a material system consisting of two or more mixed materials and bonded together to produce other material with better properties, such as higher tensile strength, rigidity, tiredness, and lower weight [1]. Particulate filled composite the reinforcement is particulate and it has become attractive due to its wide application. The polymer industry has a new interest in the potential recyclability of fillers from industrial by-products and other waste materials. Many publications have reported the possibility of fly ash being emitted from power plants as a reinforcing filler for plastics [2-4]. Powdered material can be used as fillers to maintain material with better mechanical properties and lower the prices. Preparation of polymeric composite is mainly obtained using extrusion and injection technologies.

Polyamides (PAs) are semi-crystalline thermoplastic materials known as nylon. Numerous attempts have been made to use nylon as matrix resins for composites by incorporating inorganic fillers, such as alumina trihydrate, clay, silica, mica, talc, coal fly ash, wollastonite, kaolin, and so on [4]. The filling of polymers with fly ash is one of the newest solutions. It allows for a low-cost filler that improves the material properties and eliminates waste from combustion. For example, wood ash contains lime (CaO), portlandite ($Ca(OH)_2$), Calcite ($CaCO_3$), and calcium silicate (Ca_2SiO_4) as major oxides. Among them, Olawale Monsur Sanusi et al. have described its key ingredient of CaO has improved the hardness and thermal resistance of the polymer matrix composite (PMC) as well as enhancing the bonding between the polymer matrix composite [5-6]. Nevertheless, the majority of highly filled polymer system fillers or reinforcements are incompatible with a polymer matrix due to the poor dispersion of the filler in the matrix. Therefore, the reinforcing materials are required to be modified using surface modifiers on the surface to overcome the problem of incompatibility. The reinforcing material needs modification on the surface to overcome the problem of incompatibility [7]. Surface modifiers are usually added at 1–5wt % relative to the weight of filler and bring about remarkable improvements considering the low amount needed [8].

Coupling agents are defined primarily as materials that improve the practical adhesive bond of polymer to mineral [8-10]. Silane coupling agents are widely used for surface modification of inorganic materials and for enhancing the interfacial adhesion of inorganic particulate-filled polymer composites to solve the problem of dispersion and enhance the properties of composites by enhancing chemical bonding. Gnatowski et al. have prepared a polyamide composite reinforcing fly ash which was collected from the combustion of 80% wood waste and 20% coconut shell using a twin-screw extruder technique. Ashes were silane treated to increase the compatibility and it was added 5%, 10%, and 15% dosages for determining the thermal, rheological, and mechanical properties [3]. Coupling agent treated filler increases filling/matrix interaction, and due to the greater dispersion of the filler particles into the matrix, the melt viscosity can be decreased [4]. Its usual structure, $Y\text{-}(OR)_3$ contains both organic functional and alkoxy groups in a single molecule. Y is an organo-functional group such as amine, methacryloxy, or epoxy, where OR is a hydrolyzable group such as methoxy, ethoxy, or acetoxy. Silane-type coupling agents are commonly used. The silanol group forms from the alkoxy group via hydrolysis and it interacts with polymers and forms a covalent bond with the inorganic surfaces to improve adhesion of the organic polymer and inorganic filler surfaces [11].

Ali et al. have described 3-aminopropyl triethoxysilane (3-APE) aminosilane coupling agent incorporated composite has improved tensile properties [12] and diaminosilane is a special family among the many silanes because, unlike other silanes, they dissolve in water instantaneously, the amino silane-triols are extremely unstable in water but they form clear aqueous solutions at a wide range of concentrations for long periods. They are generally oligomers even at very dilute solutions. N-2 (Aminoethyl) 3-aminopropyl triethoxy silane has a 259 ºC boiling point which can bear under higher temperature without evaporating and the recommended dosage for filler is 0.5 - 4.0 PHR [13].

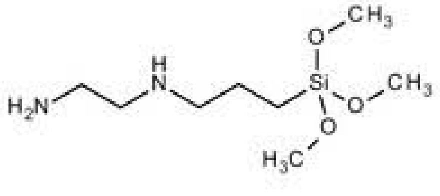

Figure 1. N-2 (Aminoethyl) 3-aminopropyl triethoxy silane [13].

Surface Modification Technologies

Surface modification is an important step for the manufacture of good reinforcing materials. There are two surface modification methods commonly used for fillers, wet and dry. In the dry and wet process, there are versatile surface modifiers used such as surfactant and coupling agents (titanate, silane, zirconates). The dry method is a short process used for large-scale production and its productivity is high. The wet surface treatment method is an effective surface modification method than the dry method [14-15]. In previous studies, various ash residues were used for polyamide 6 composites to enhance properties. Also, some of them have used titanate, silane coupling agents as surface modifiers. This research project was done to examine the effect of adding different dosages of silane treated and untreated biomass boiler ash as a reinforcing filler for polyamide 6 and analyze the thermal and mechanical properties. There are no studies that have done using 100% wood waste that occurred from the bed of the biomass boiler and using N-2 (aminoethyl) 3-aminopropyl triethoxy silane as a coupling agent recently.

Materials and Methods

Materials

Polyamide 6 (injection and extrusion grade, medium viscosity with 42.2 cm^3 /10 min (275 °C/ 5 kg) and density of 1.13 g/cm^3) was used for the study. The biomass boiler ash with different particle sizes was collected from the 3rd door of the biomass boiler bed after the combustion of wood (Elastomeric Co. Ltd, Horana). The ashes were separated using the 40-mesh sieve. The diaminosilane coupling agent, N-2 (aminoethyl) 3-aminopropyl triethoxy silane was used as a coupling agent.

Characterization of Biomass Boiler Ash

Chemical Composition Analysis

The chemical composition of ash was determined by the average value of six different spots per sample by X-ray fluorescence (HORIBA scientific XGT -5200 X-ray analytical microscope) [3].

Thermal Behavior Analysis

The thermal degradation behavior of BBA was studied using the TGA analyzer (TA TGA 5500). The sample of 5 mg was heated at a rate of 10 °C/ min in a nitrogen atmosphere at 200 °C to 1000 °C. The weight loss as a function of the sample temperature was recorded.

Surface Modification of BBA

BBA was dried at 120 °C for 1 hour to eliminate absorbed water on the surface. Then hydrolyzed solution of 0.5 wt.%, 1 wt.%, and 2 wt.% N-2 (aminoethyl) 3-aminopropyl triethoxy silane coupling agent was prepared in 20 % solution concentration dissolved in the water [16]. BBA was transferred into the high-speed blender and then hydrolyzed solution was dripped into it while blending. BBA was blended for 10 min to disperse the solution homogeneously through the ash. Finally, it was dried at 120 °C for 4 h to eliminate water from the ash. Ashes were sifted to separate clumps [17].

Preparation of Composite

A series of BBA-filled composites were prepared to refer to the Table 1 formulations using a single screw extruder with 15 screw length to diameter ratio (L/D) and screw rotation rate of 35 rpm to 60 rpm. The temperature range from barrel to die was 230 °C, 245 °C, 250 °C, and 260 °C [3]. Extruded composites were ground into appropriate sizes by using the plastic grinding mill.

Table 1. Formulation of the prepared composite series

Sample Number	Type of composition	Composition (%)		
		Resin	Filler (BBA)	CA
01	PA6	100.0	0.0	0.0
02	PA6-WA	97.5	2.5	0.0
03	PA6-WA	95.0	5.0	0.0
04	PA6-WA	92.5	7.5	0.0
05	PA6-WA	90.0	10.0	0.0
06	PA6-WA-CA	90.0	10.0	0.5
07	PA6-WA-CA	90.0	10.0	1.0
08	PA6-WA-CA	90.0	10.0	2.0

Moisture Analysis for Composites

The granulated were dried at 120 °C for 4 h in the hot air oven before the preparation of test pieces. The moisture content was analyzed by using PMB 202 moisture analyzer in the Elastomeric Co. Ltd. The samples were dried for 45 min at 130 ºC temperature to detect the moisture content. Moisture content was analyzed for each samples (Table 4) drying and after drying 4 h at 120 ºC in a hot oven.

Thermal Analysis for Composites

The degree of crystallinity and the melting behavior of the samples were characterized using Differential Scanning Calorimetry (DSC BI EVO Srtaram). The instrument has a 700 °C to -170 °C heating and cooling range. Samples of 5 mg to 10 mg were weighed and sealed in an aluminum pan. The DSC curves were recorded during the heating of specimens with the rate of 10 °C/min heating and cooling rate within the range of temperature from 35 °C to 300 °C under nitrogen atmosphere. Samples were first heated from 35 °C to 300 °C and then cooled down to 35 °C under 10 °C/min heating and cooling rate. The melting enthalpy of each sample was obtained from the area under the melting peaks. The degree of crystallinity was determined by Equation 1,

$$Xc = \frac{\Delta Hc + \Delta Hm}{\Delta Hm^{o}} \qquad \text{Equation 1}$$

Xc: Degree of crystallinity; ΔHc: Crystallization enthalpy; ΔH: Melting enthalpy; ΔHm^{o}: Melting enthalpy for 100% crystallinity for the polyamide is 230 J/g [18].

Determination of Mechanical Properties

The uniaxial tensile test was performed in Testometric (M500-50CT) win test analysis at the crosshead speed of 50 mm/min under the standard procedure specified in ASTM D638 [19]. The specimen geometry was in a dumb-bell shape and the dimensions were ascertained using Vernier calipers. The standard specimen was mounted at its ends into the holding grips of the testing machine and a uni-axial load was applied to each end of the respective samples until it fails. Tensile strength and elongation at break were decided by using the stress-strain curves. The procedure was repeated three times for each specimen and the average value was recorded.

The three-point bend test was conducted on all the composite samples according to ASTM D790 [19] using the Testometric (M500-50CT) win test analysis machine at a crosshead speed of 1.8 mm/min and supporting span length of 67.2 mm. The specimen width was 5.8 and the thickness was 4.5 mm. The span length was calculated by multiplying 4.5 mm by 16. This means the ratio between the length and thickness is 16 mm: 1 mm.

Results and Discussion

Determination of Chemical Composition in BBA

The oxides and elemental content of BBA that was deliberated by XRF are tabulated in Tables 2 and 3. Higher amounts of CaO, K_2O, and MgO were recorded with a lower amount of SiO_2, Fe_2O_3, MnO_2, TiO_2, ZnO, SrO, and Cr_2O_3 oxides according to Kalembkiewicz et al. and also Chowdhury et al. Higher Ca and K elements were recorded with a lower amount of Mg, Si, and Fe content. [20-21].

Table 2. XRF oxide analysis of BBA

Oxides	**CaO**	**K_2O**	**MgO**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**
Mass (%)	49.30	16.50	15.95	8.70	4.51	4.00

Oxides	**Cl**	**MnO_2**	**TiO_2**	**ZnO**	**SrO**	**$Cr2O_3$**
Mass (%)	3.43	0.80	0.38	0.18	0.12	0.13

Table 3. XRF elemental analysis of BBA

Element	**Ca**	**K**	**Mg**	**Si**	**Fe**	**Cl**	**Al**
Mass (%)	53.10	19.01	11.65	5.14	4.60	4.45	3.10

Element	**Mn**	**Ti**	**Cu**	**Zn**	**Sr**	**Rb**	**Ba**
Mass (%)	0.79	0.36	0.34	0.21	0.17	0.06	0.05

Thermogravimetric Analysis and Differential Thermal Analysis of BBA

The particulate needs to be stable at the temperature reached during the processing of the composite. Thermogravimetric analysis was carried out for the BBA sample to detect the thermal stability and moisture content. Figure 2 revealed the TGA and DTA weight loss at the 10 °C to 1000 °C. However, the significant mass loss of BBA was observed between 386.4 °C to 895.9 °C, and the overall mass loss was 17.8%. There was around 82.2% of BBA remained without any further decomposition as shown by the plateau in the graph. The curve displays mass loss in 3 steps (one between 386.4 °C to 420.1 °C, the second one between 590.2 °C to 706.9 °C, and the third one between 767.9 °C to 890.9 °C). The temperature range was observed according to the TGA curve, the mass loss on the first step shows the degradation of the organic components such as cellulose and lignin present in the BBA due to the incomplete combustion. The mass loss observed at 590.2 °C to 890.9 °C was due to the decomposition of carbonates of calcium and potassium. As shown in TGA curve data maximum mass loss was observed at 675.8 °C. It's caused the decomposition of carbonates of both calcium and potassium [20]. Kalembkiewicz et al. and also Chowdhury et al. reported that lime (CaO), portlandite ($Ca(OH)_2$), calcite ($CaCO_3$), and calcium silicate (Ca_2SiO_4) are the dominant phases in the wood waste ash.

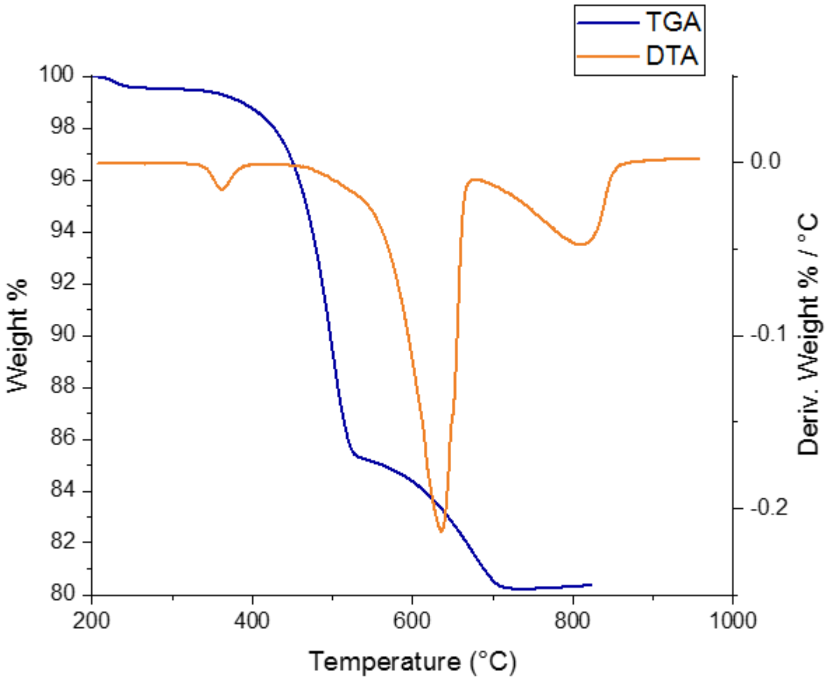

Figure 2. TGA and DTA curves

Moisture Analysis for Composites

A significant moisture loss between 0.7% - 0.8% was manifested in Table 4 in dried composites than undried.

Table 4. Moisture analysis for composite before and after drying.

Sample number		01	02	03	04	05	06	07	08
Moisture (%)	**before drying**	1.7	1.6	1.4	1.3	1.5	1.5	1.6	1.9
	after drying	0.70	0.80	0.75	0.70	0.70	0.70	0.70	0.75

DSC Analysis on Composites

Table 5. The results of DSC of composites

Sample number	Heating		Cooling		X_c (%)
	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	
01	220.467	37.184	187.820	54.257	39.76
02	221.031	37.439	187.676	56.484	40.83
03	220.680	44.314	188.524	58.191	44.57
04	220.460	46.527	186.882	56.110	44.62
05	220.239	39.037	186.419	44.084	36.14
06	220.835	43.106	186.543	52.811	41.70
07	221.739	37.583	186.410	52.222	39.05
08	221.290	40.425	185.704	46.471	37.78

T_m: Max. Melting temperature; ΔH_m: Melting enthalpy; T_c: Max. Crystallization temperature; ΔH_c: Crystallization enthalpy; X_c: Degree of crystallization

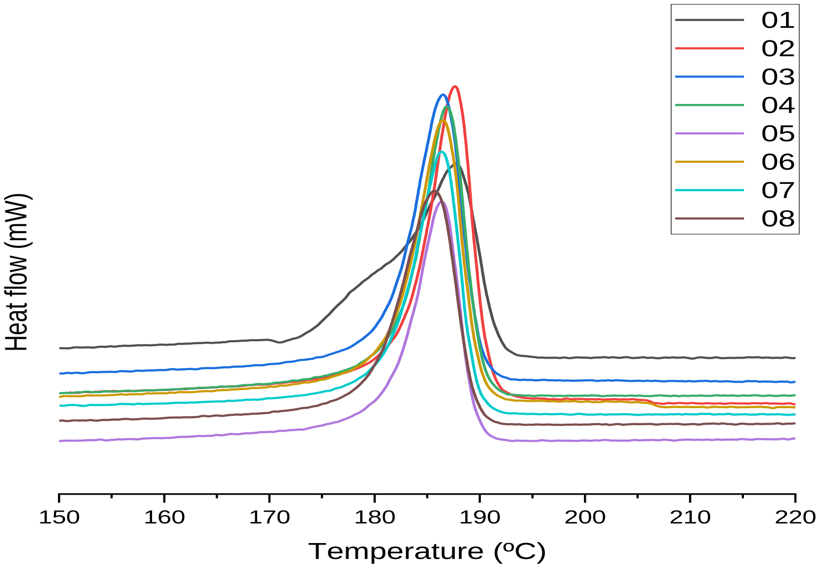

Figure 3. Variation of melting temperature of polyamide 6 composite with various BBA and SBBA content 01 - PA6/0%Ash; 02 - PA6/2.5%Ash; 03 - PA6/5%Ash; 04 - PA6/7.5%Ash; 05 - PA6/10%Ash; 06 -PA6/10%Ash/0.5 %CA; 07 - PA6/10%Ash/1%CA; 08 - PA6/10%Ash/2%CA

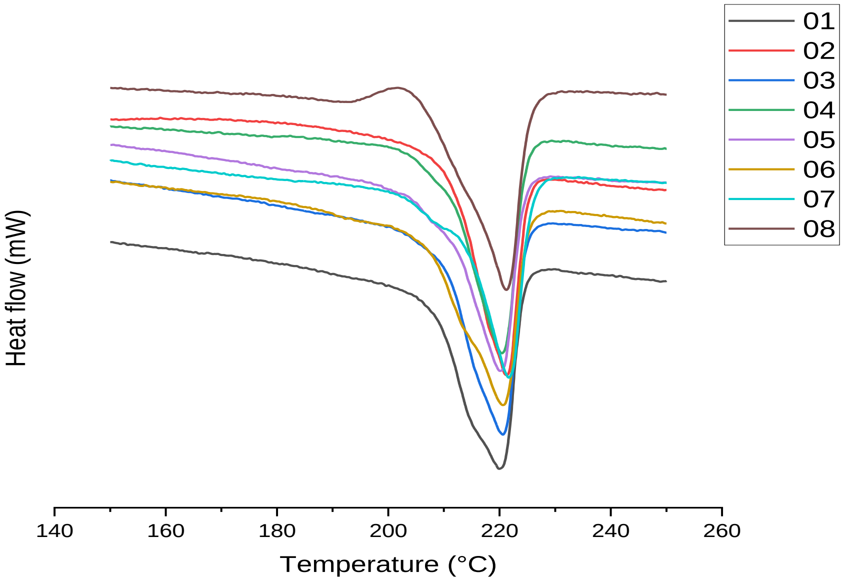

Figure 4. Variation of crystallization temperature of polyamide 6 composite with various UBBA and SBBA content 01 - PA6/0%Ash; 02 - PA6/2.5%Ash; 03 -PA6/5%Ash; 04 - PA6/7.5%Ash; 05 - PA6/10%Ash; 06 -PA6/10%Ash/0.5 %CA; 07 PA6/10%Ash/1%CA; 08 - PA6/10%Ash/2%CA.

DSC thermograms were used to study the melting and cooling behavior and degree of crystallinity. The addition of BBA has caused to gain a narrow range of crystallization temperature and has broadened the melting temperatures compared to the unfilled polyamide (UPA6). According to Figure 3 and Figure 4, a small variation was observed in the melting temperature (T_m) and a temperature enhancement was observed on the surface-modified BBA incorporated composites than the untreated BBA incorporated composites. Even though, in the crystallization temperature (T_c), a small decrement was observed in the surface-modified BBA (SBBA) than the unmodified BBA (UBBA) composites.

The highest degree of crystallinity was observed in the 7.5% UBBA filled composite. This was due to the effect of the filler, which, when cooled, causes the formation of nucleation centers, increasing the content of the crystalline phase of the polymeric matrix in the composite. However, a decrease in crystallinity was observed in the composite with the higher

10% UBBA filler loading. However, filler loading of 2.5%, 5%, and 7.5% may cause an increase in crystallinity. Due to the possibility of intermolecular interactions in the polymer, a small amount of filler may cause an increase in the degree of crystallinity, resulting in the formation of crystallization centers upon cooling. These results are similar to the experiment done by Gnatowski et al. a higher degree of crystallinity can be obtained on 5% biomass combustion ash incorporated polyamide than unfilled polyamide.

The change in structure may be the cause of the decrease in the value of the degree of crystallinity. The orientation of the filler in the sample may be affected by the increase in filler loading [3]. Furthermore, it was observed that 2% coupling agent-filled composite (PA6/ 10% Ash / 2% CA) shows lower degree of crystallinity than unfilled PA6 (PA6/ 0% Ash). It indicates that the SBBA affects the composite.

Characterization of Mechanical Properties

Table 6. Mechanical properties of the composite

Sample number	**Type of composition**	**Tensile properties**		**Flexural properties**	
		Tensile strength (MPa)	**Elongation at beak (%)**	**Stress at peak (N/mm²)**	**Bending modulus (N/mm²)**
01	PA6/0%Ash	54.261	325.270	43.79	1101.455
02	PA6/2.5%Ash	51.861	136.050	45.22	1145.584
03	PA6/5%Ash	48.620	104.500	45.86	1222.191
04	PA6/7.5%Ash	49.022	48.478	48.07	1336.020
05	PA6/10%Ash	51.389	48.602	50.07	1425.490
06	PA6/10%Ash/0.5%CA	49.322	37.839	49.08	1303.727
07	PA6/10%Ash/1%CA	50.123	47.003	49.24	1297.095
08	PA6/10%Ash/2%CA	52.398	51.469	46.29	1188.820

Tensile strength was found to decrease as the weight of the filler loading increased when compared to unfilled PA6 with UBBA incorporated samples and there is an increment noticed in samples 4 and 5. The reason for the increment of tensile strength may cause particle agglomeration due to the poor distribution. When compared to previous research experiments, a high filler content can cause a decrease in elongation at break by increasing tensile strength due to lower polymer matrix content and poor interfacial adhesion. According to the Table 6 tensile strength has been increased by 2% CA incorporated SBBA (PA6/ 10% Ash / 2% CA) compared to 10% UBBA filler (PA6/ 10% Ash). It denotes the role of the coupling agent in increasing the filler-matrix interface interaction. The elongation at break decreases drastically adding the untreated filler. But elongation has increased using the 2% coupling agent treated filler which supports the assumption of improved interface filler matrix interaction [2, 4, 22-23]. These results agree well with FA-CA-GPR composite and nylon 6 with fly ash-treated titanate coupling [2, 22]. Tensile properties have increased when CA was increased from 0.5 to 2.0% in the FA-CA-GPR composite similar to the results according to the data given in Table 6.

The flexural test measures the force required to bend a beam under three-point loading conditions. The stress at peaks and bending modulus of the USBBA and SBBA-filled PA6 composite compared to unfilled PA6. Stress at the peak was gradually increased from 43.79 N/mm^2 at unfilled PA (PA6/ 0% Ash) to the maximum value of 50.07 N/mm^2 at 10% untreated BBA loading (PA6/ 10% Ash) and then it decreased gradually to 49.29 N/mm^2 at 2% CA treated BBA filled composite (PA6/ 10% Ash/ 2% CA). The bending modulus of the samples shows a similar trend with the stress at peak data. The introduction of the particles up to 10% could improve the flexural properties. However, there is a decrement occurred with the incorporation of coupling agent into it. CA has the ability to reduce stiffness on composite by increasing the elongation properties.

Conclusion

XRF and TGA data confirmed that CaO, K_2O, MgO are mainly present in the BBA. TGA and DTA data also verified that there is no degradation of BBA occurred during the extrusion and injection molding process up to 386 °C. According to the degree of crystallinity of the composite, a higher degree of crystallinity was shown on the 7.5% UBBA incorporated composite, and it was caused by the formation of heterogenic centers of nucleating around filler while cooling in an injection mold. 2% coupling agent modified BBA has the lowest crystallinity values. The variation of tensile and flexural properties on SBBA filled composite revealed silane preparation improves the compatibility and facilitates good interfacial bonding of polymer matrix and filler. When the concentration of the coupling agent was increased, a small increment of the elongation and tensile properties were observed on 10% SBBA filler incorporated composites than 10% UBBA filler loaded composites. Out of the 10% SBBA fillers, the incorporation of a 2% coupling agent observed the highest tensile strength and elongation properties. Flexural properties were increased when filler content increasing nevertheless it was found to be decreased when the coupling agent content was increased from 0.5 to 2% by weight. So, it could be concluded N-2 (Aminoethyl) 3-aminopropyl triethoxy silane coupling agent affects the property enhancement of the composite by improving the compatibility between resin and particles.

Conflicts of Interest

The authors declare no conflicts of interests.

References

[1] A. Agarwal, M. Thombre, Chandrajeet, S. Kashyap. Preparation and characterization of polymer matrix composite using natural fiber lantana-camara. *J. Mech. Civ. Eng.* (*IOSR-JMCE),* **2014**, 60-65

[2] S. Bose, P. Mahanwar**.** Effect of titanate coupling agent on the mechanical, thermal, dielectric, rheological, and morphological properties of filled nylon 6. *J. Appl. Polym. Sci.* **2005,** 99, 266-272.

[3] A. Gnatowski, M. Ulewicz, M. Chyra. Analysis of Changes in Thermomechanical Properties and Structure of Polyamide Modified with Fly Ash from Biomass

Combustion. *J. Polym. Environ.* **2017**. 26, 647-654.

[4] S. Pardo, C. Bernal, A. Ares, M. Abad, J. Cano. Rheological, thermal, and mechanical characterization of fly ash-thermoplastic composites with different coupling agents. *Polym. Compos.* **2010,** 31, 1722-1730.

[5] O. M. Sanusi, A.K. Oyinlola. J. O. Akindapo. Influence of Wood Ash on the Mechanical Properties of Polymer Matrix Composite Developed from Fibre Glass and Epoxy Resin. *Int. J. Eng. Res. Technol. (IJERT)* **2013**, 2, 344-352.

[6] S. Chowdhury, M. Mishra, O. Suganya. The incorporation of wood waste ash as a partial cement replacement material for making structural grade concrete: An overview. *Ain Shams Eng. J.* **2015,** 6, 429-437.

[7] G. Akovali. The Interfacial Interactions in Polymeric Composites. Dordrecht: Springer Netherlands. Kluwer Academic Publishers, **1993,** pp.169-199.

[8] C. D. Armitt. Particle filled polymer composite. **2014** pp. 357-424

[9] C. Millot, L. Fillot, O. Lame, P. Sotta, R. Seguela. Assessment of polyamide-6 crystallinity by DSC. *J. Therm. Anal. Calorim.* **2015**, 122, 307–314

[10] C. DeArmitt, R. Rothon. Surface Modifiers for Use with particulate fillers. polymers and polymeric composites: A Reference Series, 2017, 29–49

[11] H. Hirano, J. Kadota, T. Yamashita, Y. Agari, Treatment of Inorganic Filler Surface by Silane-Coupling Agent: Investigation of Treatment Condition and Analysis of Bonding State of Reacted Agent, World Academy of Science, Engineering, *Int. J. Miner. Metall. Mater.* **2012**, 6, 2012

[12] M. A. Ali, T. Kaneko. Polyamide syntheses, encyclopedia of polymeric nanomaterials. **2015**, 1750–1762.

[13] H. Ishida, S. Naviroj, S. Tripathy, J. Fitzgerald, J. Koenig. The structure of an aminosilane coupling agent in aqueous solutions and partially cured solids. *J. Polym. Sci. Polym. Phys. Ed.* **1982**, 20, 701-718.

[14] Y. Ouabbas, J. Dodds, L. Galet. Chamayou A, Baron M, Modifications of powders properties by dry-coating: some examples of processes and products characteristics, 18th International Congress of Chemical and Process Engineering, Aug **2008**, Prague, Czech Republic.

[15] J. H. Cho, Y. W. Lee. Preparation of composite powder and properties by surface modification of inorganic pigments for papermaking, *KONA Powder Part. J.* **2015**, 32. 270-278

[16] M. A. Ali, T. Kaneko. Polyamide syntheses. encyclopedia of polymeric nanomaterials, **2015**, 1750–1762.

[17] H. Ismail, L. Mega, H. Khalil. Effect of a silane coupling agent on the properties of white rice husk ash-polypropylene/natural rubber composites. *Polym. Int.* **2001**, 50, 606-611.

[18] A. Konakanchi, R. K. Alla, V. Guduri. Silane Coupling Agents – Benevolent Binders in Composites Organs. *Trends Biomater. Artif. Organs* **2017**, 31, 108-113

[19] N. L. Batista, P. Olivier, G. Bernhart, M. C. Rezende. E. C. Botelho. Correlation between degree of crystallinity, morphology and mechanical properties of PPS/carbon fiber laminates. *Mater. Res.* **2016**, 19, 195–201.

[20] J. Kalembkiewicz, D. Galas, E. Sitarz-Palczak. The physicochemical properties and composition of biomass ash and evaluating directions of its applications. *Pol.*

J. Environ. Stud. **2018**, 27, 2593-2603.

[21] S. Chowdhury, M. Mishra, O. Suganya. The incorporation of wood waste ash as a partial cement replacement material for making structural grade concrete: An overview. *Ain Shams Eng. J.* **2015**, 6, 429-437.

[22] S. Guhanathan, M. Devi, V. Murugesan. Effect of coupling agents on the mechanical properties of fly ash/polyester particulate composites. *J. Appl. Polym. Sci.* **2001**, 82, 1755-1760.

[23] S. Bose, P. Mahanwar. Effect of flyash on the mechanical, thermal, dielectric, rheological and morphological properties of filled nylon 6. *J. Miner. Mater. Charact. Eng.* **2004**, 3, 65-72.