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Recycled Polypropylene Reinforced Coconut Shell Composite: Surface Treatment Morphological, Mechanical and Thermal Studies

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Abstract The mechanical, morphological and thermal stability of the recycled waste polypropylene composite reinforced with treated and untreated coconut shell particulate have been investigated under two coconut shell particulates sizes of 80 and 150μm. The thermal stability, microstructure and water absorption capacity were characterised using TGA 701, Scanning Electron Microscope model EVOMA 10 LaB6 Analytical VP-SEM at 20KV, Instron Testing Machine and Brinell Hardness Tester respectively. The surface treatment enhanced significantly the mechanical properties of the developed composites. At 10% coconut shell particulates addition, the impact energy of the developed composites and thermal stability of the treated coconut shell reinforced composite started decreasing.

Keywords Microstructure, Homogeneity, Glass transition, Surface treatment, Oxidation temperature, Degradation

1. Introduction

Thermoplastic material such as Polypropylene is characterised with high toughness, high resistance to chemical attack, electrical insulation, low coefficient of friction and easy formability but its low strength and low heat resistance have limited its use in many engineering applications. Researches have been carried out in order to optimise the physical and mechanical properties of the polymer. This has led to development of polymer based composites in which synthetic fillers such as iron particles and glass fibres are used as reinforced fillers in the polymers (Siddhartha et al. 2003). Such polymer matrix composites are used in automobile/aviation, medical implantation; fixture and furniture fittings and paper industry but the overall cost of the synthetic fibre reinforced polymer matrix composite is one of the major factors that limits its use in general day to day engineering applications.

Expensive cost of the synthetic fibre reinforced polymer matrix composite has called for the use of less expensive and efficient methods (Brahmakumer 2004) and cheap plant (natural) fibres such as rice husk, coconut shell, palm kernel shell, etcetera as reinforcement in polymers in order to develop a novel polymer composite with reduced overall cost, (Harish 2008; and Andrzej et al. 2010).

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Plant fibres such as coconut shell, palm kernel shell are hydrophilic in nature as they originate from lignocellulose which contain strongly polarised hydroxyl group (Brahmakumar et al. 2004). These fibres are not compatible with hydrophobic thermoplastics such as polypropylene leading to poor interfacial adhesion between the matrix and the fibres and mixing difficulties due to poor wetting of the fibres with the matrix. The combined effect of such fibre-matrix incompatibility and poor wetting causes poor mechanical properties of the plant fibre reinforced polymer matrix (David 2012).

Several methods have been devised in order to solve this problem of fiber-matrix incompatibility and poor wetting. These methods includes chemical treatment of the fibers, grafting of short chain molecules and polymers onto the fiber surface and the use of coupling agents or compatibilizer. Those chemicals used for surface treatment include silane, acrylic acid and maleic anhydride (Herrera-Franco 2004; Tengku-Faizal, 2010 and Salmah, 2012).

In the present study, polymer matrix composites developed from reinforced polypropylene with particulate coconut shell (which was treated with NaOH) were produced by compression molding process and their mechanical properties and water absorption behaviour were investigated. The objective was to ascertain how the particulate size of coconut shell/ NaOH treatment affect these properties. The used coconut shell and polypropylene was regarded to be a waste which their improper disposal causes environmental hazard. However, the work was aimed at improving maximally the properties of the propylene; optimizing the

surface interfacial adhesion and wetting of the coconut shell fibers with polypropylene and finally to solve environmental problem associated with improper disposal of coconut shell and non-biodegradable polypropylene.

2. Materials and Methodology

500g of crushed coconut shell was soaked in one molar solution of sodium hydroxide (NaOH) for one hour, after which it was washed in pure water; sundried; ground and sieved into different particle sizes ranging from 80 to150μm in accordance with BS 1377; 1990 standard. Plates 1-3 show the unprocessed coconut shell, ground coconut shell particulates and pelletized polypropylene respectively.

Plate 1. Unprocessed Coconut shell

Plate 2. 80μm Coconut shell Powder

Plate 3. Pelletized Polypropylene

5% volume of untreated coconut shell particulates (UCSp) were mixed with 95% pelletized recycled waste polypropylene (RWPP) in a two-roll rheomixer (Haake Rheomix 600) at a temperature of 165℃ ± 5℃. The same processes were repeated for the remaining samples at different volume fractions of UCSp/RWPP (10/90; 15/85; 20/80 and 25/75%) for two different grain sizes (80 and 150μm) for both treated and untreated coconut shell particulates (TCSp). Each blend from the mixer was cut into smaller sized pieces suitable for feeding in the three-piece stainless steel compression molds. Pieces of RWPP/5UCSp blended samples were compressed for 5minutes under controlled load of 30 tons at a temperature of 175℃ to a rectangular shape of 250x200x5mm dimensions (See Plate 4) in a Wabash V200 Hot Press.

Plate 4. Compressed Polypropylene Polymer composite

The process was repeated for the remaining samples. Each sample was cooled to room temperature and ejected from the press, and conditioned for 72hrs at a temperature of 23 ± 2℃ and a relative humidity of 50 ± 2.5%.

Samples were prepared to standard tensile coupon with 5mm gauge length for tensile and water absorption tests. See Plate 5.

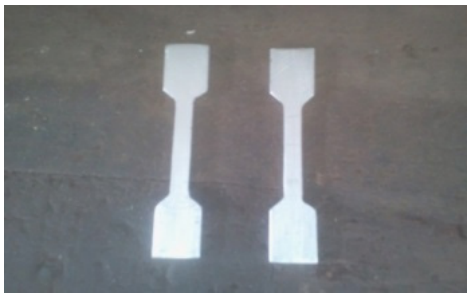

Plate 5. Prepared Sample for Tensile Test

Microstructural examination was carried out using Scanning Electron Microscope model EVOMA 10 LaB6 Analytical VP-SEM at 20KV to study the orientation and distribution of phases within the matrix of the RWPP/UCSp and RWPP/TCSp composites.

The coupon samples were subjected to tensile test using an Instron Testing Machine at a strain rate 2 X $10^{-3}s^{-1}$ in accordance with the American Society for Testing and Materials (ASTM). The response of the materials to the tensile loading was plotted as a function of percentage volume of coconut shell (See Figure 8).

The micro hardness of the samples was determined according to the provisions in American Society of Testing Materials (ASTM E18-79) using the Rockwell hardness tester on "B" scale (Frank Wellest Rockwell Hardness Tester, Model 38506). The response of samples to surface indentation was plotted against the percentage volume fraction of coconut shell (See Figure 9).

Based on ASTM D256-93, the impact energy test was carried out on the notched samples of dimensions 75 x 10 x 10mm using the Avery- Denison Universal Impact –Testing Machine (machined by Adcock Shipley Milling Machine, Model 2E operating at maximum speed 1200 rev/min).

Water absorption test was carried on the prepared samples of both RWPP/UCSp and RWPP/TCSp composites. In this method initial weight of the samples were taken and recorded, after which the samples were soaked in water, new weight of the samples were taken and recorded on daily basis until weight of the test samples remained constant, an indication that the samples can no longer absorb water. The weight gain of each sample was calculated using the equation 1.

$$\text{Weight gain} = \text{final weight} - \text{Initial weight} \quad (1)$$

The average weight gain of each samples is calculated using the equation 2.

$$\text{Average weight gain} = 1/n(\text{weight gain}_1 + \text{weight gain}_2 + \ldots + \text{weight gain}_n) \quad (2)$$

Where n = number of days

The percentage weight of water absorption of each sample was calculated using equation 3

$$\%\ \text{water absorption} = \text{average weight gain} / \text{initial weight} \times 100 \quad (3)$$

3. Results and Discussion

Compositional Analysis

The XRD analysis was carried out on the RWPP/25UCSp (150µm) and RWPP/25TCSp (150µm) composites to identify and determine counts of the compounds (found in the matrix of the tested samples) with their corresponding compound formulae. The identified compounds with their formulae are presented in Tables 1 and 2 respectively.

Figures 8 and 9 shows the XRD profiles of the compounds in the matrix of the RWPP/25UCSp and RWPP/25TCS composites. An important observation was the significant reduction in the counts of identified compounds such as calcite, sebacic acid, and titanium manganese bromide and aluminium borate. The results in Tables 1 and 2 showed that there were no new phases produced as a result of interaction of NaOH and coconut shells which was accompanied with a decrease in all the acidic phases.

Microstructural Analysis

The results of the microstructural analysis of the developed composites are presented in Plates 6-12 and the corresponding EDS in Figures 1-7. From Plate 6, it was observed that the structure of the control sample is purely uniform. The corresponding EDS result from Figure 1 shows a fairly uniform distribution within the polypropylene matrix. The value of the extrapolated UTS of the RWPP from stress-strain curve is 15Nmm^{-2}.

Plates 7-9 represent the SEM micrographs of the RWPP/TCSp composites at 80µm. it was observed that the second phase CSp is uniformly distributed within the matrix of RWPP/TCSp composites. The corresponding EDS results from Figures 2-4 reflect the similar behaviour i.e there is minimal level of second phase particulate segregation. The corresponding UTS of the composites in Plates 7-9 extrapolated from Figure 8 are 6.4, 6.8 and 11Nmm^{-2} for RWPP/5TCSp, RWPP/10TCSp and RWPP/25TCSP respectively.

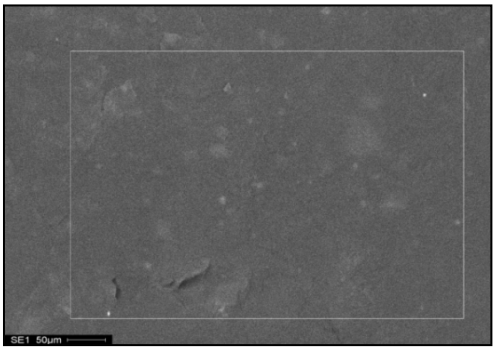

Plate 6. SEM Micrograph of RWPP

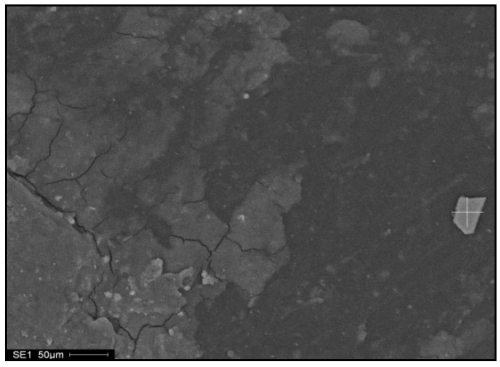

Plate 7. SEM Micrograph of RWPP/5TCSp Composite

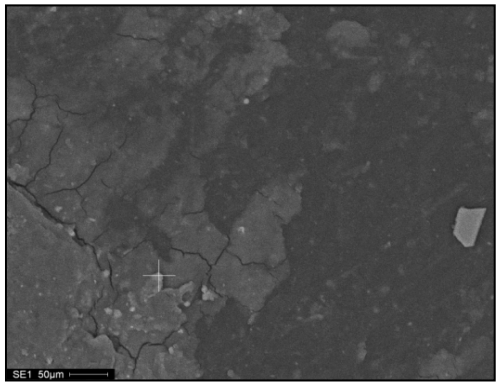

Plate 8. SEM Micrograph of RWPP/10TCSp Composite

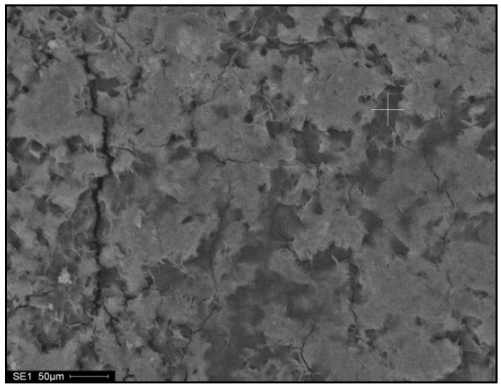

Plate 9. SEM Micrograph of RWPP/25TCSp Composite

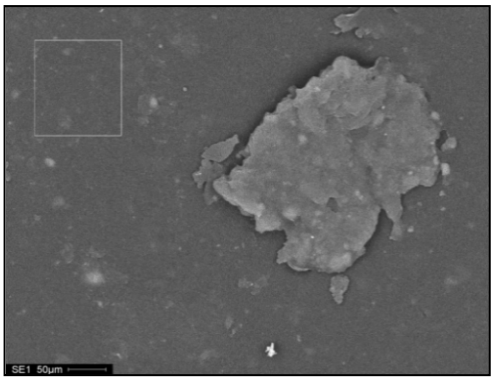

Plate 10. SEM Micrograph of RWPP/5UCSp Composite

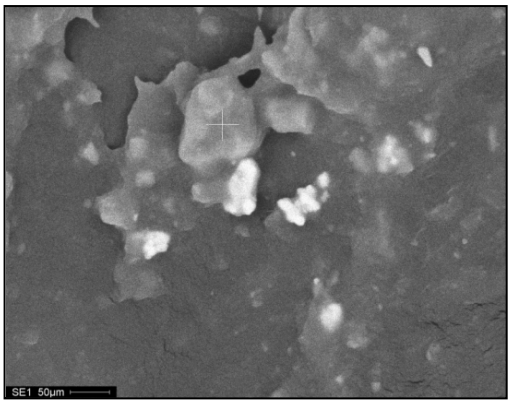

Plate 11. SEM Micrograph of RWPP/10UCSp Composite

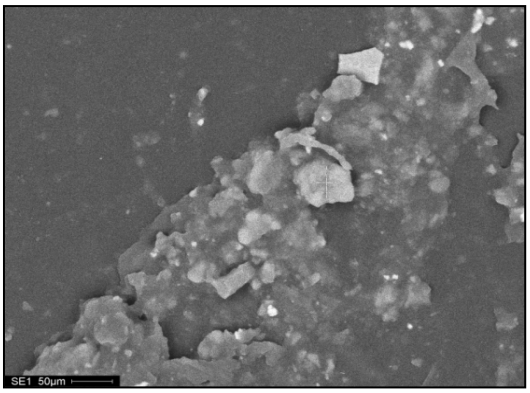

Plate 12. SEM Micrograph of RWPP/25UCSp Composite

Table 1. The identified Compounds with their Corresponding Chemical Formulae of RWPP/25UCSp (150µm)

Score	Chemical Formula	
41	Calcite, syn	$CaCO_3$
50	Sebacic acid	$C_{10}H_{18}O_4$
25	Lithium Manganese Bromide	Li_2MnBr_4
39	Aluminum Borate	$Al_4B_2O_9$

Table 2. The identified Compounds with their Corresponding Chemical Formulae of RWPP/25TCSp (150µm)

Score	Compound Name	Chemical Formula
24	Calcite, syn	$CaCO_3$
22	Aluminum Borate	$Al_4B_2O_9$
35	Sebacic acid	$C_{10}H_{18}O_4$
0	Lithium Manganese Bromide	Li_2MnBr_4

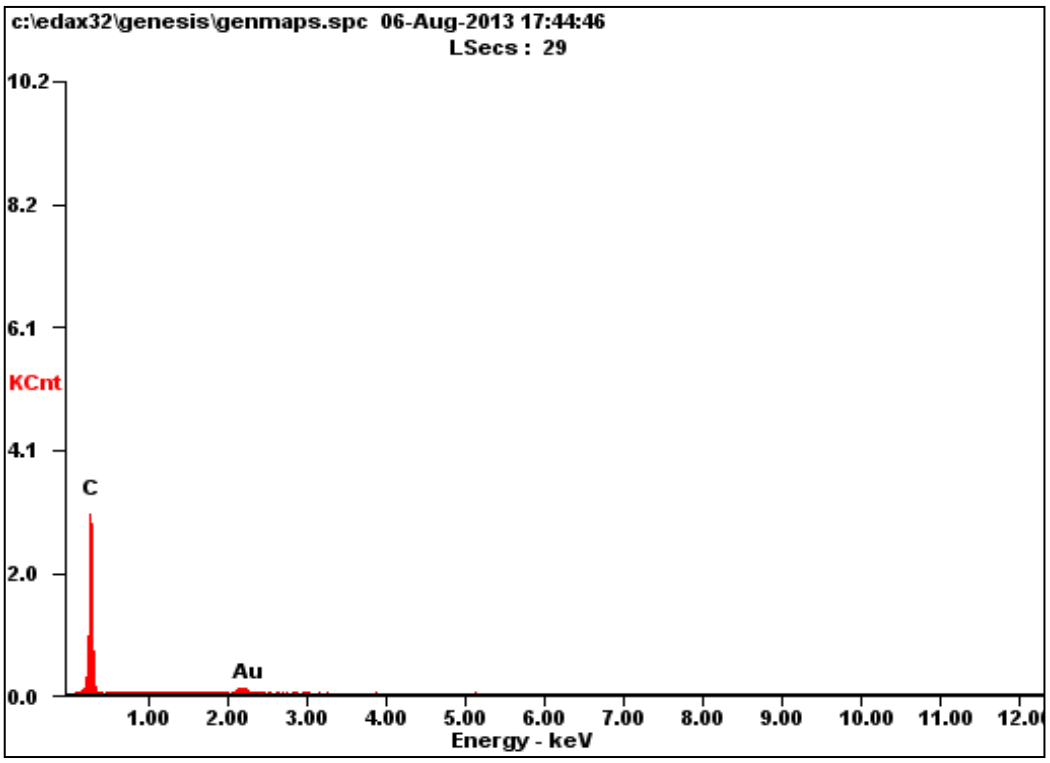

Figure 1. EDS of RWPP

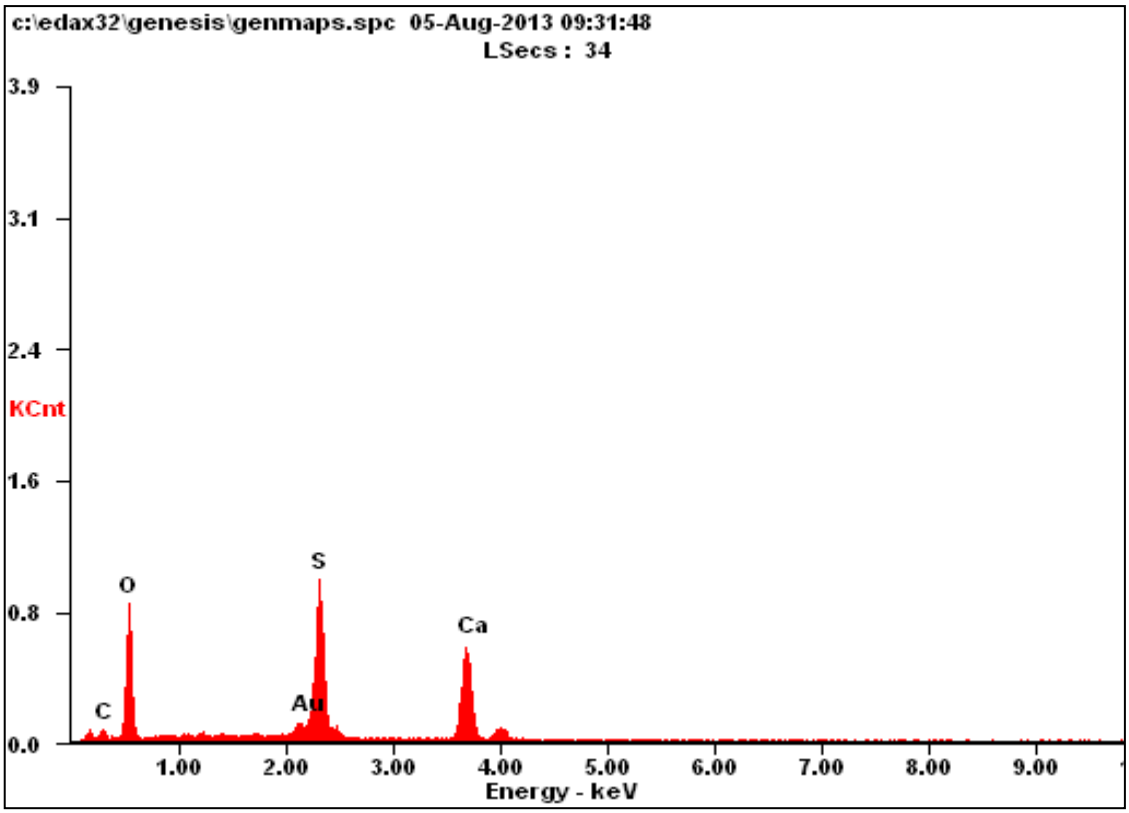

Figure 2. EDS of RWPP/5TCSp Composite

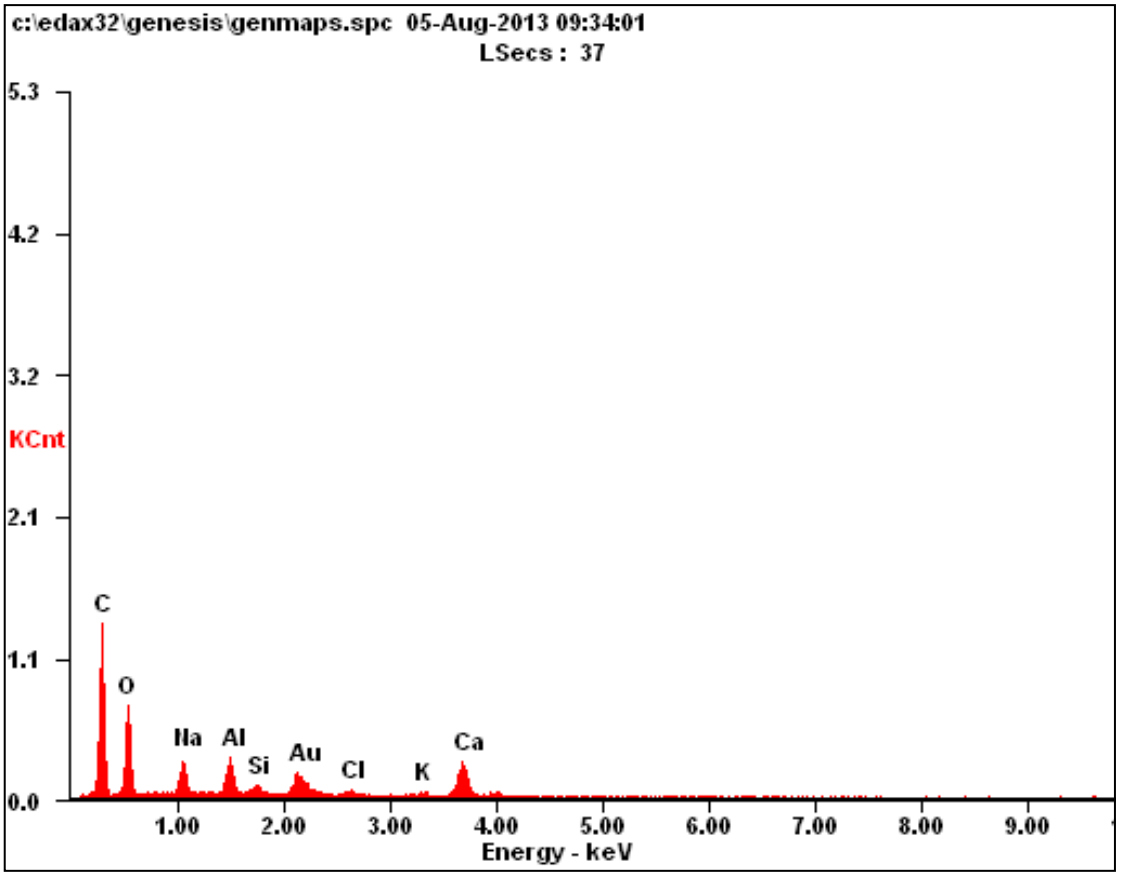

Figure 3. EDS of RWPP/10TCSp Composite

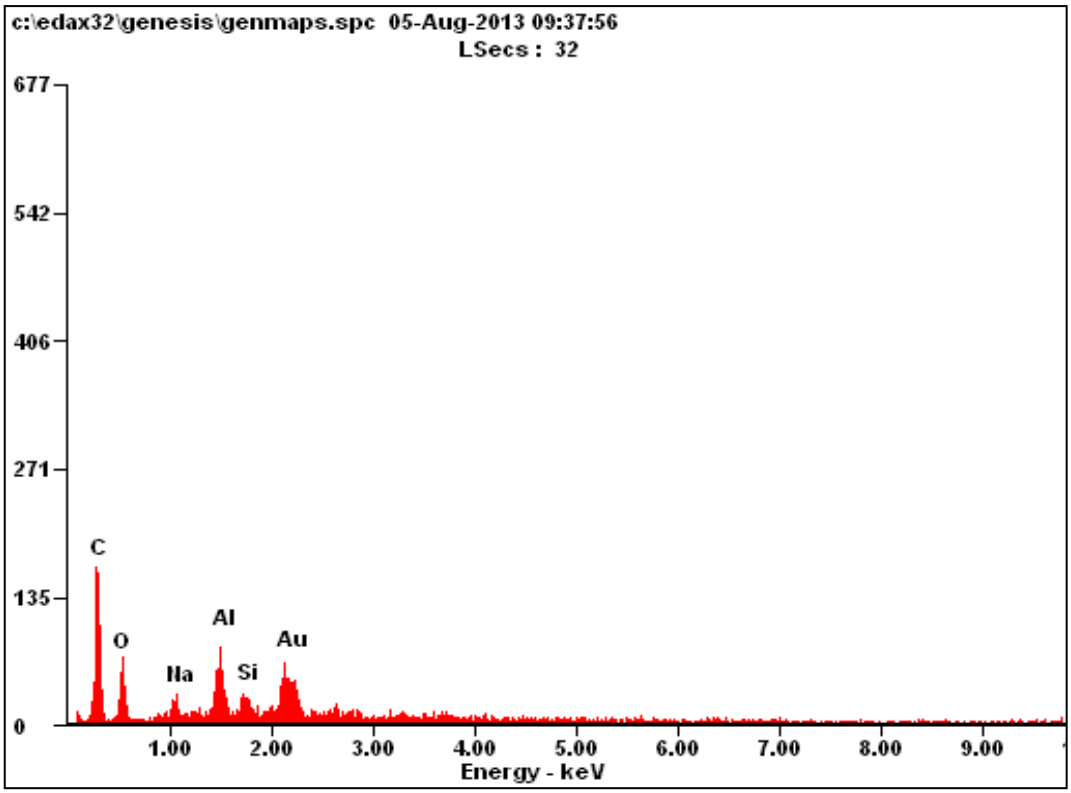

Figure 4. EDS of RWPP/ 25TCSp Composite

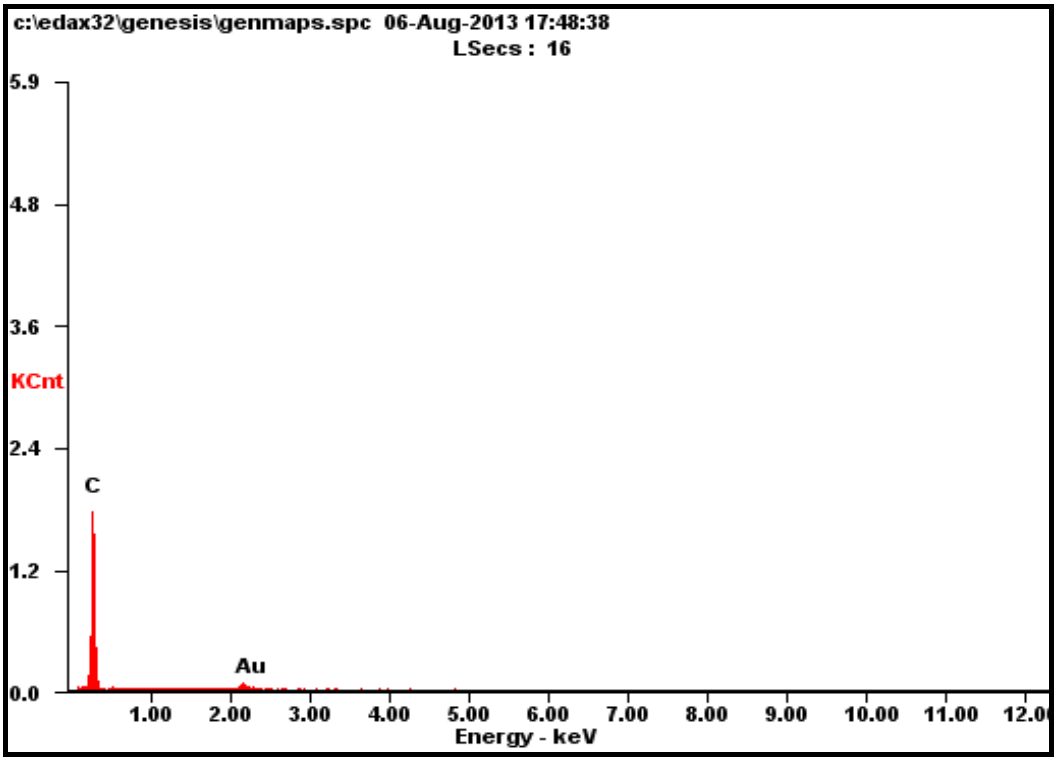

Figure 5. EDS of RWPP/ 5UCSp Composite

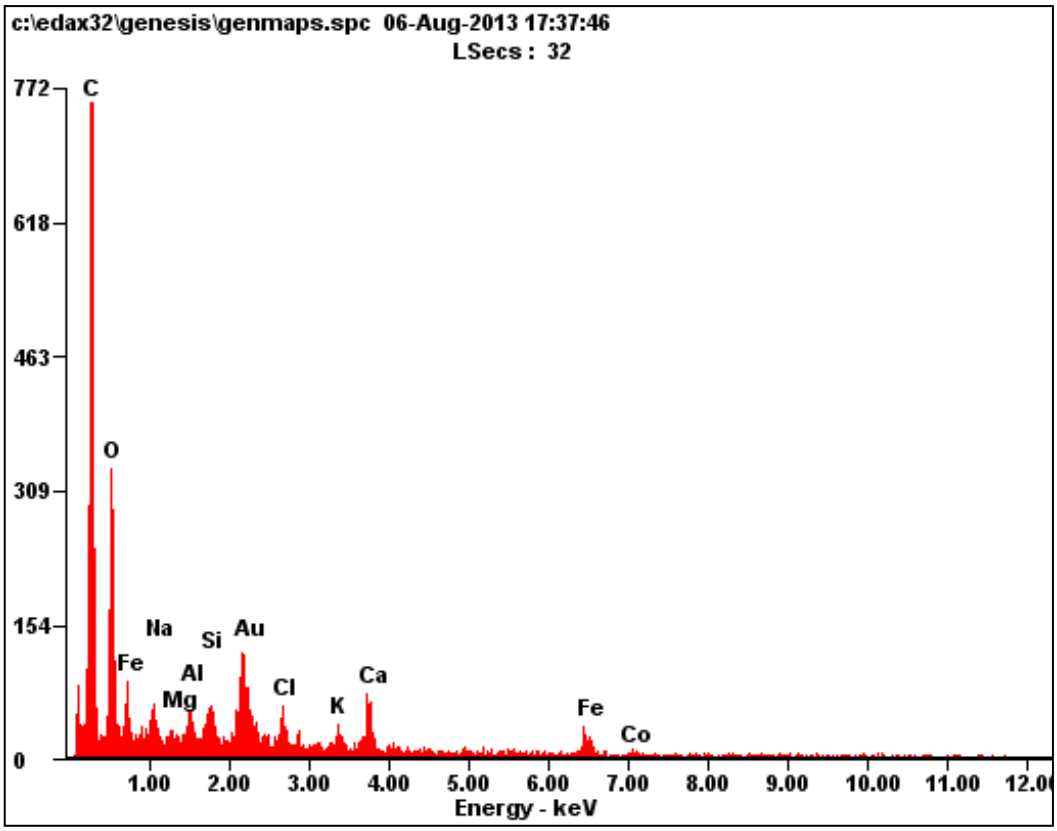

Figure 6. EDS of RWPP/ 10UCSp Composite

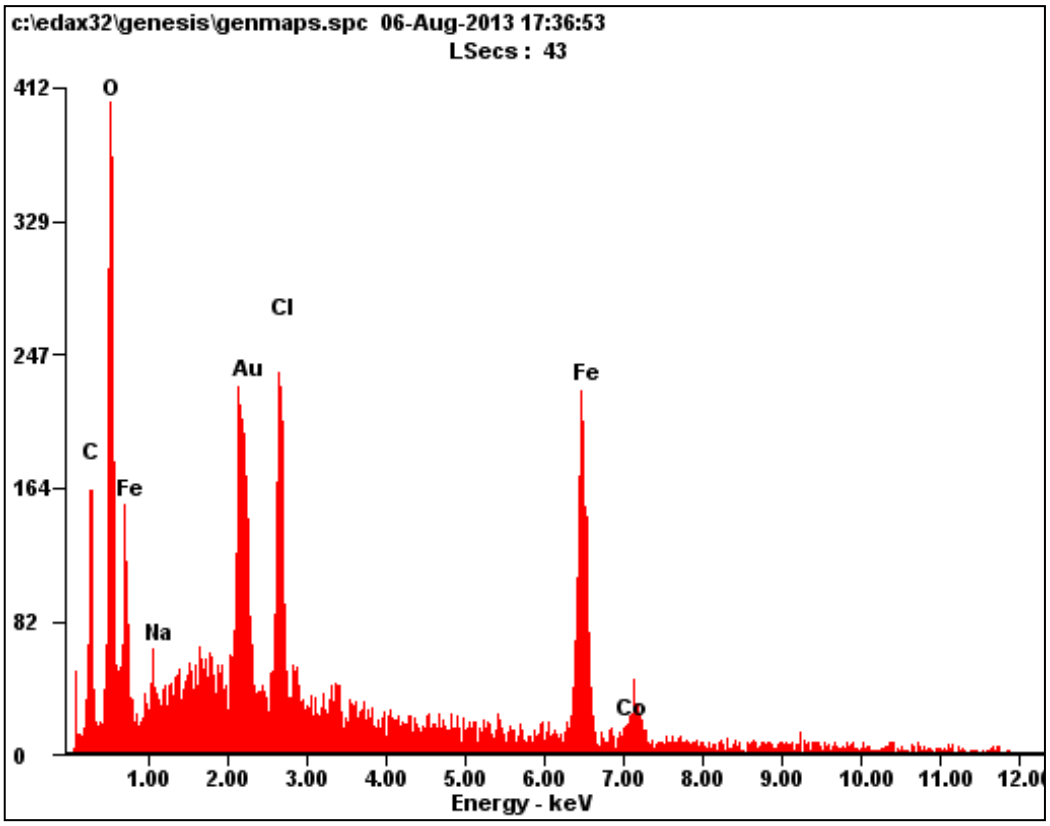

Figure 7. EDS of RWPP/ 25UCSp Composite

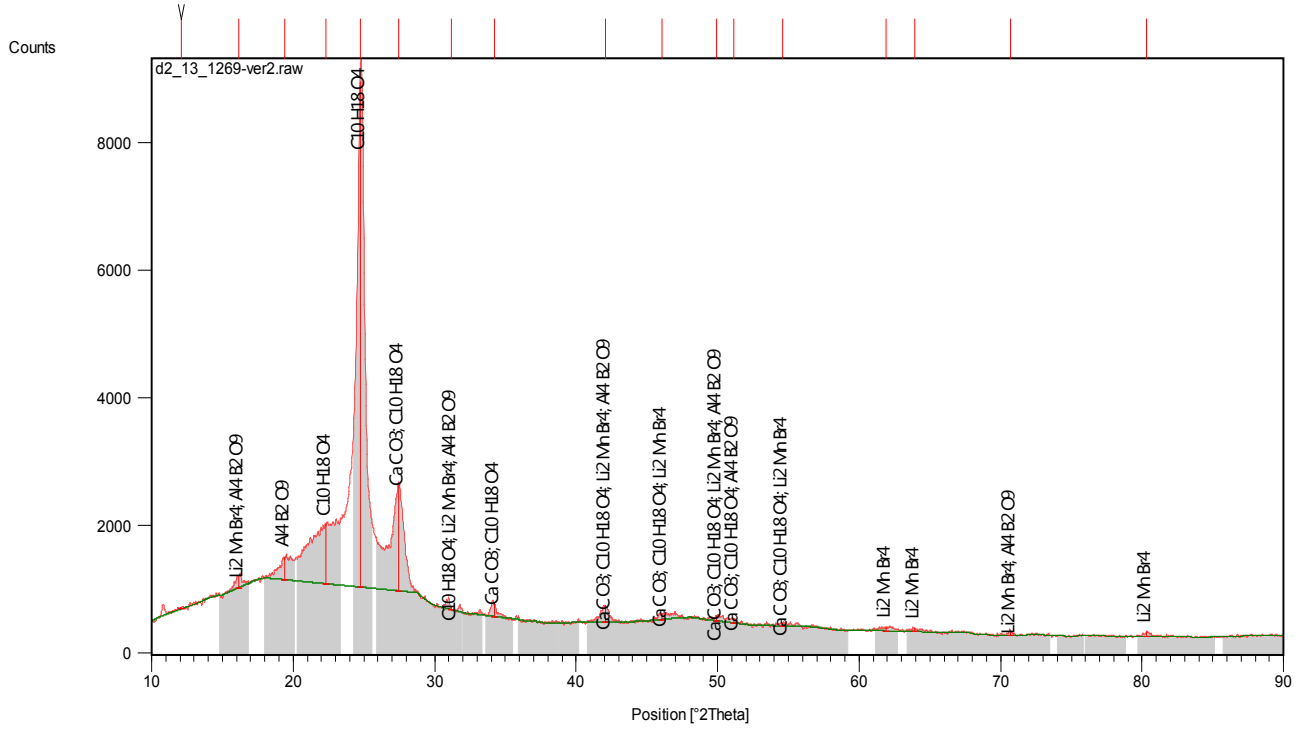

Figure 8. XRD Profile of Compound in the Matrix of RWPP/25UCSp Composite

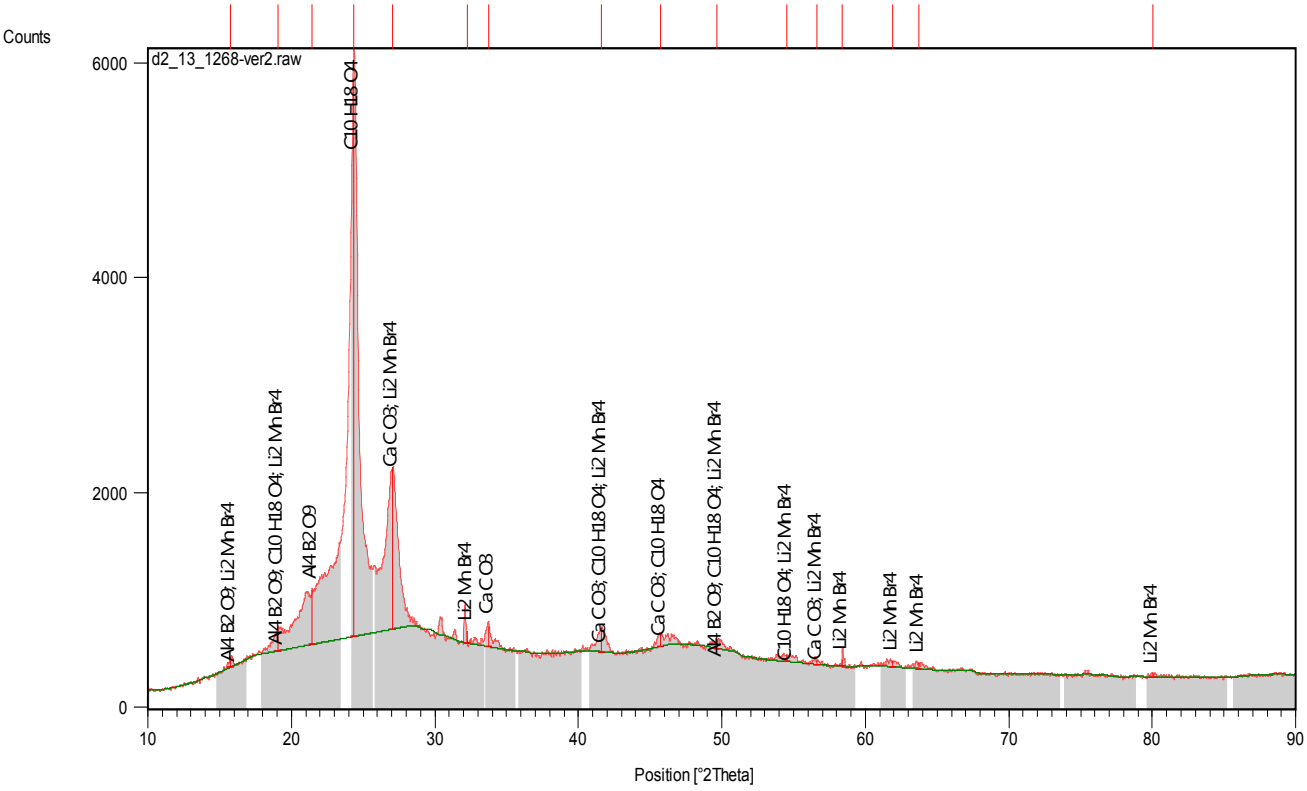

Figure 9. XRD Profile of Compound in the Matrix of RWPP/25TCSp Composite

Hardness

It was observed that the hardness of the treated coconut shell reinforced composite (RWPP/TCSp) was higher than that of untreated coconut shell reinforced composite (RWPP/UCSp) at 80 and 150 µm particulate sizes respectively (See Figure 10). With respect to 150µm particles size, about 70% increase in hardness values was observed when the coconut shells was treated with NaOH. The higher resistance to localized deformation during indentation could be attributed to the optimum improvement

in the interfacial adhesion of treated coconut shell particulates with recycled waste polypropylene which is as a result of reduction both in incompatibility and poor wetting of hydrophilic coconut shells and hydrophobic polypropylene. Also, about 38% (on average) improvement in hardness was observed both in treated coconut shell reinforced composite (RWPP/TCSp) and untreated coconut shell reinforced composite (RWPP/UCSp) as the particulate sizes of coconut shell decreased from 150 to 80µm. This might be attributed to more grafting of the coconut shell particulates with recycled polypropylene matrix.

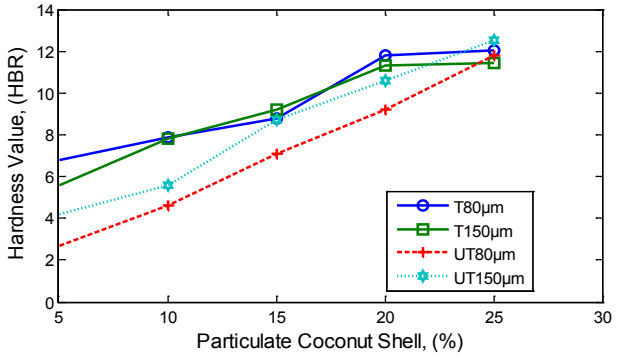

Figure 10. Hardness Values of RWPP/TCSp and RWPP/UCSp Composites as a function of %Volume Fraction of Coconut Shell

Impact Energy

It was observed that as the volume of particulate coconut shell increased, there was a corresponding increase in the impact energy up till 10% volume addition of coconut shell particulates. Beyond this point, the impact values of the composite were sacrificed. In particular, the treated coconut shell reinforced composite (RWPP/TCSp) showed higher increase in impact values than that of untreated coconut shell reinforced (RWPP/UCSp) composite (see Figure 11).

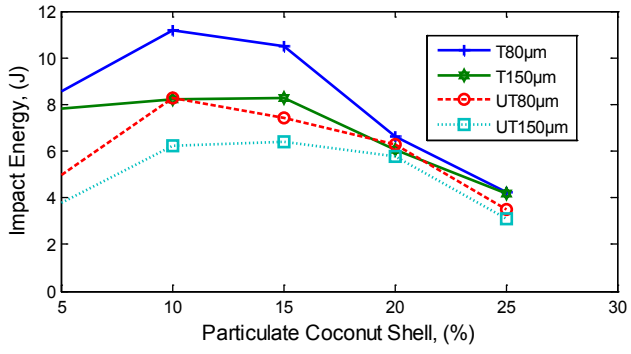

Figure 11. Impact Resistance as a Function of %Volume Fractions

Water Absorption

Figure 12 shows the relationship between water absorption and the coconut shell particulate addition. It was observed that the water absorption capacities of untreated coconut shell reinforced (RWPP/UCSp) composite was higher than that of the treated coconut shell reinforced composite (RWPP/TCSp). This behaviour may be attributed to poor interfacial adhesion between filler and matrix of the RWPP/UCSp composites. On the other hand, the poor water absorption observed for the treated coconut shell reinforced composites is as a result of the improved interfacial adhesion.

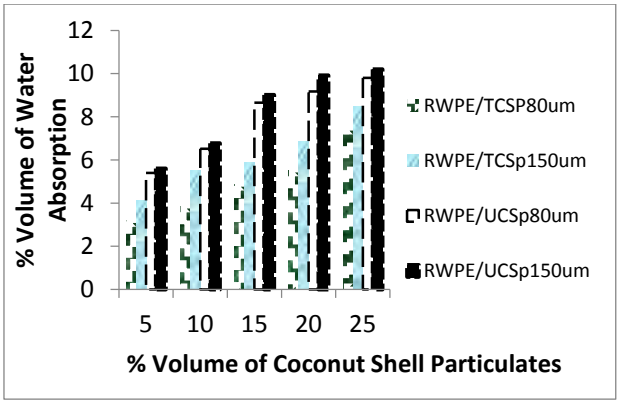

Figure 12. Water Absorption of Composites with % Volume Fractions of CSp

Thermo Gravimetric Analysis

Figures 13-14 shows the TGA results of the treated and untreated coconut shell reinforced polypropylene (RWPP/5TCSp and RWPP/5UCSp) composites. The TGA analysis was carried out in the presence of air/oxygen (oxidative) environment. The materials were heated at rate of 10℃/min from ambient temperature (25℃) to the maximum temperature (900℃) at which the weight of the sample remained unchanged i.e the temperature at which the oxidation reaction reached completion. Figure 12 shows that the treated coconut shell reinforced polypropylene (RWPP/TCSp) composite was thermally stable until when the standard (linear) line intersected the endothermic curve at 480℃ and 520℃ which were the onset temperature and oxidation temperatures (T_{on} and T_o) respectively. The onset temperature indicates the temperature at which the composite oxidation just begins and T_o the temperature at maximum oxidation rate. The degradation of the composite began at 480℃ and continues until the oxidation reaction was completed at 880℃ which was the final decomposition temperature (FDT) whereas in the case of untreated coconut shell reinforced (RWPP/UCSp) composite, T_{on} was 500℃ and T_o was 530℃ i.e the degradation of the composite just began at 500℃ and was completed at 900℃ (see Figure 13). By implication the untreated composite is more thermally stable than the treated composite.

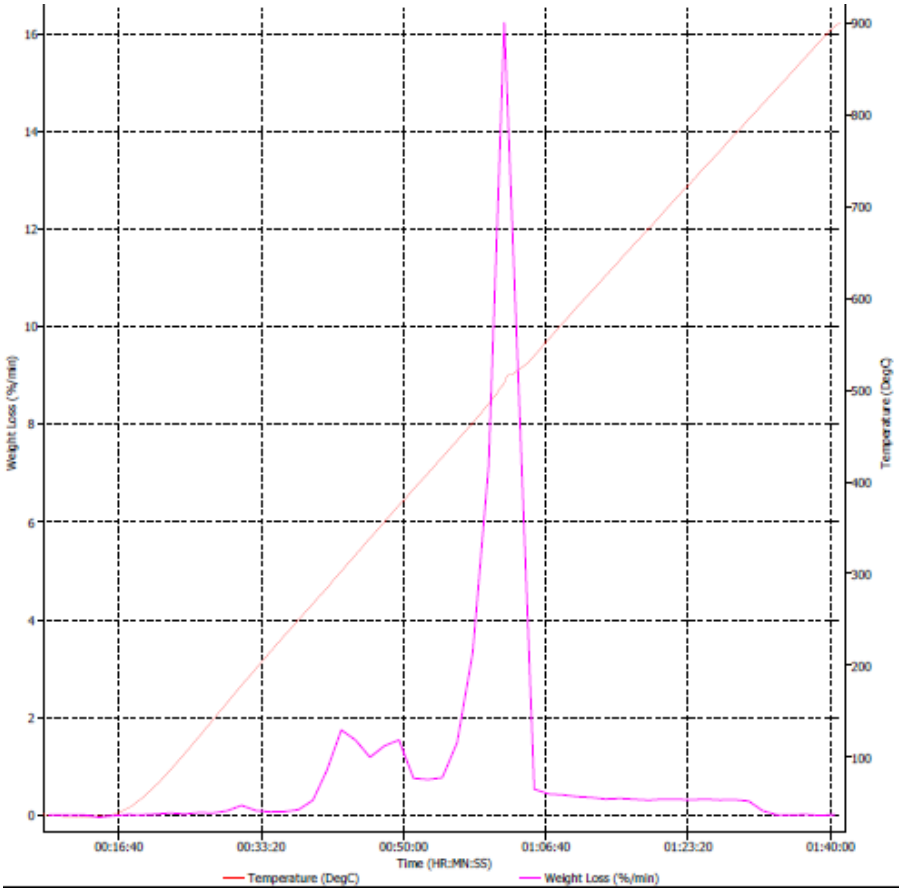

Figure 13. TGA of RWPP/5TCSp (150µm) Composite

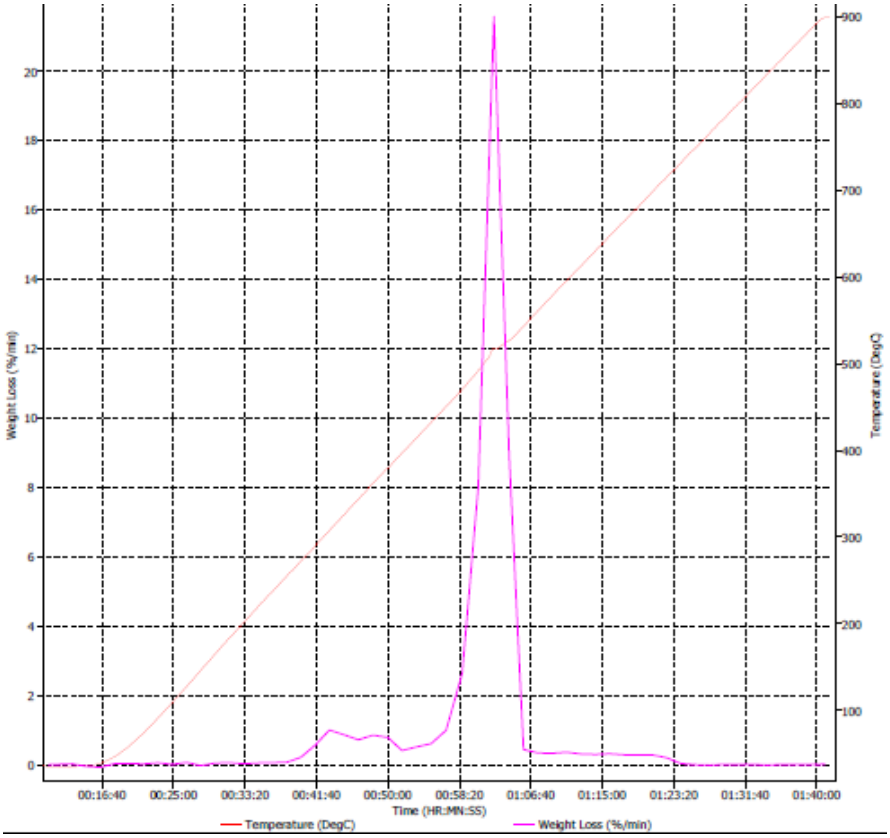

Figure 14. TGA of RWPP/5UCSp (150µm) Composite

4. Conclusions

From the results and discussion on this research, the following conclusion can be made:

1. The use of sodium hydroxide (NaOH) for surface treatment of coconut shell to enhance the adhesion property of the developed composites (RWPP/TCSp and RWPP/UCSp) reveals positive and significant results in the enhancement of the composite mechanical properties.
2. The higher the particle size, the higher the hardness and the ultimate tensile strength of the developed composites. The enhancement in the UTS may be attributable to better interfacial adhesion of coconut shell particulates to the polypropylene. Generally, there is an improvement on the UTS of the composites as the volume fraction of coconut shell particulates increase.
3. The higher the percentage of particle addition, the more segregated the distribution of the coconut shell particulates (CSp) within the matrix of the microstructure. The segregation is attributable to poor interfacial adhesion, poor wetting and incompatibility of the RWPP and UCSp.
4. The addition of coconut shell particulates (CSp) as reinforcement in recycled waste polypropylene (RWPP) is beneficial in the enhancement of its mechanical properties. However, the toughness of the composite is sacrificed when coconut shell particulates addition is above 10%. Hence the thermal stability of treated coconut shell reinforced composite (RWPP/TCSp) is also sacrificed.

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Abbreviation

RWPP = Recycled Waste Polypropylene; TCSp = Treated Coconut shell particulates; UCSp = Untreated Coconut shell particulates; TGA = Thermo Gravimetric Analysis, NaOH = Sodium hydroxide, XRD = x ray diffraction, EDS = Energy dispersion spectrum, UTS = Ultimate tensile strength, SEM = Scanning electron micrographs.

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