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Morphological Properties of High-Density Polyethylene (HDPE)/Leather Waste Composite

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Abstract

This study reports the conversion of waste cow leather into useful materials through composite design and fabrication. The fabricated composite was characterized by Fourier Transform Infrared (FTIR) Spectrophotometer to identify functional groups and Scanning Electron Microscope (SEM) to check dispersion and compatibility. In order to enhance the adhesion between the reinforcement and the matrix, 0.5g trimethylquinoline (TMQ), 3.5g Mg $(OH)_2$, 0.3g TiO_2 were used as additives. Results obtained from FTIR, showed a C-H, C-C, C=C, cis disubstituted alkene, O-H, N-O, C-O, C=O, C-N and N-H as the major functional groups. SEM revealed a ductile fracture surface as the mode of tensile deformation indicating a good dispersion, adhesion and compatible material with HDPE. This work had contributed to the reduction of tannery solid waste in the environment. Composite of HDPE/Leather waste are safe because tons of chrome is kept inside the polymer as Cr^{3+} without the risk of oxidizing to Cr^{6+} under the action of sun light and heat thereby reducing the risk of water and soil contaminations.

Keywords: Morphology, Waste cow leather, Composite, HDPE, Properties

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Introduction

Composite research and development is one way of meeting the present day-technology and material property requirement. Technology is advancing enormously in virtually all science fields due to the ease of composite design and fabrication. All that is required for composite development is to find combination of materials necessary for end user applications (Shamsun *et al*., 2013) then mixed them together by suitable techniques. Composites are made of two or more different reinforcing materials bonded together with a chemical compound called the matrix (Todd, 2015). The reinforcing or dispersed (discontinuous) phase is usually embedded in a matrix (a continuous phase) which could be in the form of particulates, flakes, spheres or fibres (Shamsun *et al*., 2013).

Scientists have long being investigating on how to convert waste to wealth, improve the properties of plastics and composite materials with cheap (low cost) yet biodegradable materials and to promote/ improve the adhesion/interaction between matrix and reinforced interface of composite. A number of composite have been developed published in literatures

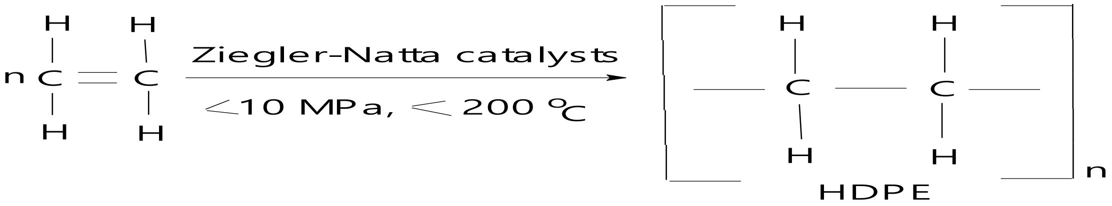
which makes composite versatile, valuable and an important family
of materials that has encompassed almost all material domains (house furnishing, packaging, sport, aerospace, automotive parts recreation equipment).

The advent of natural fiber-reinforced composite has found a place in the reinforced plastic industries where value has been added to waste and the reused of solid industrial and urban waste or residue (Chrońska and Przepiórkowska, 2009 and 2011; Ambrósio *et al*., 2011; España *et al*., 2013), and represent one of today's fastest growing industries (Souza *et al*., 2011). The leather processing industry produces large amounts of solid organic waste in the form of un-tanned (trimmings, fleshing, splits) and tanned (trimmings, splits and shavings) waste from raw hides and skins including semi-processed leather. The waste produced in leather industry far exceeds the quantum of finished leather (Zarfar *et al*., 2013 and 2014).

Though a number of solutions for the utilization and/or safe disposal have been proffered, tested, practiced and applied at pilot and industrial scales (Pecha *et al*., 2012; Yaohui *et al*., 2013), but a huge leftover of these wastes that can be managed by tanners do remain. The study is aimed at providing additional means of utilizing tannery solid waste generated in leather industry. This was achieved by dispersing solid leather waste into thermoplastic polymer (HDPE) to form composite materials as a waste management strategy that will take care of the huge quantity of solid wastes generated by tanners, a stable material which will not putrefy and suitable for a wide variety of end applications. There are many reports on the potential use and limitation of natural fibres as reinforcement in thermoplastics, available in literature (John and Richard 2005; Mohanty *et al*., 2005) Compatibilizers are used to improve adhesion between the reinforcement and the matrix (Mohammad *et al*., 2006). Physical or chemical method is usually employed to improve the interaction between the fibre and the matrix of natural fibre reinforced composite (Jerzy and Elzbieta, 2012; Jinchun *et al*., 2013). Disperscibility is necessary in order for composite materials to have good mechanical and physical properties (Chieu, 2005). Excellent disperscibility strongly depend on the micro structure of both matrix and the reinforcement. The level of dispersion can be measured directly or indirectly by the used of scanning electron microscopy (SEM) **(**Chris and Michael, 2002**).** Fourier transform infrared (FTIR) spectroscopy was employed to monitor and determine carbonyl and vinyl groups (functional groups) formation at the surface of the composites (Lundin *et al.*, 2004).

Materials and Methods

Carvers two roll mill, Model 5183 and Carvers laboratory hydraulic hot Press were used to compound (180^{0}C) and fabricate composites into standard (size and shape) (180 – 185^{0}C and 3 tons for 9mins) articles for analysis. Fracture surface and tensile strength were obtained using a Hunsfield tensometer, model W3179, H5K-S UTM; manufactured by Tinuis Olsen UK. The morphology of (the best tensile strength) composite was studied by using a JSM-5600 LV (Jeol, Tokyo, Japan) scanning electron microscope. Scanned images were taken at accelerating voltage of 2.0 and15.0 kV. Fourier transform infrared (FTIR) spectroscopy was employed to monitor and determine carbonyl and vinyl groups (check functional groups) formation at the surface of the composites. The infra-red spectra of the composite were recorded in absorbance mode, at a frequency range 650 – 4000 cm^{-1}. The commercial method of manufacturing high-density polyethylene (HDPE) is as shown in Scheme 1.



Scheme 1: Synthesis of high-density polyethylene (HDPE) by metal oxide catalysts supported over alumina-silica bases (Gowariker, 2007).

Plate I: High-density polyethylene (HDPE) physical appearance. Manufactured by Indorama Chemical Company Port-Harcourt, Nigeria

Plate II: Tanned Hide in preparation for research, obtained from Nigerian Institute of Leather and Science Technology (NILEST), Zaria.

Plate III: Dried pieces of tanned hide (leather) ready for preparation for research

Plate IV: Chrome re-tanned powder (0.5mm size, using Arthur Thomas Wiley Laboratory mill model 4 USA) ready for compounding with HDPE.

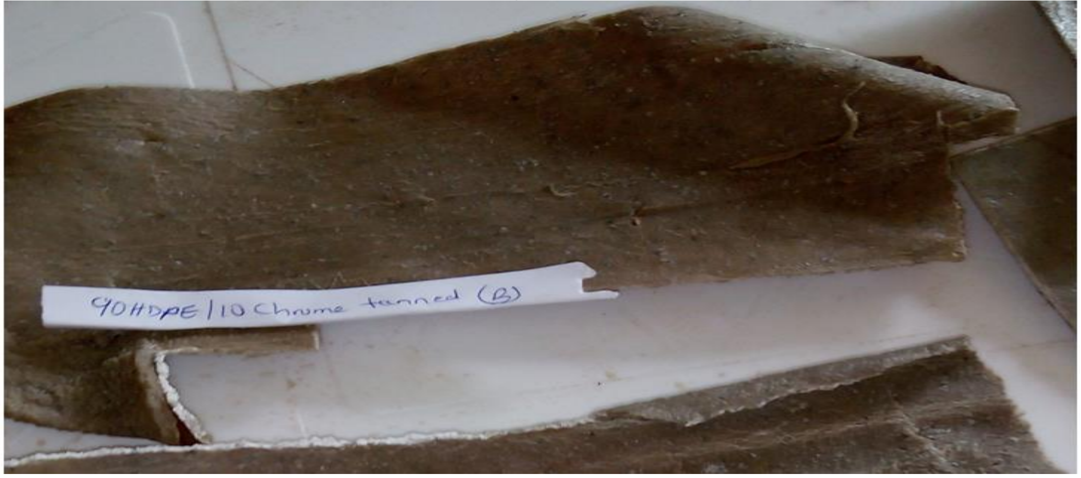


Plate V: Compounded sample with 0.5g trimethylquinoline (TMQ), 3.5g Mg $(OH)_2$, 0.3g TiO_2 were used as additives

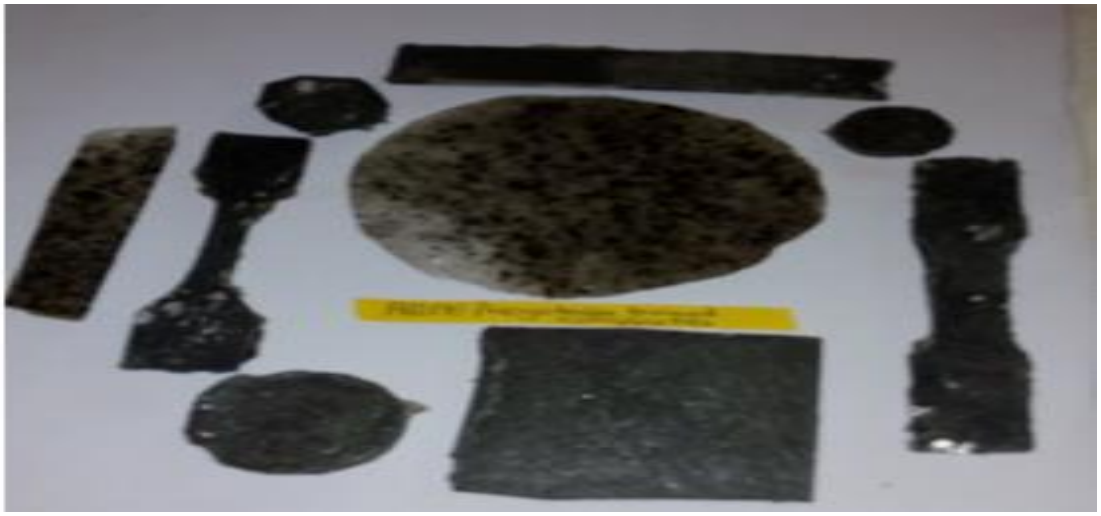


Plate VI: Fabricated samples compressed into standard shape and size for analysis.

Results and Discussion

The micrograph of Plate VII depicts a good fibre-matrix interaction, seen by links network resisting deformation. Plate VII shows micrograph of the tensile fracture surface of HDPE90/CTA10 composite (Musa *et al*., 2017). According to Mohit (2015), link network indicates good dispersion and compatible fibre-matrix interface (good tensile properties). It also means strong bonding at the fibre- matrix interface, (Rajendran *et al* 2016). The micrograph, in addition, shows white patches, and presence of structures like fibrils. The white patches were inorganic substances added as additives, the presence of structures like fibrils, suggest a poor interaction between fibre and matrix at such regions. The mode of failure in Plate VII includes tearing of the surface of composite along highly concentrated additives and fibre agglomerate. Ambrósio *et al* **(**2011) reported that accumulation of fibre in a place leads to poor adherence. Concentration of particles or fibre, acts as a flaw which could change the mode of fracture from ductile to brittle fracture as observed in Plates VII at the white patch along the fracture region.

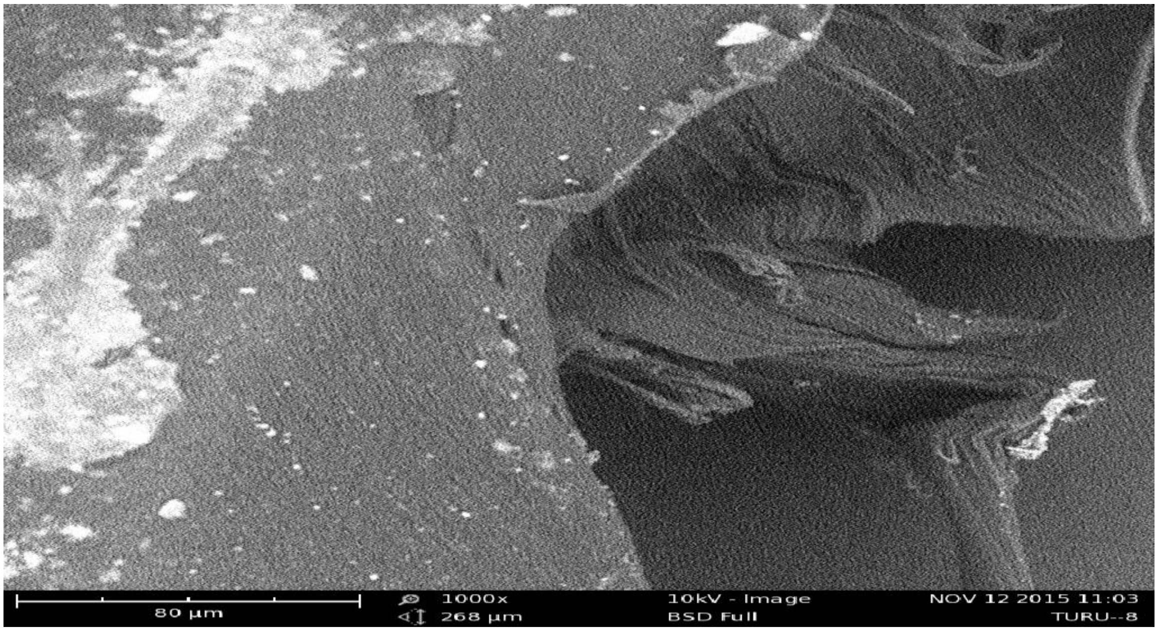


Plate VII: SEM micrograph of tensile fracture surface of HDPE90/chrome tanned10 (HDPE90/CTA10) composite

Figures 1, 2, 3 and 4 describe the FT-IR absorption frequencies for HDPE, Hide, chrome tanned leather and composite of HDPE/chrome tanned leather. FT-IR spectrum of HDPE (Figure 1) showed specific band at 2914.8, 2847.7 and 1461.1cm^{-1} (alkyl sp^3 C-H stretching) and a 719.4 cm^{-1}(cis disubstituted alkene C=C stretching) as the major strong and sharp peak intensity.

Indicating C-H, C-C and C=C functional groups which in turn attribute to hydrocarbon bond.

Figure 2 shows the FT-IR spectrum for un-tanned hide (UH) of 0.5mm particle size before compounding. A broad and strong intensity band was seen at 3298.7 and 2937.1cm^{-1} stretching frequencies, corresponding to O-H and N-H (alcohol and amide stretching) mode. Also, 1625, 1543, 1080 and 663.5 cm^{-1} for aldehyde, (nitro) N-O, (alkoxy) C-O and sp^2 C-H stretching were equally seen in the Figure 2. This gives a multi-functional groups (spectra of organic compound such protein).

Figure 3 shows the FTIR spectrum for chrome tanned of 0.5mm particle size before compounding. A broad band similar to Figure 2 but little shift at 3280.1, 2922.2, and 1080 cm^{-1}, indicating the effect of tanning on the raw hide (a modification that had taken place (some -OH has been replaced by Cr^{3+}), which is responsible for the stable material after tanning (not putrefy) in tanned hide there by making them suitable for a wide variety of end applications). A sharp and strong band of C-O, C=O and nitro at 1632.8 and 1543.1 cm^{-1} are equally seen in Figure 3. This is a modified form of Figure 2.

Figure 4 is the FT-IR spectrum for the composite of HDPE/chrome tanned. In the Figure, the 2914.8, 2847.7 and 1461.1cm^{-1} (sp^3 C-H stretching) shown in Figure 1 (HDPE) were also present, implying the present of all functional groups in HDPE. The broad band at 3280.1, 2922.2 and 1080 cm^{-1} (O-H and N-H stretching) previously shown in Figure 3 had suddenly disappeared or level up to a shape similar to that in Figure 1 (HDPE). It is likely that the proportion of HDPE to waste leather 90:10 made HDPE spectrum to overshadow that of chrome tanned hide spectrum at these wave numbers or the added additives have replaced most of the –OH functional groups at the surface. However, between stretching frequencies of 1461.1 and 719.4 cm^{-1} of N-O, C-O, C=O, C-N and N-H bonds seen in Figure 4 were stretching frequencies within 1080.9 and1953.1 cm^{-1} similar to those in Figures 2 and 3. This implies that all stretching frequencies found in un-tanned hide and chrome tanned observed in Figures 2 and 3 (finger print) were also equally present in Figure 4. This is an indication of combination of chrome tanned with HDPE to form a mixture of HDPE and chrome tanned hide spectra that formed the composite (HDPE/chrome tanned) no visible reaction. The pronounce disappearance of broad band of –OH could be attributed to the cohesive forces existing in the collagen-fibre in leather waste (i.e. strong hydrogen bonding, holding the fibre together more than the adhesive force of attraction (mechanical bonding) existing at the interface of the fibre-matrix, leading to the creation of voids, resulting into the formation of micro cracks which reduce flexibility of matrix making them brittle.

From the result of Figures 2, 3, and 4, the O-H stretching frequencies were lost to surface reaction or/and due to melt processing and N-H absorption frequencies introduced due composite development.

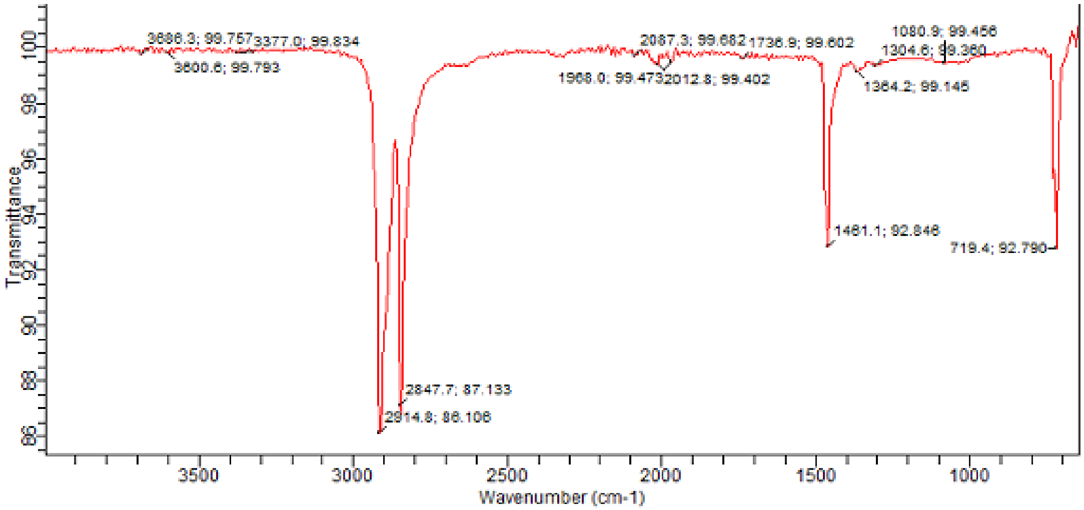


Figure 1: FT-IR for HDPE (control)

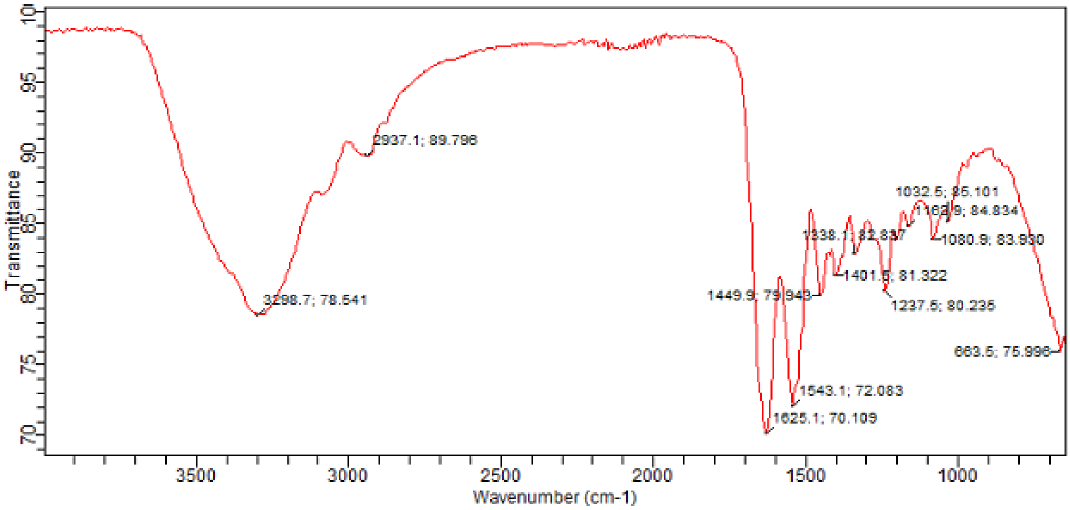


Figure 2: FT-IR for hide powder (un-tanned leather)

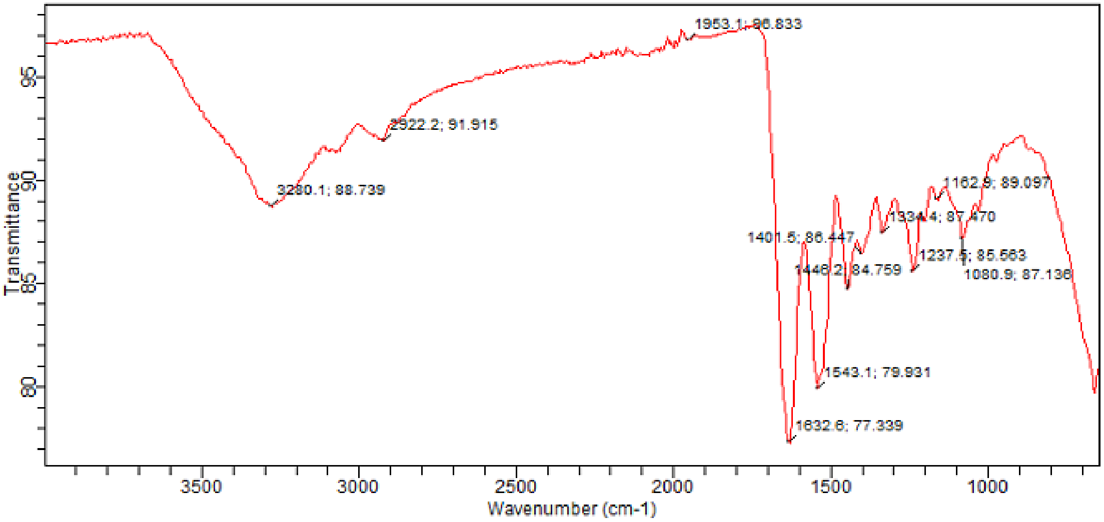


Figure 3: FT-IR for chrome tanned (0.5mm size)

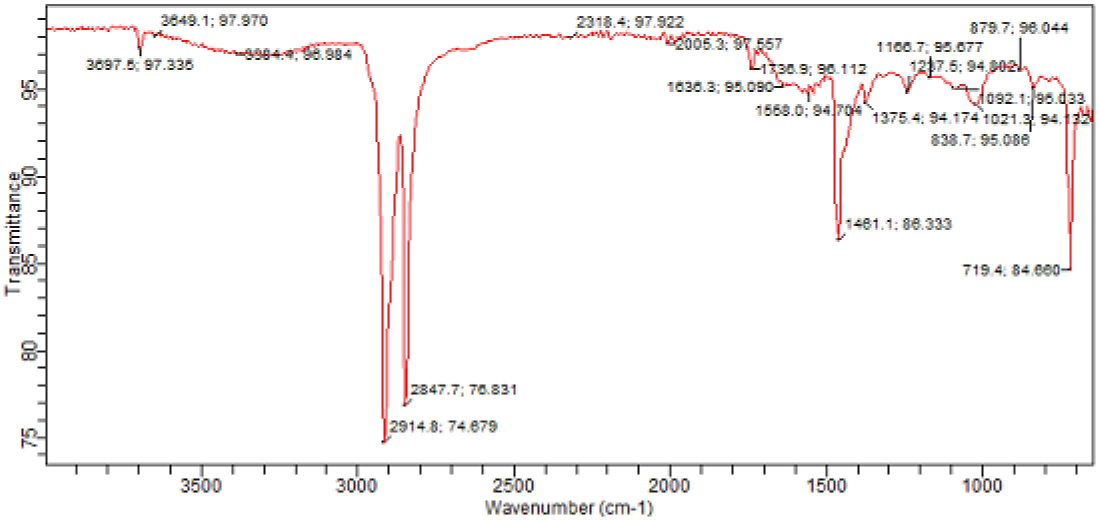


Figure 4: FT-IR for HDPE/chrome tanned composite with additives

Conclusion

Waste cow leather was successfully transformed to a valuable composite material. The adhesion between the matrix and reinforcement was improved by 0.5g trimethylquinoline (TMQ), 3.5g Mg $(OH)_2$, 0.3g TiO_2 used as additives. Results obtained from FTIR, showed a C-H, C-C, C=C, cis disubstituted alkene and O-H. SEM micrograph revealed a ductile fracture surface as the mode of tensile deformation indicating a good dispersion, adhesion and compatible material with HDPE.

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