The Recycling of Polyacrylonitrile waste filter bag blended with Polyethylene Terephthalate (PET) for structural applications

By

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Submitted in fulfilment of the requirements of the

DOCTORAL DEGREE IN TECHNOLOGY

Mechanical Engineering

In the

DEPARTMENT OF MECHANICAL, MECHATRONICS AND

INDUSTRIAL ENGINEERING

Tshwane University of Technology

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Co-Supervisor: Prof. Suprakas Sinha Ray

OCTOBER 2016
DECLARATION BY CANDIDATE

“I hereby declare that this dissertation submitted for D. Tech: Engineering: Mechanical Engineering, at the Tshwane University of Technology, is my own original work and has not previously been submitted to any other higher institution. I further declare that all sources cited or quoted are indicated and acknowledged appropriately by means of a comprehensive list of referencing”.

......................................................

Adegbola Taoreed Adesola
DEDICATION

This study is dedicated to God Almighty, the giver of wisdom, knowledge and understanding who has never left me behind.
ACKNOWLEDGEMENTS

I would like to gratefully acknowledge the support, encouragement, invaluable advice and innumerable guidance provided by my supervisors, Prof. Rotimi Sadiku and Prof. Suprakas Sinha Ray, throughout my study. They have also enlightened my personal development and professional growth.

I also wish to express my thanks to the DST-CSIR National Centre for Nanostructured Materials staff at the CSIR for their help during daily experiments and equipment set up. I wish to acknowledge Dr. Saliou Diouf and Dr. Olayinka Durowoju from the Department of Metallurgy, Tshwane University of Technology, for the X-ray diffraction analysis and Origin software application for the study.

I wish to acknowledge my close friends and family, Dr. William Kupolati, Dr. Muyiwa Ojo, Rev. Amos Adeniyi, Dr. (Mrs). Oluranti Agboola-Sadiku, Dr. Steven C. Agwunhca and Mr. Albert Olatunde Oloruntoba for their support and contribution.

I further wish to acknowledge the Department of Metallurgical and Materials Engineering of the Tshwane University of Technology for their support.

Finally, my sincere gratitude is given to my parents for their prayers, embrace, love and support throughout my life, especially my father, Mr. Suleiman Adegbola for his support and invaluable academic advice and my wife, Ms. Arinola Basirat Olaonipekun for her patience and understanding. Finally, a special thank you to my son, Master Tameem Adegbola for introducing different characters into my typing during the write-up of the thesis.
### NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Meaning</th>
<th>Units</th>
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<tbody>
<tr>
<td>$rms$</td>
<td>Root mean square (for surface roughness)</td>
<td>nm</td>
</tr>
<tr>
<td>P</td>
<td>Applied pressure</td>
<td>Bar and Pa</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
<td>$kg/m^3$</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td>$K$</td>
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**ABBREVIATIONS**

<table>
<thead>
<tr>
<th>ABBREVIATION</th>
<th>MEANING</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>ATR-FTIR</td>
<td>Attenuated total reflection-Fourier transform infrared</td>
</tr>
<tr>
<td>IC-AFM</td>
<td>Intermittent contact mode atomic force microscopy</td>
</tr>
<tr>
<td>SPM</td>
<td>Scanning probe microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal gravimetric analysis</td>
</tr>
<tr>
<td>PSD</td>
<td>Power spectral density</td>
</tr>
<tr>
<td>a.u.</td>
<td>Arbitrary unit</td>
</tr>
<tr>
<td>PAN</td>
<td>Polyacrylonitrile</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>POM</td>
<td>Polarized optical microscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray diffraction</td>
</tr>
<tr>
<td>rPAN</td>
<td>Recycled polyacrylonitrile</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene terephthalate</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
</tbody>
</table>
**ABSTRACT**

PAN has found a number of applications, mainly in material safety and other areas, such as textile industries, consumer goods and filtration plants. Moreover, with improved materials processing technologies, various methods of production are now being explored for the development of PAN products. The rise in the usage of PAN fiber constitutes environmental concerns and recycling is one possibility worth exploring. Recycling of PAN can be limited due to its high processing temperature despite the good properties, such as thermal stability and high mechanical strength. This can result in low flexibility, thermally unstable product and prone to loss molecular weight due to degradation during the melting process.

In this work, rPAN was used and blends of rPAN/PET was produced to improve the tensile modulus and impact strength of the rPAN. On the other hand, rPAN and PET are thermodynamically immiscible unlike most polymer blends, therefore, their blends usually result in phase separation morphology. This phase-separation usually results into poor adhesion of the blends compared to the neat materials. The interaction between the blends at nano-level was, therefore, influenced by the surface area to volume ratio of the fibers. The influence on the interaction of varying PET ratio in rPAN led to certain improved properties, such as; modulus and tensile strength. But a high proportion of PET also led to samples brittleness. In addition, PET slightly reduced the processing temperature of rPAN thereby increasing its possible recycling process. This also paves the way for possible applications of the blend instead of disposing of valuable material as a waste. Blends of different ratios were prepared via twin screw extrusion process. Fourier-transformation infrared (FTIR) spectroscopic measurement showed the lack of a chemical interaction between the two polymers, leading to a phase-separated morphology, as shown through SEM. The interfacial area between the two
blends at different ratios and the composition were affected by the thermal stability and mechanical properties.

Tensile test, impact test, thermal analysis and micro-structural characterizations, using: DSC, DMA, TGA, XRD, AFM, TEM and SEM were carried on rPAN, neat PET and their blends. The XRD result revealed changes in the crystal structure and phase changes as the ratio of rPAN and PET in the blended samples was varied. TGA and DSC were used to study the weight changes in materials with the effect of temperature and material crystal behaviour respectively.

Furthermore, AFM was used to study the samples surface roughness, pore formation, pore size, nearest neighbour distance analysis, perimeter, volume, bearing plot, spatial and fractal information. The findings of AFM revealed that pore formation in the samples is related to the blend ratios.

Finally, it was also observed that the addition of 70% rPAN reduced the pore formation and increased the gap of the nearest neighbour distance while the addition of 70% PET resulted in the brittleness of the blend due to increased pore formation. This is attributed to the crystals nearest neighbour distance observed in the AFM study, which led to the propagation of cracks in the blend (rPAN/PET: 30/70) sample composition. Therefore, for an effective blend of rPAN with PET, less than 50% PET addition is considered to be suitable for recycling purpose.

**Keywords:** Polymer, filtration, recycling, Polyacrylonitrile, polyethylene terephthalate, blends
Book chapter


Publications

- T.A. Adegbola, E.R. Sadiku, S.S. Ray. Atomic force microscopy and Tensile Strength Analyses of Recycled PAN and PET Blends: (Published in International Journal of Environmental Monitoring and Analysis (August 2015))
- T.A Adegbola, O. Sadiku-Agboola, I.E.A. Aghaci. SEM and AFM Microscopical characterization of rPAN fiber and PET blends (under review in Alexandria Engineering Journal)
Conferences


- Fractal analysis of AFM images of recycled PAN/PET blends obtained via melt extrusion process. Second International Conference on Composites, Biocomposites and Nanocomposites (ICCBN) 28 – 30 October 2015, Durban
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CHAPTER 1

1. INTRODUCTION

1.1 Background and Motivation

In the area of material science and engineering, works on polymer effectiveness and application are an ongoing developmental process, particularly with the trend of different polymer blends. Thus, the improvement of polymer processing techniques has a greater impact on domestic, industrial and manufacturing processes. Furthermore, with improved technological development in polymer science, different means of improving on the polymer processing for rapid production enable many industries to look for ways of improving on their products via blending.

Blending has good potentials for the development of new polymeric materials. This is done by combining the properties of more than one existing polymer in order to obtain a polymer blend and alloy with improved property. This method is based on the theoretical prospect of regulating the properties of polymers by varying their chemical compositions and molecular structures by means of a suitable selection of miscible and immiscible polymers. Miscible polymer blends are new materials with different chemical and mechanical properties. These properties are observed in the work of the following authors: Smith et al, (1981:35), Badawy et al (2001:61) and Cesteros et al, (1994:27), to mention a few. However, pure miscible polymer blends are very rare. Immiscible polymer blends poor mechanical properties are reflected by their rough morphology. Furthermore, it is possible to achieve a highly distributed blend of immiscible polymers.

Polymer processing cost implication must also be considered in order not to impair on the new blended application. Meanwhile, most blended polymers are immiscible; in order to obtain
maximum synergy compatibilization is required. The process of blending is usually less time consuming and cheaper than developing new monomers or following a polymerization route as the basis for entirely new polymeric materials (Moly 2013). An additional advantage of the polymer blend is the availability of a broad range of polymer properties within reach by simply changing the blend composition. But the significant drawback is the difficulty of recycling of some of the blended polymers in comparison with neat or reinforced polymers. Polymer blending usually takes place in a processing machine, such as single and twin – screw extruders, melt spinning, die extrusion, injection moulding, melt rheology and in situ polymerization process (White and Bumm 2011:2), which are considered standard industrial processing methods. Different processes will be explained in chapter two (Chapter 2). In addition, blends of polymers are either homogeneous or heterogeneous, this can be further classified as miscible and immiscible polymer blends. Some homogeneous polymer (miscible on a molecular level) are polystyrene (PS)–poly (phenylene oxide) (PPO) and poly (styrene-acrylonitrile) (SAN)–poly (methyl methacrylate) (PMMA) are miscible blends, while heterogeneous blends examples are: polypropylene (PP), polystyrene (PS) and polypropylene (PP), polyethylene (PE) as they are immiscible blends.

Blending of miscible and immiscible polymers, based on mechanical and chemical mixture of different polymers, is an ongoing polymer modification process. The blended polymer normally results in improved material properties, relative to the individual component of the blends. Miscible (single-phase) blends are usually homogeneous at the polymer segmental level and optically transparent. In the composition of their mixture brought about by the variations in temperature and pressure single-phase blends also undergo phase separation. Therefore, the properties of blended polymers depend on the final morphology resulting from phase behavior and the extent of the blends miscibility. In practice, depending on the type of application, the physical properties of interest are found either by immiscible or miscible pairs. Generally,
depending on the value of the Gibbs free energy of blending polymer blend can be completely miscible, immiscible and partially miscible. This important phenomenon resulting from the combination of the properties of individual polymers through improved technological blending processes, especially in the manufacturing of items with smart applications, simple and complex geometries, prompted the exploration of a blending process for the recycling of rPAN fibers in this study.

1.1.1. Polyacrylonitrile (PAN)

PAN is a highly versatile polymer due to its high carbon content. Its carbon–carbon backbone guarantees high biostability and resistance to degradation. PAN is produced by the polymerization of acrylonitrile monomer as shown in figure 1.

![Figure 1.1: Polymerization of acrylonitrile (AC) to PAN](image)

This powder in virgin form has little use in the industry; it is subsequently processed with numerous co-monomers, such as methyl acrylate, vinyl acetate, itaconic acid and sodium methyl sulphonate into another form by dissolving it in a suitable solvent at room temperature to form the desired polymer (Bajaj et al 1997:406). One of such form is polyacrylonitrile fiber with a molecular weight ranging from 10,000 to several million g/mol.
1.1.1.1. The Processing Method

PAN is difficult to process by the conventional hot-melt processing method of either moulding or extrusion. Therefore, it is advantageous to compound filler into the PAN polymer to ease its processing. Such filler will further increase its viscosity, but sometimes make processing more difficult. Processing methods will be explained in chapter 2. PAN has the following properties as listed in table 1:

Table 1 Properties of PAN (Paliwal et al 1998)

<table>
<thead>
<tr>
<th>Physical characteristic of PAN</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass transition temperature</td>
<td>~100°C</td>
</tr>
<tr>
<td>Melting temperature</td>
<td>317°C</td>
</tr>
<tr>
<td>Decomposition temperature</td>
<td>175°C</td>
</tr>
<tr>
<td>Amorphous density at 25°C</td>
<td>1.184 g/cm³</td>
</tr>
<tr>
<td>Molecular weight of repeat unit</td>
<td>53.06 g/Mol</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>24 - 65 cN/tex</td>
</tr>
<tr>
<td>Moisture content at 20°C, H.R.</td>
<td>65% (1 - 2 %)</td>
</tr>
<tr>
<td>Operating temperature (continuous)</td>
<td>130°C Max</td>
</tr>
<tr>
<td>Operating temperature (Peaks)</td>
<td>135 – 145°C Max</td>
</tr>
</tbody>
</table>

Other properties include excellent resistance to hydrolysis, acids, alkalis, oxidation and organic solvents.
1.1.2. Recycling of PAN

PAN is one of an essential fibre-forming polymer that has been broadly used because of its abrasion resistance, high strength and good insect resistance (Pan et al 2005:2127). The use of PAN products is on the increase as a result of their good properties but the waste generated as a result of their usage is of environmental concern. These challenges lead governments around the world to draft laws on the recycling and re-usage of these materials. Recycling of PAN fiber is a viable option to explore because most of the high-performance fibers used today are produced from PAN by pyrolysis under an inert gas. Hence, recycling of PAN fibers is thus interesting from both economic and ecological standpoints. This is due to their low weight and exceptional mechanical properties.

1.1.3. Polyethylene terephthalate (PET)

PET is a high-molecular weight engineering polymer developed via ethylene glycol and terephthalic acid polycondensation reaction, as shown in figure 1.2.

The polymerized monomer, with repeating C_{10}H_{8}O_{4} units, results in the formation of a thermoplastic polymer resin suitable for many different applications, such as synthetic fibres. Depending on the thermal history and processing techniques, PET may exist both as a semi-crystalline and amorphous polymers.

![Figure 1.2: Synthetic route of PET](image-url)
1.1.3.1. Processing Method

PET is processed into polyester fibres that are grouped under synthetic fibres. It can also be obtained in dry liquid form. PET films are produced by extruding molten polyester through a spinneret nozzle–shape slot, stretched and then heat treated to form the polymer. This processing method will be explained in chapter 2. The following forming properties, highlighted in table 2 are typical of PET:

Table 2: PET properties (Van der Vegt and Govaert)

<table>
<thead>
<tr>
<th>Physical characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass transition temperature</td>
<td>Varies</td>
</tr>
<tr>
<td>Melting temperature</td>
<td>285°C</td>
</tr>
<tr>
<td>Decomposition temperature</td>
<td>175°C</td>
</tr>
<tr>
<td>Amorphous density at 25°C</td>
<td>1.370 g/cm³</td>
</tr>
<tr>
<td>Crystalline</td>
<td>1.455 g/cm³</td>
</tr>
<tr>
<td>Molecular weight of repeat unit</td>
<td>53.06 g/Mol</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>55 – 75 MPa</td>
</tr>
<tr>
<td>Water absorption</td>
<td>0.16</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.24 Wm⁻¹ K⁻¹</td>
</tr>
</tbody>
</table>

Other properties include high resistance to light, excellent dielectric mechanical properties, good resistance to low and high temperatures, high resistance to aging, good resistance to dilute acids and alkalis, fats, oils, aromatic and aliphatic hydrocarbons. Low moisture absorption makes PET possible viable polymer for use in filtration processes and possible blend with PAN.
1.1.4. Thermal properties of PAN and PET

Thermal property is the temperature range in which a polymer can operate without distorting or damaging the compositional property. This property needs due monitoring in order to achieve maximum polymer performance. Thus, melt spinning is not preferred for PAN processing because a polymer degrades before melting. This prevents its fabrication via economically and environmentally attractive melt spinning process (Bahl et al. 1998:1). Furthermore, by unsettling the intra and inter-chain interactions between the nitrile groups, the melting point of PAN can be reduced to aid its processing. In general, to prepare a stable PAN polymer melt which can be melt-processed, two approaches were used to reduce its melting point temperature (Frushour and Knorr 1998:869). Firstly, by disturbing the crystal structure and nitrile-nitrile interactions using a particular amount of suitable comonomers or termonomers so that stable melt can be formed (Bhanu et al. 2002:43; Gao et al. 2009:44; Hutchinson et al. 2008:43; Bortner et al. 2004:93). Secondly, the use of non-solvents, e.g., organic plasticizers or water for PAN polymer in order to decouple the nitrile-nitrile interactions (Bashir et al. 1993:44; Atureliya and Bashir 1993:34). The very high dipole moment with a magnitude of 3.9 Debyes are the distinguishing feature of nitrile group, which govern the chain conformation for the isolated PAN polymer chain. The interaction energy between nitrile groups is the key factor controlling the fiber structure. Depending on the distance of separation, the interaction energy can be either attractive or repulsive. Also, the adjacent nitrile groups would fall into a parallel alignment if the backbone chain were placed in a plane zigzag arrangement, thus giving the net repulsion.
Research into PAN processing also revealed that free radically produced PAN exhibited a melting point temperature ($T_m$) of approximately 300°C, a glass transition temperature ($T_g$) of approximately 105°C and the carbon contents in the PAN product stabilized at a temperature of 220°C or higher during its processing. This observation is the key to preserving polymer property with the understanding of their thermal stability. This is one of the factors considered in polymer selection for both domestic and industrial applications. Different ways of determining and understanding the thermal properties of polymers are listed in numerous textbooks, journals and polymer standard index. This has been assisting in the development of many polymer products.

1.2 Problem Statement

PAN fibre has been used in hot gas filtration systems and many other applications, as done in ESKOM, South Africa, to filter fine ash particles from boiler furnace emission. Presently, ESKOM has 24 power stations of which about 14 are coal-fired. Approximately five of the stations have bag filter units installed and more are expected due to the on-going expansion program that is necessary in order to increase the power generating capacity. Each of the bag filter plants has about 27,000 bags of 18 m length X 130 mm diameter and each power station has six units of filters installed. This equates to approximately 81,000 bags (2.6m sqm. of bag filter materials) per year and it is still growing. These filter bags are made of polymeric fibres and the cost of disposing of the used polymer product is one of the major problems confronting ESKOM, with limited available landfill for the polymer waste. Therefore, there is a lot of focus on polymer accumulation because of its high visibility. This stimulated the formulation of considerable restrictive legislation regulating on polymer usage. The response has been the consideration of alternative ways of polymer disposal. Thus, the need arises for
the recycling of PAN by blending with other polymers, such as PET, in order to form a structural product that is economically viable in material development, which will be beneficial in commercial, manufacturing and industrial uses.

1.3 Research objective

1.3.1 General objective

The advantages of polymer blends depend on the ability to combine existing polymers into new products, with the aim of obtaining materials with specific properties. Thus, the purpose of this study is to blend used PAN, a polymer structural material from ESKOM with PET at different ratios in order to obtain materials with specific properties.

1.3.2 Specific Objectives

The specific objectives of this research were to achieve the following:

- To blend PAN fibre with PET in order to form structural materials with improved and good mechanical properties.
- To optimize the blending ratio of the two polymers.
- To determine the properties of the new blend and compare such with the individual properties of PAN and PET.
1.3.3 Research Questions

Based on the analysis of the existing knowledge, the following research questions were formulated:

- What are the main properties of the polymer blends under consideration that will contribute positively to the environmental and economic regimes?
- What polymer properties of PET will influence the properties of the new blend?
- What type of interaction and its mechanism take place during the blending process?
- What are the optimum operating parameters for the blend to be produced with minimum challenges?
- Possible application of the new blend?

1.4 Thesis layout

Table 1.3 shows the layout of the thesis.

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CHAPTER 2

2.0 LITERATURE SURVEY

Most polymers are classified by their average molecular weight. This gives rise to the molecular weight distribution of a particular polymer grade: most monomers are gases, a short polymer chain of low molecular weight gives a liquid and the large molecular chain gives solid material (Adrian et al, 2008, David et al, 2005:436). Higher molecular weight in polymers results in an increased strength and stiffness properties, these parameters increase the viscosity of polymer melts. Therefore, higher molecular weight polymer melt is sometimes difficult to process because it is accompanied by a high melt viscosity (Kale et al, 2004:19; Pielichowski and Njuguna, 2005). In order to reduce this viscosity, there is a need to increase the processing temperature, but this can result in polymer degradation. Therefore, the processing temperature and residence time of melt in the plasticizing unit of the machine dictate the thermal stability of the polymer (Munjal et al, 2006:95; Crowley et al, 2000:23; Lim et al, 2008:33). Hence, to avoid the degradation, limiting of the residence time by lowering the speed of cooling benefits PAN processing (Attia et al, 2009:7).

The current research in polymer blends is largely unlimited due to the variation in the polymer compositional properties, but it is limited by the compatibility of the composition (Shahul et al, 2010:26, Yang et al, 2009:21). However, an improved technological effort has been made for viable blending methods. These methods are now assisting in the polymer developments and comprehensive study has been published on the polymer, its blends and its applications (Toy and Wei-Choi 2004:60, Montheard et al 1999:39, Arshady 1992). Increasing research
interest in the development of these polymer blends and their properties has led to a rich resource of methodologies and procedures for polymer blending. Recently, the blending methods have attracted not only polymer scientist and chemists, but researchers in different field of engineering as well. Therefore, more research work needs to be done on the polymer blending development and application. This is because the study of polymer is a challenging area of research with unlimited future prospects.

Both PAN and PET can be classified as synthetic polymers. They can also be classified based on their molecular chains, such as addition chain polymers and condensation chain polymers. In addition, on the basis of structure, these polymers can be classified as linear, branched and cross-linked polymers. Furthermore, classification can be based on their crystalline structure, on the basis of morphology; polymers are classified as amorphous, semi-crystalline and crystalline polymers. Polymers can also be classified in other ways, such as homopolymers and co-polymers. Co-polymers can be further classified as alternating co-polymers, random co-polymers, block co-polymers, graft co-polymers, therefore, various homo-polymers and co-polymers are in existence of which PAN plays a vital role.

2.1 Polyacrylonitrile (PAN)

PAN is a rubbery organic polymer, most of which are co-polymer, prepared from the combination of monomers with acrylonitrile as the main component. PAN transforms to carbon at elevated temperature in many processes and it is used as precursor materials for carbon fiber manufacturing. PAN materials with its good anti-corrosion properties lose little tensile strength when used, this allowed it to be used as a replacement for polyester fibers in many applications (Almenara and Thornburrow 2004, Aidoo et al 2004:8). Also, PAN fiber, which is a low cost core material has been used as a filter material instead of the chopped strands of the composite
mat and the expensive core material of other polymers. Byung et al (2000:41) successfully blended modified PAN and cellulose acetate (CA); their findings showed partial miscibility of the blend demonstrated by the inward migration of the two glass transition temperatures (T_g), which was reproducible with the conjugate phase calculations from literature. Unfortunately, due to the poor economic benefit of processing, this system has not yet been industrialized. In other related studies, fiber-forming PAN was improved with a low quantity of amorphous vinyl monomers in order to give better process (Gupta et al, 1983:28, Dalven et al, 1985:30). Further development of the findings was in the work of Oh et al, (1995:34 and 1997:38), on the modification of PAN for improved or specific properties.

Srivastava and Anjali (2003:40) copolymerized Linalool (LIN) and acrylonitrile (AN) by using benzoyl peroxide as a crosslinking agent in xylene at 75°C for 60 mins. The TGA data show that the copolymer has a T_g of 50°C and is highly thermally stable. The mechanism of copolymerization has been elucidated, showing that with an increase in temperature the rate of copolymerization increases.

According to Yeo and Kiran (2004:37) in supercritical CO_2 methyl methacrylate and 2-chlorostyrene were copolymerised with acrylonitrile. In their work, without the use of stabilizers with a different feed of comonomer molarities, polymerizations were carried out. The selection of the comonomer was to provide a contrast while processing.

Zhong et al, (1997:36) presented the investigated results on the blends of acrylonitrile-chlorinated polyethylene-styrene copolymer (ACS) with polyvinyl chloride (PVC). In their study, attention was focused on the phase behaviour, miscibility and thermal stability of the blends. Scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) were used for analyses. Thermodynamic calculations were used to get the apparent polymer-polymer interaction parameter in the partially miscible pair PVC/styrene-acrylonitrile (SAN) in ACS.
Camino et al (2001:82) studied the thermal behaviour at the heating range of 200-300°C of a resol and a novolac resin with mixtures of nitrile-butadiene rubber (NBR). Due to the exothermic curing and cyclizing chain reactions involving the double bonds of its butadiene units and the nitrile groups of its acrylonitrile units, the NBR became hard and insoluble. In addition, NBR proved to be compatible with the novolac but not the resol. Also, due to crosslinking of the resin and the rubber, heating increased the modulus of elasticity of the mixtures. Therefore, when the mixture was heated linking of the resin resulted in phase separation in the novolac and prevented curing of the rubber.

Blake et al (2011:21) studied the fabrication and thick film characterization of macro/nanoscale aggregated and highly de-aggregated nanodiamond/PAN composite. From their investigation, the thermogravimetric analysis (TGA) traces of PAN, ultra-dispersed (ox-UDD)/PAN and nanodiamond (ox-ND)/PAN thick films revealed that ox-UDD and ox-ND additives acted as thermally stabilizing fillers. The onset of thermal degradation temperatures increased for the ox-UDD/PAN and ox-ND/PAN composite films relative to the thermal degradation onset temperature of pure PAN. This trend is consistent with the enhanced additive/PAN matrix cross-linking reaction present in these composite films, with the greatest enhancement observed in the ox-ND composite.

Agnihotry et al (2005:140) presented a study on nanocomposite electrolytes with fumed silica in polymethyl methacrylate (PMMA). Their thermal analysis result illustrated that traces of PMMA used in synthesizing the composite polymer electrolytes (CPEs) at a heating rate of 10°C/min, resulted in two different weight losses. Their results showed that the two reaction stages have a comparable weight loss; the first stage occurred at low temperature and it is endothermic while the other at higher temperature is exothermic.

Boguslavsky and Margel (2004:42), presented research data on the synthesis and characterization of polyacrylonitrile/polystyrene (PAN/PS) composite particles of narrow size
distribution by a single-step swelling of uniform PS template microspheres with methylene chloride emulsion droplets containing benzoyl peroxide (BP) and acrylonitrile (AN). The thermal analysis result from the work shows a significant shift in the decomposition temperature of the PS towards higher temperature. This shift indicates a probable potent interaction between the PS and PAN chain after crystallization.

Pourjavadi and Zohuriaan-Mehr (2003:14) studied the synthesis and thermal characterization of new polysaccharide-g-polyacrylonitrile copolymers. Their finding on thermogravimetric study showed that in the first stage the degradation of graft copolymer are very fast and then degrades rather slowly in the latter stage, thereby indicating higher thermal stability of the process. In addition, the overall thermal stability of all the graft copolymers were improved when compared to the corresponding non-grafted substrates. They concluded that the copolymers were more thermally stable than the corresponding non-grafted substrates, although they begin to decompose at relatively lower temperatures than the non-grafted counterparts.

Zou and Pan (2008:31) presented their study on the characterization of PAN/antimony-doped tin oxide (ATO) nanocomposites, prepared by solution blending. Their TGA result shows two curves; the first curve was the weight loss caused by decarboxylation of methyl acrylate in co-PAN and the second curve was the weight loss due to thermo-oxidative degradation of PAN macromolecular chain. This proves that the blend system is more thermally stable than the corresponding neat PAN system.

Semasarzadeh and Azzizalah (1997:1) worked on the thermal reactions and analysis of PAN films and their results on the thermal treatment of the films show that the weight loss before and after the treatment remain the same.

Bajpai et al 2005 studied the morphological, thermal and annealed microhardness characterization of an interpenetrating network of PAN. Their result shows that the crosslinking

Latifi et al (2010) also studied the electrospun nanofibers morphology and mechanical properties of PAN/multi-walled carbon nanotube (PAN/MWNTs) nanocomposite. Their result confirms the enhancement of the mechanical properties by increasing MWNTs content in the nanofibers, with a significant improvement over the percolation threshold value of MWNTs in fibers. Their result also shows an improvement in the tensile modulus of PAN/MWNTs composite, indicating an improved dispersion of MWNTs in the blend.

Eslami Farsani et al (2009) revealed that during stabilization of PAN fibers, the peaks related to C≡N bonds and CH$_2$ are reduced sharply in their study of FT-IR spectra of PAN fiber samples with different comonomers. These reductions are related to the stabilization procedure and cyclization of nitrile groups. From their findings, the reduction in PAN fibers containing an itaconic acid (IA) comonomer, is very intense when compared with PAN fibers containing sodium 2-methyl-2-acrylamidopropane sulfonate (SAMPS) comonomer. Therefore, the carbon fibers produced from this process have higher tensile strength due to suitable stabilization of the nitrile groups.

Biedunkiewicz et al (2011:17) using thermoanalytical methods studied the oxidation and pyrolysis of PAN in dry air. Their findings revealed that by controllable means during blending processes the pyrolysis and oxidation of PAN can be conducted.
Whitby et al (2012:48), investigated the high temperature oxidative resistance of PAN-methyl methacrylate copolymer powder, converting the copolymer to carbonized monolith. Their result indicated that chemical and thermal treatments are critical in obtaining porous PAN-based carbon monolith. In addition, their finding also shows that the process improved the thermal properties of the copolymer. Mohanty et al (2001:77) modified pineapple leaf fibers by grafting them onto PAN in order to improve their properties. Qinwu et al (2010:24) under environmental temperature and water conditions studied the performance of four fibers (polyester, PAN, lignin and asbestos) on reinforced asphalt concrete. Their results showed that the asphalt concrete rutting resistance, fatigue life and toughness was significantly improved by the fibres. It was also found that fibre content of 0.35% by mass of the mixture attained the optimum performance outputs of rutting resistance and split indirect tensile strength (SITS) for polyester fibre. Dao et al (2003:33) successfully synthesized, electrochemically, polyaniline on carbon PAN aerogel electrodes for use as active material in supercapacitor devices. In their study, two types of electrochemical phenomena were observed; the first was based on electrostatic energy storage in the double layer at the interface solution/carbon PAN aerogel, the other was associated with the redox processes in polyaniline, for which the Faradic charge depends on the potential range. Their results are very promising and demonstrated the viability of a symmetric supercapacitor, based on carbon PAN aerogel, covered by an electronically conducting polymer. Kim et al (2005:41) worked on PAN modified by copolymerizing with 2-acrylamido-2-methyl propane sulfonic acid (AMPS abbreviated as AP), methyl acrylate (MA) and blended with cellulose acetate (CA) in dimethyl formamide. The results from solution blends of the two types of modified PAN with CA showed partial miscibility, as evidenced by the inward
migration of the two $T_g$s. The migration of $T_g$ was much greater with PAN than with CA, an indication of greater solubility of CA in PAN, a result consistent with the conjugate phase calculations. Their SEM micrographs showed that phase inversion occurred at 60/40 for MA–PAN–CA and 40/60 for AP–PA–CA blends, the compositions corresponding to the minimum tensile strength predicted by the Coran–Patel model.

Peebles et al (1990:28) studied the thermal degradation of PAN under inert atmospheric conditions. They concluded that PAN can be transformed into a more stable material by prolonged heating at 225°C.

Zhu et al (2013:23) studied the properties of poly (vinyl alcohol)/PAN blended film. The results showed that to exert marked effects on the properties of PVA films PAN could be introduced to the blend.

Seydibeyoglu (2012) studied the blend of partially biobased PAN-lignin as a potential carbon fiber precursor. The results showed that with a blend of lignin and PAN it is possible to develop a new precursor material. The study also demonstrated a new application area of lignin, which in many different industries is an undervalued co-product. Furthermore, making the PAN precursor greener and a partial replacement of PAN with a renewable resource is envisaged to improve the world environment.

Feng et al (2014) worked on the thermal and mechanical properties enhancement of PAN through blending with tea polyphenol (TP). Their results revealed that PAN/TP blends with 12.5 wt % TP had a better anti-wear ability and similar hardness to those of acrylonitrile butadiene styrene (ABS). In addition, the referenced polymer ABS has a higher impact strength than all the prepared PAN/TP blends. Finally, when compared with the pure PAN the blends revealed enhanced thermal stability.
2.2 Polyethylene terephthalate (PET)

PET obtained by the polycondensation reaction of terephthalic acid and ethylene glycol is a high molecular mass polymer (Wrobel and Bagsik 2010:43). PET is one of the notably important, commercially prosperous engineering polymers that is extensively used in the form of fiber, films and in blended forms with other polymers for different applications. These blends resulted in different materials for desired applications in various polymer fields. PET has the following features that make it unique for various applications;

1) Excellent dielectric and mechanical strength attribute
2) High aging and light resistance
3) Good resistance to low and high temperatures
4) Good resistance to oils or fats, dilute acids, alkalis, aliphatic and aromatic hydrocarbons
5) It also exhibits low moisture absorption
6) Physiologically, it is indifferent and it is approved for food contact (Zuchowska 2000).

The desire to study PET, in order to further improve its properties will shed more light on its applications and future development.

Aizenshtein (2005:37) developed a process for the chemically modified PET fibers production. The aim was to eliminate polyester (PES) fibers made from traditional PET as the main product shortages. The result revealed that due to the possibility of wide variation in its physical structure PET and PET fibers exhibit an excellent capacity for physical modification. The result also concluded that the modified PET has a lowering pilling effect, higher absorption of dispersed dye and a sharp decrease in the number of abrasion cycles. The study was done using Pavlin original calorimetric applied software package.

Lou et al (2007:192-193) did some investigations on PET/PP blends with a bamboo charcoal addition in order to produce functional composites. Their result showed that the tensile stress
of the PP/PET composites decrease when the reprocessing cycles were increased. They also detected that with increasing processing procedures (melt compounding followed by injection moulding) as a result of a processing-induced degradation, the impact strength and the elongation-at-break of the PET/PP blend decreased. In their findings, with the number of the processing cycle, the flexural modulus of PET/PP composites remain relatively constant. In their conclusion, it was shown that the mechanical properties of the extruded PET/PP with 10% and 20% of polyester compositions were superior to the PET/PP injection moulded counterparts.

Evstatiev et al (2005) worked on the compatibilization effect on the microfibrillar reinforced composites properties, based on PET and polypropylene; their result indicated the possibility of recycling PET. It also demonstrated the reinforcing effect of PET fibrils and compatibilizer improvement when added to the blend.

Jarukumjorn and Chareunkvun (2006:14) carried out an experimental study on recycled high density polyethylene (HDPE)/PET blends compatibilization. Their result shows that by increasing compatibilizer content, the tensile strength and strain-at-break increased. In conclusion of their study, the compatibilized blends Young’s modulus was lower than that of the uncompatibilized blends. This outcome is in accordance with Guerrero et al. (2001:82) study of the effect of a copolymer of ethylene and methacrylic acid that was partially neutralized with zinc on the mechanical properties of HDPE/PET blends. This study shows that due to the high adhesion between the two phases the elongation-at-break and impact strength of the blends increased. Pietrasanta et al. (1999:200) pointed out that by using one-step process the HDPE/PET blends compatibilization could be achieved. Thus, the mechanical properties of the blends prepared by injection moulding were better than the blends prepared by extrusion. In addition to their observation, between the two phases, the rate of shearing in the injection moulding process was enough to ensure a better dispersion of the dispersed phase and a
reduction of the interfacial tension. Torres et al (2001:81) established that the statistical graft copolymer was less effective with the compatibilization of HDPE/PET blends. Their result shows that with the addition of the copolymers, mechanical and morphological properties of the blends were improved. They further concluded that compatibilization with graft copolymer was an appealing method because the synthesis of the graft copolymer was easier and cheaper than that of the statistical copolymer. Kalfoglou et al (1995:36), based on morphological evidence and tensile testing, investigated the effectiveness of compatibilizer for PET/HDPE blends. Their findings revealed that a copolymer containing epoxy functions was obtained because it could react with the hydroxyl and carbonyl end groups of PET. Akkapeddi and Buskirk (1992:67) finding also revealed that the toughness and heat resistance significantly improve with PET/HDPE blends. Pracella et al (2002:203) established that the type, content of the reactive compatibilizer and blending procedures could lead to the effectiveness of compatibilization of HDPE/PET systems, and this also improved the tensile properties of the blends. Lusinchi et al (2001:79) further proved that in-situ compatibilization of HDPE/PET blends, at the formation of HDPE-g-MA was first formed in the molten state and then the anhydride groups reacted with the end group of PET. When compared with the blends obtained by the addition of graft copolymer to the blends, single-step processing offered better results. Elongation-at-break and impact strength of recycled HDPE/neat PET blends was reported by Pawlak et al (2002:86). Their result also showed that the addition of maleic anhydride grafted styrene-ethylene-butylene-styrene improved the blends elongation and impact strength. They also observed that mechanical properties of the blends were due to the phase dispersion. In addition to their observation, the reaction during blending was due to the increase in the viscosities of the compatibilized blends. They concluded that the efficiency of the compatibility was determined by the compatibilizer content. For the application of post-consumer packaging materials, Pracella et al (2002:48) presented the reactive compatibilization and properties of
recycled PET/PE blends. Their result on thermal analysis revealed that type of compatibilizer and content affected the crystallization behavior of PET. Also, the blending processes, concentration of functionalized polyolefin and types of blends noticeably affects the compatibilized blend morphology. In addition, due to coalescence phenomena of the minor phase during the melt blending process, a wide distribution of the dispersed particle size was similarly observed.

According to Bonelli et al (2000:80), there was an increase in the melt flow index of the first recycled PP (PPr1) compared to that of PP in a recycled PP on PP/HDPE blends. Significant differences in molecular weight and polydispersity were not exhibited in the second recycled (PP (PPr2)) compared to PPr1. There was no substantial impairment in the polymer particle due to the extensive extraction with a solvent.

Abdolahifard et al (2011) studied the surface modification of PET fabric by graft copolymerization with acrylic acid and its antibacterial properties, their result showed that while increasing the concentration of the initiator benzoyl peroxide (BP), the grafting percentage increased. Hence, the grafted samples showed better behavior and the samples also exhibited good antibacterial properties.

Sacak and Ofiaz (1993:50) investigated the grafting of acrylic acid onto PET fibers subjected to a no swelling treatment using benzoyl peroxide. They concluded that an increase in the reaction temperature increases the graft yield. In related studies, many researchers used radiation for initiating the reaction of grafting process. Due to the fact that these fibers show a high resistance to chemical activators, the grafting method was used to initiate the graft copolymerization on PET fibers (Ahmed 2011:196, Gupta 2008:77, El-Gendy and Shanshoury 2006:101, El-Naggar et al 2001:50, Wang et al 2008:46 and El-Arnaouty et al 2008:107). Chengcheng and Zhenyagu (2003:89) researched the effects of the process parameters on graft ratio and characterization of grafting products using acrylic acid-grafted polyester fabrics by
electron beam preirradiation method. Their result indicated that using preirradiation method it is practicable and effective to graft acrylic acid onto polyester fabrics. Their result also revealed that using the SEM photos a layer of grafted polyacrylic acid was formed on the surface of the PET fibers by changing the diameter and the surface structure of the fabric fibres.

Sacak, et al (1992:44) studied the grafting of PET fibers with methacrylic acid using benzoyl peroxide. Their report showed that the graft yield increased when the reaction temperature was raised up to 85°C and decreased with further increase in the temperature. They also concluded that the increase in the concentration of monomers increased the graft yield of the polymer.


Fei et al, (2010:118) successively studied the melting and crystallization behaviour of PET and poly m-xylene adipamide blends. Their result indicated that the catalyst used, has catalysed and nucleating effects on the blends. The extent of each effect depends on the content of the catalyst applied. In conclusion, the crystalline morphology was dominated by the blend content and the crystallization temperature.

In the study of Tsai (2000), the addition of layered silicates in PET acted as heterogeneous nucleating agent, which increases the overall crystallization rate and the crystalline fraction. The result also shows that the impermeability of clay improves the barrier properties of the
PET nanocomposites to gases and water vapour. This finding was supported by the research of Wang et al (2004:94).

Costache et al (2006:17) reported on the preparation of PET nanocomposites which was presenting a challenge due to the high processing temperature of their nanocomposites. They concluded that to avoid the thermal degradation of the ammonium surfactants, neither melt blending, nor straightforward in-situ polymerization can be employed for PET and ammonium modified clays.

Ou et al (2004:91) prepared PET nanocomposites via solution blending, which does not require elevated temperatures, as a result, the surfactants does not degrade during the processing. Other researchers; Wu et al (1997:30), Imai (2002:14 and 2003:35), used surfactants of high thermal stability, which enables the use of melt blending as a means of preparing the nanocomposite. Davis et al. (2002:40) and Zhu et al. (1998:32) used alkyl chain imidazolium and phosphonium halides in their study on PET blend. These cationic surfactants are employed as modifiers for layered silicate clay fillers. It allows the blended PET nanocomposites to melt directly without requiring extensive use of organic solvents. The process posed a health and occupational risk. The observation consequently impeded the industrial applications of their work.

Tsai (2000) noted that the polarity of ethylene glycol and terephthalic acid polymer decreases and it's molecular weight increases when in-situ polymerization was used to prepare the nanocomposites. This led to phase separation of the clay and polymer, making it imperative to ensure compatibility between the clay and PET.

Reis et al (2011:25) studied the effect of recycled PET in the fracture mechanics of polymer mortar. They observed that the fracture properties of the composites obtained revealed a reduction in the specific weight of the polymer mortars and a significant improvement of their post-peak flexural behaviour. This study showed quite encouraging results and opened a new way for the recycling of PET waste in polymer mortars.
Aravinthan and Kale (2005:75) studied the rheological, electrical, mechanical and thermal properties of the blends of PET and poly (butylene terephthalate) (PBT). Their result showed that, the addition of PBT increased the processability of PET and the blends displayed higher impact properties than that of PET or PBT.

Oyman and Tincer (2003:89) worked on the melt blending of PET and PP with silane coupling agent (SCA). Their result showed that, SCA extensively improved the mechanical properties of the blends. Mechanical properties were found to be highly dependent on the numbers of extrusions. In addition, the SEM revealed different morphology with better adhesion when SCA-treated blends were compared to nontreated PP/PET blends. Lastly, the presence of individual melting temperatures and no significant changes in melting point indicated that PET and PP crystallized separately in the blends.

Mendes et al (2014:24) studied the effect of the reaction temperature on the thermal, morphological and viscosity properties of solid state polymerised PET/PC extruded blends. Their result revealed that after the solid state polymerization, at all reaction temperatures, PET glass transition and crystallization temperatures slightly decreased, melting temperature marginally increased, while the degree of crystallinity was practically unaffected. In addition, their result revealed the appearance of structures such as bridges linking the matrix and the dispersed domains. These bridges were correlated to the PET/PC block copolymer obtained by blending in the molten state.

Ujhelyiová et al (2007:15) worked on PP/PET blended fibres and focused mainly on the crystallization behaviour of PP and mechanical properties of the blends. They observed that the heating and cooling rates influence the thermal properties of the PP/PET fibres and that the tensile strength and elongation at break of the blended PP/PET fibres changed under the influence of PET and compatibilizer.
Szostak (2004:146) studied the mechanical and thermal properties of PET/PBT blends and his result showed that PET/PBT blends were processable by injection moulding only, followed by mixing on an extrusion machine and subsequently injection moulding of the blends. It was observed that the preparation manner of the blends has the greatest influence on their mechanical properties, especially on the impact strength. The study also revealed that the mixing of PET and PBT only, during the injection moulding, is not sufficient for the expected and essential improvement of the impact resistance of the PET/PBT blends. Therefore, in order to guarantee the enhanced properties of the injected PET/PBT blends, it is necessary to first mix them on the extrusion machine.

Di Lorenzo et al (2002:37) successfully polymerized PET with stearic acid coated and uncoated CaCO$_3$. They found that coated CaCO$_3$ resulted in a stronger polymer-filler interaction when compared to the uncoated particle. The strong interfacial adhesion between the phases resulted in a significant increase of the $T_g$ by 14$^\circ$C and the melting temperature by 8$^\circ$C when compared to neat PET.

2.3 Methods of polymer processing

The processing of polymeric materials is characterized by a wide range of unique methods. These methods require an adequate composition and processing which is the focus of many researches in polymer development. These methods also required the continuous manufacturing of products as required by the domestic consumers and industrial applications. These methods are melt extrusion, injection mould, electrospinning, in-situ polymerization, melt blending, intermix and brabender mixing.
2.3.1 Melt Extrusion

Extrusion process is used to create materials of a fixed cross sectional profile. This process may be continuous which is theoretically producing indefinitely long materials or semi-continuous (produces many pieces). It is one of the most widely applied processing technologies in the plastic, rubber and food industries. It is also used to prepare more than half of all plastic products including bags, films, sheets, tubes, fibers, foams, and pipes (Kruder 1985:1). Figure 2.1 shows the extrusion process.

Advantages of hot melt extrusion process are as follow: increased solubility and bioavailability of water insoluble compounds, solvent-free non-ambient process, economical process with reduced production time, fewer processing steps and a continuous operation, capabilities of sustained processes, modification of products, better content uniformity in extrudates, no requirements for the compressibility of active ingredients, uniform dispersion of fine particles, safe application, reduced number of unit operations and production of a wide range of forms. However, the process also have some disadvantages such as thermal process (polymer stability), use of a limited number of polymers, high flow properties of polymers and not suitable for relatively high heat sensitive polymers (McGnity and Koleng 2004; Jones 2008:4-9; Singhal et al 2011:2; Grunhagen and Muller 1995:1).

![HOT MELT EXTRUSION PROCESS](image)

Figure 2.1: Schematic setup of melt extrusion machine (Kruder 1985)


2.3.2 Injection Moulding

Injection moulding is the most commonly used manufacturing process for the fabrication of plastic parts. Using injection moulding technique, a wide range of products that varied greatly in size and complexity for the different application can be produced. The processes include the use of an injection moulding machine, raw plastic material, and a mould (see figure 2.2). In order to solidify the final part, the polymer is melted in the injection molding machine and then injected into the mould.

Injection moulding process has the following advantages: fast production process, material and colour flexibility, low labour cost, recycling ability of produced waste and design flexibility. However, the process also has the following shortcomings; high initial tooling cost, part design restrictions and accurate costing can be difficult (Surace et al 2012)

Figure 2.2: Injection moulding machine (Surace et al 2012)
2.3.3 Thermodynamic of polymer blends

Phase behaviour is the most important characteristics of a polymer blend because the blends performance depends not only on the polymeric components properties but also on how they are organized in space. Hence, thermodynamics and flow-induced morphology control the polymer spatial arrangement. Miscibility or phase separation can be exhibited by polymer blends at a different level of mixing in between the limits (Koning et al 1998, Utracki, 2002 and Robeson, 2007:23). This indicates that polymer blends must be exothermic, which involves interface interaction, such as hydrogen bonding, dipole-dipole and donor-acceptor interactions, between the constituents (Koning et al., 1998:23). This explains the immiscibility or partial miscibility of most polymer blends.

Polymer miscibility behaviour is strongly dependent on the processing temperature. For low molecular weight polymer materials, increasing temperature usually leads to increase in miscibility as the entropy and absolute temperature (TΔS\text{mix}) term increases, thus driving changes in the free energy of mixing (ΔG\text{mix}) to more negative values.

Robenson, (2007) proved that for higher molecular weight polymer materials, the TΔS\text{mix} term is small and factors such as non-combinatorial entropy contributions and temperature dependent ΔH\text{mix} value can also dominate and lead to the reversed behaviour, namely, decrease in miscibility with an increase in temperature. Thus, while upper critical solution temperatures (ucst) are usually exhibited by liquid-liquid and polymer-solvent mixtures (i.e. borderline in miscibility), lower critical solution temperatures (lcst) are generally exhibited by polymer-polymer mixtures, as exemplified in Figure 2.3.

Therefore, polymer blends may be classified into three groups from a thermodynamic point of view, according to Knoning et al., (1998:23). (i) **Fully immiscible** polymers (reveal that the
polymer blends have a sharp interface, rough morphological phase and the adhesion between the blend phases is poor. This shows that without being compatibilized the polymer blends are not useful. These polymer blends are generally immiscible with each phase displaying its own \( T_g \) and, therefore, resulting in phase separated morphologies, which leads to poor mechanical properties in the blends. (ii) **Partially miscible blends** are polymer blends in which one polymer is dissolved in a portion of the other polymer. The blends are generally considered compatible and exhibit fine phase morphology coupled with satisfactory mechanical properties. The two polymer blends have distinct \( T_g \)'s and their phases are homogeneous. The two blend phases are homogeneous and have their own \( T_g \)'s. The \( T_g \)'s of the blends is shifted from the values for the neat components towards the \( T_g \) of the other blend component. Therefore, the interfacial adhesion is good for such blends, resulting in a wide interphase as opposed to the sharp, thin interphase in the case of immiscible polymer blends.

Lastly, (iii) **Completely miscible blends**: due to specific components interactions in these polymer blends, the temperature dependent value \( (\Delta H_{mix}) < 0 \) lead to molecular level homogeneity. Thus, only one \( T_g \) is exhibited between the \( T_g \)'s of both blended components in a close relation to the blend composition. Therefore, it is highly important to control the morphology in order to ensure an acceptable blend.
Controlling of processing parameters (such as blends ratio and temperature) during melt blending extrusion process plays a significant role in the evolution of the phase morphology which subsequently impacts on the blends properties for immiscible blends such as rPAN/PET. Therefore, knowing the polymer rheological properties is essential in order to understand the morphological development, especially in cases where the contributions of thermodynamics to uniform morphologies are low.

In a review by Briscoe et al., (1999:81) on the immiscible blending, it is well accepted that in immiscible polymer blends flow-induced structural evolution is governed by factors, such as:
volume fraction, viscosity ratio, the mixing conditions and interfacial tension between the
phases of the polymer constituents. In addition, Taylor (1934:143) in his work summarizes the
factors that influence the shear strain required to produce break-up in a steady laminar flow as:
(i) the dispersed and continuous phase viscosities, \( \eta_d \) and \( \eta_m \), respectively, (ii) the initial
radius, \( R \) and (iii) the interfacial tension, \( \sigma \). The deformation under Newtonian flow is governed
by two dimensionless numbers: the viscosity ratio \( p = (\eta_d / \eta_m) \) and the capillary number, \( C_a \)
given by the ratio of deforming viscous stress to the restoring stress from interfacial tension in
the following form (Briscoe et al, 1999:81):

\[
C_a = \frac{\eta \dot{\gamma}}{\sigma/R} \tag{2.1}
\]

Where \( \eta_m \) is the viscosity of the major matrix (rPAN in this case), \( \dot{\gamma} \) is the shear strain rate,
\( R \) is the radius of dispersed phase (PET in this case), and \( \sigma \) is the interfacial tension. The
numerator is the deforming stresses while the denominator is the restoring interfacial stress. A
representation of the processes that occur during melt blending of two polymers was given by
Koning et al., (1998:23), as shown in Figure 2.4. Basically, at the beginning, \( C_a \) is small and
the interfacial stress withstands the shear stress and an ellipsoidal shape persists.
Above a critical value, \( C_a \), typically at the initial stage of mixing when the dispersed domains are
large, the shear stress dominates the interfacial stress and contents are stretched affinity (with the
matrix) into long thin threads. If the local radius of the thread becomes sufficiently small, interfacial
(“Rayleigh”) disturbances grow on the thread and result in the breakup of these liquid threads into
small drops. Above a certain diameter, these small contents may be stretched and broken again.
For very small particles, \( \delta/R \) is high enough to prevent further stretching and breakup.
Empirical relationships between the $C$, and viscosity ratio, $p$, have been developed and hence the droplet size, as a function of processing parameters, may then be predicted for low and constant concentrations of the dispersed phase (Koning et al., 1998:23). However, the morphology of certain blends is not in equilibrium and may change depending on post-processing treatments. rPAN has slow crystallization rate during processing when compared to PET. Therefore, annealing the blends to allow crystallization of rPAN component would lead to a probable further phase separation and deterioration of certain properties, e.g., strength. Even though PET and rPAN are immiscible, some level of the intermingling of chains of both polymers at the interface is expected. Maximizing the benefits of the two polymers would, therefore, require that the dispersed phase is not only small in size, but also the surface area per unit volume of the blend, is as maximum as it can be. In conclusion, it is apparent that in immiscible blends such as rPAN/PET, there exists very little interfacial interaction between the two phases. As such some level of miscibility is only achieved at certain compositional ratios under the processing conditions (varied content ratios and temperature).

Figure 2.4: Schematic representation of the processes occurring during melt-blending of two polymers (Koning et al, 1998)
2.4 Opportunities and challenges

The technological developments involving pure polymer, recycling process, blend compatibility and morphology revealed that this area of knowledge is continuously on the path of development at an unprecedented rate. The guiding principles behind this development are: efficiency, functionality and properties processing accuracy. However, effective application of recycled polymer blends depends on the understanding of their behaviour, blending techniques plus blend properties. In this regard, polymer sensitivity to a variety of factors, such as: temperature-dependent effects, compatibilizer, mechanical and chemical properties during processing are the pressing challenges. These intrinsic properties of polymer blends have the tendency to produce new and unexplored properties that need to be explored for further development and applications. In addition to the study, it is also important to note that, most polymers perform their dynamic roles under different conditions over an extensive temperature range. Such conditions tend to hasten their degradation and consequently, alter their functional response (Annette and Renate, 2011:2, Ke et al, 2003:34, Lustiger et al, 1998:36). Besides the technological development required in solving the identified problem areas, the need to further explore and develop blends, for both compatible and incompatible polymers for advanced applications is the prime focus of many polymer developments. In this regard, it is important to treat polymer blends as an integral part of polymer science and technological development (Bharat et al, 2000:36, Weihua et al, 2007:45, Jian et al, 2007:104, Hiltner et al, 2001:34).

The forecast of the recycled polymer properties is faced with some overwhelming challenges such as the prediction of blend output, rheology and morphology, forming, shrinkage and cracking still remain unresolved during polymer processing in some cases. Therefore, for a considerable length of time, the prediction of the precise blend property might remain a challenge. However, the application of innovative technologies now plays significant roles in
the polymer processing field. In addition, intensified efforts directed towards the development of polymer blends with enhanced adaptive capabilities in the field of smart polymer development will be of major focus in the immediate future. Therefore, it is essential to develop and adapt the existing and newly discovered techniques in the formation of polymer blends for its application and development. On this basis, further technological inquest of new materials will continue to stimulate the unique opportunities offered by the blending of polymers. These materials will have application in different sectors of engineering, medicine, manufacturing, industrial, smart material and domestic products.

2.5 Application areas of PAN and PET

Polyacrylonitrile has a wide application due to their high tensile and compressive strength in the following areas: Construction: damp proof roofing, columnisation in structures and buildings, industrial terrace, bridges, road and rail, etc. In the area of technically advanced projects: underwater and underground tunnels, jet aiming support, concrete lining, packing apron sleeper and in filtration system such as domestic, industrial and manufacturing application (Huang 2009:2; Rangarajan et al 2002:85). PAN products are also finding a wide range of potential applications in tissue engineering, drug delivery, textiles, composite reinforcements, etc. (Xu et al 2004:25), (Huang et al 2003:63) and (Greiner and Wendorff 2008).

PET has application in the following areas; Plastic applications: bottles, edible oils, non-carbonated and carbonated drinks. In packaging: wrapping for domestic and industrial application and in filtration system: acidic, organic solvents, water, fats and gas, etc. PET products are also of interest in a wide range of applications ranging from maritime ropes to
protective gloves, bullet-proof vests and other advanced composites applications (Huang et al 2003:63).
CHAPTER 3

3.0 Materials and Methods

Blending of different polymers is an important process in tailoring the polymers with optimized properties (Kukaleva et al 2000:77). On the other hand, polymers are blended in order to study their fundamental properties and there are many activities in this field both theoretically and experimentally with different blending ratios (Sadiku-Agboola et al. 2011:2, Zhang et al 2016:7, Schweizer 1993:26). It is believed that the ratio of the blend composition can strongly influence the strength of the material (Schaffer 2015:7). In this work, it is expected that the adhesion between the matrix and the disperse phase, should have some degree of compatibility and the characterization of the blends will help to choose the best rPAN/PET ratio from (30/70, 50/50 and 70/30) to achieve the desired results.

This chapter describes the processes adopted for the study: the overall approach was to analyse the data obtained for the blended samples in comparison with the pure samples of rPAN and neat PET. These include the descriptions of samples, preparations, procedures for each analysis and equipment used. The results of the different blends are discussed in chapter four. They are based on the data gathered from the different blends.

3.1 Materials

The rPAN fiber employed in this study was supplied by ESKOM, South Africa. The PET was purchased by the Tshwane University of Technology (TUT) from Ten Cate advanced composites BV, Netherlands.
3.2 Method of preparation

rPAN fibers were cleaned by soaking them in water for 12 hours, rinsed and dried for 24 hours at room temperature in order to remove ash and coal particles embedded in it. The dried rPAN fibers and PET were blended in the rheomixer (Haake Rheomix 600 OS) compounding machine at a temperature of 290°C for 5 minutes. The ratios of the blends are: 30/70, 50/50 and 70/30, as shown in Table 3.1. In the second stage of the blending process, the blends were carved at the same processing temperature of 290°C for the desired standard (ASTM) test specimens. Table 3.2 shows the operating set-up of the rheomixer used for the blending of the samples.

Table 3.1: Blend ratios of prepared samples

<table>
<thead>
<tr>
<th>Material Samples</th>
<th>PAN (%)</th>
<th>PET (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>PET</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>PAN/PET</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>PAN/PET</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>PAN/PET</td>
<td>70</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 3.2: Rheomixer operating set-up

<table>
<thead>
<tr>
<th>Temperature</th>
<th>290°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed</td>
<td>60 rpm</td>
</tr>
<tr>
<td>Time (minutes)</td>
<td>5 mins</td>
</tr>
<tr>
<td>Roller - rotor</td>
<td>R 600 for Rheomix 600 OS</td>
</tr>
</tbody>
</table>
3.3 Equipment used for blending preparation

A twin screw rheomixer was used to compound the samples. The blended samples were compounded at the temperature of 290°C. A carver machine was used to prepare the ASTM standards samples for the tests.

3.4 Characterization techniques

According to Salih et al (2013:7) and Tjong (2006:53), the strength of rPAN, PET and blended samples depend on the thermal, mechanical and chemical properties of the samples in their operational environment and the properties performance depend on these. Rana et al. (2005:249) stated that it is of technological and scientific importance in many academic and industrial research areas to understand the surface properties of materials. The chemical and physical properties of the rPAN, PET and blended samples are therefore characterized using the different approaches and techniques described below.

3.4.1 Differential scanning calorimetry (DSC)

DSC study was performed using Instrument DSC Q2000 V24.4 Build 116, Module DSC standard cell RC (TA Instruments), under a nitrogen atmosphere using approximately 4.940 mg of samples, in the temperature range of -50°C to 290°C. The same heating and cooling rate of 10 °C/min were used to test the samples in three scans: heating, cooling and heating. The previous thermal history of the samples was erased in the first heating scan from -50°C to 290°C and held at 290°C for 10 minutes. The glass transition temperature ($T_g$), crystallization
temperature \(T_c\) and enthalpy \(\Delta H_c\), melting point temperature \(T_m\) and enthalpy of fusion \(\Delta H_m\) was determined using the second heating scan at the same temperature range of -50°C to 290°C and heating rate of 10°C/min for all the samples. In most cases, the results were reproducible and two runs were sufficient, in some cases, three runs can be performed. The resulting thermal profile information of the DSC experiment are reflected on the thermal profile curves. These curves were used to examine the thermal behavioural properties of the prepared samples by observing the heating (melting) and cooling (crystallization) rates of the samples.

DSC also monitors the thermal decomposition and degradation temperatures of polymers which are a useful prior knowledge during processing in order to assist with their development.

### 3.4.2 Thermogravimetric analysis (TGA)

According to Coats and Redfern (1963:88), a procedure that measures the physical changes in materials (weight) as a function of increasing temperature at a constant heating rate or as a function of time at a constant temperature is referred to as TGA. TGA relies on three measurements from the sample; temperature, temperature change and mass with respect to a high degree of precision for characterization. Thus, by cutting a small piece (8±2 g) of the sample in order to maintain the interior sample temperature close to the measured gas temperature, samples can then be investigated. Therefore, with blending processes in many cases carried out at an elevated temperature, investigating the thermal stability which is one of the most important aspects of polymer technology is, therefore, necessary.

Thermogravimetric (TGA) model Q500, (TA instrument, the USA) under a nitrogen atmosphere was used to study the neat and blended samples thermal stability. This is done in a
micro-balance controlled environment. A sample size of ~17.47 mg, temperature ramp from room temperature to 900.00°C and at a heating rate of 10.00°C/min were used. TGA measures very small weight changes in a material as a function of temperature. It also provides information on the volatility behaviour of the samples subjected to different temperature ramps. TGA provides information on the samples thermal characterization, degradation, moisture content, weight loss and residue information. The rate of decomposition, which is the first derivative of weight loss over time, was obtained. This comprises of a different sample peak profiles that indicate different phases of the sample weight loss during the temperature ramp profile. The information obtained from the TGA experiment was used to analyse the thermal behaviour of the blended rPAN/PET samples within the temperature range specified (i.e. from room temperature to 290°C). This characterization gives detailed information on the thermal profile of the blended samples, the decomposition process and the residue in the heating pan. Thus, in the blend development, TGA characterization plays a crucial role.

In addition, it is significant to note that the TGA experiment was carried out in an extremely sensitive and high precision computer controlled environment. This enables an accurate detection of weight loss against increasing temperature. The samples that were investigated in this work are listed in Table 3.1.

### 3.4.2.1 TGA characterization Procedure

The blended sample of 5 mg each, in table 3.3, was placed in the sample pan and attached to the sample loading assembly. During the TGA measurement, the balance chamber was purged with inert gas in order to balance evolved gases. This, in turn, prevents back diffusion during the TGA process. The temperature ramp operating from (0 to 900)°C and at a heating rate of
10.00°C/min was set for the experiment and the device controller program maintained the sample environment at the selected heating rate. Data from four channels were then stored on the computer as follows: time [mins], temperature [°C], mass [g] and the time derivative of mass loss [%min] at the end of each experiment.

### 3.4.3 Dynamic mechanical analysis (DMA)

DMA characterization of rPAN, PET and the blended samples was done using a TA instrument (DMA8000 dynamic mechanical analyser, PerkinElmer) in the dual cantilever bending mode. The sample characterization was done in a deformation mode at a frequency of 1Hz, a heating rate of 2°C/minute from 0°C to 300°C and upper stiffness limits: 1.0E+08 and lower stiffness limit 2.0E+02. The dynamic mechanical properties which are expressed in terms of the storage modulus, loss modulus and tan delta is a manifestation of the response of polymer when subjected to a periodic force. The moduli values of polymers usually ranges from $10^6$-$10^{12}$ dyne/cm² depending upon the nature type of polymer, frequency, modulus and temperature. In addition, the viscoelastic polymer will also respond with a sinusoidal strain for low amplitudes of stress when an applied stress varies with time. This sinusoidal variation in time is generally designated as a rate quantified by the frequency ($f$ = Hz; $\omega$ = rad/sec). The out-of-phase with the stress applied to the phase angle, $\delta$ is the strain of a viscoelastic body. This phase lag is due to the excess time necessary for molecular motions and relaxations to occur in the samples. Dynamic stress, ($\sigma$) and strain, ($\varepsilon$), are given as:

$$\sigma = \sigma_0 \sin(\omega t + \delta)$$  \hspace{1cm} (3.1)

$$\varepsilon = \varepsilon_0 \sin(\omega t)$$  \hspace{1cm} (3.2)
Where $\omega$ is the angular frequency. Using the expression in equation 3.1 and 3.2, stress can be divided into an in-phase component ($\sigma_o \cos \delta$) and an out-of-phase component ($\sigma_o \sin \delta$) and rewritten as,

$$\sigma = \sigma_o \sin(\omega t) \cos \delta + \sigma_o \cos(\omega t) \sin \delta$$  

3.3

Dividing stress by strain to give the modulus and using the symbols $E'$ and $E''$ for the in-phase (real) and out-of-phase (imaginary) moduli, gives:

$$\sigma = \varepsilon_o E' \sin(\omega t) + \varepsilon_o E'' \cos(\omega t)$$  

3.4

However,

Storage modulus, $E' = \frac{\sigma}{\varepsilon} \cos \delta$  

3.5

Loss modulus, $E'' = \frac{\sigma}{\varepsilon} \sin \delta$  

3.6

Complex modulus, $E^* = \frac{\sigma}{\varepsilon} (\cos \delta + i \sin \delta) = E' + i E''$  

3.7

Equation (3.7), shows that from dynamic mechanical test consisting of “real” and “imaginary” parts the complex modulus can be obtained. Therefore, the ability of the material to store potential energy and release it upon deformation is referred to as the real (storage) part, while imaginary (loss) part is the portion associated with energy dissipation in the form of heat upon deformation. Therefore, equation 3.7 can be modified for complex shear modulus as:

$$G^* = G' + i G''$$  

3.8

Where the storage modulus is $G'$ and the loss modulus is $G''$. The damping and phase angle (dissipation factor or phase lag), $\delta$ are given by:

Loss tangent, $\tan \delta = \frac{G''}{G'}$  

3.9

The “stiffness” of a material which is related to the Young’s modulus, $E$ is often times, associated with the storage modulus. The “internal friction” often associated with the dynamic
loss modulus is sensitive to different kinds of relaxation processes, morphology, molecular motions, transitions and other structural heterogeneities. Thus, for the understanding of the polymer mechanical behavior the dynamic properties provide information at the molecular level. Figure 3.1 shows the typical DMA curves for a polymer. DMA will be used to study the properties of rPAN, PET and the blended samples and the information obtained will be very vital in the development of rPAN/PET blend and its applications.

![Figure 3.1: Typical DMA Curve of storage modulus, loss modulus and tan delta](image)

3.4.4 Scanning Electron Microscopy (SEM)

The cryogenically fractured-surface morphology of rPAN, PET and the blended samples was determined using a JEOL-SEM model JSM-7500 field emission scanning electron microscopy (SEM) (JEOL, Japan). An accelerating voltage of 3 kV was used under the gentle beam (low mode) in order to prevent the beam from damaging the samples. The samples were prepared by immersing in liquid nitrogen, cryogenically-fractured, sputter-covered with gold for 2 minutes using EMITECH K950X machine in order to enhance conductivity and avoid
charging. The samples were mounted on stubs edge-on before being imaged by the electron beam.

The signals generated from the interaction of electron beam generate information on the sample's surface topography, morphology, chemical composition, crystalline structure, orientation and the compositions that make up the polymer sample. Data were collected at selected area of the sample in 2- and 3-dimensional image; this display generates the related properties of the samples being analysed, in most applications. Therefore, using the conventional SEM techniques with magnification ranging from 20X to 30,000X and spatial resolution of between 50 nm to 100 nm, area, ranging from approximately 1 to 5 micron in size was imaged in the scanning mode in this study. Hence, in determining the semi-qualitative or quantitative polymer chemical compositions, crystal orientations and crystalline structure that are vital in polymer characterization, this approach is useful for the blends.

3.4.4.1 ImageJ Software

The ImageJ software is a public domain Java image analysis and processing program, inspired by the National Institute of Health (NIH, USA). The SEM images were further analyzed using NIH ImageJ software at the magnification of X500000. ImageJ allows the systematic extraction of key parameters such as: total area of imaged samples, average size, the % area of imaged sample, mean grey value, maximum and minimum grey value, standard deviation, angle, centroid, skewness, kurtosis, etc. It was decided that the tool be employed to elucidate a number of these parameters relevant to polymer structure. For the purpose of this work, average height, kurtosis and skewness were studied.
3.4.5 Transmission electron microscopy (TEM)

The transmission electron microscope is a very powerful tool for polymer science. A high energy beam of electrons is beamed through a very thin sample and the interactions between the electrons and the atoms can be used to detect features such as the crystal structure and features in the structure like disruptions and grain boundaries. TEM can also be used to study the growth in polymer layers, their composition and defects. High resolution feature in the equipment can be used to analyse the quality, shape, size, density and pores in neat and blended polymer samples.

TEM operates on the same basic principles as the light microscope but uses electrons instead of light. Because the wavelength of electrons is much smaller than that of light, the optimal resolution attainable for TEM images is many orders of magnitude better than that from a light microscope. Therefore, TEM can reveal in detail the finest internal structure of the polymer.

3.4.5.1 TEM Process for the study

The particles distribution in rPAN, PET and their blends was investigated through TEM using DualVision camera from Gatan on a JEOL TEM model JEM-1230 operated at an accelerating voltage of 120kV. This provides a highly magnified micro- and nano-structure image of rPAN, PET and their blends.

TEM technique uses high energy electron beam to process the samples. The electron beam with a wavelength of about a million times shorter than light waves behaves like a wave front when passing through the prepared thin-section of a polymeric material. This process characterised the material electrons through the scattering of light. An arrangement of electromagnetic lenses
is used to focus the scattered electrons into an image. The nano-analytical spectrum or a
diffraction pattern of the image depends on the composition of the polymer.
This imaging gives an insight into the polymer properties of the material by providing in high
resolution imaging mode a highly magnified view of the micro- and nanostructure, resulting
from the direct mapping of the structure in the composition. In addition, the diffraction mode
of TEM can reveal accurate information about the polymer local crystal structure. TEM also
provides valuable information, such as, the crystalline structure and morphology of a material
useful for researchers that are developing new polymer for different applications.

3.4.6 X-Ray diffraction (XRD)
X-ray diffraction (XRD) is a rapid analytical technique primarily used to provide information
on a polymer crystalline structure. The crystals in the structure act as three-dimensional
diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice.
XRD is based on the constructive interference of monochromatic X-rays and the polymer
sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic
radiation, collimated to be concentrated and directed toward the sample.
The sample interaction with the incident rays produces constructive interference and a
diffracted ray when Bragg’s Law \((n\lambda=2d \sin \theta)\) conditions are satisfied. This law relates the
diffraction angle to the wavelength of electromagnetic radiation and the lattice spacing in a
crystalline sample. These diffracted X-rays are then detected, processed and counted. By
scanning the sample through a range of 20 angles, all possible diffraction peaks of the lattice
should be attained due to the random orientation of the polymer molecules. The calculation of
the d-spacing from the diffraction peaks allows the identification of the material crystal
structure because each material has a set of unique d-spacing. Typically, this is achieved by comparison of d-spacing with standard reference patterns.

### 3.4.6.1 X-Ray diffraction (XRD) operational principles

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament in order to produce electrons, accelerating the electrons toward a sample by applying a voltage, and bombarding the sample with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the sample, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being Kα and Kβ. Kα consists, in part, of Kα1 and Kα2. Kα1 has a slightly shorter wavelength and twice the intensity of Kα2. The specific wavelengths are characteristic of the target material such as copper, iron, chromium and molybdenum. Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. Kα1 and Kα2 are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with CuKα radiation = 1.5418 Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak occurs. A detector records and processes this X-ray signal and converts the signal to a count which is then sent out as an output to a device such as a printer or a computer monitor.

For our study, XRD patterns of rPAN, PET and the blended samples were determined using a PanAnalytical X’pertPRO diffractometer (PanAnalytical, the Netherlands) (Cu Kα radiation; wavelength (λ) = 0.154 nm) operated at 45 kV and current of 40 mA with line collimation
geometry. Scanning was performed between $2 \theta = 0^\circ - 80^\circ$, with a scanning step size of 0.0263° and a step time of 132.09s. A point collimated SAXSess was used in obtaining sample intensity profiles and was recorded with a 2D-imaging plate. The distance of the detector-to-sample was 261.2 mm and 260 mm was the radius of detector curvature. The pixel size and the $q$-scale obtained were used in calculating the read-out angles, this was cross-checked by measuring silver behenate diffraction peaks whose equidistant peak positions are known. 5 mins were the exposure time for each of the experiment. XRD investigates the polymer crystalline structure, which includes the atomic arrangement, crystallite size, lattice distortions, phase composition, orientation and imperfection in the samples. All these are highly important characterization parameters in the field of polymer-based materials development for different applications.

3.4.7 Atomic Force Microscopy (AFM)

3.4.7.1 Principle of AFM

Mohammed et al. (2011:40) pointed out that by scanning a microscopic tip at the end of a cantilever over a material surface, topographical images can be produced in AFM. AFM does not use lenses for imaging like an optical microscope. Therefore, for AFM to form an image of the three-dimensional shape (topography) of a sample surface at a high resolution, the reaction of the probe to the forces that the sample imposes on it can be used. With respect to the tip and recording the height of the probe that aligns with a constant probe-sample interaction, this was achieved by raster scanning the position of the sample (see Figure 3.2).

The vertical deflection of the cantilever is measured by an optical system, as the tip gets in contact with the surface, (a laser beam is bounced off the cantilever onto a dual element photodiode (Wiesendanger, 1994) and (Wyart et al., 2008:315).) To converts the signal into a
voltage, the photodetector measures the difference in light intensity between the upper and the lower photodiodes. This method allows the AFM to provide a 3D profile of the surface topography on the nanoscale in conjunction with computer software (WSxM 5.0 development 6.4 and digital instruments/VEECO multimode which are currently finding wide application in polymer surface imaging topography at high resolution). The probe interacts with the sample by the forces involved in the tip-sample interaction. The probe will be in contact mode if it experiences a repulsive force, but attractive forces dominate if the probe moves further away from the surface, thus making the probe be in non-contact mode.

![Schematic representation of AFM](image)

**Figure 3.2: Schematic representation of AFM (Wiesendanger, 1994)**

There are three common imaging modes in AFM: the contact mode: where the tip scan of the sample is in close contact with the surface. In the contact mode for the repulsive regime, the cantilever bends if the spring constant of the cantilever is less than the surface; then the force on the tip is repulsive. An image of the surface is obtained when the forces between the probe
and the sample remain constant by maintaining a constant cantilever deflection. Wilson and Bullen (2007) stated that (i) contact mode is fast in scanning, used in friction analysis, good for rough samples; they can also be applied to soft samples by imaging the samples in liquids.

(ii) Non-contacting mode: In this mode, the probe oscillates above the material and does not touch the sample during scanning, the tip moves about 5-15 nm above the sample surface. Boussu (2007:27) mentioned that by scanning the tip above the surface, topographic images are constructed of the attractive inter-atomic forces between the cantilever tip and the sample surface. The non-contacting mode advantage is that a very low force is exerted on the samples ($10^{-12} \text{N}$), thus, by means of a piezoelectric element and changes in resonance frequency as a result of tip-surface force measured, the cantilever is driven to vibrate near its resonance frequency.

(iii) Tapping mode: In this mode, the cantilever vibrating at its resonance frequency is driven by a piezoelectric actuator in mapping the sample. Upon approaching the sample, the tip temporarily taps the surface at the bottom of each strike, causing a decrease in oscillation amplitude. Putman et al. (1994:64) stated that the decrease in the preset value is kept by the feedback loop and the sample surface topographical image can be obtained. In the AFM tapping mode, due to the relative movement of the tip with respect to the sample, the destructive influence of the lateral forces is virtually eliminated, as mentioned in the non-contact mode AFM, because the duration of tip-sample contact is short (Zhong et al 1993). The lateral resolution being determined by the tip sharpness has nonetheless been as high as in AFM contact mode. According to Matsko et al. (2011:2), high quality factor (Q), which substantially increases the sensitivity of the AFM system and permits the true atomic resolution lateral force microscopy in ultrahigh vacuum (UHV) is one of the advantages of the piezoelectric actuator. An extension of AFM tapping mode is the phase imaging. Phase imaging is not really an operation mode in itself. It is carried out in intermittent contact mode (IC-AFM). In commercial
AFMs, depending on the instrument, IC-AFM may be referred to as vibrating tapping mode. Different material properties measured by the oscillation and the phase difference between the oscillations of the cantilever are the main characteristics of the tapping mode process. The change in phase is not only related to the topography change but also to the properties of the surface. In many cases, the phase image can give better resolution and some information about material properties. Boussu (2007:27) reported that, in phase imaging, the cantilever oscillation during scanning and the difference in phase angle between the freely oscillating cantilever in the air resulted in the phase shift. Therefore, freely resonating in the air is what convention of phase scaling is based on. Hence, where there is no interaction between the sample surface and the cantilever tip, the phase shift is zero. Therefore, a phase lag is induced if the interaction is attractive and a phase advance appears if the interaction is repulsive, in the case of sample interaction.

AFM has been continuously used in polymer processing since the 1990’s to analyse the surfaces of pure and blended polymer materials (Achalla et al 2006:44, Jagtap and Ambre 2006:13, Ulaganathan et al 2012, Tranchida et al 2009:20, Fang et al 2005:36, Jee and Lee 2010:29 and Camargo et al 2009:12). It has also been used in studying, the estimated pores size and shape on the material surfaces (Li and Golovchenko 2009:544), (Shulga et al 2007:19) (Juszczak et al 2003:55), (Podobnik et al 2015:5) and (Hilner et al 2014). Bowen and Doneva (2000:129) reported that in the interpretation of pore diameters obtained by AFM in the case of smaller pores of pure and blended polymers, a great caution needs to be exercised because of the convolution effects between the samples pore and the contact of the cantilever tip. According to Bowen and Doneva (2000:129) and Hilal and Bowen (2002:150), AFM has also been applied in polymer surface technology by direct measurement of the adhesion force between a particle and the probe tip in quantifying the surface and molecular forces.
3.4.7.2 AFM sample process

Agilent Technologies 5500 Scanning Probe Microscope (PicoPlus-Atomic Force Microscopy Series 5500) was used to perform Non-contact AFM imaging. The cantilever tip was made of silicon (Nanosensors) with a resounding frequency of ~60 kHz, a nominal spring constant of 7.4 N/m with a typical tip radius of less than 7 nm. Neat PET, rPAN and their blends were also cut into smaller pieces, fastened onto a sample holder and processed at a relative humidity of ~ 30% air atmosphere. Thus, applying the nanotechnology research tool, AFM images with the flattened order of 1 and the root-mean-square (RMS) value of the roughness can be obtained (Horcas et al., 2007:78). It was also discussed by (Boussu et al., 2005:286) that the sample roughness depends on the scan section; therefore, for the comparative analysis, it is important to obtain the roughness value from images within the same scan areas. The phase shift, roughness and force-distance were measured for all the samples using areas of 5.0 µm x 5.0µm and each measurement were done five times on all the sample areas in order to obtain the root mean square.

3.4.7.3 AFM characterization

The development and application of scanning probe microscopy (SPM) have revolutionized the nanoparticle materials development and characterization, by a revolution in software technology. In fact, this is now playing a significant role in improving the material processing techniques by the data acquisition and control, data analysis and image processing (Horcas et al 2007:78). WSXM 5.0 software program is widely used in SPM to extract sample roughness parameters from AFM topography and phase image. The software can also be used to augment the contrast for the distinguish features between the sample phases, by providing additional
information on the topography image projections (Taylor et al 2007:8). Stawikowska et al. (2013:425) also stated that the phase imaging is used to improve the contrast for the features of importance, or to distinguish phases in the material and provide extra information on the topographical projections.

3.4.7.4 SPM Image Process - Roughness Analysis

Scanning probe microscope (SPM) is designed to acquire images, measure and generate statistical properties of materials. The surfaces of rPAN, PET and their blends were analysed, characterised and compared in terms of roughness parameters, such as root mean square $rms$ (nm), the mean roughness $ra$ (nm), the height distribution function, gradient, curve, average height, surface fractal analysis, power spectral density, average surface roughness and average surface area, together with the diameter of the nodules (Lehmani et al 1998:68, Nazzarro et al 1998:44, Singh et al 1998:142, Bowen et al 1998:139). In addition, the size of the cantilever tip, the curvature and the treatment of the captured surface data (i.e. plane fitting, flattering, filtering, etc.) governs the sample’s roughness parameters. The statistical measurement of the relative roughness of a material surface is referred to as the root mean square ($rms$) roughness parameter and is primarily the standard deviation of the heights of all the pixels in the image from the arithmetic mean. The root mean square of the roughness varies with the interval range; it is given by the following expression:

$$
\text{Root mean square, } rms = \sqrt{\frac{\sum_{j} (a_{ij} - < a >)^2}{N}}
$$

3.10
Where $a_{ij}$ = height value for a particular point on the image (nm), $\langle a \rangle$ = average/mean height of all the pixels in the image (nm) and $N$ = a total number of pixels within the image.

The height difference between the lowest and highest pixels in the image is the maximum range. The mean value of the surface relative to the centre plane is the mean roughness, the plane for which the volumes enclosed by the image above and below this plane are equal; it shows how rough the sample is. It is given by the following expression:

$$\text{Mean roughness, } r_a = \frac{\sum_{ij} |a_{ij} - \langle a \rangle|}{N}$$  \hspace{1cm} (3.11)

The average height ($\langle a \rangle$) = the mean height of the pixel in the image Eq. 3.12.

$$\langle a \rangle = \frac{\sum_{ij} a_{ij}}{N}$$  \hspace{1cm} (3.12)

The surface skewness (S) = the measure of the direction of the asymmetry of the distribution of heights in the sample. This statistical parameter is given by the following expression:

$$\text{Skewness } S = \frac{\sum_{ij} (a_{ij} - \langle a \rangle)^3}{N\sigma^3}$$  \hspace{1cm} (3.13)

The numerical value of the surface skewness (S) gives the information about the direction of the asymmetry of the distribution of height as follows:

If S>0: positive asymmetry

If S=0: symmetric distribution

If S<0: negative asymmetry

55
The surface kurtosis (K) is the measure of the degree of peakedness in the distribution of heights in the membranes comparing it to the normal distribution. This statistical parameter is given by the expression in Eq. 3.5.

\[
K = \frac{\sum (a_{ij} - <a>)^4}{N\sigma^4}
\]

3.14

Where the reflection coefficient \(\sigma\) is given by the relation in (Eq. 3.1) as:

\[
\sigma = \sqrt{\frac{\sum (a_{ij} - <a>)^2}{N}}
\]

3.15

3.4.7.5 Force spectroscopy

The force spectroscopy was done with Kelvin Probe Microscopy. It was used to improve the contrast for the features of importance, providing additional facts about the force of interaction near the surface of the rPAN, PET and blended samples (Horcas et al., 2007:78). The applied force was controlled by obtaining force plots between the tip and samples to quantify the distance from the starting point values. The force-distance curves were done with non-contact mode principle, here the cantilever is vibrated by an extra piezoelectric transducer; the amplitude of the cantilever oscillations is collected as a function of tip-sample distance which is the effective distance.

3.4.8. Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR)

Attenuated total reflectance (ATR) Fourier-transform infrared (FT-IR) spectroscopy using a Perkin-Elmer Spectrum 100 spectrometer was performed on the samples, in the wavelength
region of between 250 and 2500 cm\(^{-1}\) in order to check for any chemical interaction in rPAN, PET and the blended samples. The disk-shaped samples were 25 mm in diameter and had a thickness of ~ 1.62 mm.

Attenuated total reflectance is a sampling technique used in conjunction with Fourier Transform infrared spectroscopy in order to enable surfaces to be examined directly for infrared (IR) analysis. The part of the electromagnetic spectrum between the visible and microwave regions is known as the Infrared (IR) radiation. Therefore, the transition intensities and the vibrational frequencies of most polymers together with the characteristic of the functional group frequencies can be determined by the IR spectrum. Hence, for structure identification and chemical processes, infrared spectroscopy is an important technique to apply. Also, the advances in nanomaterial surface analysis are made possible using the infrared spectroscopy with the theories of reflection. Although the IR spectrum is a representative of the entire polymer, according to Silverstein, Webster and Kiemle (2005), it is true that some groups of atoms give rise to bands at or near the same frequency irrespective of the structure of the rest of the polymer. It is the resolution of these characteristic bands that permits the analyst to acquire valuable structural data by simple examination and reference to universal charts of characteristic group frequencies. Silverstein, Webster and Kiemle (2005) further stated that the geometry of the atoms, the atoms relative masses and the bonds force constants depends on the wavelength of propagation or the frequency.

### 3.4.8.1 FTIR process

In order to reflect at least once off the internal surface in contact with the polymer samples, a beam of infrared light is passed through the sample’s crystal during the FTIR process (see Figure 3.3). The reflection is the momentary wave connection covering the samples. Therefore,
the size of reflections is varied by varying the angle of incidence and by using a detector while the light is exiting the crystal the beam was collected. The FTIR spectra of the polymers were usually recorded in the 4000-250 cm\(^{-1}\) region, on a Perkin Elmer 16PC FT-IR instrument with 32 scans in each at a resolution of 4 cm\(^{-1}\).

Figure 3.3: Schematic of an FTIR spectrometer (Adapted from Silverstein Webster and Kiemle, 2005)

3.4.9 Polarized optical microscopy (POM)

The morphology of rPAN, PET and their blended samples were studied for spherulite growth using the polarized optical microscope (POM) equipment. Two glass slides were used to hold the samples while being heated on Linkam THMS hot stage (Linkam Scientific Instrument, Ltd). The samples were processed from (0 to 300)\(^{\circ}\)C at a heating rate of 20\(^{\circ}\)C/min and held at this temperature for 10 mins before being cooled to 120\(^{\circ}\)C at a rate of 10\(^{\circ}\)C/min to observe the crystal formation. The samples were maintained under the isothermal condition for 90 mins,
during which period images were collected using Carl Zeiss imager Z1M POM (Germany). The images result from this characterization will be discussed in chapter 4.

3.4.10 Rheology

The science of material flow and deformation is referred to as rheology. All materials do flow given sufficient time; in this context polymer time for flow are of the same order of magnitude as their processing time for injection and extrusion processes. Therefore, the material may behave as solid in a very short processing time, while in extensive processing time the material may behave as a liquid. This state of solid-liquid during processing is called viscoelastic behavior.

Rheological measurements can be applied to determine material processability, characterization and as an idea data for computer simulations. Furthermore, rheology has an advantage over other polymer processing techniques in material characterization because of its sensitivity to certain aspects of the structure such as the material chain branching and high molecular weight. Therefore, with rheology, it is possible to decide whether or at what conditions will the polymer be processable and many problems can be avoided through rheology characterization (Kelly et al 1999:20), (Coates et al 1999).

3.4.10.1 Viscosity and flow index

Viscosity is the utmost significant flow property in a material and it can also be described as the resistance to flow. Figure 3.4 shows the shear flow and viscosity which is defined as the ratio of the enforced shear stress (force F, applied tangentially, divided by the area A) and the
shear rate (velocity V, divided by the gap h) as shown in equation (Vlachopoulos and Wagner 2001):

\[ \eta = \frac{Shear\ stress}{Shear\ rate} = \frac{F}{A \cdot F / V / h} = \frac{\tau}{\gamma} \]  

3.16

Where \( \tau \) = shear stress and \( \gamma \) = shear strain

In this study, the melt state rheology of rPAN, PET and blended samples were studied using a Physical MCR501 stress/strain – controlled rheometer with 25 mm diameter parallel plates from Anton Paar, Austria. In order to eliminate any residual thermal history, the blended samples were melted in a parallel plate spindle at the processing temperature of 290°C for 5 mins. In addition, a dynamic strain sweep was also done on the sample in order to determine the common linear region. Finally, for the performance of a dynamic frequency sweep of the pure and blended samples, a small amplitude oscillatory shear was also attempted.

![Figure 3.4: Schematic drawing of simple under shear deformation](image)

**3.4.11 Tensile strength**

In this current work tensile tests were performed on rPAN, PET and their blends to determine the stress, modulus, the strain, yield strength, elongation-at-break and ultimate tensile strength using Instron 5966 tester (Instron Engineering Corporation, USA) with a load cell of 10 kN in agreement with ASTM D638 standard. Samples were prepared using compression molding.
The experiments were done in tension mode at a single strain rate of 5 mm/mins at room temperature. The results presented are an average of at least five independent tests per samples. The maximum stress that a material can endure while being strained or stretched before fracture or failing is called the tensile strength. It can also be articulated as the minimum tensile stress (force per unit area) required to section polymer material. Different polymers have different tensile strength that dictates their application in the relevant area of applications. Therefore, the understanding of tensile test properties in polymer development is highly essential for its applications and performance.

3.4.12. Impact test

According to ISO 179 standard, a Charpy impact test specimens with a dimension of approximately 80 x 10 x 4 mm (L x W x B) were compression moulded for the test. Using CEAST Notchvis Plus (Italy) polymer samples were notched on one side, with a notch root radius of 0.25 mm at 2 mm depth, while CEAST Pendulum Resil Impactor II (Italy) at room temperature measured Notched Charpy impact strength (ISO 179). The hammer energy is 7.5 J with a drop velocity of 3.7 m/s and 40 mm was the fixed span between supports for the tests. The results of the averages of six independent tests per sample were presented.

3.4.12.1 Impact test operating procedure

The impact testing machine operates on automatic principle to achieve a precision of the impact loading, the hammer released system is pneumatic actuation and was programmed to a holding force after the test to avoid the second impact on the samples.
The measured properties and dimensions of pure rPAN, PET and their blends were set on the comments on lot of the impact testing machine before the commencing the test. The hammer was calibrated with 12 oscillations after which, the samples were loaded on the anvil. The process was repeated for all the samples and the result generated saved on the comment on lot. The generated results will be discussed in chapter 4.

3.4.13 Origin 8.0 software

Computer simulation has turned out to be an indispensable part of science and engineering. A computer simulated environment is the transformation of the real-world scenario using physical laws into virtual reality form for detail study. The resulting model accuracy was determined by the number of simplification that takes place in the translation procedure. Origin 8.0 software is a flexible platform that permits users to plot all the significant data relating to material analysis. Origin 8.0 gives the user confidence to analyze the plots with real-world precision. Origin 8.0 requires that data being analyzed gives adequate and precise information on the material behaviour in the real world. This stern requirement reflects what take place in the real world, thus the reason why origin 8.0 software was used to plot and analysed the curves of the data obtained in this study.
CHAPTER 4

4.1 RESULTS AND DISCUSSION

4.2 Introduction

The data collected from the equipment in chapter 3 were analysed and discussed in this section. The investigation and discussions showed the performance of rPAN, PET and the blends. The discussions are in line with the processes mentioned in table 3.1. Finally, the interpretations of each sample results are explained in the relevant sections and the overall conclusion was also stated at the end of each section.

4.3. Materials characterization

4.3.1 DSC Curves discussion

DSC was one of the methods used to characterise the thermal behaviour of the polymers. The assessment of the thermal properties of rPAN, PET and their blends would aid the understanding of the interaction between the two polymer blends. Figures 4.1-4.4 showed the cooling curves of rPAN, PET and the blended samples, while cooling the samples from 300°C to -50°C at the rate of 10°C/min. The same figures revealed the matching heating curves attained while heating the samples from -50°C to 300°C. Visually, the samples did not reveal any glass transition temperature ($T_g$) and there is only one melting and crystallization peaks each, for rPAN, PET and rPAN/PET (70/30 and 30/70) (see Figures 4.2b and 4.3a), while two peaks were observed in rPAN/PET (50/50) (see Figure 4.3b). Obviously, the crystallization temperature of PET decreased with increasing rPAN content, in cases where rPAN was the main matrix (see Table 4.1). In addition, PET also acted as the nucleating site for rPAN at a temperature ranging between ~263°C – 266.64°C and this did not influence the growth of the rPAN crystals formed. Therefore, as the composition of PET increases, the amount of crystals...
formed in the blend increased. Furthermore, as the melting temperature of rPAN decreased the melting temperature of PET increased. Hence, rPAN crystallization (crystal formation) is influenced by PET addition. Similar trends can also be seen in the percentage crystallization data (Table 4.2). Therefore, the addition of PET, in the composition, improves the crystallinity of rPAN in the blend as revealed by the reduction and shift to the left (lower temperature) for both the melting and crystallization (see Figure 4.4). This shift to lower temperature should assist in the processing of rPAN. The enthalpy heat of melting and crystallization, tabulated in Table 4.1, are low for the blends of rPAN/PET (30/70 and 50/50) but highest in the blend rPAN/PET (70/30). This phenomenon revealed that the enthalpy trend might be related to the ratios of the blends composition.

Table 4.1: Summary of DSC Data

<table>
<thead>
<tr>
<th>Samples</th>
<th>Peak crystallization temperature (°C)</th>
<th>Onset crystallization temperature (°C)</th>
<th>Peak melting temperature (°C)</th>
<th>Onset melting temperature (°C)</th>
<th>Enthalpy heat of crystallization (J/kg)</th>
<th>Enthalpy heat of melting (J/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rPAN</td>
<td>234.83</td>
<td>240.94</td>
<td>277.03</td>
<td>263.56</td>
<td>29.55</td>
<td>21.81</td>
</tr>
<tr>
<td>rPAN/PET (30/70)</td>
<td>234.07</td>
<td>242.10</td>
<td>277.73</td>
<td>266.55</td>
<td>5.33</td>
<td>3.04</td>
</tr>
<tr>
<td></td>
<td>196.96</td>
<td>208.14</td>
<td>249.95</td>
<td>239.17</td>
<td>16.14</td>
<td>11.68</td>
</tr>
<tr>
<td>rPAN/PET (50/50)</td>
<td>237.40</td>
<td>242.10</td>
<td>277.5</td>
<td>266.64</td>
<td>10.17</td>
<td>5.98</td>
</tr>
<tr>
<td></td>
<td>194.83</td>
<td>208.14</td>
<td>247.86</td>
<td>235.72</td>
<td>11.43</td>
<td>10.17</td>
</tr>
<tr>
<td>rPAN/PET (70/30)</td>
<td>237.40</td>
<td>244.82</td>
<td>277.50</td>
<td>266.64</td>
<td>16.67</td>
<td>8.86</td>
</tr>
<tr>
<td></td>
<td>194.83</td>
<td>203.73</td>
<td>247.86</td>
<td>235.72</td>
<td>3.08</td>
<td>4.30</td>
</tr>
<tr>
<td>PET</td>
<td>212.97</td>
<td>216.92</td>
<td>245.31</td>
<td>236.30</td>
<td>26.86</td>
<td>20.54</td>
</tr>
</tbody>
</table>
Table 4.2 Percentage crystallinity

<table>
<thead>
<tr>
<th>Samples</th>
<th>% crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>rPAN</td>
<td>23.25</td>
</tr>
<tr>
<td>rPAN/PET (30/70)</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>0.21</td>
</tr>
<tr>
<td>rPAN/PET (50/50)</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>0.16</td>
</tr>
<tr>
<td>rPAN/PET (70/30)</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>0.51</td>
</tr>
<tr>
<td>PET</td>
<td>14.31</td>
</tr>
</tbody>
</table>

Figure 4.1: DSC curve of rPAN
Figure 4.2: DSC curves of: (a) PET (100%) and (b) rPAN/PET (70/30)
Figure 4.3: DSC curve of (a) rPAN/ PET (30/70) and (b) rPAN/PET (50/50)
Blends stability is one of the essential characteristics of polymer technology, thus, the blends, rPAN and PET samples thermal stability was investigated. TGA is a thermal analysis method that measures the physical properties of a material as a function of temperature or time (with constant heating rate). TGA was performed on the rPAN, PET and the blended samples in order to understand their structural thermal and degradation behaviour that will influence their application. Figures 4.5 – 4.9 show the thermal degradation stages of rPAN, PET and their blends. The plots of the samples first derivative TGA (dTGA) curves were plotted as a function of temperature (see Figure 4.5 and 4.6), the curves showed increased thermal stability of rPAN/PET (50/50 and 70/30) while there is a reduction in the thermal stability of rPAN/PET.
Hence the thermal stability of the blend increases with the increasing rPAN content and vice versa for PET.

Figures 4.7-4.9 shows the curves of percentage weight losses in the samples. The thermograms show two degradation stages for rPAN and neat PET (the first stage shows that the intermediate products are thermally stable and in the second stage, in which the intermediate products degrade rapidly) and the blends exhibit three stage % weight losses. It is shown in Fig. 4.9 that at around 390°C, all samples are thermally stable before the start of degradation. Furthermore, there are sharp mass losses of the rPAN sample at about 500°C. Mass losses at a temperature above 400°C for the blends could be attributed to the breakdown of the carbon-carbon double and triple bonds in both the rPAN and PET and the dipole-dipole interaction of the nitrogen group in the rPAN composition. The mass loss at 400°C in the first stage of degradation can be attributed to the removal of moisture and small molecules of water as well as OH groups. The loss of binding elements that remaining in the samples caused the second weight loss and the third degradative stage is caused by the complete degradation of the polymer. The third degradative stage in the blends demonstrates an intermediate between those of the two components (rPAN and PET). This suggests that the inter-macromolecular bonding caused interactions between the two polymers.

In addition to the samples degradation, phase change can also be a contributing factor affecting the weight loss. This phase changes in the blend might also be attributed to the breakdown of the CN and CH (double and triple bonds) and the dipole-dipole bond in rPAN. This affects the shape and size of the crystals formed in the blends which modify samples properties. Therefore, the result shows that high amount of rPAN improves the blend properties while high PET content resulted in the brittleness (weakened mechanical property) of the blend. The TGA further revealed that both the rPAN and PET samples degrade independently typical of many
polymer blends and the addition of PET increases the thermal stability of the blends since the
temperature at which PET degraded increased with increasing amount of rPAN in the blend
(see Figures 4.8 and 4.9).

In addition, the blended samples revealed % char formation in the following order; 14.8; 21;
26.2 for rPAN/PET (70/30; 50/50; 3070) when compared to PET. These chars could be related
to undecomposed PET within the range of processing temperature. Lastly, Table 4.3
summarises the temperature profile while figures 4.5 – 4.9 revealed the temperature curves and
the weight loss summary in Table 4.4.

Table 4.3: Summary of TGA data

<table>
<thead>
<tr>
<th>Blended samples</th>
<th>Peak temperature (°C)</th>
<th>Intermediate temperature (°C)</th>
<th>Char (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rPAN</td>
<td>643.52</td>
<td>495.60</td>
<td>4.74</td>
</tr>
<tr>
<td>rPAN/PET (ratio 30/70)</td>
<td>583.52 (PAN)</td>
<td>421.33 (PET)</td>
<td>506.00</td>
</tr>
<tr>
<td>rPAN/PET (ratio 50/50)</td>
<td>614.75 (PAN)</td>
<td>419.55 (PET)</td>
<td>514.87</td>
</tr>
<tr>
<td>rPAN/PET (ratio 70/30)</td>
<td>634.38 (PAN)</td>
<td>415.09 (PET)</td>
<td>511.91</td>
</tr>
<tr>
<td>PET</td>
<td>423.65</td>
<td>520.80</td>
<td>35.9</td>
</tr>
</tbody>
</table>
Table 4.4: Samples weight loss

<table>
<thead>
<tr>
<th>Samples</th>
<th>Weight loss (%) in stages</th>
<th>Temperature (°C)</th>
<th>Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(%)</td>
</tr>
<tr>
<td>rPAN 100%</td>
<td>96.80 ~ 465.87</td>
<td>64.22 ~ 572.43</td>
<td>4.74</td>
</tr>
<tr>
<td>rPAN/PET(30/70)</td>
<td>98.44 ~ 354.01</td>
<td>62.56 ~ 471.15</td>
<td>26.16</td>
</tr>
<tr>
<td></td>
<td>51.61 ~ 561.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>rPAN/PET(50/50)</td>
<td>98.71 ~ 346.08</td>
<td>65.07 ~ 471.16</td>
<td>20.97</td>
</tr>
<tr>
<td></td>
<td>47.65 ~ 580.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>rPAN/PET(70/30)</td>
<td>98.23 ~ 362.21</td>
<td>82.00 ~ 457.93</td>
<td>14.81</td>
</tr>
<tr>
<td></td>
<td>61.55 ~ 561.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PET 100%</td>
<td>98.87 ~ 348.73</td>
<td>45.23 ~ 455.29</td>
<td>35.89</td>
</tr>
</tbody>
</table>
Figure 4.5: TGA curve of: (a) rPAN and (b) PET
Figure 4.6: TGA curve of (a) rPAN/PET (30/70) and (b) rPAN/PET (70/30)
Figure 4.7: TGA curve of: (a) rPAN/PET (50/50) and (b) all samples curves
(a) PAN 1\textsuperscript{st} step weight change

Residue = 4.74%

(b) PET 1\textsuperscript{st} step weight change

Residue = 35.89%
Residue = 26.18%

(c) PAN/PET (30/70)

PET 1\textsuperscript{st} step weight change

PAN 1\textsuperscript{st} step and PET 2\textsuperscript{nd} step weight change

PAN 2\textsuperscript{nd} step weight change

Residue = 20.97%

(d) PAN/PET (50/50)

PET 1\textsuperscript{st} step

PAN 1\textsuperscript{st} step and PET 2\textsuperscript{nd} step weight change

PAN 2\textsuperscript{nd} step weight change

Residue = 20.97%
Figure 4.8: weight change in (a) rPAN, (b) PET, (c) rPAN/PET (30/70), (d) rPAN/PET (50/50) and (e) rPAN/PET (70/30)

Figure 4.9: Combined curves of weight loss in samples
4.3.3 DMA results discussion

In the understanding of the behaviour of polymer materials, DMA has emerged as one of the utmost accessible dominant processing tools. DMA provides vital information on the thermal and structure of the polymer, such as: tan delta (damping), loss modulus (viscous) and storage modulus (stiffness). Polymer materials can easily be deformed when it exhibits low storage modulus while high storage modulus reveals the toughness in the material. Furthermore, the degree of crystallinity in the material can serve as a relative indicator of the storage modulus reduction observed through the glass transition temperature.

Figures 4.10 and 4.11 show the DMA curves for the rPAN, PET and their blends. Due to the increase in temperature, a gradual decline in $E'$ was detected in all the samples. This reveals the fact that, the addition of a low amount of PET (<50%) to rPAN, slightly improves the toughness (storage modulus) of the blends when compared with the rPAN and neat PET. In addition, the loss modulus decreases with the addition of 70% by weight of PET which resulted in the sample (rPAN/PET (30/70) brittleness. Thus, the mechanical properties of the rPAN as a matrix in the blends were influenced by the amount of PET added.

Furthermore, rPAN/PET (50/50) composition reveals the optimum modulus in the blend. Above 50% addition of rPAN in the blend, there was a reverse in the material property. Therefore, the blend of rPAN/PET (50/50) gave the optimum storage modulus, which improved the toughness of the sample.

Also important to note is that;

- As the percentage of PET increases in the blend, changes in the glass transition temperature ($T_g$) becomes obvious. This might increase the crystallinity of the sample and subsequently improve the blends toughness and damping properties.
An increase in the structural mobility of the polymer chain indicated by the rapid rise in the loss modulus, permits motion along larger portions of the individual polymer chains due to the relaxation process that might not be possible at a temperature below the glass transition temperature. At the glass transition which is the prevailing and most significant relaxation region, polymers structure that is not either cross-linked or crystallised become capable of moving freely within the regions. Thus, the polymer mobility will take the form of organised flow or movement under an applied load.

Furthermore, the $T_g$ is identified as the peak of the loss modulus even though the DMA plot visibly shows that the glass transition process spans over a temperature range. In addition, the determinations made by other thermal analysis methods are in agreement with the information provided by the loss modulus. The immiscibility of the blends was revealed by the lack of shift in the $T_g$. The loss modulus is the contribution of the viscous constituents in the polymer, the material region at flows under the conditions of applied stress.

The result also revealed that, the higher the amount of rPAN added in the blends, the lower storage modulus value. This is clearly observed in Figure 4.11. Also important to note is that, low PET content improved the $T_g$ of the blend to $\approx 130^\circ C$ as shown with the 50/50 and 70/30 blends in Figure 4.10 (d and e). These $T_g$s are higher than the individually quoted $T_g$s of the polymer and the increase might be related to the blends ratio. Furthermore, the occurrence of a simple strong tan $\delta$ peak in all the blends shows possible homogeneous mixing. Lastly, in the blends, the leathery region is almost non-existent, this might also be related to the blends compositional ratio, processing method adopted and phase changes in the blend.
(a) Modulus $E'/\text{Pa}$ versus Temperature $^\circ\text{C}$

(b) Modulus $E'/\text{Pa}$ and Loss Modulus $\text{Pa}$ versus Temperature $^\circ\text{C}$
Figure 4.10: DMA curves for: (a) rPAN, (b) PET, (c) rPAN/PET (30/70), (d) rPAN/PET (50/50) and (e) rPAN/PET (70/30)
Figure 4.11: Curves of (a) Tan delta and (b) Storage Modulus (MPa)
4.3.4 XRD CURVES ANALYSIS

Wide-angle X-ray diffraction patterns of the materials were collected using the XRD machine as described in chapter 3. The WAXRD peak profiles were observed at 2 theta as shown in Figures 4.12 and 4.13. The main use of X-ray diffraction is to identify sample components by a search/match procedure.

From Figure 4.13, a common (rPAN/PET) strong diffraction peak occurred at $2\theta = 18^\circ$, in all samples, except rPAN/PET (30/70) blend where this peak completely disappeared. However, 2 small diffuse peaks appeared at about $2\theta = 16^\circ$ and $17^\circ$, which a PET peak appeared at about $2\theta = 28^\circ$. It is pertinent to note that new crystals were formed for blends 30/70 and 50/50 with diffuse intensities at $2\theta = 16^\circ$ and $17^\circ$ and also at $2\theta = 22^\circ$. It is assumed that < 50% PET, this phenomenon is rife suggesting a possible co-crystallization < 50% PET addition.

Furthermore, the areas under the peak relate to the different phases present in the blends (see Figure 4.13). These peaks were used to calculate the crystallite size and the degree of crystallinity. The expressed heights of the scattering intensity at 2 theta and the percentage crystallinity of the samples were calculated using the following equations:

- **Bragg’s equation**:

\[
n\lambda = 2d \sin\theta
\]

Where n equal to order of reflection; $\lambda$ equal to X-ray wavelength; d equal to interplanar d-spacing of the set of planes of this order; $\theta$ equal to angle between “diffracting plane”, “incident X-ray beam”, the “diffracting plane” and the “reflected beam”

- **Scherrer equation**

The crystallite size of rPAN, PET and their blends were calculated using the Scherrer equation:
\[ D_p = \frac{0.94\lambda}{\beta \cos \theta} \]

Where \( D_p \) = Average crystallite size, \( \beta \) = Peak width i.e. full-width half maximum (the line broadening measured in radian), \( \theta \) equal Bragg angle and \( \lambda \) = X-ray wavelength \( (1.5\ldots\text{A}^\circ)^{1/2} \).

The results generated by using the Scherrer’s equation are tabulated in Tables 4.5 – 4.9

**Percentage Crystallinity**

The percentage crystallinity of the materials (from xrd curve) is defined as the total area of crystalline peaks divided by the area of crystalline peaks plus the area of amorphous peak.;

\[ \% X_c = \frac{\text{Area of crystalline peaks}}{\text{Area of crystalline peaks} + \text{Area of amorphous peak}} \]

Using the intensity of the peaks,

\[ \% X_c = \frac{I_a + I_b + I_c \ldots \ldots \ldots \ldots \ldots I_n}{I_a + I_b + I_c \ldots \ldots \ldots \ldots \ldots I_n + I_A} \]

The area of rPAN, PET and blended samples were calculated from the curves generated using origin 8.0 software. The result from the calculations is tabulated in Table 4.10.

**4.3.4.1. XPert High score discussion**

The XRD results were further analysed by using XPert HighScore software in order to detect the intensity profiles, compound name, chemical formula and crystal systems of rPAN, PET and blended samples (see table 4.11). The software also confirmed the crystallinity of the two polymers in the blended samples. The intensity peaks changes were based on the compositional ratios of the rPAN and PET in the blended samples. In addition, the crystal structure of the samples changed due to the ratios of the elements in the blends, see Table 4.11. This changes can be attributed to the disappearing and reappearing of new phases in the blended composition,
as follows: ‘phenyl’ appear in all (neat and blended samples); ‘Hyroxyl’ appears in the all the 
blends (rPAN/PET[30/70;50/50;70/30]); ‘Phenylpentanoade only appears in rPAN/PET 
(70/30); ‘Metheoxypheny’ appears in PET and rPAN/PET (50/50) and lastly “Carbohyrazide” 
compound appears in rPAN/PET ([30/70 and 50/50]). This effect of the phase changes in the 
blended samples could be attributed to the toughness of matrix in rPAN/PET (70/30 and 50/50) 
and the weakness in the matrix of rPAN/PET (30/70) blend.

In conclusion, as the amount of PET added to rPAN increases, the crystallinity increases. The 
crystal structure of the matrix in the blend plays a significant role in the polymer-based blends 
system properties determination (Tchmutin et al 2003:4; Radhakrishnan et al 2004:9). Also, 
based on the XRD intensity profiles of rPAN, PET and the blends of rPAN/PET (Figures 4.12), 
the following X-ray patterns of the blends were displayed: (rPAN70/PET30; PAN30/PET70 
and PAN50/PET50) revealed the presence of peaks at 2theta = 20.98°, 26.49° and 21.03° 
corresponding to the crystal reflections of (8587), (6679) and (6483). While the pure rPAN and 
PET show the peaks at 2theta = 20.07° and 26.57° respectively, their intensity counts are 
(10983) and (7285), respectively. The result also shows that the blend of rPAN/PET (70/30) 
has the highest intensity and rPAN/PET (50/50) has the least intensity count. Lastly, in the 
blends, rPAN composition affects the type of crystals formed due to its rubbery state. In 
addition, the overall crystallinity depends on the individual material in the blends. Moreover, 
the XRD confirmed that rPAN/PET blends are immiscible as manifested by their individual 
peaks.
Table 4.5: rPAN crystallite size calculation

<table>
<thead>
<tr>
<th>Sample 1</th>
<th>Peak width (degree)</th>
<th>Peak position (degree)</th>
<th>Crystallite size (nm)</th>
<th>Lattice strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>0.56727</td>
<td>19.2566</td>
<td>14.84</td>
<td>0.0146</td>
</tr>
<tr>
<td>Peak 2</td>
<td>1.4433</td>
<td>20.7332</td>
<td>5.85</td>
<td>0.0344</td>
</tr>
<tr>
<td>Peak 3</td>
<td>0.5616</td>
<td>25.7739</td>
<td>15.16</td>
<td>0.0107</td>
</tr>
<tr>
<td>Peak 4</td>
<td>0.6353</td>
<td>27.62293</td>
<td>13.45</td>
<td>0.0113</td>
</tr>
</tbody>
</table>

Table 4.6: PET crystallite size calculation

<table>
<thead>
<tr>
<th>Sample 2</th>
<th>Peak width (degree)</th>
<th>Peak position (degree)</th>
<th>Crystallite size (nm)</th>
<th>Lattice strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>0.7685</td>
<td>16.85615</td>
<td>10.92</td>
<td>0.0226</td>
</tr>
<tr>
<td>Peak 2</td>
<td>0.7684</td>
<td>18.2480</td>
<td>10.94</td>
<td>0.0209</td>
</tr>
<tr>
<td>Peak 3</td>
<td>0.9979</td>
<td>23.3950</td>
<td>8.49</td>
<td>0.0210</td>
</tr>
<tr>
<td>Peak 4</td>
<td>1.4622</td>
<td>26.6776</td>
<td>5.83</td>
<td>0.0269</td>
</tr>
</tbody>
</table>

Table 4.7: rPAN/PET (30/70) crystallite size calculation

<table>
<thead>
<tr>
<th>Sample 3</th>
<th>Peak width (degree)</th>
<th>Peak position (degree)</th>
<th>Crystallite size (nm)</th>
<th>Lattice strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>0.6328</td>
<td>19.4034</td>
<td>13.31</td>
<td>0.0161</td>
</tr>
<tr>
<td>Peak 2</td>
<td>1.3528</td>
<td>21.0316</td>
<td>6.24</td>
<td>0.0318</td>
</tr>
<tr>
<td>Peak 3</td>
<td>0.8146</td>
<td>26.0999</td>
<td>10.46</td>
<td>0.0153</td>
</tr>
<tr>
<td>Peak 4</td>
<td>0.9964</td>
<td>28.0169</td>
<td>8.59</td>
<td>0.0174</td>
</tr>
</tbody>
</table>
Table 4.8: rPAN/PET (50/50) crystallite size calculation

<table>
<thead>
<tr>
<th>Sample 4</th>
<th>Peak width (degree)</th>
<th>Peak position (degree)</th>
<th>Crystallite size (nm)</th>
<th>Lattice strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>0.6242</td>
<td>16.8362</td>
<td>13.44</td>
<td>0.0184</td>
</tr>
<tr>
<td>Peak 2</td>
<td>0.6242</td>
<td>18.2217</td>
<td>13.47</td>
<td>0.0170</td>
</tr>
<tr>
<td>Peak 3</td>
<td>0.7737</td>
<td>21.2154</td>
<td>10.92</td>
<td>0.0180</td>
</tr>
<tr>
<td>Peak 4</td>
<td>0.9297</td>
<td>23.4738</td>
<td>9.12</td>
<td>0.0195</td>
</tr>
<tr>
<td>Peak 5</td>
<td>1.2418</td>
<td>26.6776</td>
<td>6.87</td>
<td>0.0229</td>
</tr>
</tbody>
</table>

Table 4.9: rPAN/PET (70/30) crystallite size calculation

<table>
<thead>
<tr>
<th>Sample 5</th>
<th>Peak width (degree)</th>
<th>Peak position (degree)</th>
<th>Crystallite size (nm)</th>
<th>Lattice strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>0.7069</td>
<td>19.7448</td>
<td>11.92</td>
<td>0.0177</td>
</tr>
<tr>
<td>Peak 2</td>
<td>1.2960</td>
<td>21.2942</td>
<td>6.52</td>
<td>0.0301</td>
</tr>
<tr>
<td>Peak 3</td>
<td>1.2960</td>
<td>26.9139</td>
<td>6.59</td>
<td>0.0236</td>
</tr>
</tbody>
</table>

Table 4.10: Percentage crystallinity of samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Percentage crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>rPAN</td>
<td>13.81</td>
</tr>
<tr>
<td>PET</td>
<td>15.13</td>
</tr>
<tr>
<td>rPAN/PET(30/70)</td>
<td>15.82</td>
</tr>
<tr>
<td>rPAN/PET(50/50)</td>
<td>15.46</td>
</tr>
<tr>
<td>rPAN/PET (70/30)</td>
<td>12.67</td>
</tr>
</tbody>
</table>
Table 4.11: XPert HighScore Report of the pure and blended samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Compound name and codes</th>
<th>Chemical formula</th>
<th>Crystal structure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>rPAN</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4020557</td>
<td>C\textsubscript{22}H\textsubscript{208}N\textsubscript{16}</td>
<td>Orthorhombic</td>
<td></td>
</tr>
<tr>
<td>4021113</td>
<td>C\textsubscript{40}H\textsubscript{24}N\textsubscript{4}</td>
<td>Orthorhombic</td>
<td></td>
</tr>
<tr>
<td>7001404</td>
<td>C\textsubscript{42}H\textsubscript{48}N\textsubscript{12}</td>
<td>Anorthic</td>
<td></td>
</tr>
<tr>
<td>2008693</td>
<td>C\textsubscript{60}H\textsubscript{52}N\textsubscript{12}</td>
<td>Monoclinic</td>
<td></td>
</tr>
<tr>
<td>8101251</td>
<td>C\textsubscript{240}H\textsubscript{176}N\textsubscript{30}</td>
<td>Orthorhombic</td>
<td></td>
</tr>
<tr>
<td><strong>PET</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2&lt;i&gt;E&lt;/i&gt;-5&lt;i&gt;E&lt;/i&gt;-2,5-)Difurfurylidene cyclopentanone</td>
<td>C\textsubscript{60}H\textsubscript{48}O\textsubscript{12}</td>
<td>Monoclinic</td>
<td></td>
</tr>
<tr>
<td>1,4-bis(4-methoxyphenyl)but-1,3-diyne</td>
<td>C\textsubscript{72}H\textsubscript{56}O\textsubscript{8}</td>
<td>Monoclinic</td>
<td></td>
</tr>
<tr>
<td>4100096</td>
<td>C\textsubscript{56}H\textsubscript{64}O\textsubscript{8}</td>
<td>Monoclinic</td>
<td></td>
</tr>
<tr>
<td><strong>rPAN/PET(70/30)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2102316</td>
<td>C\textsubscript{108}H\textsubscript{216}O\textsubscript{8}N\textsubscript{8}</td>
<td>Monoclinic</td>
<td></td>
</tr>
<tr>
<td>2014432</td>
<td>C\textsubscript{40}H\textsubscript{28}O\textsubscript{12}N\textsubscript{4}</td>
<td>Monoclinic</td>
<td></td>
</tr>
<tr>
<td>(3S,4S)-tert-Butyl 4-amino-3-hydroxyl-5-phenylpentanoate</td>
<td>C\textsubscript{60}H\textsubscript{92}O\textsubscript{12}N\textsubscript{4}</td>
<td>Orthorhombic</td>
<td></td>
</tr>
<tr>
<td>Sebacic acid—4,4’-bipyridine(1/1)</td>
<td>C\textsubscript{40}H\textsubscript{52}O\textsubscript{8}N\textsubscript{4}</td>
<td>Anorthic</td>
<td></td>
</tr>
<tr>
<td>2003187</td>
<td>C\textsubscript{32}H\textsubscript{60}O\textsubscript{12}N\textsubscript{12}</td>
<td>Orthorhombic</td>
<td></td>
</tr>
<tr>
<td><strong>rPAN/PET(30/70)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-(4-Nitrophenoxy)biphenyl</td>
<td>C\textsubscript{72}H\textsubscript{52}O\textsubscript{12}N\textsubscript{4}</td>
<td>Monoclinic</td>
<td></td>
</tr>
<tr>
<td>4021930</td>
<td>C\textsubscript{120}H\textsubscript{168}O\textsubscript{24}N\textsubscript{8}</td>
<td>Monoclinic</td>
<td></td>
</tr>
<tr>
<td>3-Hydroxy-N’-phenylanaphthalene-2-carbohydrazide</td>
<td>C\textsubscript{72}H\textsubscript{56}O\textsubscript{12}N\textsubscript{8}</td>
<td>Monoclinic</td>
<td></td>
</tr>
<tr>
<td>7200092</td>
<td>C\textsubscript{16}H\textsubscript{28}O\textsubscript{12}N\textsubscript{4}</td>
<td>Monoclinic</td>
<td></td>
</tr>
<tr>
<td><strong>rPAN/PET(50/50)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4,4’-Methylenediphenol—4,4’-bipyridine(2/3)</td>
<td>C\textsubscript{112}H\textsubscript{96}O\textsubscript{8}N\textsubscript{12}</td>
<td>Monoclinic</td>
<td></td>
</tr>
<tr>
<td>3-[4-(Dimethylamino)phenyl]-2-(4-methoxyphenyl)acrylonitrile</td>
<td>C\textsubscript{72}H\textsubscript{72}O\textsubscript{4}N\textsubscript{8}</td>
<td>Monoclinic</td>
<td></td>
</tr>
<tr>
<td>3-Hydroxy-N’phenylanaphthalene-2-carbohydrazide</td>
<td>C\textsubscript{72}H\textsubscript{56}O\textsubscript{12}N\textsubscript{8}</td>
<td>Monoclinic</td>
<td></td>
</tr>
<tr>
<td>4023178</td>
<td>C\textsubscript{24}H\textsubscript{30}O\textsubscript{12}N\textsubscript{2}</td>
<td>Monoclinic</td>
<td></td>
</tr>
</tbody>
</table>
4.3.4.2 XRD curves for the samples

Figure 4.12: XRD intensity curves of samples

Predominantly rPAN peak might be due to high content of rPAN in the blend

Predominantly PET peak might be due to high content of PET in the blend

rPAN dominates the composition and subdue some of PET peaks by shifting the intensity to lower 2theta

Figure 4.12: XRD intensity curves of samples
4.3.5 SEM Analysis

It is necessary to investigate the blends morphology because its interfacial adhesion is governed by: the viscosity ratio of constituents, volume fraction, interfacial tension between the phases, the mixing conditions and the processing temperature. Therefore, the higher the processing temperature, the smaller were the PET dispersed phase sizes (Lin and Cheung 2003:88). The processing temperature influenced the blends viscosity resulting into an increase in viscosity ratio, which favours better mixing in rPAN/PET (70/30 and 50/50) blends. Likewise, with high processing temperature (290°C), there is the possibility of low molecular weight components formation as a result of degradation (as discussed under TGA). These low molecular components from rPAN/PET blends have better combination prospects and are able to entangle with each other at the interface, thus resulting in better morphology (see Figure 4.14e). Figure 4.14 shows the Scanning Electron Microscopy (SEM) cryogenically-fractured surfaces of rPAN, PET and their blends at a magnification (x 50,000). At this magnification, the samples...
appear to be smooth, dense and its structure shows inter-winning fibrous network with numerous pores that are more prominent in neat PET and rPAN/PET (30/70). In order to explore the effects of PET content on the blends, SEM images of the fractured blend surfaces were taken and compared with rPAN and neat PET. SEM images were analysed with ImageJ software in order to determine the surface roughness from these images (see figure 4.15). The images obtained using ImageJ for rPAN, PET and their blends are shown in Figure 4.15. The topographical feature of rPAN has a fine fibrous-like network structure. It was also observed that the roughness increases due to the high rPAN content in the blend (rPAN/PET (70/30)).

The roughness characteristics from the SEM images, analysed with ImageJ give more clarity on the structure of the samples.

Hence, the visual observation of the SEM micrographs and ImageJ revealed the following:

- Figures 4.14a and figure 4.15a show the morphology of 100% rPAN fiber and the micrograph unveil a complex interconnected network of fibers. Clearly, the morphology of the fiber provides a compounding pathway that can enhance an effective blending in order to improve the blend properties if carefully explored.

- Figures 4.14b and figure 4.15b reveal the morphology of the neat PET sample with numerous pores, this shows possible matrix network for new material development. The morphology further reveals the possibilities of fiber penetration into such pores that may lead to network formation in the PET matrix; this is a good prospect for rPAN fiber blending.

- Figures 4.14c and figure 4.15c reveal the morphology of rPAN/PET (30/70) sample. The blend shows some degree of homogeneity (smooth surface) of the two polymers, but it further revealed the formation of pores in the blend which resulted in the material
weakness thereby leading to sample brittleness as a result of poor adhesion between the components. This ratio is not viable for recycling processes.

- Figures 4.14d and figure 4.15d reveal the morphology of rPAN/PET (50/50) sample. The micrograph shows good homogeneity of the rPAN/PET blend. This shows an almost homogeneous structure between the two polymers with interpenetrating networks, although some pores are also observed.

- Figures 4.14e and figure 4.15e shows the (70/30) blend of rPAN/PET. This blend reveals a near total dispersion of PET in the rPAN matrix. This dispersion shows improved homogenization between the polyacrylonitrile and polyethylene terephthalate: better than that of blends in figure 4.14c and figure 4.14d.

In conclusion, the blend of (rPAN/PET (70/30)) shows a well dispersed sea island, this means that the dispersed phase (PET) was well distributed in the polymer matrix (rPAN). It is also significant to note is that: (i) at low temperatures, in the vicinity of the melting point of PET, some PET pellets might not have fully melted, resulting in less mixing homogeneity. (ii) The processing time also had an effect on the resultant blends morphology. At a very low processing time, the morphology was quite poor, but it improved slightly at an intermediate processing time. However, a further increase in processing time results into poor morphology, this is attributed partly to coalescence and degradation of the polymers contents. Therefore, for optimal rPAN/PET morphological development, processing time in the region of 5 minutes was good enough for the blends. (iii) Despite the fact that PET and rPAN are immiscible, at the interface the adhesion between the phases is possible, due to the possibility of their chains intermingling. As a result of chain intermingling, if the surface area of the dispersed phase exposed to the major matrix is maximized, marginal adhesion may be enhanced between the blends. Hence, it is anticipated that the best synergies of the properties of the two polymers
should be achieved in the domain of rPAN/PET (70/30) composition, in the case where PET is the dispersed phase. Thus, any effort on compatibilization of the rPAN/PET blends would appropriately be positioned around blends with the weight fraction of PET in the vicinity of 30%.

Figure 4.14: Morphology of freeze-fractured surfaces of: (a) rPAN and (b) PET. Images were collected at x 50000 at a voltage of 2 kV.
Figure 4.14: SEM micrographs of freeze-fractured surfaces of: (a) rPAN, (b) PET, (c) rPAN/PET (30/70) (d) rPAN/PET (50/50) and (e) rPAN/PET (70/30). The images were collected at x 50000 at a voltage of 2 kV.

- **a)** PAN/PET (30/70)
  - Pores formation in the blend
  - 100 nm

- **b)** PAN/PET (50/50)
  - Pores formation in blend
  - Good homogeneity
  - 100 nm

- **c)** PAN/PET (70/30)
  - Improved homogeneity of matrix-phase dispersion in the blend
Figure 4.15: ImageJ micrographs of freeze-fractured surfaces of: (a) rPAN, (b) PET, (c) rPAN/PET (30/70), (d) rPAN/PET (50/50) and (e) rPAN/PET (70/30). The images were collected at x 50000 at a voltage of 2 kV.
4.3.6 TEM Analysis

Figure 4.16 shows the TEM images of rPAN, PET and their blends, it is quite difficult to separate rPAN and PET components in the blends. This implies that simple visual analysis of TEM image is not enough for the characterization of the samples. The dark patches observed in the samples were due to the overlapping of the sliced sample layers and not component composition. Therefore, AFM was employed to examine the TEM images.

Table 4.11 shows the samples: number of pores, first neighbour distance, pores area, pores volume and bearing ratio data generated from AFM. The information gathered are explained as follows:

- The numbers of pores and pore size decreased in the following order: rPAN/PET (30/70) < rPAN/PET (50/50) < rPAN/PET (70/30) when compared with rPAN and PET. This perchance is attributed to the blending ratio, chemical composition and the type of crystals formed in the samples (see Figure 4.17).
- The first neighbour distance increases in the following order: rPAN/PET (70/30) < rPAN/PET (30/70) < rPAN/PET (70/30). This shows an increased in the near neighbour when compared to rPAN and PET, this can be attributed to the newly developed structure, restructuring of the chemical bonds and blend ratios.
- The pore area and volume also increased in the following order: rPAN/PET (70/30) < rPAN/PET (30/70) < rPAN/PET (50/50). This is in line with the nature of the parent polymer (rPAN and PET) (see Figure 4.17).

Lastly, Figure 4.18 revealed the flooding result of the TEM images by investigating the behaviour of the pores (i.e. regular, random, cluster, regular-cluster or random-cluster) (Anson and Gruzleski 1999). Random-cluster pore distribution can be observed in the blend of
rPAN/PET (50/50) (see Figure 4.18 (d)), revealing why this sample was the optimum. Regular-cluster pore distribution was observed in the blend of rPAN/PET (30/70 and 70/30) (see figure 4.18 (c and d). But the clustering of pore is more concentrated in the blend of rPAN/PET (30/70), revealing poor mechanical properties exhibited by the blend during an impact test (see Figure 4.18 (c)).

In conclusion, the pore size distribution and the distance to its nearest neighbour are some of the determining factors in the characterization and performance of blends (Exner and Schwarz 1983). These provide a quantitative representation of the dimension of pore sizes existing in a given sample and it further provides information on the disperse phase and matrix failure in a blended material. Therefore, AFM topography imaging of rPAN, PET and their blends was helpful in providing statistical data on the pore size distribution. This has helped in the understanding of the samples structural characterization and the improved mechanical properties of rPAN/PET (70/30; 50/50) and weak mechanical properties of (rPAN/PET (30/70) in relation to their composition.

Table 4.12: TEM Data using AFM

<table>
<thead>
<tr>
<th>Sample</th>
<th>Number of pores</th>
<th>First neighbour distance (pm)</th>
<th>Pores area (a.u)</th>
<th>Pores volume (a.u)</th>
<th>Bearing ratio (a.u)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rPAN</td>
<td>8864</td>
<td>0.395247</td>
<td>0.520905</td>
<td>21.4976</td>
<td>11362.5 (47.76%)</td>
</tr>
<tr>
<td>rPAN/PET(30/70)</td>
<td>5861</td>
<td>0.441143</td>
<td>0.64032</td>
<td>20.0573</td>
<td>21652.1 (64.76%)</td>
</tr>
<tr>
<td>rPAN/PET(50/50)</td>
<td>1224</td>
<td>0.531193</td>
<td>0.892393</td>
<td>27.3546</td>
<td>12068.9 (87.01%)</td>
</tr>
<tr>
<td>rPAN/PET(70/30)</td>
<td>17565</td>
<td>0.378083</td>
<td>0.42139</td>
<td>8.42085</td>
<td>10771.8 (40.70%)</td>
</tr>
<tr>
<td>PET</td>
<td>17745</td>
<td>0.377966</td>
<td>0.424683</td>
<td>11.7742</td>
<td>18183.2 (42.80%)</td>
</tr>
</tbody>
</table>
Figure 4.16: TEM image of: (a) rPAN, (b) PET, (c) rPAN/PET (30/70), (d) rPAN/PET (70/30) and (e) rPAN/PET (50/50)
Figure 4.17: Pore size distribution of: (a) rPAN, (b) PET, (c) rPAN/PET (30/70), (d) rPAN/PET (50/50) and (e) rPAN/PET (70/30)
Figure 4.18: TEM images flooding analysis of: (a) rPAN, (b) PET, (c) rPAN/PET (30/70), (d) rPAN/PET (50/50) and (e) rPAN/PET (70/30)
4.3.7 Atomic force microscopy analysis (AFM)

Surface roughness and the nodular structure are important structural features that determine the resultant properties of polymers and these can be measured by atomic force microscopy (AFM). According to Adams (1993:28) and Kfoury (2003), the surface roughness of a particle is one of the significant consideration in evaluating the efficiency of polymer, such as toughness since the characteristic can influence the performance and application potentials of the polymer. Bowen and Doneva (2000:29) also pointed out that other material characteristics, for instance: pore size distribution and interpore spacing which are related to polymer toughness and ductility can also be correlated with surface roughness.

Figure 4.18 shows non-contact mode images of rPAN, PET and their blends in 2D and 3D configuration. The topography, frequency, phase, height, flatten and roughness of samples was obtained from the non-contact mode AFM. According to Boussu et al. (2005:286), in the polymer samples scanned area the phenomenon of increasing roughness with increasing scan area can be related to the roughness on the spatial wavelength. Boussu et al. (2005:286) also stated that when polymer molecules are assembled into nodules or aggregates of nodules the formation of a fractal structure on the polymer samples surface could be due to increasing roughness with increasing scan size. Therefore, it is important that the surface roughness is compared for identical scan sizes due to different roughness parameters effect on image size.

The topography images of rPAN, neat PET and blended samples presented the detailed information on the samples top views in the Z-direction, in coded colour intensity (the peaks having the highest points are represented by the light region while the pores are represented by the dark region). The images of rPAN and PET show a topographical feature with fine fibrous-like network structure and the 3D orthographic images show the occurrence of the valleys and tiny peaks. The tiny peaks of rPAN and PET are responsible for the higher roughness when
compared with the blends high peaks. It was also observed that the images of the blends have a dense and smooth surface with visible pores. Furthermore, the high surface roughness of the blends when compared to the neat polymers can be ascribed to a factor in proportion to the nature of the chemical composition, bond formation and the strength of the parent materials (rPAN and neat PET). Therefore, the AFM photographs support the quantitative image characterization obtained through AFM data of the samples (Anson and Gruzleski 1999:43, Ma et al 2007:19). The results obtained further confirmed the influence of rPAN and PET ratios that influenced the pore size and size distribution; as this affects the mechanical property of the blended samples.
PAN Analysis

Roughness Analysis

Image Statistics

rPAN
rPAN/PET (30/70)
rPAN/PET (50/50)

Roughness Analysis
rPAN/PET ((70/30)
Figure 4.19: 3D AFM images of rPAN, PET and blended samples
4.3.7.1 Scanning probe microscopy (SPM) Image Process – Roughness Analysis

AFM was used to analyse the samples surface roughness and the results generated are shown in table 4.13. The surface roughness and the number of events of the blends, as shown in Table 4.13 and Figure 4.20 reveal the extent of the importance of the different ratios of PET and rPAN in every composition. rPAN/PET (50/50) revealed the optimum root mean square and mean roughness, followed by rPAN/PET (70/30) and lastly by rPAN/PET (30/70). The observation supports the findings in the mechanical tests (impact and tensile) for the blends. For example, the brittleness (cracks) observed during impact test preparation of rPAN/PET (30/70) sample was supported by the high root mean square value (63.232nm) and the mean roughness value of (49.781nm). The brittleness observed was due to the weakening of rPAN carbon-carbon bond and the dipole-dipole bond in the chain of the blends as a result of the high percentage of PET. Therefore, high PET addition negatively affects the blend more than high rPAN and this also has effects on the blends mechanical properties.

Table 4.13: Sample roughness

<table>
<thead>
<tr>
<th>Samples</th>
<th>Img. Rms (Rq) (nm)</th>
<th>Mean Roughness (Ra) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rPAN</td>
<td>80.304</td>
<td>65.739</td>
</tr>
<tr>
<td>rPAN/PET (30/70)</td>
<td>20.924</td>
<td>15.806</td>
</tr>
<tr>
<td>rPAN/PET (50/50)</td>
<td>70.371</td>
<td>53.693</td>
</tr>
<tr>
<td>rPAN/PET (70/30)</td>
<td>63.232</td>
<td>49.781</td>
</tr>
<tr>
<td>PET</td>
<td>49.508</td>
<td>38.698</td>
</tr>
</tbody>
</table>
Figure 4.20: Histogram of roughness: (A) rPAN, (B) rPAN/PET (30/70), (C) rPAN/PET (50/50), (D) rPAN/PET (70/30) and (E) PET
4.3.7.2 AFM flooding images analysis

The image in Figure 4.21 represents the samples flooding analysis. The images displayed a progressive pores increase in the rPAN matrix due to high PET composition and vice versa for PET matrix. The pores progression is small in the composition of rPAN/PET (70/30), this shows an improvement in the roughness, following the addition of 30% PET (see Figure 4.21d). Blend of rPAN/PET (50/50) showed improved compatibility with pores sparingly distributed (see Figure 4.21c). Lastly, rPAN/PET (30/70) blend revealed increased pores (see Figure 4.21b). These pores are reduced in the rPAN as a matrix, resulting in the material brittleness. This observation is supported by the impact test results of the sample during preparation which manifested extensive cracks in rPAN/PET (30/70) blend. This resulted in the catastrophic failure of the sample.

In conclusion, the addition of PET (above 50%) in rPAN blends weakens the blend and makes the blend unsuitable for the proposed application as filter material, while the addition of PET below 50%, improves the recycling probability of the blends. This observation is also supported by the mechanical property and microstructural characterization of the 30% and 70% of rPAN in the blends.
Figure 4.21: Flooding analysis of holes distribution in: (a) rPAN, (b) rPAN/PET (30/70), (c) rPAN/PET (50/50), (d) rPAN/PET (70/30) and (e) PET

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4.3.7.3 Bearing Analysis

The bearing analysis method was used to determine the height information in pixels. This method is briefly described as follows: The term bearing refers to the relative roughness of the pure and blended sample surfaces with regard to the high and low pixels and the measured area. In the bearing analysis, the depths of all pixels of the image with a particular reference point are noted. This gives the estimate of the surface covered by the material, the material depth and height distribution that is possible for either the entire image or for a selected area of analysis. The bearing ratio also gives the percentage of the surface that lies above and below the arbitrary chosen height. For the rPAN, PET and the blends, bearing analysis was used to determine the roughness with regard to height distribution. This gives quantitative information for a sample that lies above or below a specific plane, as shown in Figure 4.22 and 4.23.
Figure 4.22: Bearing surface area analysis for: (A) rPAN, (B) PET, (C) rPAN/PET (30/70), (D) rPAN/PET (50/50) and (E) rPAN/PET (70/30)
Figure 4.23: Bearing volume analysis for (A) rPAN, (B) PET, (C) rPAN/PET (30/70), (D) rPAN/PET (50/50) and rPAN/PET (70/30)
4.3.7.4 FRACTAL ANALYSIS

Fractal analysis is a contemporary approach of understanding defying patterns with traditional Euclidean concepts by applying non-traditional mathematics (Kasimanickam et al 2010:8). Fractal data of rPAN, neat PET and blended samples are presented in Figure 4.24. The digitized images of the samples were converted to a graphic form in Figure 4.24, by using Marr-Hildreth convolution algorithm (Marr and Hildreth 1980:207), from grey scale to binary silhouettes. These silhouettes were used to obtain one-pixel-wide border of the sample structure image, which was used as the entity for the quantitative studies. Digitized AFM images of rPAN, PET and their blends were analysed by the square covering (box-counting method), as shown in Figure 4.24 (Mandelbrot 1983; Smith et al. 1989:27; Peitgen et al. 1992; Cross et al. 1994a:17). The dimension of the registered binary border-image of each sample examined was 200 nm × 200 nm. The binary border-images of the rPAN, PET and their blends were analyzed in a succession of square grids, containing an increasing number of squares (with decreasing edge lengths of each of them). The logarithm number of squares counted was plotted against the logarithm of the box edge length, was given by the equation:

\[ D_B = \lim_{\varepsilon \to \infty} \frac{\log N(\varepsilon)}{\log 1/\varepsilon} \]  \hspace{1cm} 4.4

Where \( D_B \) equals the box-counting fractal dimension of the digitized image of the material at the given magnification level,

\( \varepsilon \) equals the side length of one box within the grid,

\( N(\varepsilon) \) equals the smallest number of box of side length

NOTE: \( \varepsilon \) requires to completely covering the border of the object being measured (Smith et al. 1989:27).
This result gives additional evidence that fractal analysis is a reliable method, which can be used to analyse blends of rPAN and PET. In conclusion, fractal analysis of rPAN/PET blends is a useful complementary approach to experimental data collection.

Figure 4.24: Fractal analysis of: (A) rPAN, (B) PET, (C) rPAN/PET (70/30), (D) rPAN/PET (50/50) and (E) rPAN/PET (30/70)
4.3.7.7 Power Spectral Density

The data generated from AFM profile provide the surface roughness power spectral density (PSD) of samples, as shown in Figure 4.25. This provides useful information on the morphological microstructure of the rPAN, PET and the blended samples. The PSD curves generated were fitted with appropriate analytic function and material characterizing parameters in order to obtain useful morphological properties.

The root mean square height of a surface around its mean value represented by the morphological parameter of the material surfaces is the root mean square (rms) roughness; this was discussed in section 4.3.7.3. However, this statistical representation, although reliable and simple, makes no contrast between the image valleys and peaks. It also does not account for the lateral distribution of surface features (Gavrila et al 2007:10).

For material surface characterization, PSD function is an important tool, it represents ways of describing the surface quality as it is connected with the amount and angular scattered light. Therefore, scattering theories can be used to predict the surface that limits the angular distribution of scattered light from the material surface topography, as follows (San et al 2007:14):

\[ IS (\mu; \ Á) = C (\mu; \ Á) \cdot PSD (fx; fy) \]

Where \( IS (\mu, \ Á) \) = the scattered solid angle unit in the (\( \mu \), \( \Á \)) direction,

\( PSD (fx; fy) \) = the 2-D PSD of the surface topography,

\( fx, fy \) are the spatial frequencies, related to the incident (\( \mu_i \)) and scattering (\( \mu, \ Á \)) angles,

\( C (\mu, \ Á) \) = an optical factor which depends on the refractive indexes of the incident medium (generally air), material surface, illumination and observation conditions (wavelength, geometry, polarization).
Figure 4.25: Curves of power spectral density of: rPAN, PET and the blended samples
4.3.7.6 Spatial Frequency Analysis

The spatial frequency displays information on the samples interacting macromolecular distribution governs by intermolecular forces. This characterization tool also investigates the interacting forces between nanometer-scale samples. It produces spatially resolved insights into the structure and characterizing process of the sample surface properties. Based on the spatial frequency correlation value of the samples, image fittings indicate the possibility of good blending between rPAN and PET materials. This prospect is important to further improve the properties of the blends of rPAN.

4.3.7.7 Force-volume imaging Analysis

Over the polymer surface, an array of force curves in the x–y plane were collected and translated into the force volume see Figure 4.26. This force-volume information set (FVDS) consists of an array of force curves and the height of the image. An array of z-piezo positions at the turn around points (points of maximal deflection) of the force curves is the force-volume height image (FVH). Therefore, using a relative deflection trigger the force curves making up a force-volume (FV) were collected. The force-volume height (FVH) is a surface of equal force, not necessarily a height image in the sense of topography. The combination of FV and FVH provides the rPAN, PET and their blends three-dimensional images, shown in Figure 4.19. This is the emphatic description of the forces over and within the pure and blended samples. For sufficient force curves collection, the interacting dependence distance of the structural materials was related to the lateral resolution of force-volume imaging. Thus, the lateral resolution varies within the volume and cannot be defined easily.
The data-acquisition times was limited by the size of most FVs. This is due to the fact that, the acquisition time for a single force curve is often between 0.1 and 10 sec. Therefore, in the Z-direction, there is no specific limit to data compilation, despite the fact that data-acquisition rates of <100 kHz can be achieved in most commercial instruments. A great deal of samples information is incorporated in FVDS and the information when extracted can be communicated in numerous ways. Therefore, the force distributions at different z-positions, the surface mapping, the isoforce surfaces and the samples properties can all be characterised by information gathered in the FVDS was shown in Figure 4.26 (Heinz and Hoh, 1999:17).

Figure 4.26: Volume histogram of: rPAN, PET and their blends
4.3.7.8 AFM Force distance discussion

The interpretation of AFM force curves depends almost exclusively, on the standard force laws. These laws describe the $z$-piezo position as a function of force. Therefore, in order to further understand the forces generated by van der Waals and electrostatic interactions in the samples force measurement was done using AFM. The electrostatic forces depended on the long range distance i.e. the forces acting on the material surfaces were due to the atoms or molecules at the material tips. The force-distance obtained in this work was due to the associating electric field originating from a voltage difference between the interfacial contact potential of the cantilever. Upon approach, a slight repulsion was detected by the probe which could be due to instrument noise prior to encountering a strong repulsive force. The repulsive force produced an almost linear increasing force between the samples and the tip. This suggested that a strong repulsive interaction exists between the samples surfaces and the cantilever tip prior to contact on close approach due to near linear behaviour of the approach of the tip. The length of bridging between cantilever separation tip and the material samples was indicated by the long-range distance (~350 Å).

4.3.7.9 Pore size distribution

The pore size distribution of rPAN, PET and their blends are shown in Figure 4.27 and Table 4.14. The pore size and its effect on the blend are better understood by their distribution (regular, random and cluster). Figure 4.18 shows the number of event in the rPAN, neat PET and their blends. The event-to-event distance in each sample is the intervention distance of the
blend composition. The effect of pore distribution, which affects the blends, is better understood by the method of nearest neighbour (Anson and Gruzleski 1999:43). The result of the material pore distribution, based on the nearest neighbour is dependent on the limiting inter-event distance and as the limiting inter-event changes, so does the distribution of pores. This is shown in Figure 4.27a, where the rPAN material appears dense and relatively smooth with few visible pores distance, referred to as regular pore distribution (the pores are formed at a distance from their immediate neighbour). In Figure 4.27b, PET shows a fibrous network with numerous pores, referred to as clustering pores (the pore distributions are at a close distance from their nearest neighbour). In Figure 4.27c, rPAN/PET (70/30) reveals the possibility of good blend due to few visible pores distribution. The event analysis shows that the pores distance from the nearest neighbour is wide. This explains the good mechanical property of the blend as earlier discussed under SEM and TEM. In Figure 4.27d, rPAN/PET (50/50) shows a fiber network with improved pores when compared to PET. The pores distances to their nearest neighbours are regular, however, clustering pores were also observed in the blend. This was the optimum blend ratio for rPAN/PET blend and above this ratio, the material becomes very brittle. In Figure 4.27e, rPAN/PET (30/70) blend resulted in clustering pores distribution, similar to PET pore size distribution, this supports the brittle nature of the blend as reported earlier (impact test).

In conclusion, the pore size distribution and the distance to its nearest neighbour are some of the determining factors in the characterization and performance of blends (Exner and Schwarz 1983:129). Figures 4.18 and 4.27 provide a quantitative description of the pore size ranges present in a particular given sample. This further provides a description of the disperse phase and matrix failure in a blended material. Therefore, AFM topography imaging of rPAN, PET and their blends was helpful in providing the pore size distribution information. This has helped
in understanding the mechanical properties of the improved (rPAN/PET (70/30; 50/50) and weak (rPAN/PET (30/70) blends in relation to their composition.

Figure 4.27: Pore size distribution of: (a) rPAN, (b) PET, (c) rPAN/PET (70/30), (d) rPAN/PET (50/50) and (e) rPAN/PET (30/70)
4.3.7.10 Image Mapping (Spatial distribution)

The main method of determining sample topography is by using the constant-force imaging mapping in AFM. During the mapping process, the sample being analysed is always in contact with the cantilever tip and the set constant cantilever deflection was maintained in the feedback loop. However, it is also possible to produce isoforce surfaces in a non-contact regime in the presence of a long-range force (Manne, and Gaub, 1995:270, Senden, et al, 1994:10). As the cantilever tip moves above the sample and varying magnitude of sample forces interact with the tip, the feedback loop repositions the stage so that the cantilever deflection remains constant. Current AFM cantilevers are extremely sensitive to temperature changes causing it to bend slightly with time and any drift of the cantilever would make it impossible to assemble the volume properly. In practice, however, because of the cantilever drift this is essentially impossible with the current technology. Thus, as long as a relative trigger is used when collecting arrays of force curves, the cantilever drift is not a problem during AFM process (Radmacher et al 1995:17). In conclusion, the mapping of rPAN, PET and their blends as shown in Table 4.14 and Figure 4.28, supports the findings of the flooding analysis, pores diameter, nearest neighbour analysis, tensile test, SEM and impact test discussed in this work.

Table 4.14 Distance analysis on image mapping

<table>
<thead>
<tr>
<th>Sample</th>
<th>Number of pores</th>
<th>First neighbour distance (nm)</th>
<th>Pores area (nm²)</th>
<th>Pores volume (nm³)</th>
<th>Bearing ratio (μm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rPAN</td>
<td>29</td>
<td>28.76</td>
<td>928147(92.9%)</td>
<td>1,79364e+006</td>
<td>1.00722(91.05%)</td>
</tr>
<tr>
<td>rPAN/PET(30/70)</td>
<td>74</td>
<td>48.54</td>
<td>806759(80.68%)</td>
<td>1.5172e+006</td>
<td>1.07189(76.30%)</td>
</tr>
<tr>
<td>rPAN/PET(50/50)</td>
<td>80</td>
<td>33.22</td>
<td>924486(92.44)</td>
<td>1.70295e+006</td>
<td>1.20247(85.87%)</td>
</tr>
<tr>
<td>rPAN/PET(70/30)</td>
<td>21</td>
<td>45.29</td>
<td>982462(98.25%)</td>
<td>2.45529E+006</td>
<td>1.04395(96.50%)</td>
</tr>
<tr>
<td>PET</td>
<td>59</td>
<td>56.70</td>
<td>913846(91.38%)</td>
<td>1.81583e+006</td>
<td>1.40038(84.79%)</td>
</tr>
</tbody>
</table>
Figure 4.28: Particles distribution in: (A) rPAN, (B) PET, (C) rPAN/PET (70/30), (D) rPAN/PET (50/50) and rPAN/PET (30/70)
4.3.7.11 Summary of AFM Results

The pore size distribution observed in the blends revealed an improved interpenetrating network for samples with low PET content (rPAN/PET (70/30 and 50/50)), while a poor interpenetrating network was observed in the sample with high PET content (rPAN/PET (70/30)), but this can be improved with possible application of additives to the matrix. Therefore, the addition of PET above 50%, in the composition, weakens the blend and makes the blend unsuitable for the proposed application.

The roughness values decreased as PET content increased, as shown in Table 4.14. Sample rPAN/PET (70/30) shows a better-refined grain size, followed by rPAN/PET (30/70) and rPAN/PET (50/50) in the composition when compared with the samples of rPAN and PET. Furthermore, the weakness observed in the mechanical properties of the blends was support by the pore size distribution, pores nearest neighbour distance and the diameter of the pores observed in the AFM.

4.3.8 ATR-FTIR Spectroscopy

ATR-FTIR spectra of rPAN, neat PET and their blends were measured using the ATR-FTIR spectroscopy. At the wavelength region of 4000-500 cm\(^{-1}\), the FTIR spectra of the samples were recorded on the Perkin Elmer 16PC FTIR instrument at a resolution of 4 cm\(^{-1}\) at the glancing angle of 72° with 32 scans in each. Types of chemical bonds (functional groups) were studied by detecting the vibrational characteristics of the chemical functional groups in the rPAN, PET and their blends. ATR-FTIR spectra of all the samples are given in Figures 4.29 and 4.30. For rPAN, the peaks observed at 1571 cm\(^{-1}\), 1470 cm\(^{-1}\), 1180 cm\(^{-1}\), 1091 cm\(^{-1}\), 10080 cm\(^{-1}\), 806 cm\(^{-1}\), 553 cm\(^{-1}\) and 478 cm\(^{-1}\) are attributed to the C-H stretching vibrations, CH\(_2\) bending vibration,
aromatic C=N stretching vibration and (CH₂) groups, respectively (Kanwal et al 2012:9) and the asymmetric N-H stretching absorptions and the carboxylic groups in the acrylonitrile. For neat PET, the peaks observed at: 1712 cm⁻¹, 1490 cm⁻¹, 1342 cm⁻¹, 1240 cm⁻¹, 10930 cm⁻¹, 1017 cm⁻¹, 871 cm⁻¹, 721 cm⁻¹ and 437 cm⁻¹, are due to the presence of hydroxyl ethyl group resulting from the asymmetric C-H stretching, O-H stretching, COOH stretching and the carboxylic groups. Silverstein et al (2005) stated that the peaks positions depend on the degree of hydrogen bonding and thus, on the physical state of the compound. Furthermore, with the bands originating from interacting vibrational modes the absorption pattern in this region is frequently complex.

The peaks observed in the blends are mostly related to the respective contents of rPAN and PET in the blend. It further shows that in the material development the materials ratios in the blends play a significant role.
Figure 4.29: FTIR spectrum of rPAN, PET and blended samples shown over the range of 250 cm\(^{-1}\) - 2500 cm\(^{-1}\).
Polarising optical microscope was used to observe crystal characteristics and their formation in the rPAN, PET and their blends. The samples were observed at different temperature stages for crystal formation. No crystals were observed as shown in Figure 4.31a-l. The rPAN transition to a rubbery state in the blends makes it quite impossible for the formation of crystals. In addition, the rapid cooling of rPAN also affected the formation of PET crystals in the blend. Therefore, the crystallization forming state was absent in the blends because of the spatial
irregularity of its macromolecules. This was due to the rapid cooling of rPAN in the blend preventing crystal formation (Bashir 2001:40 and Kalashnik et al 2010:52).

In conclusion, polarised optical microscopy for rPAN/PET blends did not detect any crystals formation in the samples. Therefore, further study on this development is required in order to characterise the blends. This confirmed the fact that the samples are either semicrystalline or amorphous.
Figure 4.31a - l: Polarising Optical Microscope images of: r PAN, PET and their blends at the heating rate of 40°/300°C to 10°/70°C for crystal formation
4.3.10 Rheology

As a result of torque build-up in the rheometer, the experiment was aborted in order not to damage the facility.

4.3.11 Tensile test discussion

The results of the tensile test are tabulated in Tables 4.15 and 4.16 and their curves are shown in the Figures 4.32 – 4.35. The composition of the blends plays a substantial part in determining the mechanical properties, such as: stress, modulus and strain of the samples. The preliminary study based on the amount of PET in the composition shows that, by increasing the content of PET in the sample, the modulus also increased. The blend of rPAN/PET (50/50) has the highest, followed by the rPAN/PET (70/30), which is higher than the modulus of the neat PET and rPAN, as shown in Figure 4.33. The blend rPAN/PET (30/70) possesses the highest modulus (because of its low strain) and hence, it is the most brittle of the samples. This is due to the high content of PET (the lowest strain of all samples) and thus, exhibited poor mixing with the rPAN fiber.

The stress-strain plots of all samples are displayed in Figure 4.32a. With increasing PET content in the blends, it can be seen from Figure 4.34 that the tensile strength (UTS) and modulus increased. There is an increase in the toughness of rPAN/PET (50/50 and 70/30) while, rPAN/PET (30/70) shows very low strain at failure and lower UTS than the other samples. This lower UTS could possibly be attributed to the weak bonding between the dispersed phase (i.e. rPAN) and the matrix (PET) of the blend. Although the moduli of the blend of the blend (rPAN/PET (30/70)) was good, the gross defects in the system resulted in the crack progression in the material which caused rapid failure, even at low strain level, thus the high brittleness of the material.
4.3.11.1 Discussion of Tensile Data

In this study, rPAN, PET and their blends were analysed in order to determine whether or not there was improved mechanical properties of the blends. The blends, except for rPAN/PET (30/70) showed good tensile property. The samples also showed improved mechanical properties as compared to the pure samples (rPAN and PET).

The following result was also noted during the tensile test;

- The addition of 70% PET increases the modulus of the sample (see figure 4.33). This contributes to the brittleness observed during the preparation of samples for the impact test. The addition of 70% rPAN reduces the modulus (see Figure 4.33). This stands out as better blend composition, followed by 50% composition as far as modulus is concerned.

- The Toughness of rPAN/PET (70/30 and 50/50) improved when compared to PET. rPAN/PET (30/70) revealed the lowest toughness of the blends, this can be attributed to the poor interfacial adhesion between the matrix and the dispersed phase in the blend. Therefore, high content of rPAN improves the toughness of the blend while, it’s vice versa for PET (see Figure 4.32b).

- On the yield load, the blends of rPAN/PET (70/30) and (50/50) have better integrity than (30/70) blend as shown in Figure 4.35.

- The ultimate tensile strength, shown in Figure 4.34, also follows the trend observed in the modulus and yield load. It revealed the fact that blended of rPAN/PET (70/30) has a better mechanical integrity.
- Lastly, the maximum tensile strain of the blends shows that rPAN/PET (70/30) gave the highest tensile strain, followed by the rPAN/PET (50/50) and rPAN/PET (30/70), which shows the least strain.

The result of the tensile strength is supported by the findings of the impact test.

Table 4.15 Tensile result of the pure and blended samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus (MPa)</th>
<th>load at yield</th>
<th>UTS (MPa)</th>
<th>Max Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET100</td>
<td>0</td>
<td>3251.1</td>
<td>1118.8</td>
<td>115.5</td>
</tr>
<tr>
<td>rPAN/PET 30/70</td>
<td>30</td>
<td>3311.6</td>
<td>973.7</td>
<td>99.5</td>
</tr>
<tr>
<td>rPAN/PET 50/50</td>
<td>50</td>
<td>2811.7</td>
<td>1075</td>
<td>106.6</td>
</tr>
<tr>
<td>rPAN/PET 70/30</td>
<td>70</td>
<td>2372.8</td>
<td>1136.88</td>
<td>111.4</td>
</tr>
<tr>
<td>rPAN 100</td>
<td>100</td>
<td>1834</td>
<td>1319.22</td>
<td>124</td>
</tr>
</tbody>
</table>

Table 4.16 Stress/strain result of rPAN, PET and their blends

<table>
<thead>
<tr>
<th>Samples</th>
<th>Average stress (MPa)</th>
<th>Average strain</th>
<th>Young modulus E (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rPAN</td>
<td>76</td>
<td>0.46</td>
<td>1652</td>
</tr>
<tr>
<td>PET</td>
<td>52</td>
<td>0.02</td>
<td>2600</td>
</tr>
<tr>
<td>rPAN/PET(30/70)</td>
<td>47</td>
<td>0.032</td>
<td>1469</td>
</tr>
<tr>
<td>rPAN/PET(50/50)</td>
<td>80</td>
<td>0.036</td>
<td>2222</td>
</tr>
<tr>
<td>rPAN/PET(70/30)</td>
<td>73</td>
<td>0.035</td>
<td>2086</td>
</tr>
</tbody>
</table>
Figure 4.32 (a): Stress vs strain curves of all samples

Figure 4.32b: Toughness bar chart of rPAN, PET and their blends
Figure 4.33: Modulus of: rPAN, PET and their blends.

Figure 4.34: Ultimate tensile strength of: rPAN, PET and their blends
4.3.12 Impact test analysis

rPAN, neat PET and their blends were prepared for notching and impact test according to the ASTM standard, this was used to determine the samples impact properties. The operating condition of the Instron impact machine is tabulated in Table 4.17 and the results obtained are tabulated in Table 4.18.

It was observed that, at a slight notching impact on the rPAN/PET (30/70) sample, the samples cracked and could not be processed any further (see Table 4.17). This shows that the blend is very brittle and as it reflects very poor mechanical integrity. This corroborates the finding in the tensile test and this might be due to the weakening of the dipole-dipole interactions of the nitrile groups of the rPAN matrix as observed in the work of Kim et al 2000:41 and 1998:2, Cates and white 1956:20. The rPAN/PET (50/50) blend shows the highest impact energy followed by rPAN/PET (70/30).

Figure 4.35: Load at yield of: rPAN, PET and their blends
Table 4.17 Operating set-up of impact machine

<table>
<thead>
<tr>
<th>Charpy</th>
<th>ASTM 123</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charpy</td>
<td>ISO 179 A</td>
</tr>
<tr>
<td>Temperature</td>
<td>$23^\circ C$</td>
</tr>
<tr>
<td>Hammer</td>
<td>7600.007 Charpy</td>
</tr>
<tr>
<td>Hammer angle</td>
<td>$150^\circ$</td>
</tr>
</tbody>
</table>

Table 4.18 Impact Test Results

<table>
<thead>
<tr>
<th>Samples</th>
<th>Width (mm)</th>
<th>Absorbed Energy (Abs en) %</th>
<th>Repeatability (Re) (kJ/m²)</th>
<th>Energy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rPAN</td>
<td>7.3</td>
<td>0.81</td>
<td>1.93</td>
<td>0.061</td>
</tr>
<tr>
<td>rPAN/PET (30/70)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This sample exhibits progressive cracks during notching and broke during notching process. It is very brittle</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>rPAN/PET (50/50)</td>
<td>7.55</td>
<td>1.24</td>
<td>2.72</td>
<td>0.093</td>
</tr>
<tr>
<td>rPAN/PET (70/30)</td>
<td>7.95</td>
<td>0.90</td>
<td>1.90</td>
<td>0.068</td>
</tr>
<tr>
<td>PET</td>
<td>8.1</td>
<td>1.23</td>
<td>2.63</td>
<td>0.093</td>
</tr>
</tbody>
</table>
CHAPTER 5

5.1 Summary and Concluding Remarks

5.2 Conclusions

The objective of the research is to explore the viability recycling PAN fiber and blend it with PET in order to develop new material instead of disposing of rPAN as waste. Samples of rPAN, PET and their blends were prepared using the rheomixer and the methods listed in Table 1 were used to obtain quantifiable data needed to ascertain (or otherwise) this objective.

Literature has shown that recycling of polymer products through various compounding routes can be successful in reclaiming an otherwise unserviceable material. Although, in most cases, the recycled products can have difficulty in competing with pure polymer products.

This study evaluated and compared blends of rPAN/PET samples with rPAN and neat PET. The evaluation approaches, include: the use of atomic force microscopy, scanning electron microscopy, differential scanning calorimetry, thermogravimetric analysis, dynamic mechanical analysis, transmission electron microscopy, X-Ray diffraction, FTIR (Attenuated Total Reflectance–Fourier Transform Infrared), polarized optical microscopy, rheology (relatively less successful), tensile test and impact test as methods of sample characterization and thermal analysis. Atomic force microscopy was used to determine the surface roughness, pore distribution, nearest neighbour pore, power spectral density, fractal analysis, flooding analysis and bearing analysis of the samples. The AFM results of the rPAN/PET blends were better when compared to the rPAN and PET. The higher roughness due to the high compositional content of rPAN strengthens the phase and matrix of PET in the blend while the high compositional content of PET weakens the blends. This is due to the brittleness
characteristics of PET, which led to high pore distribution in the matrix of PAN. The end result of high content of PET in the blend led to the weak mechanical property of the blend.

Firstly, WSXM 5.0 software that was introduced as a program was used by the scanning probe microscopy (SPM) as a relatively novel characterization technique for rPAN, PET and blended samples. It was also applied to all the samples analysed. A new set of experimental data (the bearing analysis) regarding the surface characteristics of the samples was used to characterize the pure and blended samples. This novel characterization technique was used to investigate the bearing profile of the AFM images in order to give additional information beyond the standard roughness measurement. For all samples, bearing analysis was done to determine the surface roughness with regard to the height distribution. For the blends, bearing analysis gives quantitative information about the fractions of each component that are located above or below a specific bearing plane.

Scanning electron microscopy (SEM) was used to visualize the surface morphology of all the samples. Since the height information of the samples was not given in the 2D images of the scanning electron microscopy, it was difficult to estimate the height variation (roughness) from the images. The SEM images were therefore analysed with ImageJ software in order to determine the height roughness and pores distributions. It was observed that pores distribution is related to the composition of (rPAN and PET) in the blends. High rPAN content, improves the pore distribution in the blends of rPAN/PET (70/30:50/50) while high PET content increases the pore distribution in the blend of rPAN/PET (30/70) (was very porous). This porosity resulted in high brittleness of that particular blend (rPAN/PET (30/70)) and makes it unsuitable for further analysis. The chemical characterization of samples surface was performed with Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) in order to analyse the chemistry of the samples top layer and identify the types of chemical bonds (functional groups) by detecting the vibration characteristics of the chemical functional groups.
in the samples. All the samples show some characteristic peaks that were due to the presence of primary amines resulting from asymmetric N-H stretching absorptions and the carboxylic groups in the polymer layer.

- From the impact test data of the samples, the rPAN/PET (30/70) blend is considered not viable due to its brittleness, while rPAN/PET (70/30 and 50/50) show promising results that warrant further development.
- The DSC data confirmed that the introduction of rPAN depresses the melting temperature of PET in the polymer blend samples. This assisted in the production process of the blends.
- The TGA tests indicated that the introduction of rPAN of a different amount in the samples reduced the maximum degradation temperature of the PET in the blend. In addition, the weight loss observed in the blend is due to the degradation of both components in the blend.
- The tensile tests showed that the tensile strength of the blended samples increased with increasing rPAN content.
- XRD showed the characteristic properties of the blended samples which support the crystallization in DSC. rPAN crystallinity suppressed by the addition of PET, only the main intensities (1 each) of the components showed in the rPAN/PET (50/50) blend.
- DMA result supports the tensile strength and modulus findings in this work.

The novelty of the study was the use of a new set of experimental data (bearing analysis) regarding the surface property of the samples. This novel characterization technique was used to give additional information, beyond the standard surface roughness measurement. For rPAN, PET and their blends, the bearing analysis was used to determine the roughness with regards to the height distribution of the lamella crystals in the samples and for blended samples, the
bearing analysis was used to give quantitative information about where the matrix and dispersed phase are located above or below a specific bearing plane.

5.3 **Recommendations and further study**

On the basis of the experimental data obtained in this study, the following recommendations are suggested for the development of rPAN fiber blends:

- **Exploring means of analysing the rheology of the blended samples**

  Rheology analysis plays a vital role in the polymer development. In this study, the blended samples were not suitably processed by the processing equipment due to the nature of the material and in order to avoid damaging the equipment.

- **Propose additives to improve the material properties**

  Exploring additives suitable for rPAN and PET are another important area of development. In this present study, the blends are phase-separated because no additives were added. Therefore, the need to explore the possibility of property improvement and appropriate additive for the blends needs to be explored.

- **Investigating probability of smart application for the blends**

  The possibility of rPAN/PET blends in smart applications is another area of interest for further study. Smart application of materials is another growing area of polymer development that could be explored with polymer blends. The lightweight packaging material is another area of interest which the blends possibly can fit into.
Mathematical modelling

Further use of a mathematical model is necessary in order to understand the physics of samples and material properties because they can have a great effect on the application of the material in a diversified economy.
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