

CHARACTERISATION OF WASTE POLYOLEFIN BLENDS USING THERMAL AND IMAGING TECHNIQUES AIMED AT PRODUCT DEVELOPMENT

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ABSTRACT

A major gap exists in research and development when it comes to valorising solid waste (SW), namely of polymeric origin, targeted at product development for market use. Such opportunities can be of immense environmental and operational benefits in the future, for which materials characterisation techniques can be of immense support in providing a scientific rationale. To this end, commingled plastic solid waste (PSW) blended with virgin commercial grade resin of linear low-density polyethylene (LLDPE), were subjected to scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) with the aim of investigating various properties that determine product integrity. The blends comprised PSW in the following percentages (by wt.%): 0, 25, 50, 75 and 100 wt.%. The blends were compounded by weighing, extruding, and blow-filming using a single screw extruder (L/D = 30, 45 bars and 85 RPM) and a film-blowing machine (monolayer) with a water cooling temperature maintained between 16 and 17°C. The die head temperature (DHT) was maintained at 175°C to preserve the mechanical integrity of the LLDPE resin. The images obtained showed the distinctive impact of waste content which can cause the deterioration of products used in outdoor environments. A comparative assessment with weathered samples also revealed knowhow development opportunities for such applications. The thermograms obtained distinguished the polyolefin material degradation profile clearly, which can be used as a basis for thermal degradation kinetics determination.

Keywords: plastic solid waste, thermogravimetric analysis, scanning electron microscopy, extrusion, polyolefin.

1 INTRODUCTION

Mechanical recycling of polymeric waste is one of the most established methods in valorising solid waste (SW). This is due to the fact that such type of waste can be treated using established methods that are typically associated with the plastic industry conversion processes. These include plastic conversion by extrusion, blown filming, injection moulding, etc. Incorporation of plastic solid waste (PSW) with virgin resin has been conducted previously, namely for price driven reasons and reduction of environmental pollution. This type of recycling schemes can serve the environmental and ecological system, and reduce energy demand. Mechanical recycling of polymeric waste provides numerous advantages that can be summarised thus:

- It reduces oil and energy consumption by comparison to virgin resin conversion;
- It reduces the disposal of PSW;
- It generates income and creates job opportunities.

It is of major importance that the substituted PSW performs a similar function to the virgin resin, in order to, have the concept of mechanical recycling proven [1]. This is typically conducted when the PSW is mixed with the virgin polymer with the aim of achieving an acceptable standard for the desired product [2]. Researchers should be vigilant



to the fact that mechanical recycling, although it utilises similar techniques, is typically confused with what is termed as closed loop (primary) recycling. The former is typically conducted in-house the conversion facility utilising process scrap, whilst the latter (also termed downgrading) is done with reclaimed (recovered) SW [3]. Primary recycling of scrap plastic is conducted to a great extent. This is due to the fact that such type of PSW is very pure, available and compatible to the product converted since it results from the same type of process the scrap originates from [4]–[5]. However, primary recycling doesn't solve the accumulate PSW problem in urban environments considering the fact that post-consumer waste is some five times greater in volume than waste generated from industry and commerce [6]. Hence, prime focus should be on mechanical recycling where recovered plastic is put into an application that would not use virgin resin but utilizes polymeric waste (i.e. plastic lumber) as an alternative to higher cost/shorter lifetime plastic grades [7].

SW is considered a major problem in various developing countries, including the state of Kuwait, where it is estimated according to recent statistics to comprise 17% of the MSW generated [8]. Fig. 1 shows the distribution by type of municipal solid waste (MSW) distribution in Kuwait. The generation of PSW goes hand in hand with the dependency of consumers on these articles. It is evident that dependency on plastics is namely from household items, where PSW constitutes 13% of its total distribution in Kuwait [9]. Hence, and by closer examination to household activities; dependency is typically on plastic films which has not been research and assessed in the past to a great extent and literature is very limited and scant to this effect. Recently, Al-Salem et al. [10] and Al-Salem [11] reported that plastic film waste constituting polyolefin (PO) polymers in Kuwait can substitute virgin resin by 90 wt.% to produce superior market products with accepted market standards. Extrusion with blown filming was used and a die head temperature (DHT) that was suitable was reported to be 175°C in accordance with recommended processing conditions to the virgin linear low-density polyethylene (LLDPE) used in the dry blends. Albano and Sanchez [12] used waste high density polyethylene (HDPE) and virgin HDPE, as well as virgin polypropylene (PP) to assess various properties in the obtained blends. The breaking point of the blends was noticed to decrease with the addition of both virgin and recycled HDPE to the virgin PP. La Matina [13] assessed the effect of blending virgin polyethylene (PE) with mixed plastic waste originated from bottle collections consisting of 39% polyvinyl chloride (PVC), 33% PE and 28% polyethylene terephthalate (PET). The Young's Modulus was reported to increase with the addition of waste, attributed to the high Young's Modulus of the waste polymers acting as a reinforcing agent. Starpasson et al. [14] evaluated the mechanical properties of virgin PE and PP blends. It was reported that the increase in low density polyethylene (LDPE) percentage by weight reduced the strength and Young's Modulus of the blends. Madi [15] blended recycled HDPE with virgin PP blends with a weight ratio up to 30% of PP. It was reported that the addition of HDPE had a strong correlation to the maximum stress measured.

Research and development (R&D) recycling and reclaiming PSW comes as a necessity rather than anything else. It goes hand in hand with the ever-increasing demand on plastics which witnessed a booming increase as of late reaching a production rate of 322 mtpa [16]. It is also crucial to have a sound rationale with scientific basis to be able to develop products for market use, especially from the PSW stream. Testing for the durability of waste materials can be conducted using various laboratory methods. For instance, weathering (aging) tests can be used as a means to examine the durability of products against influential outdoor environment parameters [16]–[19]. In addition, thermal stability and imaging techniques have been employed previously with polymeric samples

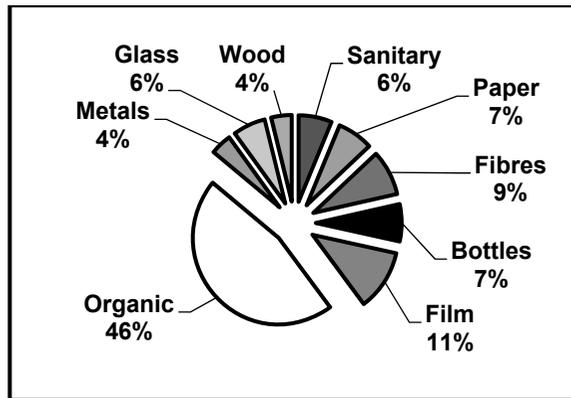


Figure 1: Municipal Solid Waste (MSW) distribution by type in the state of Kuwait according to Al-Jarallah and Aleisa [8].

characterisation namely using scanning imaging microscopy (SEM) and thermogravimetric analysis (TGA) [20]–[22]. Henceforth, this work was initiated, in order to, characterise various blends of PSW (originating from plastic waste packaging films) with virgin commercial grade plastic (i.e. LLDPE) typically used in plastic film conversion. The work conducted in this study is a part of a continuing effort that stems out experimental results with the aim of having a comprehensive and novel picture of plastic film products rich in waste content. To best of knowledge the aim of the original research project and this paper's specific objectives have not been attempted in the past.

2 EXPERIMENTAL

2.1 Materials

PSW in the amount of 200 kg, was secured from NWMC in the form of plastic films reclaimed from various sources in the State of Kuwait. Constituting elements of PSW and differential scanning calorimetry (DSC) investigation could be found elsewhere [23]. Readers are referred to Al-Salem [23] and Al-Salem and Al-Dousari [24] for the materials preparation and conditioning procedures. LLDPE grade EFDC-7050 was graciously supplied by EQUATE Petrochemical Company and used in this work as white translucent pellets with a particle density (ρ) of 0.918 g cm⁻³ and a melt flow index (MFI) of 2 g/10 min. For the purpose of confidentiality, the company did not provide details of the additives in this commercial grade.

2.2 Specimens compounding

Dry blends (i.e., blends with no additives at the blending stage) of both virgin and waste polymers were weighed, extruded, and blown using a single screw extruder (Tecnova, L/D = 30, 45 bars and 85 RPM) and a film blowing machine (Kung Hsing monolayer) with a water cooling temperature maintained between 16 and 17°C. Three DHTs were originally used to determine the effects in the later stages of DHT on properties studied. These were: 175 – as per supplier's recommendation, 185, and 195°C. The three temperatures were chosen to showcase the extremes of melting points surpassing those of the

constituting polymers in order to study the processing effect on the measured properties. The six extruder zones were maintained between 175 and 185°C. Fig. 2 shows the blown film machine used with a schematic diagram of the main processing parts used in this work. Samples of a DHT (175°C) were later used and are discussed in this work, as these specimens proved higher in integrity and more comparative to products used in the local market [11]. Weathering tests, mechanical and physical characterization are discussed elsewhere [23]–[24].

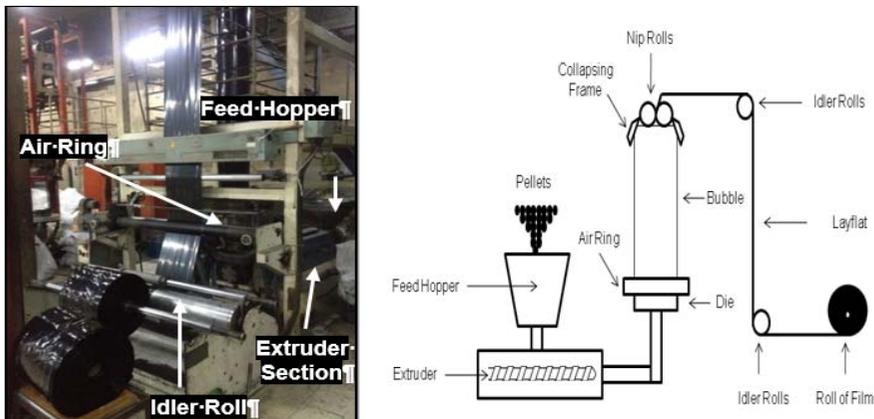


Figure 2: Blown film machine used in compounding the samples in this work.

2.3 Scanning Electron Microscopy (SEM).

The sample surfaces were placed on a double-sided carbon tape positioned on a metal holder then coated with a layer of platinum with a thickness of 8–10 nm by sputtering using a JEOL-JFC-1600 sputter coater for 30 seconds. Samples were then analysed by placing them under JEOL-JSM-6010 LA SEM using a voltage of 5 kV (to prevent damage of polymeric film) resulting in various micrographs taken with a 100- to 10,000-fold magnification. All samples were stored in the dark before analysis at laboratory temperature with controlled relative humidity (RH) of 50%. Furthermore, a cross section of each sample was imaged after dipping each film in liquid nitrogen by placing the samples vertically on a double-sided carbon tape in 90 degrees position. The samples were coated by platinum using the same sputter coater and analysed by the same SEM.

2.4 Thermogravimetric analysis (TGA)

Thermal degradation of virgin/waste blend samples was investigated using a Shimadzu TGA-50 thermo-balance equipped with a data acquisition/analysis software (TA Instrument) under five heating rates (β) (i.e. 5, 10, 15, 20 and 25°C min⁻¹). A constant flow of pure (99.99%) dry nitrogen with a flow rate of 50 ml min⁻¹ was maintained throughout the experiments. The measurements were conducted using 5±0.2 mg samples from room temperature to 550°C made with triplicates showing high repeatability with standard deviation not exceeding 1% in accordance with the International Confederation for Thermal Analysis and Calorimetry (ICTAC) recommendations previously published in Vyazovkin et al. [25]–[26] for non-isothermal (dynamic) thermogravimetry; to diminish sample size

influences on the kinetics [27]. Furthermore, samples of 1 ± 0.01 mg were subjected to thermogravimetry in the same instrument under a constant flow of pure oxygen gas (99.99%) with a flow rate of 50 ml min^{-1} (β equal $15^\circ\text{C min}^{-1}$).

3 RESULTS AND DISCUSSION

Analysis of examined specimens revealed various influential factors regarding the products considered in this work. Fig. 3 shows the thermogram obtained for the virgin LLDPE specimens, showing influence of various β on the onset, inflection point and maximum degradation temperature obtained. A residual mass of less than 3.5% was obtained with the lowest heating rate detecting a clear change in degradation reaction mechanism under pyrolytic conditions using the 5°C min^{-1} rate [28]. In addition, it was suspected that blends of virgin and waste materials subjected to thermogravimetry will indicate a two degradation curves (thermograms) in the TG curves. However, it was noted that samples of the waste and waste blends were acting in a pseudo polymer manner under inert media. Fig. 4 shows the 75/25 (virgin/waste) sample and Fig. 5 shows the 0/100 (virgin/waste) samples examined (other formulations not shown in this communication. This indicates that the degradation reactions kinetics can be considered in an iso-conversion (i.e. iso-kinetics) manner. This is also attributed to the fact that blending has occurred on a physical level rather than co-polymerisation bonding in the materials matrix.

Residual masses obtained in the TG analysis of all samples showed less than 3.5% between onset temperature and maximum degradation temperature. In addition, a sequential change in onset temperature was noted in the specimens of all formulation similar to past works [29]. However, oxidation temperature investigation using TG in reactive media (i.e. O_2) revealed a distinct onset curve for the second degradation stage which can be attributed to the degradation of polypropylene (PP) in the waste (Fig. 6). This shows that gasification with the aim of recovering products of similar nature should account for the reaction in the second degradation curve, unlike the pyrolytic behaviour noted in the previous examination under N_2 .

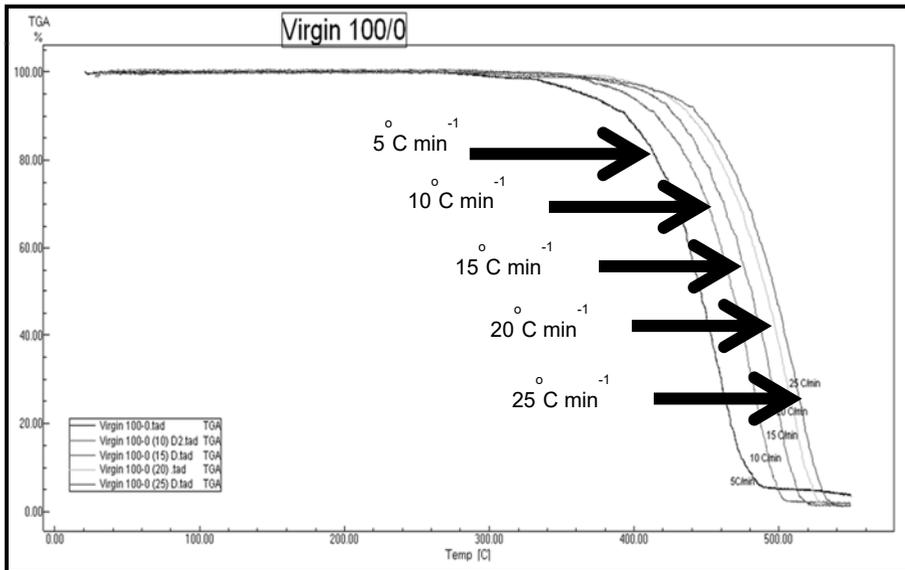


Figure 3: Thermogram of 100/0 (Virgin/Waste) sample obtained in this work.

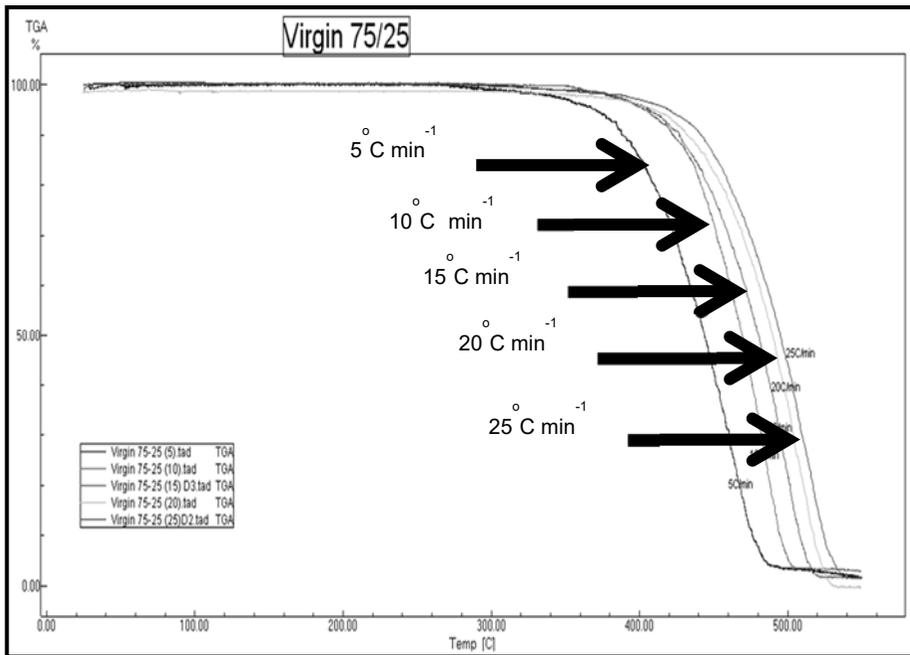


Figure 4: Thermogram of 75/25 (Virgin/Waste) sample obtained in this work.

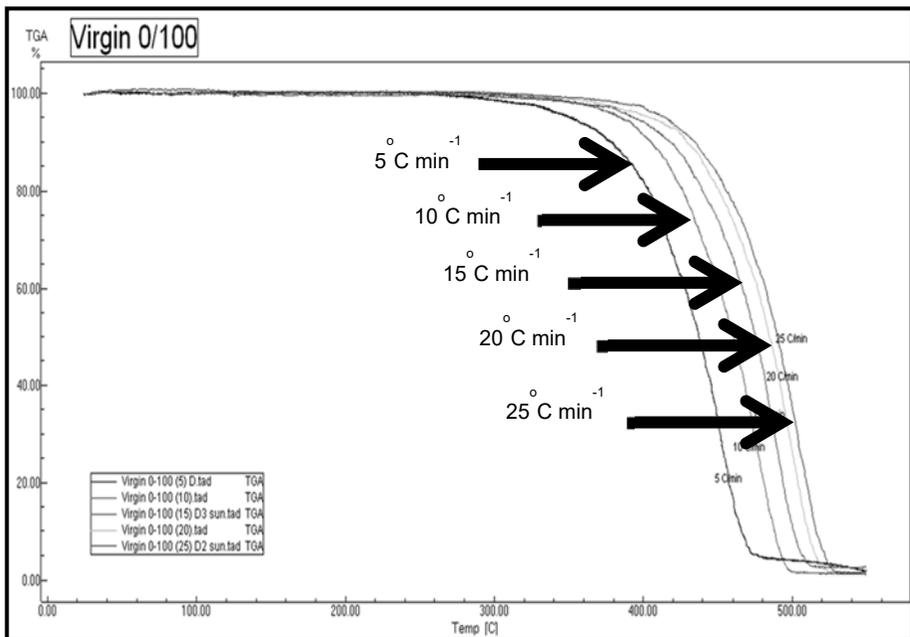


Figure 5: Thermogram of 0/100 (Virgin/Waste) sample obtained in this work.

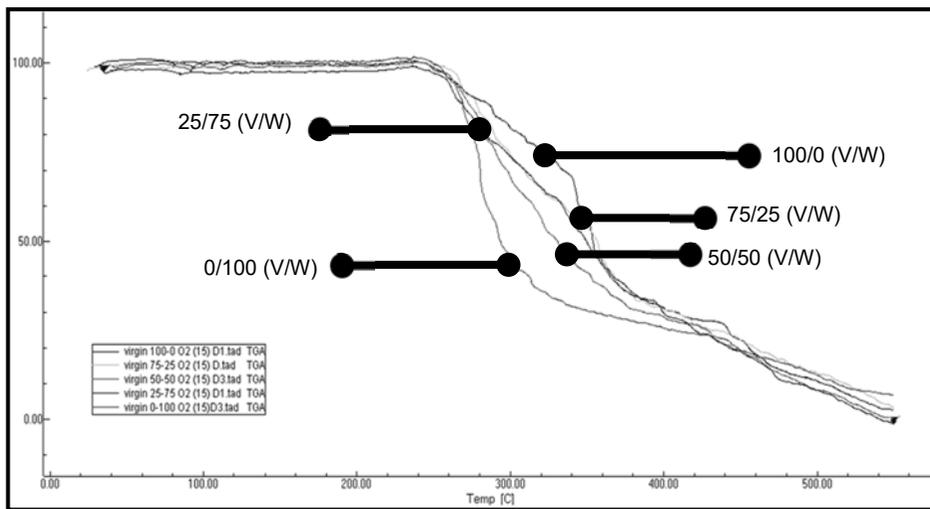


Figure 6: Thermograms obtained for specimens analysed in oxygen media showing samples of virgin/waste formulations considered.

Identifying a knowhow based on analytical and experimental technique for the identification of products developed from PSW is the main objective of this work, which SEM analysis has aided in doing so. Photomicrograph depicted in Fig. 7 shows the LLDPE samples subjected to two magnifications. The surface was smooth as the material was non-degraded as past investigations have shown [30]. No visible cracks were, holes or defects were noted. Apparent non-uniformity from extrusion and processing at compounding stage was visible (Fig. 7(b)) showing some crystalline (blistering) behaviour. Waste specimens with no LLDPE present in the formulation also revealed compatibility among examined samples (Fig. 8). However, samples of the various blends show some microcracks namely resulting from processing. Samples in cross sections also revealed crystalline incompatibility (not shown). The continuation of the work shall reveal a development of a methodology for analyzing and evaluating waste based materials namely after exposure to various accelerated weathering exposure duration, complimenting the work also will be a degradation kinetics reaction model and infrared spectroscopy analysis for identifying the ageing of the materials.

4 CONCLUSION

Compounded specimens resulting in various formulations between virgin linear low-density polyethylene (LLDPE) and plastic solid waste originating from plastic films, were subjected to thermal and imaging analysis. A knowhow based profile is expected to be established based on eth final analysis and results obtained by eth end of this continuing effort. Onset temperatures were noted to change, indicating a degradation mechanism change, with inert media pyrolytic analysis. However, no degradation was noted for specific materials. In addition, SEM analysis revealed compatibility of pseudo polymer plastics rather than the blends in both modes of examination (i.e. imaging and cross sections).

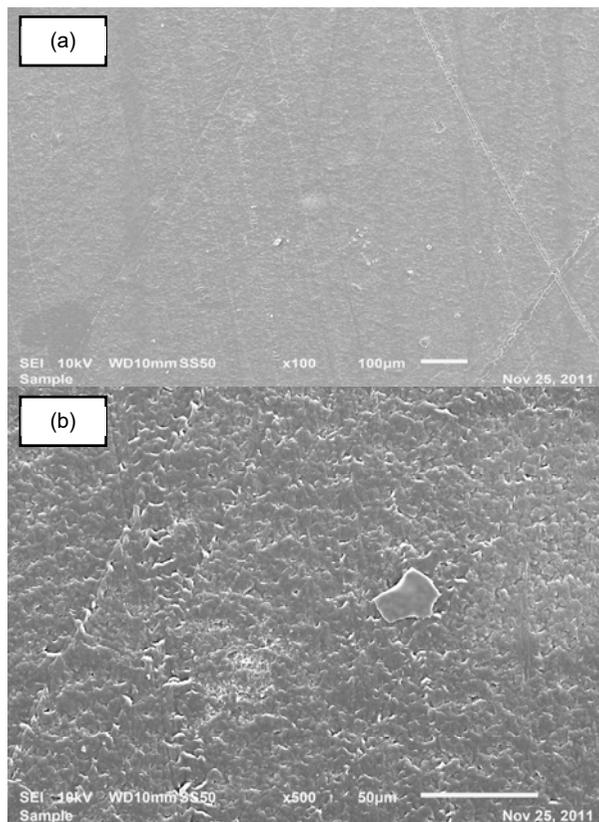


Figure 7: Micrograph of Virgin LLDPE Sample Subjected to (a) 100X and (b) 500X magnification.

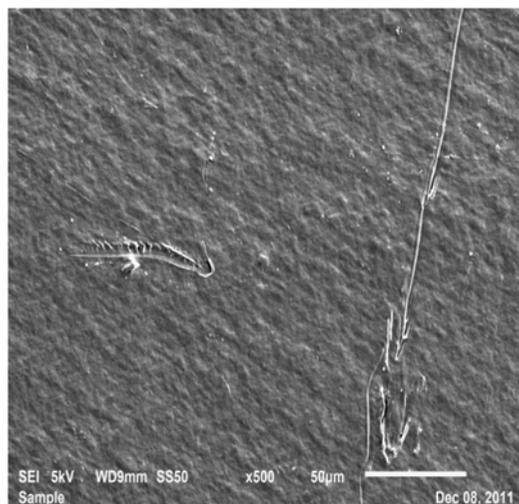


Figure 8: Micrograph of Waste Sample Subjected to 500X magnification.

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