

PYROLYSIS TECHNIQUES AS TOOL FOR DETERMINING THERMAL HISTORY OF CABLE INSTALLATION POLYMERS.

Armaya'u usman¹, Zakariyya Uba Zango², Wada Nuraddeen³ and Nasiru Musa Malan⁴
(+2348037866622 armayau.usman@auk.edu.ng, +2347030793012, zakariyyazango@auk.edu.ng,
+2348034487386 wada.nuraddeen@auk.edu.ng, +2348066186585, nasiru.nmalan@auk.edu.ng)

^{1, 2, 4}College of Natural and applied sciences Department of Chemistry Al-Qalam University Katsina.

³College of Natural and applied sciences Department of Biology Al-Qalam University Katsina.

Abstract: A thermal history of polymer used as cable insulations was studied using a system equipped with thermogravimetric analysis, Fourier transform infra-red and finally pyrolysis-gas-chromatographic analysis. Polymers used as insulation materials were obtained; one set was pre-treated at different temperature rates, while the other set was not pre-heated. Both sets were first run under FTIR spectroscopy to detect and analysed the compounds present, TG technique was used to characterise and evaluate their thermal history, Pyrolysis-gas-chromatography was performed to determine their thermal history and the two were compared. Findings indicated that FTIR spectra of the pre-heated samples produced very similar and reproduced spectral peaks different from the non-pre-heated samples. The TG curves obtained provides a clear characteristics decomposition profiles of each pre-heated samples different from the non-pre-heated samples, the thermograms of all the three different heating rates indicate good similarities between the samples as well as their different thermal treatment. The results on the Py-GC showed that it can be relied upon and can be used to determine the thermal history of polymers used as electrical insulations and it was found that the optimal Py-GC conditions is at high temperatures above 400 °C and 600 °C to 700 °C would give an optimum needed results.

Key words: Pyrolysis, Gas-Chromatography (GC), Thermogravimetry (TG), Fourier Transformed Infra-red (FTIR), Polymers.

1.0 INTRODUCTION

A polymer is a large molecules obtained by building up of numerous smaller molecules, these smaller units are joined relatedly in order to form the desired polymer molecule. These large molecules may be simple linear, can still be slightly branched depending on the method of polymerization or even highly interconnected, while the smaller molecules used as the basic building blocks for these molecules are called monomers. [7, 9]

Polymers are seen everywhere, from natural materials like wood or silk to synthetic plastics, fibres and gels. The improvement of methods for the controlled synthesis of polymers is one of the most important technological advances of this century, because it plays an enormously important role in modern society. [8] but the significance of polymers are often taken for granted, but apparently; polymers are fundamental to most aspects of modern life such as communication, building, transportation, clothing, packing and in electricity (modified for different purposes). To these; a good understanding of the structures as well as properties of polymeric materials is very important. The first man-made polymer (Bakelite) was completely made in 1905 and the industry became fully operational after the Second World War, with development in schemes for polymerizing polyethylene and polypropylene as well as in the production of synthetic fibres. Very recently, "speciality polymers" have come into focus, because it is possible to tailor specific properties, as a high strength (in fibre) or electrical conductivity. [8]

Polymers have a richer range of structures, which are being distinguished on the basis of the flow behaviour rather than molecular organization, example rubber, which is a compound with high elastic response and as a plastic material used in all households. PVC (example the ones used in electrical insulation) has a very high hardness and more of mechanical properties as well, this increase with increasing molecular weight and decrease with increase in temperature. [8]

1.2.1 CLASSIFICATIONS OF POLYMERS

Polymers are classified using various numbers of methods; one is by using the way polymers respond to thermal treatment this classified them into thermoplastics and thermosets (considered in this research). Another classification system is based on the nature of the chemical reactions employed in the polymerisation, with the major groups as *condensation* and *addition* polymers. Our research is considering the first classification i.e. thermoplastics and thermosets. [7, 17]

1.2.1.1 THERMOPLASTICS

Thermoplastics are plastics (polymers) that require heat to make them process-able, as they can melt when heated and re-solidified when cooled. After cooling, such materials retain their shape. More over these polymers may be re-heated and reformed, often without significant changes to their properties, they comprises of essentially linear or lightly branched polymer molecules. [17]

1.2.1.2 THERMOSETS

Thermosets' class constitutes a mixture of reactive compounds with low molecular masses which when heated react with each other to transform from a liquid into a solid material due to crosslinking or curing. This class of polymer cannot be melted or recycled in very ordinary simpler way like thermoplastics. Example vulcanised rubber or synthetic elastomers. Not much is going to be discussed here as this class of polymer was not considered in this research. [17,11]

1.2.2 POLYMERS AS ELECTRICAL INSULATORS

Polymers have very low electrical conductivity which was why they are considered greatly as electrical insulators. The presence of any small electrical conductance happened due to the presence of impurities which brings in some minutes charge in the form of electrons or ions. When sufficiently high fields is applied a different processes will happen that would cause a complete breakdown of the polymeric material present there as insulator. For this reason a compounds (mostly referred to additives) are added to the polymeric insulator to protect and prevent the possible occurrence of these breakdowns. [8, 11]

1.2.3 POLYMER ADDITIVES

Polymers mixed along with a variety of additives such as plasticizers, processing lubricants, flame retardants, stabilizers, light and thermal stabilizers, fillers, colorants, processing aids, impact modifiers and biocides are commonly used for commercial purposes. [8, 11] But the specific application or processing requirement will determine the actual formulation. For example, poly vinyl chloride PVC (which is commercially one of the important polymers) is thermally unstable, when PVC is exposed to temperature above 140°C it will start to melt and its melting temperature is 160°C. In order to obtain a flexible and resilient-grade resin of PVC for use in wire insulation, the polymer must be blended with an additives and plasticizers so as to reduce its T_g (Glass transition or kinetic temperature) and to improve its thermal stability at processing temperature. [11]

Plasticisers make up one of the largest segments of the additive market, it is added to a material (plastic) to make the material elastic, flexible and usually easy to work with (mostly used for PVC). [8] Plasticized PVC is one of the most widely used electrical insulation materials today, Its main function is to reduce the modulus of a polymer at the usual temperature which is done by lowering its T_g , and its transition (plasticized polymer) occurs over a wide range of temperatures than for the un-plasticized polymer There are other importance additives in plastics, that are used in addition to plasticizers and fillers. [8, 11]

1.2.4 Thermal properties of polymers

Polymers are used world-wide for different applications depending on the purpose of usage; the polymers are treated extensively to attain a desirable level of properties needed for the purpose. Characterization of properties of polymers for cable insulation wire purposes are of very utter most importance so as to guarantee its constant quality. The PVC has a very poor stability to heat; and melts at a temperature of 160 °C, and a very small linear expansion coefficient. The oxidation index of PVC is about 45, the needs for the addition of heat stabilizers is very necessary to polymers during processing to ensure the desired properties. [8, 11] The classes below present the most important classes;

1.3 THERMAL ANALYSIS

The techniques (thermal analysis) have been in use for characterization of polymer material for many years ago in which the stability of various polymeric and non-polymeric material are being assessed using various methods.[21]The development of thermal methods were done by many scientist workers, it was made necessary to agree on a common definition terms; given by the 'The international Confederation for Thermal Analysis and Calorimetry' (ICTAC); defined thermal Analysis as 'A group of techniques in which a property of the sample is monitored against time or temperature while the temperature of the sample in a specified atmosphere, is programmed. [13]The procedure may necessitate heating or cooling at definite rate of temperature change, or may be at constant temperature or any course of these and the properties chosen should solemnly depend on the area and needs of the specific measurements. When a substance (sample) is heated to certain temperature, its chemical nature as well as its physical state changes, and the stages in these changes can be obtained from the information obtained from the graphical results called 'thermal analysis curve'. [13, 10, 21, 6]The thermal stability is defined as a general term indicating the ability of a substance to maintain its properties as nearly unchanged as possible on heating while taking it from a practical point of view; thermal stability needs to be considered in term of the environment to be imposed on the material and the functions it has to perform. [6]

1.3.1 Thermogravimetry (TG)

The thermal analytical technique of thermogravimetry (TG) is one in which the change in mass (i.e. mass loss or gain) is completely decided by a function of temperature and /or time in a controlled temperature. In the thermogravimetric analysis (TGA), the mass of the sample is continuously recorded as the temperature increases at a constant rate, while the weight losses occur when volatiles absorbed by the polymer are driven off and at higher temperatures when degradation of the polymer occurs with the formation of volatiles products. [10] The resulting mass-change versus temperature curve (thermogram) give information concerning the thermal stability and composition of the initial sample, and for any intermediate compounds that maybe formed, and the composition residue (if any). Measurements in thermogravimetric analysis are primarily employed in the

determination of the composition of materials and to predict their thermal stability at different measurable temperature up to 1000 °C.

1.4.1 Principles of Pyrolysis

The pyrolysis technique is used to thermally decompose samples and the decomposition products (called pyrolyzates) are analysed by gas chromatography. [3] Analytical pyrolysis-GC differs from other thermal techniques in one important way: the temperatures used in carrying out the experiment are intentionally high so as to cause the needed chemical changes in the sample material. It is a specialized sample introduction procedure where by a large molecular sample is continuously heated to very high pyrolysing temperatures of up to 900 °C under non-oxidizing temperature. Large molecular weight samples will breakdown into lower fragment under this conditions and Gas Chromatography is used to get the fingerprint of the molecular samples. The main reason behind pyrolysis, however, is to create smaller, volatile molecules from a larger molecule so that GC is used to study and identify the smaller or macro-molecule with the clear understanding that it is a destructive technique. [4] The reactions that happened in the pyrolysis-GC include dehydration, decarboxylation as well as bond dissociations by forming free radicals with typical reactions and rearrangements of such entities. [4]

1.4.2 Principles of chromatography

Chromatography is an extensive method widely used for the separation, determination and identification of chemical components present in compounded mixtures. [19] It is generally believed that gas chromatography is a premier analytical technique for the separation of volatile compounds, as it joins speed of analysis, resolution and ease of operation, excellent quantitative results and the cost of the machine is moderately affordable. [1]

The effective separation of components in chromatography is on the basis of differences in the rates at which the component mixture are carried along through a stationary phase that is fixed by a gaseous or liquid mobile phase. The chromatography's stationary phase is fixed in place either in a column or in a planar surface, while the chromatography's mobile phase is the one that moves along through the stationary phase taking the analyte mixture through, and it can be a gas, liquid or supercritical fluid. [19] The sample is vaporised and carried by the mobile phase (the carrier gas) through the column. Samples partition (equilibrate) into the stationary liquid phase, based on their solubilities at a given temperature. The components of the samples (usually called solutes or analytes) separates from one another base on their reactive vapour pressures, and affinities for the stationary bed.[1]If the sample to be analysed is non-volatile, then one can call upon the technique of Pyrolysis Gas Chromatography. This is a modification where by a non-volatile sample is pyrolysed under high temperature prior to its entering the column. Decomposition products are separated in the gas chromatographic column after which they are quantitatively determined. [2]When the GC instrument is hyphenated with Pyrolyser (Pyrojector) then the name changes to pyrolysis Gas chromatography (Py-GC). Quantitative analysis by gas chromatography is based on the concept of retention characters of sample compounds. [12] Analytical results are obtained from the pyrogram (a chromatogram obtained resulting from the detection of pyrolysis products). The general fact about the term analytical pyrolysis is "the study of chemical changes that occur to a molecule at high temperatures under vacuum or an inert atmosphere". [4] The volatiles that constitute the GC analysis are compound that are isolated from the matrix and transported to the GC intact and therefore the identification of a particular compound as a peak presented in the chromatogram means that the compound was present in the

sample originally. This can be applied in the thermal sampling and determination of many compounds.[4] The molecular fragmentation caused by pyrolysis and the final products formed and identified, all depends on how strong the bonds found in the molecule is and how the free radicals formed when the bonds dissociate and stabilize to make products. The strength of Py-GC depends greatly on the detection system, and in this research work the flame ionisation detector is used (as its frequently used) because it provide both qualitative information based on the retention time and fingerprints.

This work is aimed to determine the thermal history of cable wires polymers using pre-heated and non-pre-heated samples by employing the techniques of thermogravimetric and pyrolysis-GC analysis.

2.1 MATERIALS AND METHODS

i. POLYMERS;

Insulation cables were collected from the school departmental store and used as samples. While a different plastic materials were randomly collected around the University.

2.2 FOURIER TRANSFORM INFRA-RED (FTIR);

The FTIR instrument used in the experiment is the THERMO Nicolet 450 FTIR-ATR model which is equipped with smart orbit diamond ATR accessory that is convenient in identifying and verifying the sample. The FTIR was conducted on each of the polymer samples and a computerised library search performed. The spectrometer was operated in Absorbance mode running from 5000 to 500 cm^{-1} .

2.4 THERMOGRAVIMETRY (TG);

Thermogravimetric analysis was carried out with the METTLER TCA 15 TA controller instrument and the analysis was obtained in three different temperature conditions

- (1) Programmed from 25 $^{\circ}\text{C}$ (room temperature) to 300 $^{\circ}\text{C}$ (hold to the end of analysis) at 10.00 k/min under Nitrogen at 50 ml/min flow rate.
- (2) Programmed from 25 $^{\circ}\text{C}$ (room temperature) to 500 $^{\circ}\text{C}$ (hold to the end of analysis) at 25.00 k/min under nitrogen at 50 ml/min flow rate.
- (3) Programmed from 25 $^{\circ}\text{C}$ (room temperature) to 500 $^{\circ}\text{C}$ (hold to the end of analysis) at 50 k/min under nitrogen at 200 ml/min flow rate.

2.7 PYROLYSIS-GC;

Solid samples of average of 100 μg polymers were used, they were cut (no any further preparation was carried out on them) and inserted directly into the bore of the pyrolysis solid-injector and then placed on the quartz tube of the furnace Pyrolyser Pyrojector II. The Pyrolyser programmed pressure is 9.00 kPa hold to the end of analysis and was (the Pyrolyser) operated under constant temperatures of 400 $^{\circ}\text{C}$, 550 $^{\circ}\text{C}$, 600 $^{\circ}\text{C}$, and 700 $^{\circ}\text{C}$ on each sample respectively. In carrying out the Pyrolysis-GC the Pyrolyser was connected to a Variant CP-3900 Gas Chromatography equipped with Flame Ionization detector (FID) operated in an electron impact ionization (EI) mode. The GC column is a supelcowaxTM 10 column. The temperature limit of the column is 280 $^{\circ}\text{C}$ but

250 °C was used in performing the experiment and the GC has a CP-1177 split ratio of 20 -1 and the split/splitless injector was 330 °C the purge pressure of the whole experiment is approximately set between 1-2. The GC column temperature is 50 °C carried to the end of the experiment to 250 °C as a GC condition.

3.0 RESULTS AND DISCUSSION

A sample of cable insulation wire of both pre-heated, non-pre-heated and the other selected polymers were thermally analysed using Thermogravimetric analysis TG under 500 °C, and eventually the samples were Pyrolysed at 400 °C, 500 °C, 550 °C, 600 °C and 700 °C respectively to know if the thermal analysis as well as Pyrolysis-GC can be used to determine the thermal history of polymers used as electrical insulation. But after carrying out multiple Py-GC analysis under the different temperatures mentioned above, two temperatures (600 °C and 700 °C) were found to be suitable for these kind of analysis and therefore they are considered in reporting the analysis. Other analysis such as Fourier transform infra-red spectroscopy (FTIR) was carried out apart from the already mentioned above. The results of the analytical experiments were summarised in the respective order of how they were performed below. Due to the large number of analysis carried out only a few selected graphs and curve results were used and a general summary of all the results were tabulated during discussions.

3.1 FOURIER TRANSFORM INFRA-RED (FTIR);

The main differences resulting from comparing the spectra were presented in Figure 1. The FTIR spectra show the pre-heated samples producing almost very similar and reproducible spectral peaks in their absorption bands in all the five different temperature-heated cables, the appearance of the peaks only differs in intensity which is attributed to the differences in temperature at which the samples are heated. FTIR (figure 1) stacked shows gradual appearances of peaks from the pre-heated sample of 100°C to 250°C with an increase appearance being most pronounced at 6th peak in sample heated at 300 °C from 2920.9 to 2922.3 cm⁻¹. The spectra bands obtained indicate the effects of heating at different temperature rates on the pre-treated samples, as the heating temperature is increased, the peak intensity is increased. The appearance of the peaks shows that basically the same micro-structure is present in all the samples. But on the other hand, the spectrum of the non-pre-heated sample shows a different structural band as shown in (figure 1 with non-pre-heated sample 23) indicating a non-distracted microstructure as it was not pre-heated. The IR-Spectral Interpretation results showed that there are methyl group (CH₃) asymmetric deformation vibration that occurs at 1470-1440cm⁻¹ which overlapped (the band) with the CH₂ scissors vibration that occurs at 1490-1440 cm⁻¹, and a sulphur compound was indicated to be present in the compound.

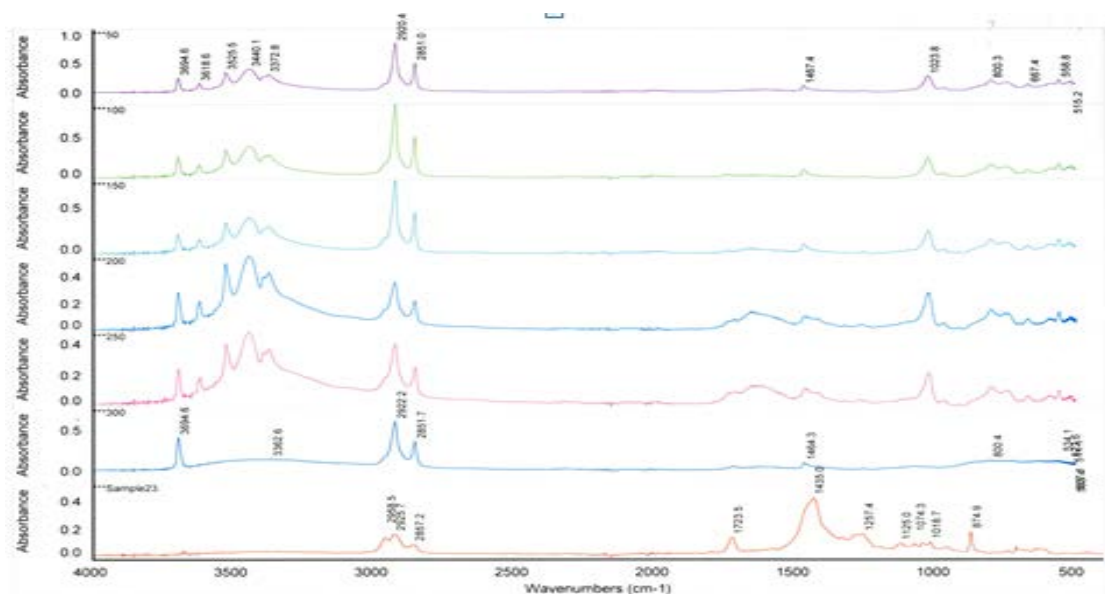


FIGURE 1; FTIR stacked spectrum of pre-heated and non-pre-heated samples

3.3 THERMOGRAVIMETRIC ANALYSIS (TG);

The TG analyses of all the polymer samples were recorded under dynamic conditions from room temperature (25⁰C) to 500⁰C at a different heating rate of 10 K/min, 25 K/min, and 50 K/min under nitrogen atmosphere. The representations of thermometric curves are presented in TG tables 2, 3 and 4 and the figures 2 and 3. The thermogram clearly displayed the thermal degradation of the different pre-heated samples showing practically an identical behaviour which indicates a high degree of characteristic similarities between them, even though they were pre-heated under different temperatures and under different reaction times. The thermogravimetric curves obtained clearly provide the characteristics decomposition profiles of each pre-heated sample when compared with the non-pre-heated sample, the difference starts from the onset of the weight loss which often defines the upper limit the polymer sample can attain in term of thermal stability. The TG data obtained for non-pre-heated samples clearly shows a major one-stage weight loss in all the three different heating rates of 10K/min, 25K/min and 50K/min with a mass loss of 46.2 %, 43.1 % and 27.1 % both of which falls in temperature around 160-330⁰C respectively and a second stage (minor or shorter stage) weight loss of 6.9 %, 5.9 %, and 3.3 % both within a temperature range of 440-500 ⁰C respectively. The thermograms of all the three different heating rates indicates a good similarities between the samples which proves that the samples are from the same macro molecules, with all of the three samples having two weight loss steps; the first is caused by the separation of moisture then secondly, the pyrolysis step from where the weight loss starts.

On the pre-heated samples, it is apparently clear that there is a difference in pattern between the two thermograms (pre-heated and non-pre-heated samples), the pre-heated thermogram appears to have an undefined pattern of two to three weight loss stages, but for the purposes of this research, emphasis was given on the two major stages to give a clear view of the changes that occurred due to pre-heating which makes the molecules in the polymer samples to be distorted and to have different molecular properties with the non-pre-heated polymer samples. Weight loss that occurred in all the pre-heated samples happened in the last stages unlike the non-pre-heated samples that occurred at the early stages.

Table 2; TG THERMOGRAMS CHARACTERISTICS ON PRE-HEATED SAMPLES AT 10 K/min

Heated at 10K/min	1 st Weight loss (%)	Temperature (°C)	2 nd Weight loss (%)	Temperature (°C)
250 ⁰ C	-9.0	390.5-350.0	-33.8	400.0-480.5
200 ⁰ C	-4.1	150.0-340.0	-40.4	370.0-480.5
150 ⁰ C	-8.6	240.0-340.0	-27.8	410.5-490.0
100 ⁰ C	-7.7	140.5-360.0	-16.1	440.5-490.0
50 ⁰ C	-7.6	270.0-350.0	-30.5	430.0-490.0

Table 3: TG THERMOGRAMS CHARACTERISTICS ON PRE-HEATED SAMPLES AT 25 K/min

Heated at 25K/min	1 st Weight loss (%)	Temperature (°C)	2 nd Weight loss (%)	Temperature (°C)
250 ⁰ C	-12.6	170.5-370.5	-29.5	390.0-500.0
200 ⁰ C	15.5	160.0-400.0	-30.3	420.0-500.0
150 ⁰ C	-19.2	150.5-420.5	-37.4	430.5-500.0
100 ⁰ C	-14.4	120.5-360.5	-33.0	400.0-490.5
50 ⁰ C	-11.0	100.0-310.0	-32.0	410.0-500.0

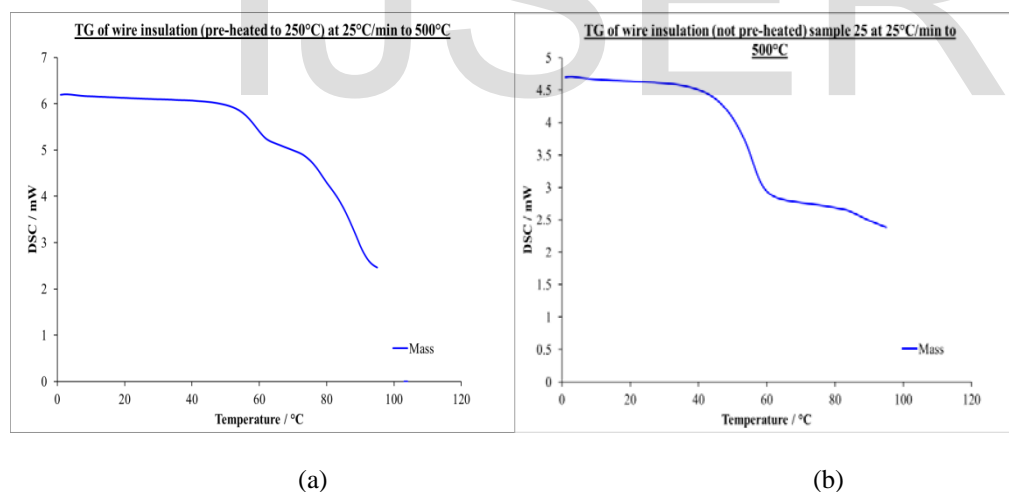
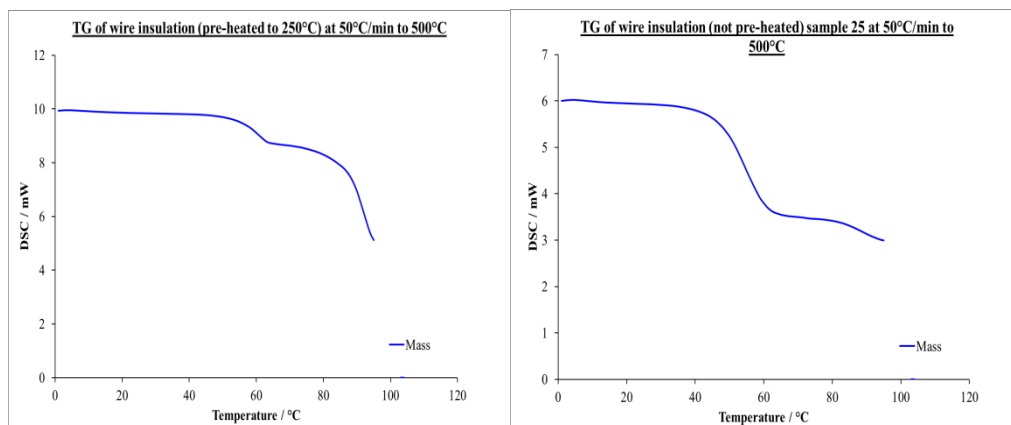


Figure 2:TG graph of (a) pre-heated and (b) non-pre-heated at 25 K/min to 500 °C

Table 4; TG THERMOGRAMS CHARACTERISTICS ON PRE-HEATED SAMPLES AT 50 K/min

Heated at 50K/min	1 st Weight loss (%)	Temperature (°C)	2 nd Weight loss (%)	Temperature (°C)
250 ⁰ C	-9.3	170.0-380.5	-27.2	410-500
200 ⁰ C	-9.9	150.0-360.5	-28.7	390.0-490.0

150 ⁰ C	-10.3	90.0-350.5	-30.5	370.5490.5
100 ⁰ C	-11.3	170.5-360.0	-30.4	370.0-490.0
	-9.1	130.0-360.0	-25.4	390.0-490



(a)

(b)

Figure 3: TG graph of (a) pre-heated and (b) non-pre-heated at 50 K/min to 500 ⁰C

In all the five pre-heated samples the thermal degradation clearly indicated by the thermograms (figure. 2) showed a basically identical behaviour, illustrating the high degree of similarity between them and indicating a great difference between the thermogram patterns obtained from the non-pre-heated (figure 3) and the one obtained in the pre-heated samples, which revealed the thermal effects the insulation cable have on pre-heating it before undergoing the TG analysis.

3.4 PYROLYSIS-GC

The five different pre-heated samples were analysed by pyrolysis-GC under different temperature ranges of 600 ⁰C and 700 ⁰C (three runs on each samples) and the pyrograms were stacked to observed the differences in the pattern of the fingerprints. Generally the fingerprints (pyrograms) presented as the patterns of each injection obtained showed a very distinct characteristic properties proving the samples to be from the same macro molecules for both the pre-heated, non-pre-heated and the other polymers used in the analysis. However, there were some samples which differ slightly.

3.4.1 PRE-HEATED SAMPLES AT 600 ⁰C

Taken individually, in the pre-heated 50 ⁰C patterns of the pyrogram, two out of the three runs were literally the same; they only differ with the third (bottom) pyrogram in response (figure 4a and 4b) and when compared between the different pyrolysis temperatures. The pyrograms below (pre-heated 50 ⁰C and non-pre-heated all at 600 ⁰C) present a clear difference when the same original sample (one with pre-heating treatment and one without undergoing any pre-heating treatment) undergoes analysis under the same pyrojector temperature of 600 ⁰C. Here the fingerprint pattern obtain are completely different, but there is a rise in the baseline that occur in

around 7 minutes retention time in both the two samples in all the injections, this indicates the origin of the samples to be from the same macro-molecules but the thermal history differentiates them all.

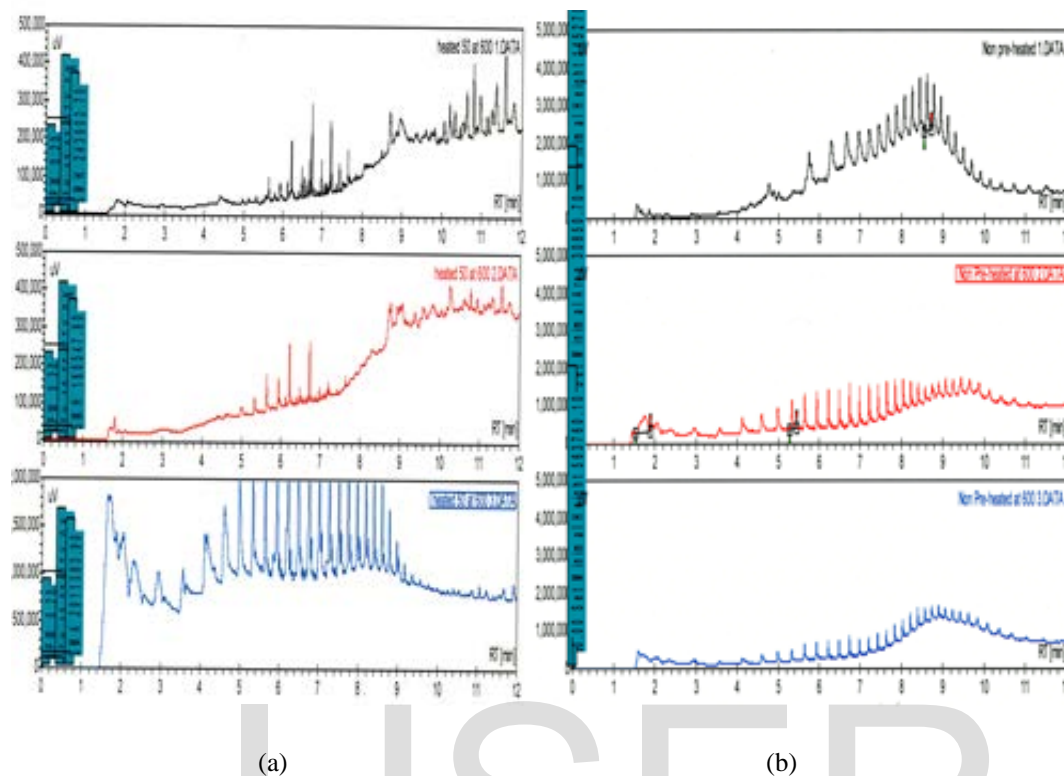
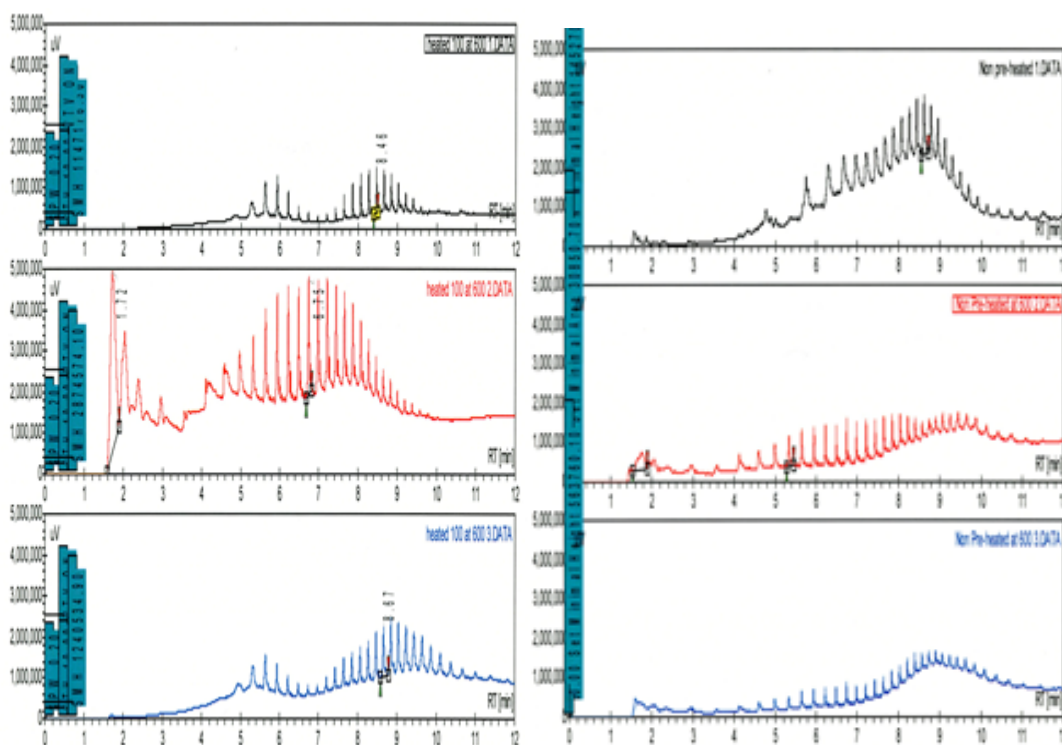


Figure 4a and 4b: Stacked pyrograms of pre-heated 50 °C and Non-pre-heated samples pyrolysed at 600 °C at three different injections each.

Pre-heated sample at 100 °C shows two identical pyrograms too (first and third fingerprints) with both having the highest peak at the retention time of 8.46 and 8.67, while the second pyrogram has a highest peak at the retention time of 1.72 responses and a rise in a baseline. When compared with the non-pre-heated sample the two samples differs a lot in their fingerprint's pattern, but on o closer look; the non-pre-heated pattern is a minor pattern of the pre-heated as the peaks appears in a very shorter pattern as in the middle injection of the pre-heated, which is the indications of the sample being the same but the molecular structure is distorted by thermal treatment it undergoes.



(a)

(b)

Figure 5a and 5b: Stacked pyrograms of pre-heated 100 °C and Non-pre-heated samples pyrolysed at 600 °C at three different injections each.

The fingerprints obtained by pyrolysis of pre-heated sample at 150 °C are identical in all the injections only the baseline in the first pyrogram shows a highest response at a retention time of 1.60 and peaks shown was higher than the ones in the first and third, the fingerprint's pattern obtained on the non-pre-heated sample shows a higher peak compared to the second and third pyrogram of both and an initial response peak appears which was not pronounced in the pre-heated sample at the retention time of 1.60.

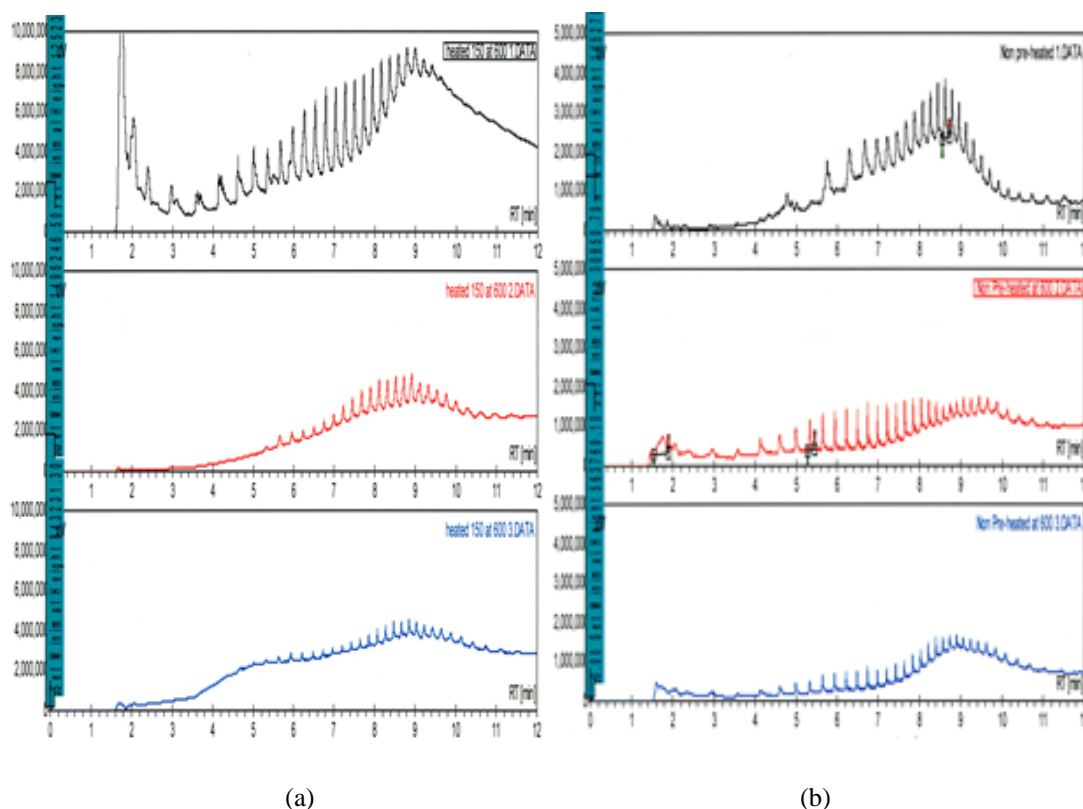


Figure 6a and 6b: Stacked pyrograms of pre-heated 150 °C and Non-pre-heated samples pyrolysed at 600 °C at three different injections each.

Pre-heated sample at 200 °C shows very identical patterns in all the three pyrograms when compared, only that the peaks are higher in the first, with the highest peak at a retention time at 8.2, followed by second injection which loses some peaks towards the end, the highest peak appear at a retention time of 8.2 (the same range with first injection) while some of the peaks in the last pyrogram were missing in the initial stages and appearing clearly towards the end, between 9 to 10 minutes retention time.

Pre-heated sample at 250 °C shows a clear identical pyrograms in all the three injections too, even though the response are reducing from the first to the last injection which makes the last injection to appear more smaller in peaks than the rest. Pyrograms below shows an effect of thermal pre-treatment of two samples treated under the same pyrojector temperatures. It can be seen clearly that the response in pre-heated 200 °C pyrogram is 5 million while in 250 °C is 4 million.

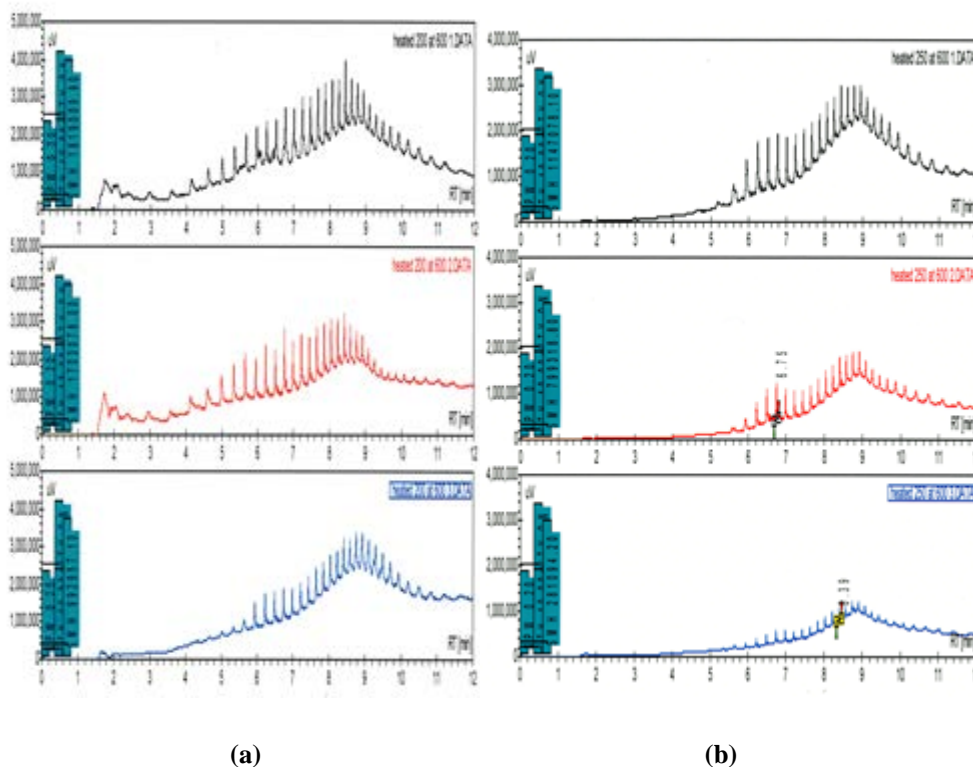


Figure 7a and 7b:Pyrograms of pre-heated samples 200 °C and 250 °C pyrolysed at 600 °C

3.4.2 PRE-HEATED SAMPLES AT 700 °C

Due to the large number of analysis carried out some pyrograms are specifically chosen and presented here. Pre-heated sample at 50 °C; two pyrograms (second and third) shows a very identical fingerprints only differs in the peak response; the response in peak is high in the third injection than the second. The baseline in the first injection appears high which makes it different from the rest. The fingerprints pattern obtained in the pre-heated 50 °C sample differs more when compare with non-pre-heated sample at 700 °C heating rate, which explain the effect the sample have on thermal treatment as shown in the figures below;

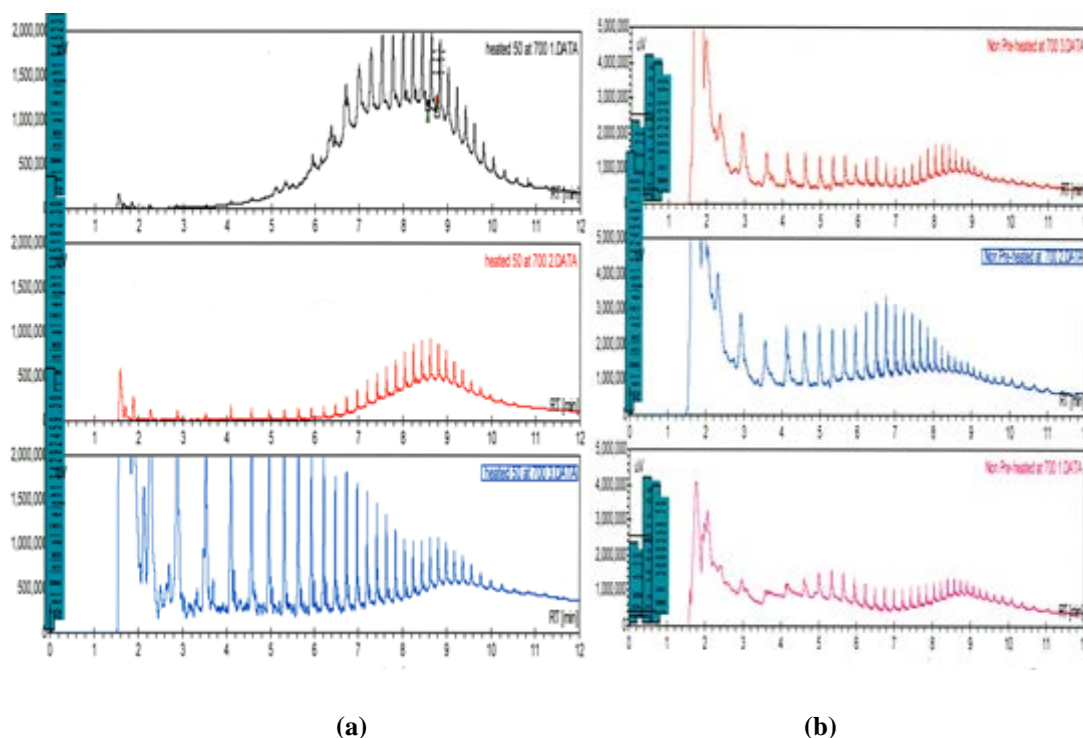


Figure 8a and 8b: Stacked Pyrograms of pre-heated samples 50 °C and non-pre-heated pyrolysed (both) at 700 °C

Pre-heated sample at 100 °C; the pyrograms in these analysis show more apparently identical fingerprints, with an upward surge of the baseline appearing in the 1st peak of all the three injections and a hill-high appearing at a retention time of 7 minutes in all the pyrograms. The response here does not have much effect on the fingerprints, while the pyrograms on the side of the non-pre-heated samples were all clearly identical in all the three injections and a clear different pattern with the pre-heated sample.

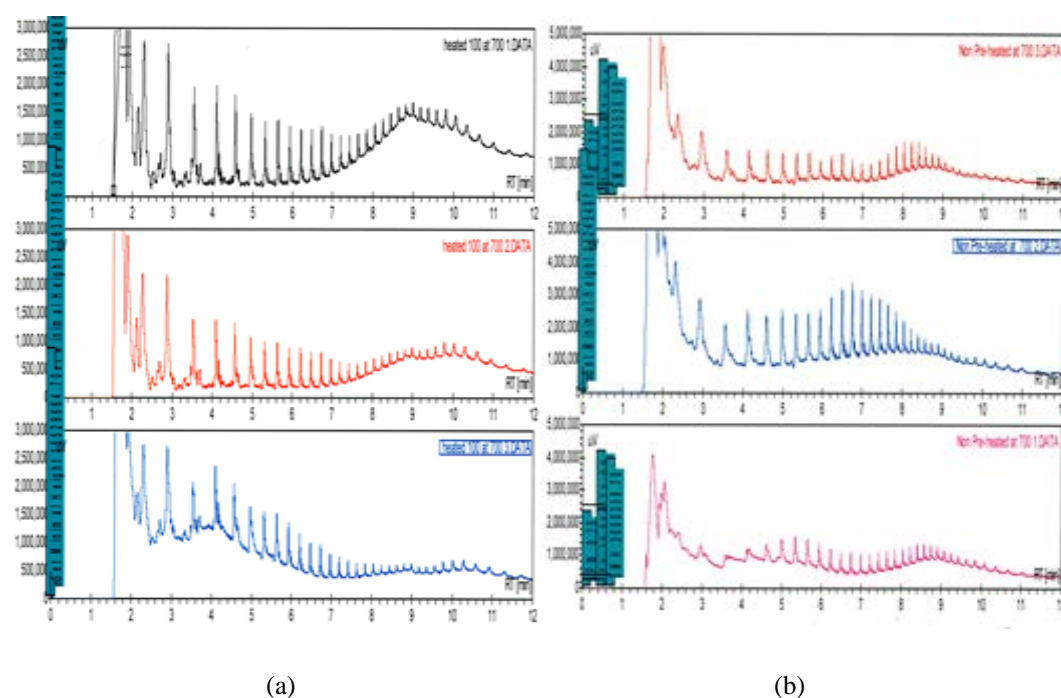


Figure 9b and 9b: Stacked Pyrograms of pre-heated samples 100 °C and non-pre-heated pyrolysed (both) at 700 °C.

Pre-heated sample at 150 °C; as expected the fingerprints obtained are very identical structurally, these appeared broadly clear in the first and second injections but the third injection can only be ascertain when observed closely because of the response nature of the baseline that made the peaks so height which makes it difficult to differentiate at a glance. In the pre-heated sample at 200 °C; the second and third injections shows very clear identical fingerprints, the first injection can be said to be familiar in all the peaks but only the baseline pattern that went up high, and the peaks around 3 minutes that appears to be two, which are one in the rest of second and third.

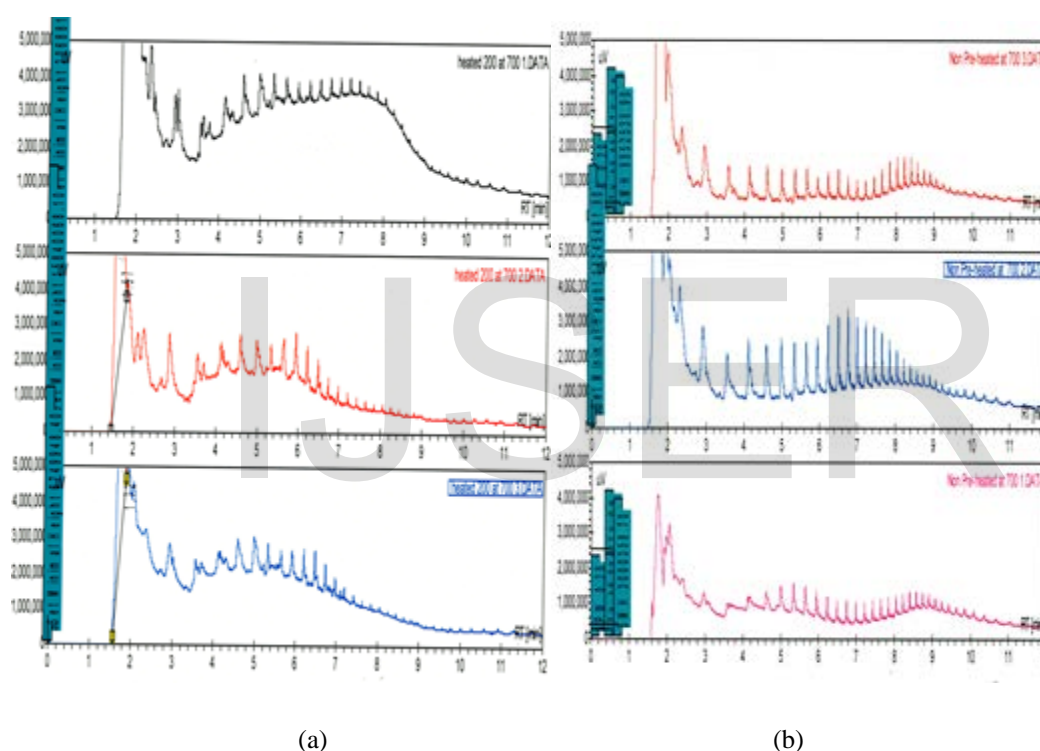


Figure 10a and 10b: Stacked Pyrograms of pre-heated samples 200 °C and non-pre-heated pyrolysed (both) at 700 °C.

Pre-heated sample at 250 °C; the pattern of the pyrograms appear to be similar but the appearance of peak height differs and the baseline appear to be high in the second injection.

3.4.3 NON-PRE-HEATED SAMPLES AT 600 °C AND 700 °C

The analysis of non-pre-heated samples pyrolysed at 600 °C and 700 °C showed a different pyrograms pattern with the rest of the pre-heated samples (as stated earlier), only that when looked at a glance it may be assume as it resemble some of the fingerprints in the pre-heated samples but on a closer look it appear to be different fingerprints entirely, this is so because the samples are initially from the same parent molecules. Moreover the

non-treated pyrolysed samples at 600 °C and 700 °C greatly differ when they are compared between, this is due to the change in the thermal temperature.

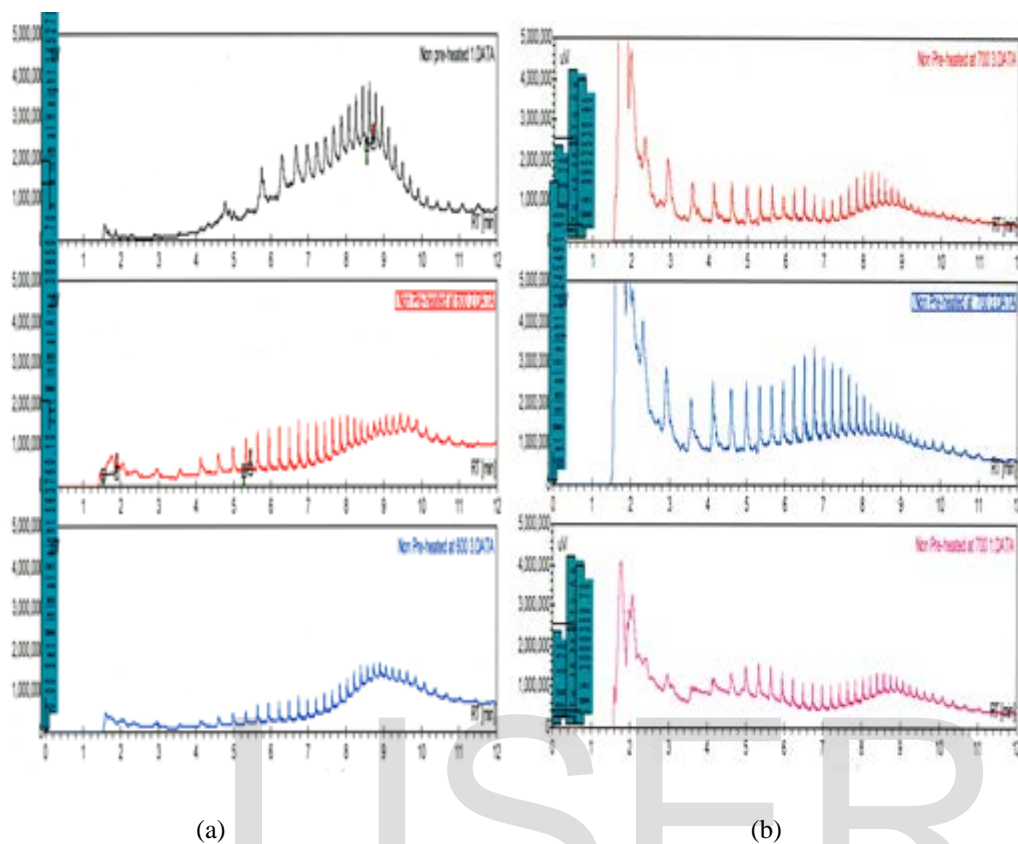


Figure 11a and 11b: Stacked Pyrograms of non-pre-heated samples, pyrolysed at 600 °C and 700 °C respectively.

3.4.4 OTHER POLYMERS

Four out of twenty four other polymers (randomly selected polymers around the University environment) were pyrolysed three times each (as done to the treated and non-treated samples) and their fingerprints analysed (the general pyrograms are in the last pages of the project) the results showed that the pyrojector used is reliable as the fingerprints (three resulting injections pyrograms) were reproduced identically in all the four randomly selected samples, as shown in figures 41a and 41b below;

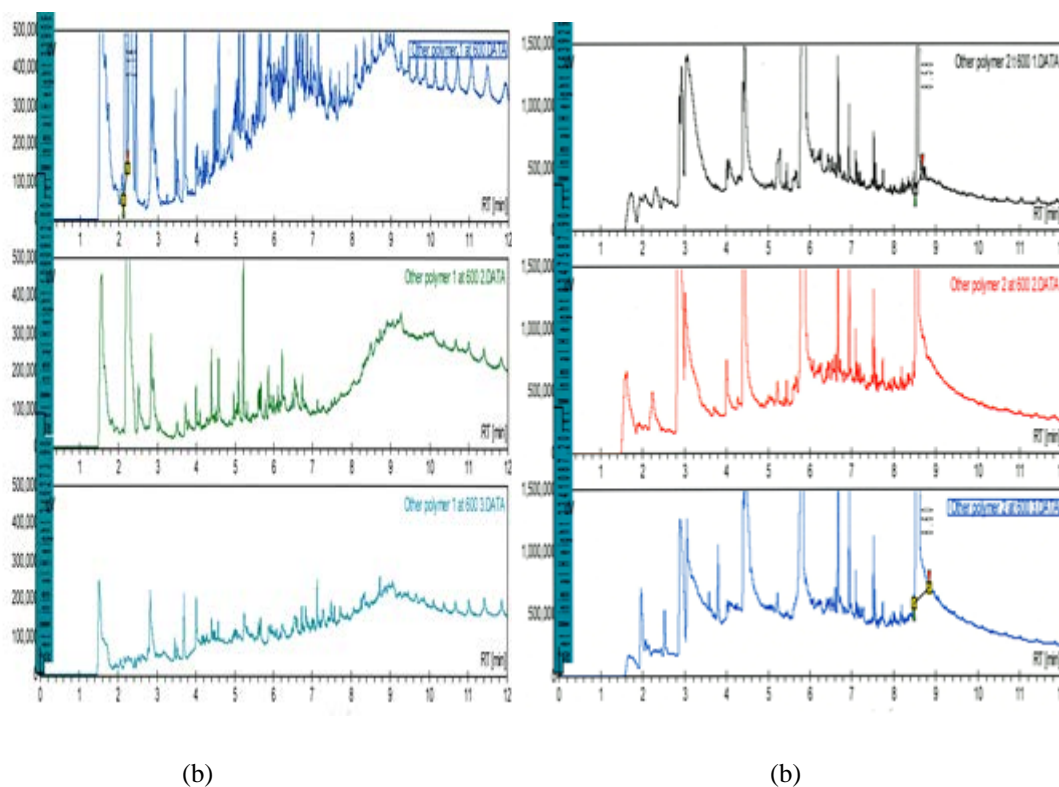


Figure 12a and 12b: Stacked Pyrograms of other polymer samples, non-pre-heated pyrolysed at 600°C.

4.0 CONCLUSIONS

Pyrolysis-gas chromatography (Py-GC), thermogravimetric TG and some other methods can be used to study the thermal history of cable insulation wire. Initial FTIR analysis shows that the insulation cable properties were affected by pre-heating the sample because the peak appearances between the wavenumbers 4000 to 3000 (cm^{-1}) of the pre-heated samples were absent in the non-pre-heated sample and on the decreasing wavenumbers the peaks in the non-pre-heated samples starts to appear which are not as much in the pre-heated samples. Subsequent analysis by TG shows that the thermograms on TG has a two steps weight loss, with an average major weight loss between the temperatures of 120 °C to 370 °C of the non-pre-heated sample and on the pre-heated sample the major weight loss between 370 °C to 500 °C and a TG graphs plotted on TG curve and the temperature plotted against time and the TG curve plotted against temperature for both the pre-heated and non-pre-heated results obtained from the thermograms point out the difference between the thermally treated samples and non-treated samples.

Pyrolysis-GC analysis performed shows the pyrograms of each injection to be of identical patterns in the set of three injections producing a clear thermal history of each of the polymer samples. The results on the Py-GC showed that the Py-GC pyrojector can be relied upon and can be used to determine the thermal history of polymers used as electrical insulations because it simply and physically differentiates the samples that are pre-treated (thermally) with those ones that are not pre-treated as indicated by the pyrograms patterns obtained. And the pyrogram's patterns from each of the three resulting injections were mostly reproduced identically and easily interpreted in the entire analysis taken. In the analysis it was found out that the optimal pyrolysis-gc conditions (for best result) would be at high temperatures above 400 °C. And for moderate results a temperatures of 500 °C

to 550 °C will be considered suitable and 600 °C to 700 °C would give an optimum needed results. These were identified following an extensive analysis at different temperatures (from 400 °C up to 800 °C). Because at lower temperatures the polymers tend to melt (instead of evaporate) blocking the glass tube in the quartz furnace causing an uncharacteristic fingerprints (pattern of the pyrograms) that are not the actual characteristic of the concerned polymer. And at higher temperatures the polymer samples tends to burn out, but at temperatures 600 °C to 700 °C the pyrograms shows the best characteristics of the polymer sample.

ACKNOWLEDGEMENT

We wish to acknowledge the contributions of Dr. Gareth Parkes, Post graduate course Leader in the Department of Chemical and Biological Sciences, University of Huddersfield, United Kingdom, Dr. Abdulkadir Sani Maisanda of Kano state University of Science and Technology, Nigeria and Dr. Muhammad Saleh Salga of Umaru Musa Yar'adua University, Katsina, Nigeria. We are also grateful to the department of chemistry of Al-Qalam University Katsina, Nigeria for supporting this research.

REFERENCES

1. McNair, H.M. & Miller, J.M. 2009, *Basic gas chromatography*, John Wiley & Sons, Inc, Hoboken, NJ.
2. Wendlandt, W.W. 1964, *Thermal methods of analysis*, Interscience, New York.
3. Poole, C.F. 2012, *Gas chromatography*, Elsevier, Oxford.
4. "Nomenclature and terminology for analytical pyrolysis", 1995, *Journal of Analytical and Applied Pyrolysis*, vol. 31, pp. 251-256
5. Wendlandt, W.W. 1986, *Thermal analysis*, Wiley, Chichester.
6. Nicholson, J.W. 2012, *The chemistry of polymers*, RSC, Cambridge.
7. Hamley, I.W. 2000, *Introduction to soft matter: polymers, colloids, amphiphiles and liquid crystals*, Wiley, Chichester.
8. Stuart, B. 2002, *Polymer analysis*, John Wiley, Chichester.
9. Campbell, D., Pethrick, R.A. & White, J.R. 2000, *Polymer characterization: physical techniques*, Stanley Thornes, Cheltenham.
10. Fried, K.J. 1995, *Polymer science and technology*.
11. Dressler, M. 1986, *Selective gas chromatographic detectors*, Elsevier, Amsterdam.
12. Wang, F.C. 1999, "Polymer analysis by Pyrolysis Gas Chromatography", *journal of Chromatography A*. vol. 843, no. 4, pp. 413-423.
13. Haines, P.J. 1995, *Thermal methods of analysis: principles, applications and problems*, Blackie Academic & Professional, London.
14. Dodd, J.W., Tonge, K.H., Currell, B.R. & ACOL 1987, *Thermal methods: analytical chemistry by open learning*, Published on behalf of ACOL by Wiley, Chichester.
15. Morris, A.L., T 1996, "Comments on the interpretation of differential scanning calorimetry results for thermoelastic martensitic transformations: Athermal versus thermally activated kinetics", *Scripta Materialia*, vol. 34, no. 9, pp. 1361-1363
16. Challa, G. 1993, *Polymer chemistry: an introduction*, Ellis Horwood, New York.

17. Calvert, R. 2007, "Applied pyrolysis handbook: by Thomas P. Wampler (ed): CRC Press, Taylor and Francis, Boca Raton, FL, USA, 2006, ISBN: 978-1-5744-4641-8, p 304, Price: USD 159.95, GBP 92.00", *Chromatographia*, vol. 66, no. 9, pp. 827-827.
18. Skoog, D.A., West, D.M., Holler, F.J. & Crouch, S.R. 2014, *Fundamentals of analytical chemistry*, Brooks/Cole, Australia.
19. Challinor, J.M. 1996, "Characterisation of wood extractives by pyrolysis-gas chromatography/mass spectrometry of quaternary ammonium hydroxide extracts", *Journal of Analytical and Applied Pyrolysis*, vol. 37, no. 1, pp. 1-13.
21. Zaharescu, T. 2000, "New assessment in thermal degradation of polymers", *Polymer Testing*, vol. 20, no. 1, pp. 3-6
22. Milczarek, J.M. & Zięba-Palus, J. 2009, "Examination of spray paints on plasters by the use of pyrolysis-gas chromatography/mass spectrometry for forensic purposes", *Journal of Analytical and Applied Pyrolysis*, vol. 86, no. 2, pp. 252-259.
23. Zieba-Palus, J., Zadora, G., Milczarek, J.M. & Kościelniak, P. 2008, "Pyrolysis-gas chromatography/mass spectrometry analysis as a useful tool in forensic examination of automotive paint traces", *Journal of chromatography. A*, vol. 1179, no. 1, pp. 41-46..
24. Zieba-Palus, J., Zadora, G. & Milczarek, J.M. 2008, "Differentiation and evaluation of evidence value of styrene acrylic urethane topcoat car paints analysed by pyrolysis-gas chromatography", *Journal of chromatography. A*, vol. 1179, no. 1, pp. 47-58.
25. Usami, T., Itoh, T., Ohtani, H. & Tsuge, S. 1990, "Structural study of polyacrylonitrile fibers during oxidative thermal degradation by pyrolysis-gas chromatography, solid-state carbon-13 NMR, and Fourier-transform infrared spectroscopy", *Macromolecules*, vol. 23, no. 9, pp. 2460-2465.
26. Mao, S., Ohtani, H. & Tsuge, S. 1995, "Compositional analysis of multicomponent acrylic resins by pyrolysis-capillary gas chromatography", *Journal of Analytical and Applied Pyrolysis*, vol. 33, pp. 181-194.
27. Wang, F.C. & Smith, P.B. 1997, "Composition and Microstructure Analysis of Chlorinated Polyethylene by Pyrolysis Gas Chromatography and Pyrolysis Gas Chromatography/Mass Spectrometry", *Analytical Chemistry*, vol. 69, no. 4, pp. 618-622.
28. Calvert, R. 2007, "Applied pyrolysis handbook: by Thomas P. Wampler (ed): CRC Press, Taylor and Francis, Boca Raton, FL, USA, 2006, ISBN: 978-1-5744-4641-8, p 304, *Chromatographia*, vol. 66, no. 9, pp. 827-827.
29. Peter Kusch 2013, "Identification of Organic Additives in Nitrile Rubber Materials by Pyrolysis-GC-MS", *LC GC North America*, vol. 31, no. 3, pp. 248.
30. White, D.M., Garland, D.S., Beyer, L. & Yoshikawa, K. 2004, "Pyrolysis-GC/MS fingerprinting of environmental samples", *Journal of Analytical and Applied Pyrolysis*, vol. 71, no. 1, pp. 107-118.

31. Wang, F.C. 1999, "Composition and Microstructure Determination of a Latex System by Pyrolysis Gas Chromatography", *Analytical Chemistry*, vol. 71, no. 20, pp. 4776-4780.
32. Wang, F.C. & Burleson, A.D. 1999, "The development of pyrolysis-fast gas chromatography for analysis of synthetic polymers", *Journal of Chromatography A*, vol. 833, no. 1, pp. 111-119.
33. Project advises from my supervisor (Gareth. P)
34. "PANalytical provides new standards for XRF analysis of polymer additives", 2006, *Additives for Polymers*, vol. 2006, no. 9, pp. 10-10.
35. Nakano, K., Nishi, C., Otsuki, K., Nishiwaki, Y. & Tsuji, K. 2011, "Depth elemental imaging of forensic samples by confocal micro-XRF method", *Analytical chemistry*, vol. 83, no. 9, pp. 3477.
36. Badawy, S.M., Sokker, H.H. & Dessouki, A.M. 2006, "Chelating polymer granules prepared by radiation-induced homopolymerization. II. Characterizations", *Journal of Applied Polymer Science*, vol. 99, no. 3, pp. 1180-1187.
37. Schenker, B., Widmann, G. & Riesen, R. 1997, "Wave shapes in alternating DSC", *JOURNAL OF THERMAL ANALYSIS*, vol. 49, no. 2, pp. 1097-1104.
38. Y. H Roos, 2010 Glass Transition Temperature and its Relevance in Food Processing. Annual Review of Food Science and Technology, 1469496
39. Rial-Otero, R., Galesio, M., Capelo, J. & Simal-Gandara, J. 2009, "A Review of Synthetic Polymer Characterization by Pyrolysis-GC-MS", *CHROMATOGRAPHIA*, vol. 70, no. 3-4, pp. 339-348.
40. Ishida, Y., Kawaguchi, S., Ito, Y., Tsuge, S. & Ohtani, H. 1997, "Characterization of copolymer type polycarbonates by reactive pyrolysis gas chromatography in the presence of organic alkali", *Journal of analytical and applied pyrolysis*, vol. 40-1, pp. 321-329.