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Atomic Force Microscopy and Tensile Strength Analyses of Recycled PAN and PET Blends

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Abstract: This investigation focuses on blend of recycled polyacrylonitrile fiber with neat polyethylene terephthalate in order to develop a new product and to improve on the properties of PAN/PET blend for possible new application. The micro-structural characterization using AFM shows possibility of blends development. The AFM images revealed an interpenetrating network of phases in the blends. The mechanical properties: modulus and tensile strength of the blended samples improved when compared to the recycled PAN and pure PET samples. This mechanical property improvement is due to a high ratio of PAN in the composition. This also paves way for possible reuse of PAN fibers rather than disposing it as a waste.

Keywords: Recycling, Blends, PAN, PET, Impact Test, Characterization

1. Introduction

In the field of polymer development, pure and blended polymers have been discovered for different applications. Many of these discoveries revealed that blending improves some properties of the polymers due to the matrix interpenetrating network [1-3]. Polymer recycling is another major development because many of these polymers are not easily disposable, thus the need for their recycling for possible new applications, instead of disposing them as wastes that will end-up in the landfill. Polyacrylonitrile fibers (PAN) have become a very important polymer in many industrial applications [4]. PAN fibers and polyethylene terephthalate (PET) have high commercial volume, annually and have been blended with other synthetic polymers that are rarely compatible because of its strong dipole-dipole interaction of the nitrile group [5, 6]. In many processes, optimizations of materials (pure and blended) properties are highly important, while maintaining adequate mechanical and chemical stability of the material. The study of recycled blended polymers for different applications is now being increasingly realized. However, there is no single compounding polymer process that can satisfy all the technical needs and economic requirements. The main focus in this report is the recycling process of used PAN fiber and PET-based polymers that are widely used in the filtration process of the ESKOM power generating process.

Many investigations have revealed that PAN is one of the most important fiber-forming polymers and it has a wide range of application, due to its high mechanical and excellent chemical properties [7]. The various ways of improving PAN properties have been reported in the literature [8–18]. Their reports have shown tremendous improvement in blending application of PAN. In addition, great effort has also been applied in the blending and development of PET as reported in literatures [19–23]. Little success has been reported in the compatibility of PAN with PET, hence the need for this study. The major focus of this study is to blend and improved on the properties of blended PAN and PET for possible product development.

2. Experimental

2.1. Materials

The PAN 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. The processing and analysis were carried out at the CSIR and TUT.

2.1.1. The Recycled PAN Fiber and PET Processing

PAN fibers used in this present study were cleaned by soaking in water for 12 hours, rinsed and dried for 24 hours at room temperature to remove dust, ash and coal particles embedded in the fiber. The PET and PAN fibers were further dried in air for 2 hours before the blending process took place. The dried PAN fibers were randomly chopped to fit into the rheomixer (Haake Rheomix 600 OS) compounding barrel. The two polymers were compounded at 290^{o}C.

2.1.2. The Blending Process

The dried PAN fiber was randomly chopped and mixed with the PET pellet at the ratio of 30/70, 50/50 and 70/30. These ratios were compounded in the rheomixer at a temperature of 290^{o}C for a 5 minute cycle time. 100% PAN fiber and 100% PET were used as controls for the blended systems. In the second stage of the process, the blends were carved at the same processing temperature of 290^{o}C for the desired standard test specimens and for subsequent analysis. Table1 shows the operating set-up of the rheomixer used, for the blending of the samples.

Table 1. *Rheomixer operating set-up for the blend.*

Temperature	290^{o}C
Speed	60 rpm
Time (minutes)	5 mins
Roller - rotor	600 rpm
Sample Mass	25 g
Density	1g/cm^{3}

2.2. Analytical Methods

2.2.1. Atomic Force Microscopy (AFM)

AFM was carried out using Agilent Technology 5500 scanning probe Microscope (PicoPlus-Atomic Force Microscopy Series 5500). The scanning probe microscope (SPM) was designed to acquire images, measures and generates statistical data of properties over a small area of the materials [24-27]. The data acquisition generates 2D and 3D-images used for PAN and PET detailed analysis.

2.2.2. Impact Test

The prepared ASTM standard samples were notched using notching NOTCHVIS CEAST 9050 machine. The Resil Impactor CEAST instrument (7.5J Hammer head) impact testing machine operating on automatic principle to achieve precision of the impact loading was used. The hammer released system is pneumatic actuation and this was programmed to a holding force after the test to avoid second impact on the tested samples.

2.3. Tensile Strength

Tensile test were performed on the pure PAN, PET and blended samples in order to determine the modulus, yield strength, ultimate tensile strength and elongation at break of each of the samples using Instron 5966 tester (Instron Engineering Corporation, USA) with a load cell of 10 kN in agreement with ASTM D638 standard. The samples were prepared using compression molding. The analyses were performed in tension mode at a single strain rate of 5 mm/mins at room temperature. The results presented, are the averages of 5 tests per samples.

3. Results and Discussion

3.1. AFM Flooding Analysis

The flooding analysis reveals the pores in the pure and blended samples as shown in figure 1. The blend of PAN/PET (70/30) (figure 1D) shows an improvement in the matrix roughness analysis and it shows PET sparingly distributed in the composition, followed by PAN/PET (50/50) (figure 1C). Furthermore, PAN/PET (30/70) (figure 1B) revealed increased pore size which resulted in the brittleness of the sample during impact analysis testing. From this analysis, PAN/PET (70/30) revealed maximum interpenetration network of PAN/PET and addition of PET above 50% weakens the blend composition and makes the blend unsuitable for the proposed recycling application.

3.2. Analysis of PAN, PET Surface Roughness

Table 2 showed the AFM roughness results of the sample surfaces performed under standard controlled environment. The roughness depends on the scan size; for comparative analysis, it was required that roughness is obtained from image within the same scan area. From table 2, surface roughness of pure PAN and PET samples were used as control for PAN/PET blended sample roughness parameters, i.e. root mean square Rms (nm) and the mean roughness Ra (nm). In conclusion, the roughness values decreased significantly due to the samples compositional ratio. The blend of PAN/PET (70/30) has the least mean roughness value, followed by PAN/PET (30/70) and lastly by PAN/PET (50/50), when compared to the pure samples of PAN and PET. The result showed the dispersion of PET in the PAN matrix which improves the mechanical property in PAN/PET (70/30:50/50) blends and weaken mechanical property in PAN/PET (30/70) blend.

Table 2. *Roughness of PAN, PET and blended samples.*

Sample	**Img. Rms (Rq) (nm)**	**Mean Roughness (Ra) (nm)**
PAN (100%)	80.304	65.739
PAN/PET (30/70%)	63.232	49.781
PAN/PET (50/50%)	70.371	53.693
PAN/PET (70/30%)	20.924	15.806
PET (100%)	49.508	38.698

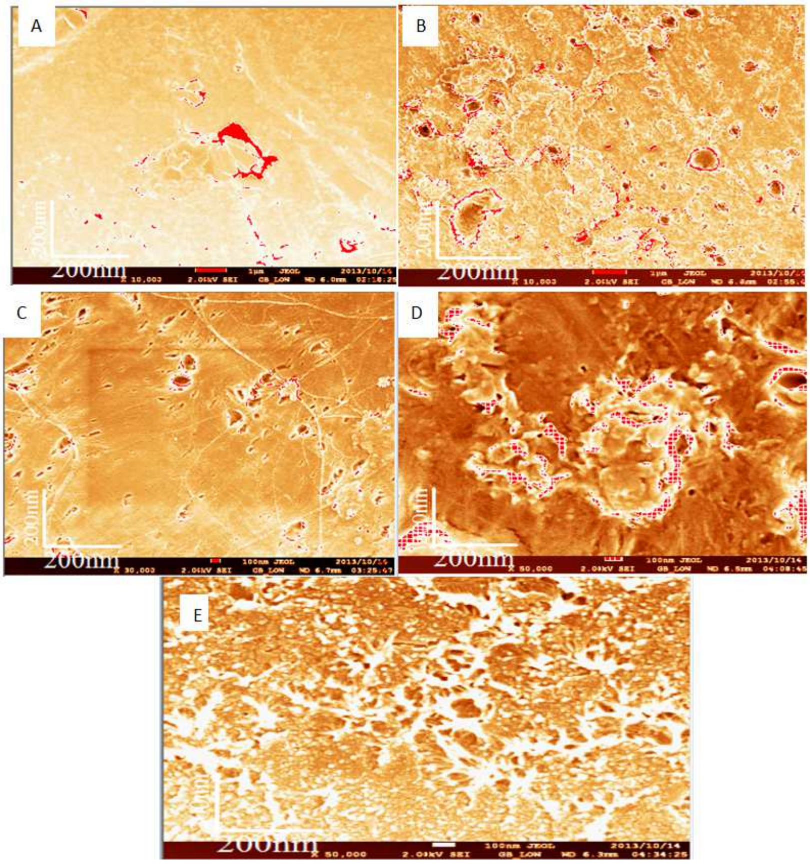

Figure 1. *Flooding analysis of poles distribution in (A) PAN, (B) PAN/PET (30/70), (C) PAN/PET (50/50), (D) PAN/PET (70/30) and (E) PET.*

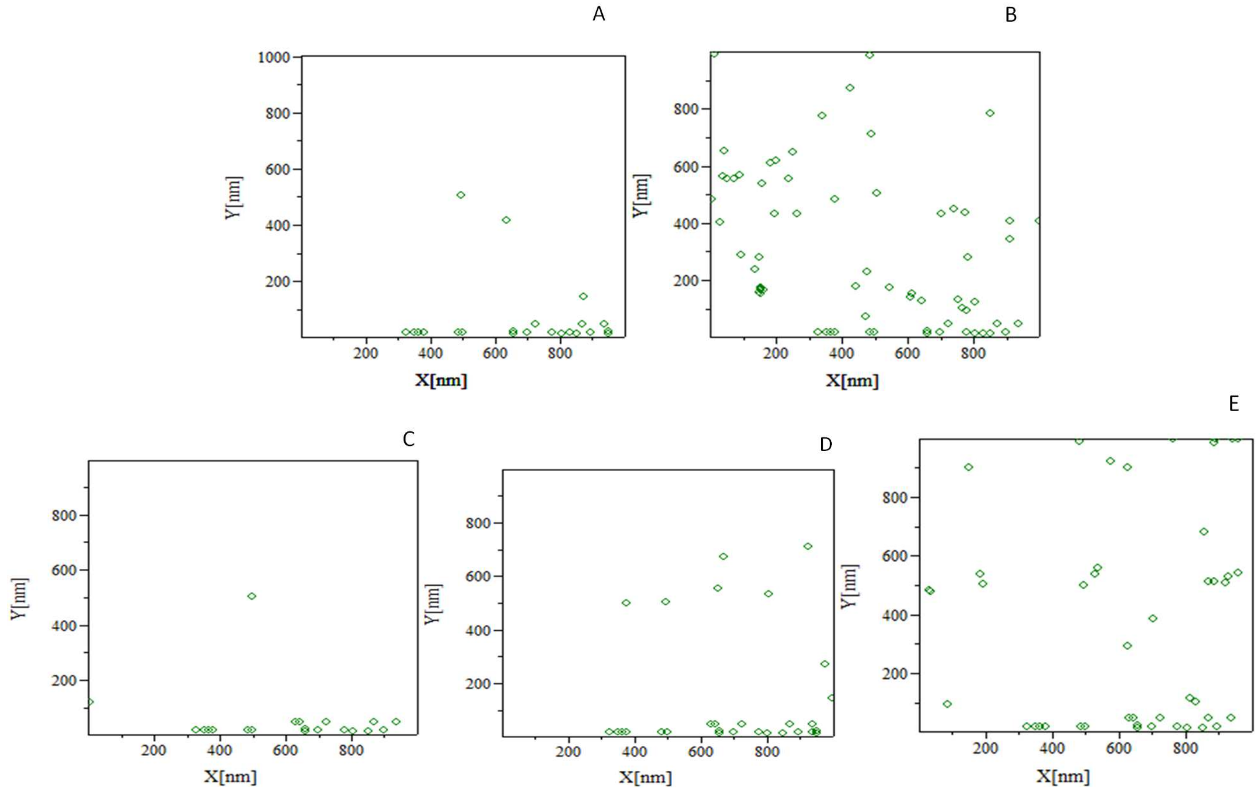

Figure 2. *Particles distribution in (A) PAN, (B) PET, (C) PAN/PET (70/30), (D) PAN/PET (50/50) and PAN/PET (30/70).*

3.3. PAN, PET AFM Image Mapping

The mapping of PAN, PET and the blended samples shown in figure 2, supports the findings of the roughness and flooding analysis, tensile and impact test of this work. The AFM image mappings showed that, particle distributions are well dispersed in PAN/PET (70/30) followed by PAN/PET (50/50) and lastly by PAN/PET (30/70) see figures 2c-2e. The particle distribution also improves and weakens with the constitutional ratios of PAN and PET in each blend. This assisted in understanding the matrix improvement of PAN/PET (70/30:50/50) and weakness in matrix of PAN/PET (30/70) observed during the tensile test. Furthermore, the result revealed that high ratio of PET is not viable for recycling purpose in this study.

3.3.1. Impact Test

It was observed that, at a slight notching impact on PAN/PET (30/70) blended sample, the samples cracked and could not be processed any further. This shows that the blend was brittle by revealing poor mechanical property. This corroborates the finding of the AFM mapping and tensile strength analysis. This weakness observation might be due to the weakening of the strong dipole-dipole interactions of the Nitrile groups of PAN [28-30]. In addition to the impact test conducted, PAN/PET (50/50) blended composition shows higher energy impact followed by blended composition of PAN/PET (70/30).

3.3.2. Tensile Strength

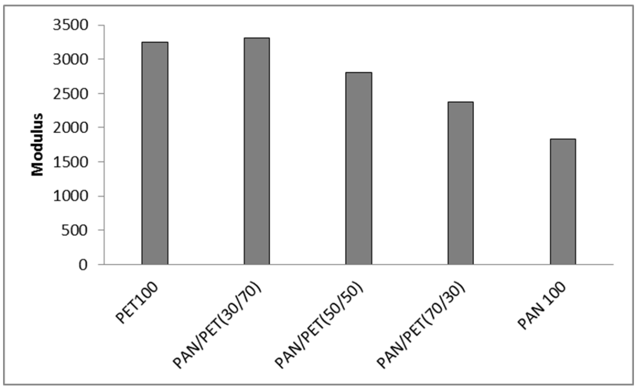

Figure 3. *Modulus of the Pure and Blended PAN/PET Samples.*

The result of the modulus and tensile strength of the finding analysis are shown in figures 3 and 4. In this study, the blended samples exhibits increased mechanical properties based on the blends ratios when compared to the pure samples of PAN and PET. The mechanical properties of all the samples are shown in figures 4 and 5. The results from the chart are discussed as follows:

- Figure 3 shows that the addition of 70% PET increases the modulus of the sample and it resulted in brittleness. This was observed during the material impact test. The addition of 70% PAN reduces the modulus and improves the stiffness of the blend. PAN/PET (70/30) reflects better composition in the blended, followed by the composition of PAN/PET (50/50).
- From figure 4, the result of the tensile strength of the blended samples shows that, the addition of 70% PAN improves the tensile stress of the blended samples, follows by the 50% blended composition.

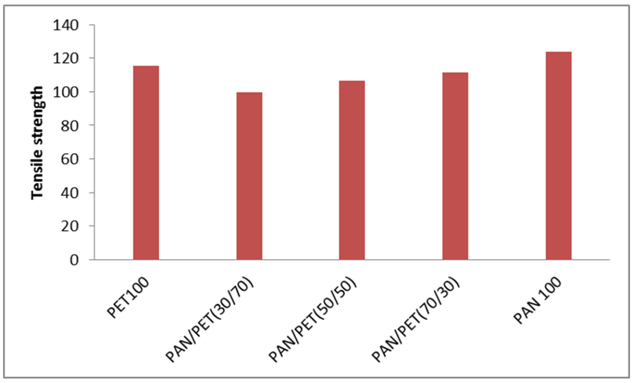

Figure 4. *Tensile strength of the Pure and Blended Samples.*

4. Conclusion and Further Study

The blended samples optimum viable blend was observed at PAN/PET (50/50), beyond this ratio of PET (70%), the material becomes brittle. PAN/PET (70/30) revealed maximum tensile strength which shows improve mechanical property of the blend. The AFM findings support the finding on the impact test, modulus and tensile strength of the samples. This will further assist in the development of PAN/PET blends.

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