Thermogravimetry Analysis of Epoxy and Unsaturated Polyester Filled With Some Agricultural Waste of Dates Palm *(Phoenix dactylifera)* and African elemi (*Canarium shweinfurthii*) Particulate Composites

Abstract

Investigation of the thermal stability of epoxy and unsaturated polyester filled with some agricultural waste of Dates palm *(Phoenix dactylifera)* and African elemi (*Canarium shweinfurthii*) pits particulate composites has been conducted at a heating rate of 10^{o}C/min using thermogravimetric analysis (TGA). The study showed that the composites can withstand temperature up to 340^{o}C in inert atmosphere before decomposition and thus had good thermal stability as increased in temperature had little effect on the composites before the onset of degradation. The results show that the composites prepared from both fillers showed high thermal stability because onset of degradation of date palm pits/epoxy (DTP/EP) commenced at about 340^{o}C which was unsual for lignocellulosic material while atili pits/ unsaturated polyester (ATP/UP) was 320^{o}C. Literatures have shown that most lignocellulosics filler degrades at their processing temperature below 250^{o}C. Thus, both fillers could be used in engineering plastics.

Keywords: Temperature, Thermal Stability, Degradation, Lignocellulosics

1.0 Introduction

Thermosetting resins are the most widely used resins in composites. The main characteristic of thermosets (literally setting under heat) is that they require curing, in which they undergo a molecular cross-linking process which is irreversible and renders them infusible. They therefore offer high thermal stability, good rigidity and hardness, and resistance to creep. This also means that, once cured, the resin and its laminate cannot be reprocessed except by methods of chemical breakdown, which are currently under development. For practical purposes, therefore, cured thermosetting resins can be recycled most effectively if ground to fine particles, when they can be incorporated into new laminates or other products as fillers [1,2].

Thermosetting resins have little use on pure resin, but require addition of other chemicals to render them process able. For reinforced plastics, the compounds usually comprise a resin system (with curing agents, hardeners, inhibitors, plasticisers) and fillers and /or reinforcement. The resin system provides the 'binder,' to a large extent dictating the cost, dimensional stability, heat and chemical resistance, and basic flammability. The reinforcement can influence these (particularly heat and dimensional stability) but the main effect is on tensile strength and toughness. High performance fibres, of course, have a fundamental influence on cost [3].
Special fillers and additives can influence mechanical properties, especially for improvement in dimensional stability, but they are mainly used to confer specific properties, such as flame

retardancy, ultraviolet (UV) stability or electrical conductivity. Thermoset was the first organic resins used for composites making and they still represent around two-thirds of the overall composites market and about the same fraction of the overall market value as represented in Figure 1.

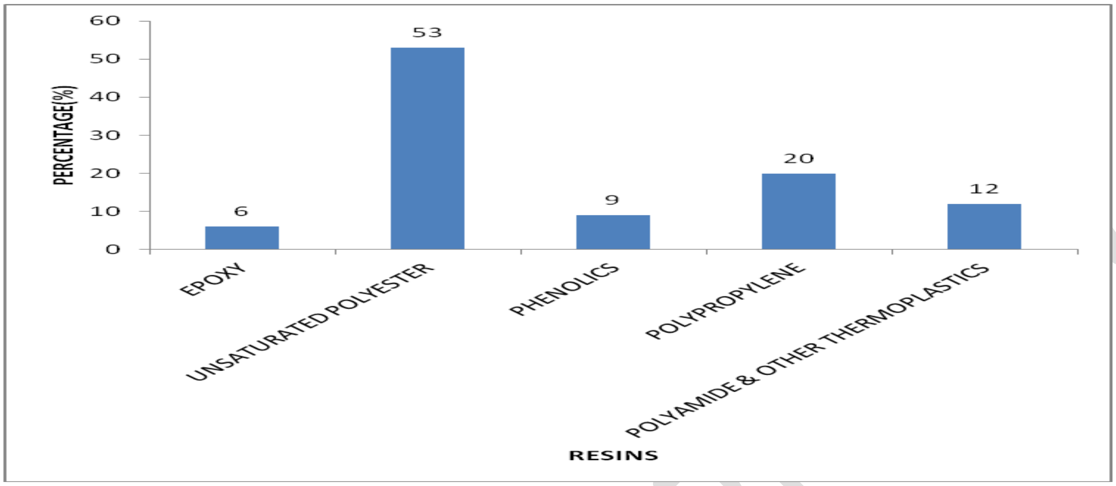

Figure 1: The overall composite market uses showing about two-thirds thermosetting resins and one-third thermoplastics as matrix materials [4].

The plastics industry produces far more thermoplastics than it does thermosetting plastics, approximately in the ratio of 4:1; however, this ratio is not maintained in the area of composite materials which represent about 3 % of the total plastics industry. Approximately twice as much thermosetting matrix material is used for composites than thermoplastics matrix material [4].

1.2 Date Palm Fruits: Palm date fruits consist of three main parts: date flesh, date pit, and skin. That is, it is a drupe, an indehiscent fruit in which an outer fleshy part (exocarp, or skin; and mesocarp, or flesh) surrounds a shell (the pit, stone, or pyrene) of hardened endocarp. The main sugars of date flesh are glucose, fructose and sucrose. At early stages of maturing the fruit, it has a high content of sucrose, but during the maturation process it is converted to glucose and fructose [5].

It contains a single seed (kernel) about 2–2.5 cm long and 6–8 mm thick. The kernel is a major by-product of the date palm-processing industry. They contained 7.1–10.3 % moisture, 5.0–6.3 % protein; 9.9–13.5 % fat; 46–51 % acid detergent fibre; 65–69 % neutral detergent fibre; and 1.0–1.8 % ash. Date pit is mainly used as animal feed [6].

Plate 1: Date palm raw fruits, and stony pits

1.3 African elemi (Atili): It is one of the tropical trees whose fruits contain oils in its pulp and seed kernel. The pulp is of oily consistency and edible. It is a drupe with an outer skin (exocarp), a 3 mm layer of fleshy mesocarp that is the edible portion and a hard (five-sided, 2 cm long and 1 cm wide) stony endocarp (pit) surrounding the tiny seed kernel that is edible. The endocarp (pit or stone) is thrown away after the fleshy part is eaten. In some culture, the pits are strung into necklaces or attached to traditional instruments, and in some cases used as local beads for feet [7].

Plate 2: African elemi (Atili) fruits, and stony pits

The research is aim at investigating the thermal stability of thermosets (epoxy and unsaturated polyester) composite prepared with fillers from some agricultural wastes.

2.0 MATERIALS AND METHODS

2.1 Materials: Date palm fruits, aluminium foil, Epoxy Resin (commercially available epoxy resin (3554A) of density 1.17 g/cm^3) and polyamine amine (Hardener3554B) of density 1.03 g/cm^3 were procured from a local supplier in Ojota, Lagos, Nigeria. The date palm fruits and African elemi (Atili) fruits were obtained from Gwagwalada market, F.C.T; Nigeria.

2.2 Methods

2.2.1 Filler Preparation: The date pits (DTP) and African elemi or atili pits (ATP) were separated from their fruits manually, thereafter, they were washed and cleaned to remove contaminants. They were then dried and grounded with hammer mill to obtain filler powder. The fillers were made to pass through wire mesh screen to obtain different particle sizes of 150 μm The fillers were then oven dried for 24 hrs at temperature of about 70 ^{o}C before use so as to reduce the moisture content. Samples were thereafter stored in a sealed container prior to compounding.

2.2.2 Compounding: Five levels of filler loading (10, 20, 30, 40, & 50 wt %) were made from fillers with the matrixes (epoxy and unsaturated polyester). Neat resins without filler were equally prepared to serve as control.

2.2.2.1 Date and Atili pits Epoxy Composites (DTP/EP and ATP/EP): The composites with varying degrees of filler percentage (i.e. 0, 10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt%) were prepared. This was achieved by mixing the various ratios of the prepared fillers with the epoxy to form homogenous blends. The mixing was achieved via manual stirring method for 10 minutes. The volume ratio of resin to hardener was 2:1, and after thorough mixing with the filler, the resin was poured onto the cavity of glass mould of dimensions 160 mm x 70 mm x 4.5 mm overlaid with aluminium foil so as to serve as releasing agent. The mixture was allowed to cure at room temperature for 24 hours before removal from the mould.

2.2.2.2 Date and Atili pits unsaturated polyester composites (DTP/UP and ATP/UP): Unsaturated polyester composites with varying degrees of filler percentage ((i.e. 0, 10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt%)) were also prepared. This was achieved by mixing the various ratios of the prepared fillers and the unsaturated polyester resin to form homogenous blends. The mixing was achieved via manual stirring method for 7 minutes. For example, 10 % filler loading was prepared by adding 0.2 % of the accelerator cobalt napthenate to mixture of resin and the filler and stirred for 3 minutes before the final addition of the catalyst i.e methyl ethyl ketone peroxide in ratio 2 % of the resin, the mixture was poured onto the cavity of glass mould overlaid with aluminium foil so as to serve as releasing agent. The mixture was allowed to cure at room temperature for 24 hours before removal from the mould. The composites were kept for 20 days at room temperature for complete curing.

2.3 Thermogravimetric Analysis: The thermogravimetric analysis (TGA) was performed on the date pits/epoxy (DPT/EP 1), date pits/ unsaturated polyester (DTP/UP), atili pits/epoxy (ATP/EP), atili pits/unsaturated polyester (ATP/UP) composites using TGA Q500 machine. The Samples were subjected to pyrolysis in nitrogen environment to a maximum temperature of 900 °C at a heating ramp rate of 10 °C/min. The weight loss was recorded in response to increasing temperature, with final residue yield on set of degradation temperature.

3.0 Results: The results of the thermogravimetry conducted are as presented in Figure 2 to 7.

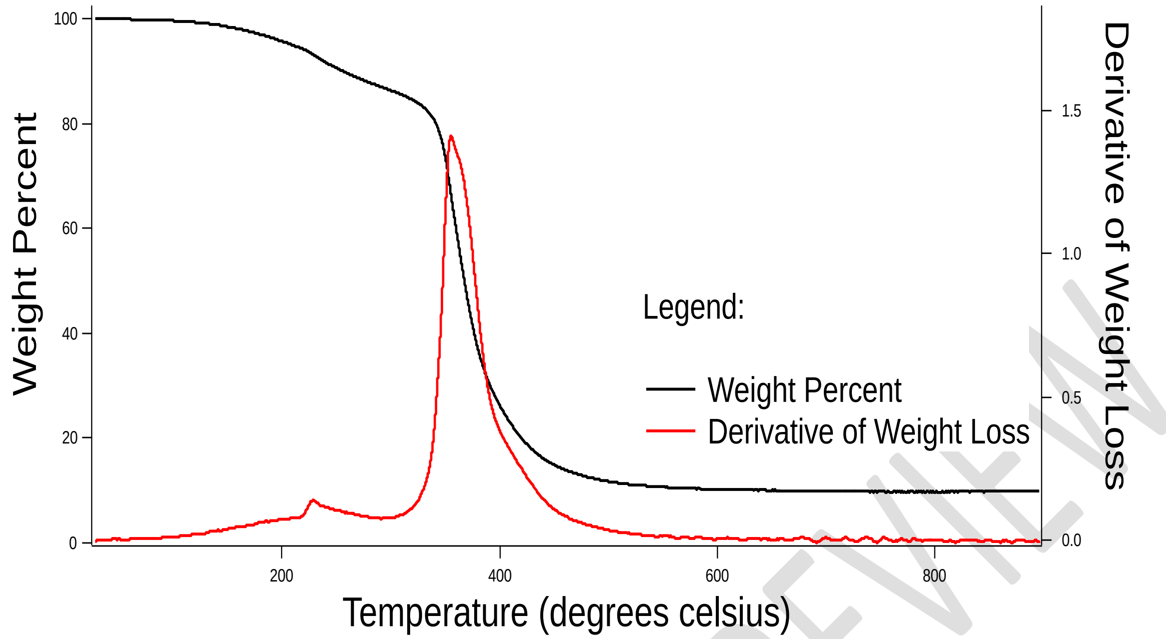

Figure 2: Thermogravimetric analysis (TGA) and derivatographic analysis curves of the neat epoxy resin (EP).

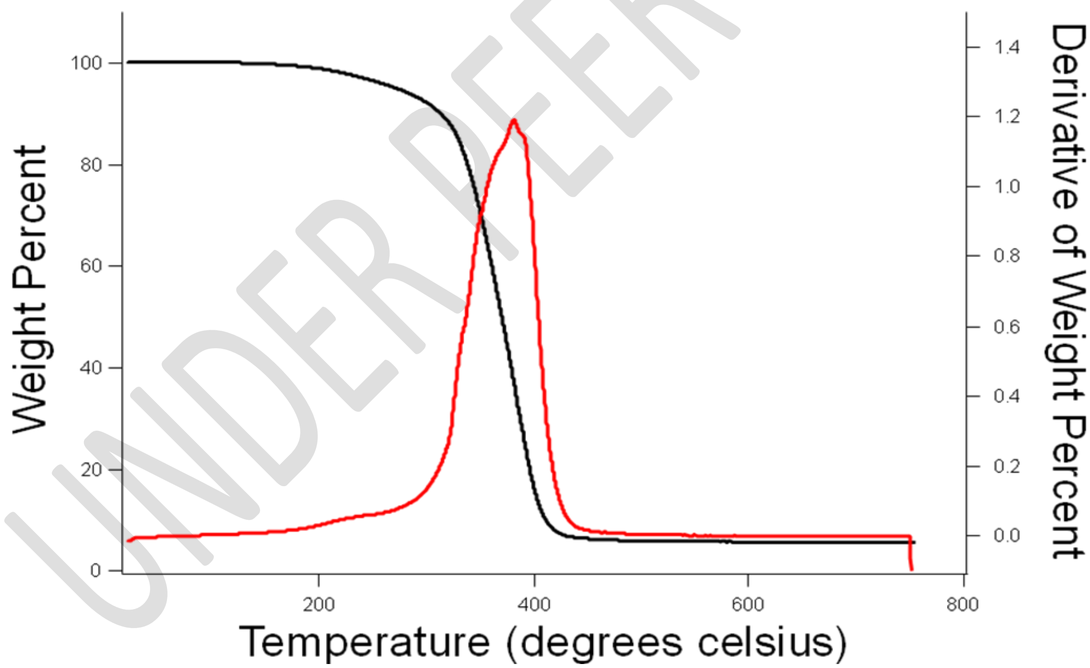

Figure 3: Thermogravimetric analysis (TGA) and derivatographic analysis curves of neat unsaturated polyester (UP).

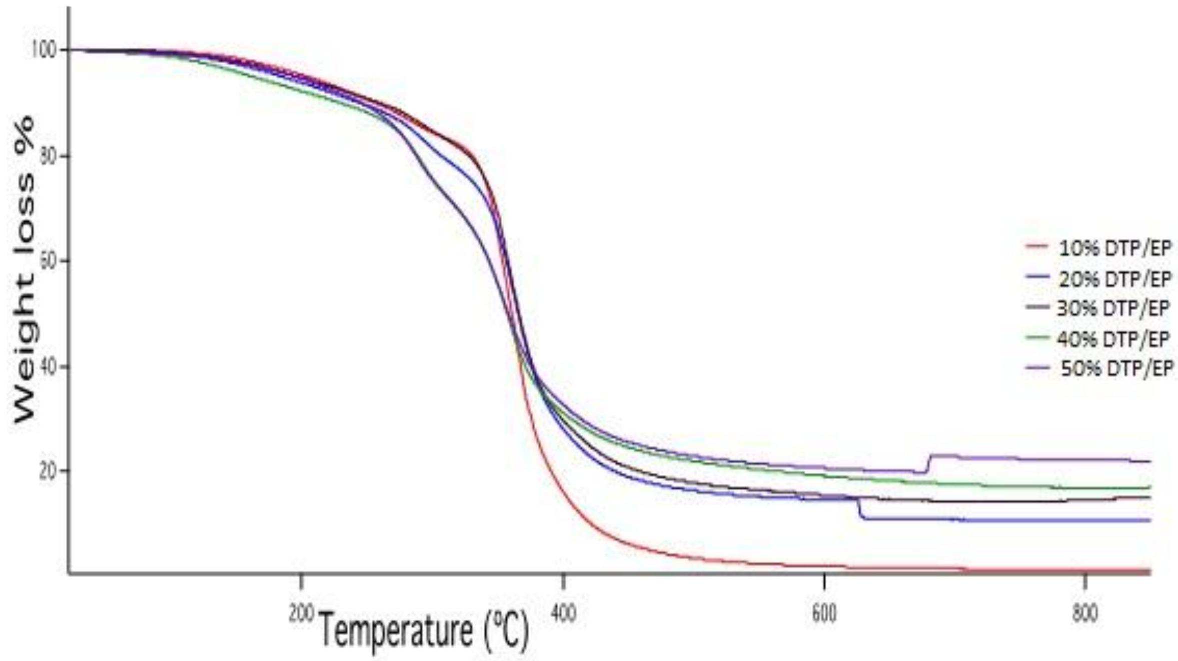

Figure 4: Thermogravimetric analysis (TGA) analysis curves of date pits filled epoxy (DTP/EP 1) composites.

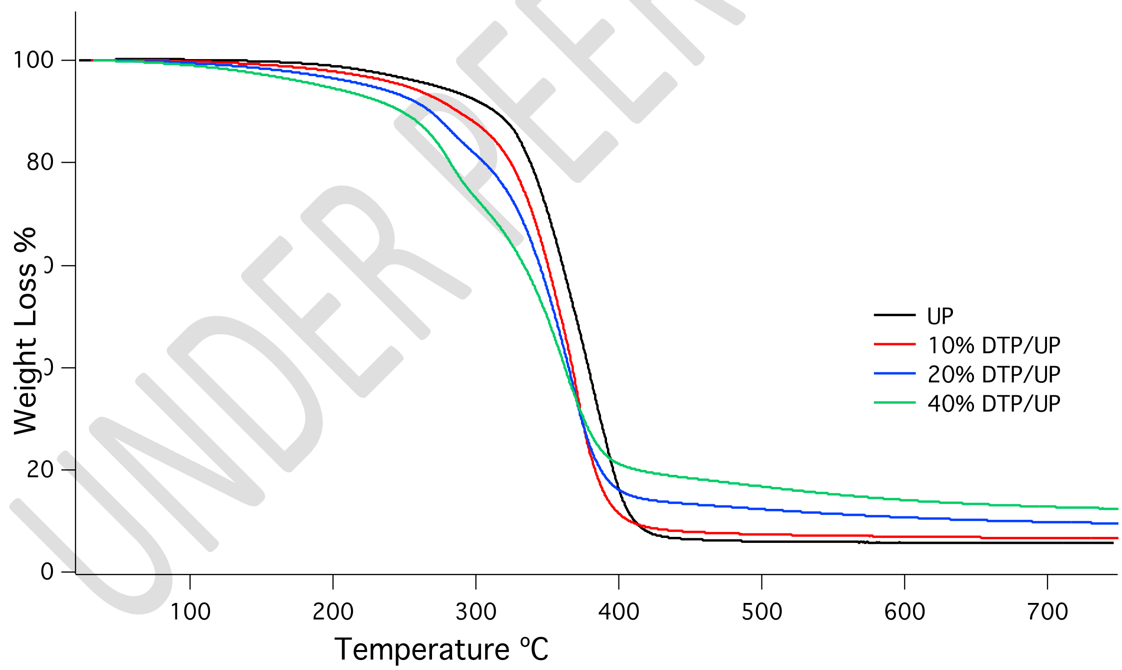

Figure 5: Thermogravimetric analysis (TGA) analysis curves of date pits filled (DTP/UP) filled unsaturated polyester composites.

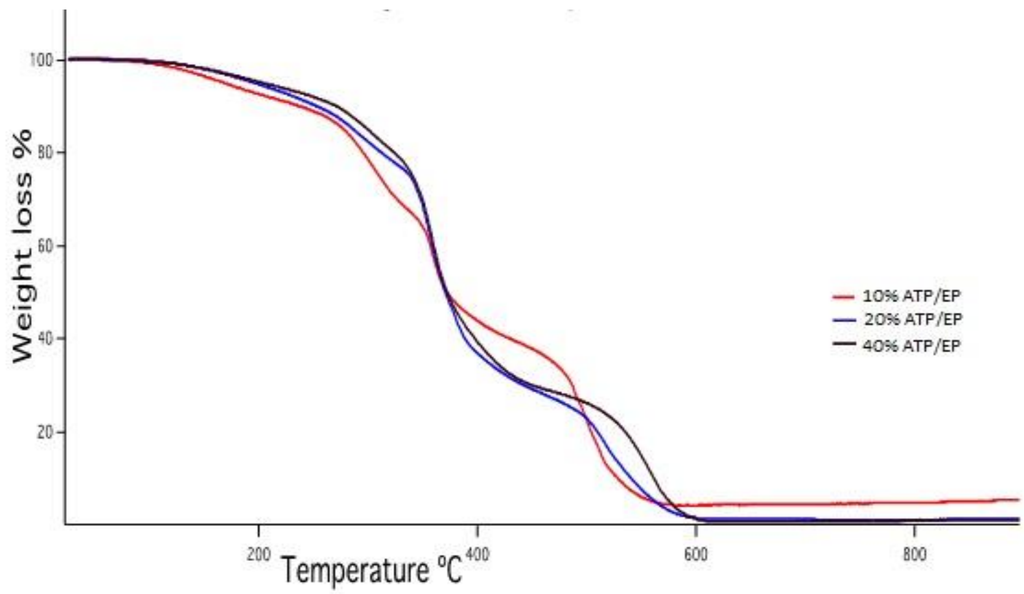

Figure 6: Thermogravimetric analysis (TGA) analysis curves of atili pits filled epoxy (ATP/EP) composites.

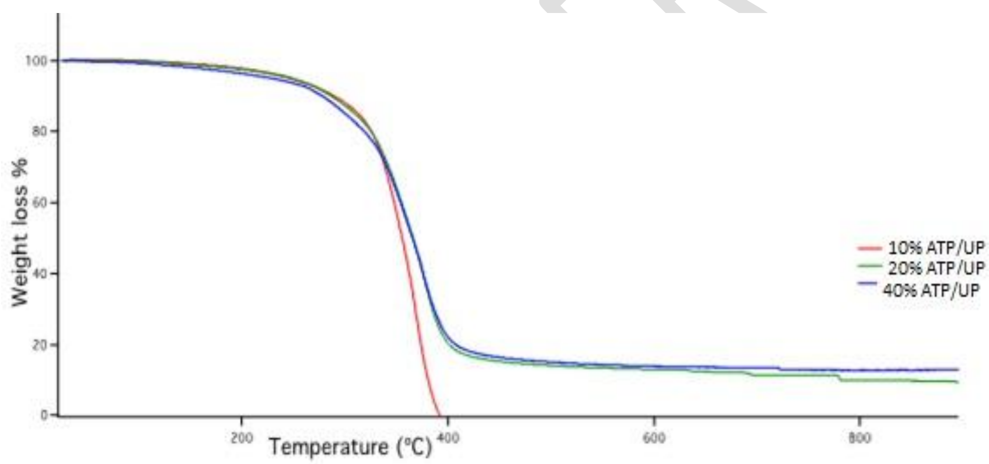

Figure 7: Thermogravimetric analysis (TGA) analysis curves of atili filled unsaturated polyester (ATP/UP) composites.

4.0 Discussion

Figure 2 shows the thermogravimetric curve of the unfilled epoxy resins. The results show a single step decomposition pattern. However, a gradual mass- loss of about 0.4% at 100 ^oC was observed, while at 130^oC, the resin lost 0.91% of its mass and this can be traced to loss of moisture content of the material. Shortly before the onset of decomposition temperature, the resin lost 9.3% of its mass due to loss of occluded water and other component at temperature of 250^{o}C. Onset of decomposition commenced at about 340^{o}C till the final decomposition temperature of about 420^{o}C in which 80 % of the material mass have been lost. At 500^{o}C the mass loss was 88.2% while at 600 ^{o}C, 650^{o}C and 700^{o}C, the mass loss was 90% meaning that the material must have experience total decomposition leaving 10 % residue or ashes.

Figure 3 shows the thermogravimetric analysis of the unfilled unsaturated polyester resins and a single step decomposition pattern can be observed. However, unlike epoxy which experienced a gradual mass- loss of about 18% before the onset of decomposition, unsaturated polyester shows minimal loss in weight before the onset of decomposition temperature. That is, unsaturated polyester was more stable than epoxy at temperature below 100^{o}C, this is because unsaturated polyester recorded no loss in mass and this was confirmed by the low moisture content. At 130 ^{o}C, the resin lost only 0.02 % of its weight compares to epoxy with value 0.91% at the same temperature. Shortly before the onset of decomposition temperature, the resin lost only 3.5% of its mass due to loss of bounded water and other component at temperature of 250^{o}C. Onset of decomposition commenced at about 317^{o}C till the final decomposition temperature of about 400 ^{o}C in which 92% of the material weight have been lost. At 500 ^{o}C , 600 ^{o}C, 650 and 700 ^{o}C, the mass loss was 94% meaning that the material must have experience total decomposition leaving 6 % residue. From the result in Figure 2 and 3, epoxy is more thermally stable than unsaturated polyester.

Figure 4 shows the TGA curve of date pits filled epoxy (DTP /EP) composites at filler loading of 10 wt% to 50 wt%, it can be seen that the 40 wt% and 50 wt% DTP/epoxy composites lost their weight earlier than the other samples. This is attributed to the high moisture content of the filler due to hydrophilic nature of lignocellulosic filler at higher filler loading. The percentage of weight reduction at 500°C of 50 wt% filler loading was 78% which mean about 22% of residues left after the composites were degraded. From the results shown in Figure 3 it can also be seen that 10 % date pits filled epoxy (DTP/EP) composite has the lowest residue due to the absence of char followed by 20 wt% DTP/EP composites. Lignin in filler is responsible for charring thus 40 wt% and 50 wt% DTP/EP composite will have more char [8]. Thus, the higher the filler content, the higher the residue after decomposition. The onset of decomposition temperature of 10 wt% DTP/EP composite started around 310 ^{o}C and lasted till the decomposition temperature of 441^{o}C while that of 50 wt% DTP/EP composite was observed at 281^{o}C and lasted till 444^{o}C. Thus, the ash content of the composites increased as the filler loading increases. The 10 % DTP/EP seems to be more thermally stable when compared to other composites since it shows less variation in weight as the temperature increases. Some researchers have found that the addition of natural fibres causes reduction in the thermal stability of the composite due to the influence of the less stable fibres [9]. It was equally observed from the result that the epoxy filled 10 wt% date pits (DTP/EP) composite experienced mass-loss of 16.7% at the onset of decomposition temperature

(310^{o}C) while 0.5% was lost at 130^{o}C. At 500^{o}C, the mass – loss for 10 wt%, 40 wt%, and 50 wt% are 96.5%, 77.03% and 77.6%, respectively.

Figure 5 shows the TGA for date pits filled unsaturated polyester (DTP/UP) composites. It can be seen that the filler followed similar pattern in unsaturated polyester with that of epoxy composites in Figure 4, except that the DTP/UP composites experienced high degree of stability at temperature below 13^{o}C.

That is, unsaturated polyester was more stable than epoxy at temperature below 100^{o}C, this is because unsaturated polyester recorded no loss in mass. At 130^{o}C, the unfilled unsaturated polyester (UP) lost only 0.02% of its weight compares to the unfilled epoxy with value 0.91 % at the same temperature. The 10 wt%, 20 wt%, and 40 wt% date filled unsaturated polyester, respectively, lost: 0.35%, 0.7% and 0.89% of their mass at 100^{o}C, and at 130^{o}C, 0.6%, 0.91%, and 1.7 % mass was lost, respectively. At the decomposition temperature of about 420^{o}C, the char left for the respective 10 wt%, 20 wt%, and 40 wt% date filled unsaturated polyester composites are 17%, 32% and 21% respectively.

The Figure 6 represents the thermogravimetric curve of atili pits/ epoxy (ATP/EP) composites. The results seem to be different from the pattern of curve shown in Figure 4 and 5. The graph shows multiples steps of decom position which might be due to non consistency in filler – matrix interaction. The 10%, 20%, and 40% atili filled epoxy composites respectively lost 2.3%, 1.07% and 1.1% at 130^{o}C, while at 400^{o}C, the mass-loss was 56%, 63% and 61% as it can be seen from Figure 6.

Figure 6 shows the decomposition pattern of atili pits filled unsaturated polyester (ATP/UP) composites. A single stage decomposition step was seen, in which 10 wt% atili pits unsaturated polyester (ATP/UP) showed more thermal stability than 20 wt% and 40 wt% atili pits unsaturated polyester (ATP/UP) composites. The 10 wt% gave no residue after decomposition at about 400^{o}C. It can be observed from Figure 7_that the onset of decomposition for 10 wt% and 20 wt% atili pits unsaturated polyester (ATP/UP) is at 298^{o}C and 242^{o}C, respectively, while the final combustion temperature is 400^{o}C and 405^{o}C respectively. The 40 wt% filler loading left more char after combustion than 20 wt% filler loading as expected due to higher lignin content. The initial weight loss of 0.6%, 0.8% and 1.44% for 10 wt%, 20 wt% and 40 wt% filler ratio respectively was observed for the sample at about 130^{o}C while the unfilled unsaturated polyester gave 0.02 % loss of weight at the same temperature. The initial mass – loss can be attributed to loss of moisture content at that temperature indicating the higher the filler loading, the higher will be the percentage loss of moisture. This is due to the hydrophilic nature of the filler.

At the onset of degradation, 10 wt%, 20 wt% and 40 wt% ATP/UP composites lost 11.42%, 4.5% and 6.6% of their weight while 99%, 82% and 80% was lost at the decomposition temperature of 400^{o}C, 405^{o}C and 413^{o}C, respectively.

Conclusions

Thermogravimetric analysis of composites prepared from both fillers showed high thermal stability. Literatures have shown that most lignocellusics filler degrades at their processing temperature of below 250^{o}C. Thus, both fillers could be used with thermosets to produce composites that will be of use for outdoor materials and in engineering plastics.

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