

Biodegradability Study of Footwear Soling Materials in Simulated Compost Environment

by

^{a#}Moumita Mukherjee, ^aT. Loganathan, ^{*b}Sujata Mandal, and ^{*a}G. Saraswathy,

^aShoe and Product Design Centre (SPDC),

^bCentre for Analysis, Testing, Evaluation and Reporting Services (CATERS),

*Council of Scientific and Industrial Research- Central Leather Research Institute (CSIR- CLRI),
Adyar, Chennai – 600020, India.*

#Ordnance Factory Board, Ministry of Defense, Kolkata, India

Abstract

Aim of the present study is to investigate the biodegradability and decomposing properties of footwear soling materials by standard biodegradability test method. Biodegradability tests were performed by aerobic exposure of the selected six soling materials to the soil matrix and measuring the degradation and decomposition occurred with time. All soling materials were characterized for physical and physicochemical properties such as weight loss, hardness, density, tensile strength, abrasion resistance, thermal and morphological properties before and after exposing to the simulated compost environment. In the present study, the end-of-life nature of footwear soling materials currently used by the footwear industries are explored, which will further emphasize the importance of development and use of biodegradable materials in the footwear manufacturing.

Introduction

The global environment is increasingly deteriorating as a result of the socio-economic activities. Recently protection of the environment has become a global issue. Environmental sustainability refers to the synchronised conquest of environmental, social, and economic balance. Leather product industry occupied a prominent position in the world's economy but also it is accountable for the respective environmental consequences.¹⁻³

The global market value of leather goods was worth approximately 239.78 billion U.S. dollars⁴ whereas the global leather footwear market size was valued at USD 166.53 billion in 2018 and is expected to grow with a CAGR of 2.8% from 2019 to 2025.⁵ Depending upon the fashion forecast the utilization of number of pairs of footwear per person in every country is increasing nowadays. Being an essential commodity in today's world, worldwide footwear consumption had reached 24.2 billion pairs in 2018, raised by 2.7% over 2017 and this figure continues to rise.⁶ Now India is the second largest producer of footwear globally accounting for 13% of global footwear production of 16 billion pairs.⁷ India produces 2065 million pairs of

different categories of footwear which includes leather footwear of 909 million pairs, leather shoe uppers of 100 million pairs and non-leather footwear of 1056 million pairs.⁸

Undoubtedly, synthetic polymer materials play very important roles in our daily lives. Synthetic polymeric materials in footwear are increasingly replacing the natural ones. For example, polymeric materials such as polyurethane (PU), ethylene vinyl acetate (EVA), thermoplastic rubber (TPR), and thermoplastic polyurethane (TPU) are slowly replacing the natural materials, leather and natural rubber (NR), as shoe sole materials.⁹ Although extensive research has been performed on biodegradable plastics, the critical processing methods and high cost limited their application in many industries including footwear industry.¹⁰⁻¹³ Irrespective of the material used for making footwear, shoes are simply thrown away to the open environment without knowing the adverse effect they may cause in future. This creates an enormous amount of post-consumer shoe wastes that is currently being disposed in landfill sites around the universe that creates soil and water contamination. This may lead to various health issues in future. So, research and development on preparing biodegradable materials suitable for footwear application have become emergent need of the society.¹⁴ It is well known that leather is degradable.¹⁵⁻¹⁷ However, Pantazi et. al. found that the biodegradation capacity of vegetable-tanned leather is higher than the chrome-tanned leather while that of synthetic leather is very low as required by EN ISO 13432:2002.¹⁸ So in the present study, leather has been chosen to identify the leather shoe soles end-of-behavior in the specific compost environment and also as one of the control biodegradable material to compare with the plastics. The aim of the present study is to investigate the biodegradability and decomposing properties of different types of present day footwear soling materials by standard biodegradability test (soil burial) method (ASTM D5998) while exposing the sample materials to simulated compost environment.¹⁹ The physico-chemical and mechanical properties of these footwear materials are analyzed before and after exposure to the simulated compost environment. Properties such as weight loss, hardness, density, tensile strength and abrasion resistance are studied. Characterizations such as infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), differential scanning

*Corresponding authors email: saraswathyg@clri.res.in; sarasjohns@gmail.com; sujata@clri.res.in; sujatamandal@rediffmail.com

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calorimetry (DSC) and scanning electron microscopy (SEM) are performed. The results of this study will add knowledge about the polymeric materials that are used currently in footwear making and help to minimize the adverse effect to the environment by making necessary changes in the footwear manufacturing.

Materials

Total six different types of footwear soling materials such as vegetable tanned leather (LA), natural rubber (NR), ethylene vinyl acetate (EVA), polyurethane (PU), thermoplastic rubber (TPR) and thermoplastic polyurethane (TPU) were chosen and collected from the domestic market. Roughing process was done for all soling materials by using surface roughing machine to expose the basic soling material and also to maintain the uniform surface. By using clicking machine and standard dies, samples were cut into two different shapes (rectangular and dumbbell). Each sample specimen was marked with specimen number and sample code. Before conducting the biodegradability test, the samples were conditioned in the laboratory climatic conditions as per the ISO 2419 standard (temperature: $20^{\circ} \pm 2^{\circ}\text{C}$ and relative humidity: $65\% \pm 5\%$), for a period of 48 hours.

Compost Composition

The composition of the compost (dry weight) (Figure 1) per 5000 g was 2040g of cow dung, 570g of sawdust, 790g of newspaper and computer paper, 100g of white bread, 390g of shredded leaves, 960g of food waste (dry milk, potato, carrot, onion, pumpkin, tomato and other vegetables), and 150g of urea.²⁰

Methods

Soil is an extremely species-rich source of inoculum for evaluation of the biodegradability of plastics in the environment. The natural and fertile soil was collected from the surface layers of CLRI garden.

A laboratory mixture of equal parts (by weight) of soil samples obtained from at least three diverse locations, an agricultural field, a forest and a pasture or meadow was made. Soil from multiple and diverse locations were collected to maximize the biodiversity. To avoid significant perturbations of the microbial population, soils that have been exposed to pollutants were rejected. Preferably, the soil was used as fresh as from the field to assure active microbial content. The soil was sieved to less than 2-mm particle size, and obvious plant materials, stones, or other inert materials were also removed. The soil was stored in a sealed container at $4^{\circ} \pm 1^{\circ}\text{C}$ for one month. The moisture content of the soil was determined with moisture balance equipment. The compost was prepared by maintaining a particular ratio of component as described earlier. Open pots of 4L volume made up of clay were filled with the mixtures of compost and soil in 1:25 ratio, according to the standard test method ASTM D5998. The moisture content of the mixture was determined by following the equation $[(\text{Weight of fresh solids} - \text{Weight of dry solids} / \text{Weight of fresh solids}) * 100]$ as per the method of APHA-AWWA-WPCF 2540D and G respectively (as described in the method ASTM D5998). The percentage moisture content of compost and soil was $28.4\% \pm 1.5\%$ and $92.2\% \pm 2.1\%$ respectively. The moisture content of the soil mixture was maintained by spraying water at regular time intervals (250 mL/day). The degradation study of the samples was carried out at ambient temperature, between 30° - 40°C . Six empty pots of same specification were used, each for a particular soling material. 25% of the composting pot was filled with the mixture of soil and compost; and the specimens were placed in a cyclic order one after another. The pot was then filled with the mixture of soil and compost covering the sample specimens, until 4 cm down from the edge of the pot, as shown in Figure 2. Each pot containing nine specimens of a particular sample and filled with soil-compost mixture, was buried uncovered under the field in CLRI garden. The samples (three specimens for each sample of soling material) were removed manually from the pot after 30, 60 and 90 days, rinsed thoroughly with distilled water, dried to a constant weight at ambient temperature (30° - 40°C) and subjected to physicochemical,

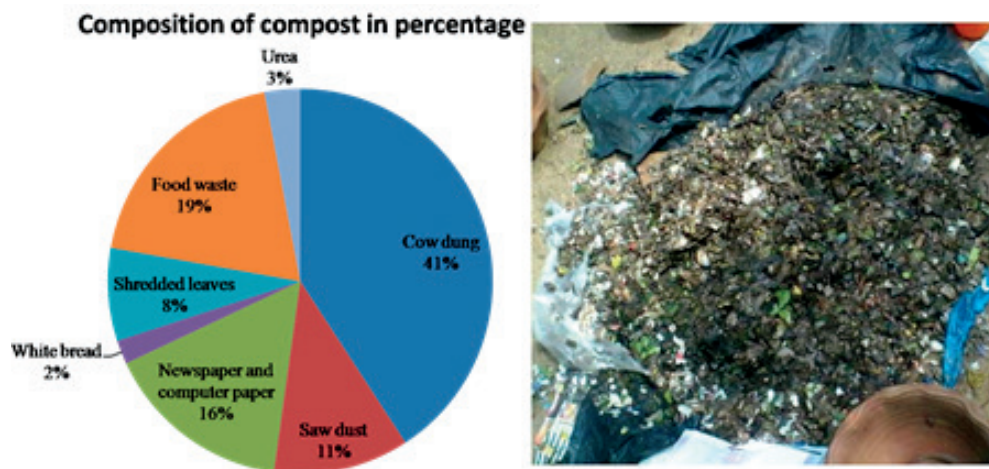


Figure 1. Compost composition and prepared compost.



Figure 2. Step-wise procedure for the placement of samples and filling of the pot with soil - compost mixture (i) clay pot for composting, (ii) 25% filled pot, (iii) placement of sample specimens, and (iv) covering of the sample specimens with soil - compost mixture.

morphological and thermal characterizations. The sole samples before exposure to the simulated compost environment are designated as BD and those after exposure are designated as AD.

Characterization

The weight of the samples were measured using an analytical balance. The weight loss of the samples after exposure to simulated compost environment was measured following the below equation,

$$\% \text{ weight loss} = [(W_b - W_a) / W_b] \times 100$$

where,

W_b = weight of the initial sample before exposure to compost environment, and

W_a = weight of the sample after exposure to compost environment for time t .

All the physical properties were measured by standard SATRA test methods as per the recommendations for shoe soles. Hardness is defined as the resistance of a material against deformation, particularly permanent deformation, indentation or scratching. There are two most common test methods for hardness i.e., Rockwell and Durometer. The hardness numbers derived from any of these tests are numbers without units. The Rockwell is generally used for hard plastics whereas for softer materials, Durometer is used. The Durometer is used to determine the relative hardness of the soft material. The test method is based on the penetration of a specific indenter forced into the material under specific condition. There are two types of Durometer which are commonly used, type A and D, i.e. Shore A and Shore D. The basic difference is according to the shape and dimension of the indenter. Type A is used for soft materials while type D is for relatively harder materials. Hardness is a major characteristic of any outsole, midsole or foam foot bed as it relates with ease of flexing and cushioning effect. The hardness of the sole samples were characterized by Durometer hardness tester (SATRA TM 205). The density of all materials was measured by SATRA TM 134 except leather. In this method, the density or specific gravity

is measured by measuring their volume displacement in water. For solid structured, soling materials most accurate method to determine volume is by adapting Archimedes' principle i.e. the weight in air, weight in water method. This method requires an analytical balance that has facilities for hanging samples above the weighing pan and for supporting a beaker with water above the pan. Density is calculated as follows.

A = weight in air, g

B = weight of sinker in water, g

C = weight of sample + sinker in water, g

D = $(C - B)$ weight in water, g

E = $(A - D)$ volume of water displaced, cc

F = (A/E) density, g / cc

The density of leather and cellular materials was measured using SATRA TM 68. As leather and cellular materials absorb water, it is not recommended for volume displacement method. The dimensions of the test specimen were measured and their volume was calculated. The mass of the specimen was then measured and the average density determined. Three circular test specimens were cut from the sole, patterns were removed and the surfaces were made flat and smooth so as to have an adequate degree of accuracy. Diameter was measured using Vernier calipers and thickness using dial gauge. Density was calculated using the following formula.

For circular specimen,

$$\text{density, g / cc} = M / (3.14 \times r^2 \times h)$$

where,

M = mass of the specimen in g;

h = height or thickness of the circular specimen in cm ;

r = radius of the circular specimen in cm.

The tensile strength was determined using INSTRON model 3369 equipped with 1kN load and the jaws separating speed of 500 mm/min (SATRA TM 137). The sample length and the width between the

clamps were 20 mm and 6 mm respectively. Thickness at the normal position is measured using dial gauge and width using Vernier calipers. System generated value was recorded and average value reported.

$$\text{Tensile strength, Mpa} = F / (T \times W)$$

where

F = force in Newtons.

T = thickness in mm;

W = width in mm.

The abrasion resistance of leather was determined by reciprocating method (SATRA TM 84). All other material's abrasion resistance was determined by rotating drum method (SATRA TM 174). A moving carriage is fitted to the equipment to hold the test specimen applying a force of 10N over the test specimen. It has a mechanism of automatically lifting the holder after 84 revolutions or 40 meters, so that the test specimen is prevented from contact with the abradant. The specimen was abraded along the length of a cylinder so that it traverses a helical contact path with the abrasive. The mass loss of the test specimen and its density were measured and volume loss calculated.

$$\text{Relative volume loss, mm}^3 = 200 \times T_n / \text{Density} \times 0.5 \times (C_n + C_{n+1})$$

where

T_n = mass loss of the test specimen,

C_n & C_{n+1} are two successive mass loss of the standard rubber piece.

The attenuated total reflectance-infrared spectroscopy (ATR-FTIR) data was collected using JASCO FTIR-4200 by non-destructive technique to measure the wavenumber dependent transmission of sample between the range of 4000–600 cm^{-1} at 25°C with a resolution of 4 cm^{-1} and 32 scans. The background spectra were collected for the air and subtracted from the sample spectra. Thermal analysis was carried out using TA Instruments Q200 Differential Scanning Calorimeter (DSC), USA in the temperature range from -70°C to

300°C at a heating rate of 10 °C/min under nitrogen atmosphere. Prior to the measurement, the sample was sealed in aluminum pan before cooling to -70°C and equilibrated at that temperature before heating up to 300°C. The system generated graph is used to analyze the thermal characteristics of the materials tested. Thermo Gravimetric Analysis (TGA) was carried out by using TA Q50 in the temperature range from room temperature to 800°C at a heating rate of 20°C/min under nitrogen atmosphere. The system generated graph was then used for analysis. To study the morphological characteristics of samples before and after the biodegradability test, samples were scanned in FEI-Quanta 200 scanning electron microscope (SEM). The SEM instrument was operated at 5kV. Prior to scanning, the samples were sputter coated with a thin layer of gold. An incident electron beam is raster-scanned across the sample's surface, and the scattered electrons from the sample are gathered to collect an image of the surface. The electrons interact with the atoms that contain the sample producing signals that reveal information about the sample's topography.

Results and Discussion

Physical Properties

Weight loss

The biodegradation studies of the different soling materials in same composting environment showed different outcomes. The aerobic exposure of the soling material shows that the weight of the leather sole gradually decreases during the period of the study (30 to 90 days), due to decomposition of leather sole. In natural rubber (NR) sole, there is no loss in weight for first 60 days whereas after 90 days, there is some weight loss (1.5%) noted in the sole. In case of EVA, PU, TPR and TPU soles, there is no change in weight for first 60 days of study, but after 90 days, there is slight weight loss of less than 0.4% observed, which may be because of some physical changes due to exposure to the compost/wet environment. After 90 days, the percentage weight loss recorded for LA, NR, EVA, PU, TPR and TPU is 26.14, 1.48, 0.38, 0.01, 0.22 and 0.22 respectively (Figure 3a).

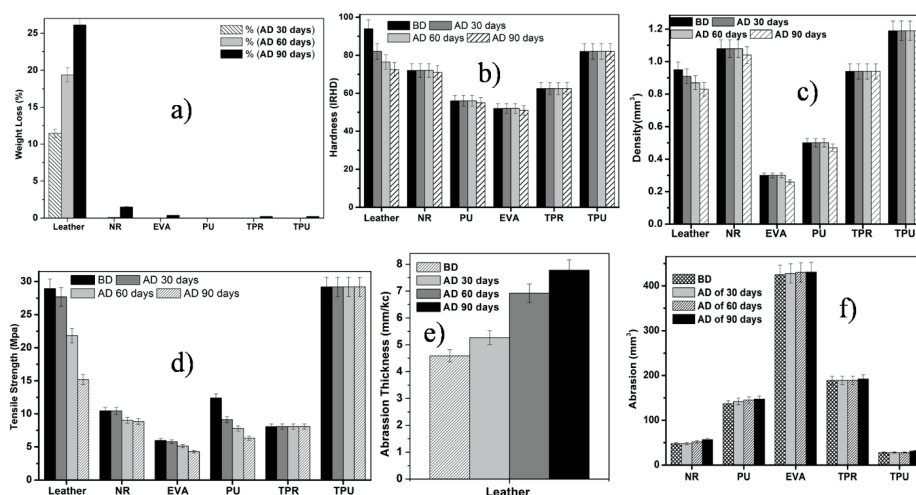


Figure 3. Physical characterization of the sole samples before (BD) and after (AD) 30, 60 and 90 days of exposure to the simulated compost environment a) Weight Loss, b) Hardness, c) Density, d) Tensile Strength, e) Abrasion Resistance of Leather, and f) Abrasion Resistance of all other samples.

Hardness

The hardness values show that the hardness of the leather sole also gradually decreased from 30 to 90 days, due to decomposition of the leather sole. Although in NR, PU and EVA soles there was no difference in hardness for first 60 days, the hardness reduced slightly after 90 days. In case of TPU and TPR soles, there was no change in hardness for first 60 days. Even after 90 days, there was no significant change found, which may be due to the strong resistance towards degradation (Figure 3b).

Density

The density of the leather sole also gradually decreases from the original sample during 30 to 90 days of exposure to simulated compost environment. In case of NR, PU and EVA soles, during the first 60 days, there is no change in density. But after 90 days, there is a significant change of density due to weight loss of the sole. In case of TPR and TPU soles, there is no change in density during the period of 90 days, which is in good agreement with other physicochemical characterization (Figure 3c).

Tensile Strength

The tensile strength of the leather and PU sole gradually and significantly decreases with the increase in time of exposure to the compost environment from 30 to 90 days. This is due to decomposition of the leather sole and hydrolysis of the ester bonds in PU. The tensile strength of EVA and NR also decrease gradually during 60 to 90 days which may be due to the deterioration of product quality but it is unaffected in case of TPR and TPU even after 90 days which shows the strong resistance to degradation (Figure 3d).

Abrasion Resistance

The abrasion of the leather sole gradually increases with the increase in time of exposure to the compost environment from 30 to 90 days, as a result of decomposition of the leather sole (Figure 3e). The abrasion of PU sole and EVA increased gradually which may be due to the atmospheric effect on properties. But this doesn't affect the soles such as NR, TPR, and TPU on first 30 days. Although after 60 days, there is no change in TPR and TPU but insignificant changes are noticed in NR. After 90 days very little increase in abrasion is observed in these samples which may be due to aging of the samples in the compost environment (Figure 3f).

ATR-FTIR Measurement

To investigate the chemical changes in the soling material due to their exposure to the simulated compost environment, the ATR-FTIR spectroscopy was performed for all the soling material samples before and after the experiments (Figure 4).

Leather

Basic IR peaks (cm^{-1}) were detected in leather sample as it is for a typical leather containing additives. The protein is detected by bands at 3307 cm^{-1} due to $-\text{NH}$. After 90 days burial of the leather sample, the formation of the aldehyde is identified by the presence of the new

peaks at 1725 cm^{-1} , 2932 cm^{-1} and a small shoulder at 2844 cm^{-1} . These new peaks at 2932 cm^{-1} and 2844 cm^{-1} correspond to the asymmetric and symmetric stretching of the $-\text{CH}$ group respectively.²¹ Also, the new peak at 1727 cm^{-1} is due to the stretching of $>\text{C}=\text{O}$ group. The formation of new peaks indicates the formation of the aldehyde group due to initial decomposition of the leather samples. Another new peak at 1207 cm^{-1} corresponds to $-\text{CH}$ stretching. The peaks observed at 3325 cm^{-1} , 1610 cm^{-1} and 1066 cm^{-1} are corresponding to $-\text{NH}$ stretching, bending and outer plane bending respectively, which further confirms that the protein structure is still remaining even after 90 days. Hence the decomposition of the protein as a part of biodegradation was just started but not completed which is in good agreement with SEM analysis as well as physical characterization (Figure 4a).

Natural Rubber

After 90 days burial of the rubber sample, the formation of the aldehyde is identified by the presence of the new small peak at 1725 cm^{-1} , due to the stretching of $>\text{C}=\text{O}$ group. The formation of small new peak after 90 days indicates the starting of biodegradation process for the rubber samples and formation of aldehyde group (Figure 4b). It is well known that natural rubber is a biodegradable material.²²

EVA

In the ATR-FTIR spectra of EVA, the absorption peaks at 2914 cm^{-1} and 2849 cm^{-1} are attributed to the symmetric and asymmetric stretching vibration of ethylene, respectively. The peak at 1458 cm^{-1} represents the deformation vibration and the peak at 721 cm^{-1} represent the rocking vibration of ethylene group. The flexural vibration of methyl group is represented by the peak at 1365 cm^{-1} . Characteristic absorption peaks of vinyl acetate groups are observed at 1735 , 1238 and 1015 cm^{-1} that corresponds to stretching vibration of $\text{C}=\text{O}$ band, asymmetrical stretching vibration of $\text{C}-\text{O}$ band and symmetric stretching vibration of $\text{C}-\text{O}-\text{C}$ band, respectively. All the characteristic bands of EVA present even after 90 days of exposure to simulated compost environment but there is a bizarre change in the ATR-IR spectra.^{23,24} As EVA sole are generally microporous cellular material, there may be soil contamination in the gaseous foam structure. The sharp peak at around 3334 cm^{-1} and a broad peak at around 1120 cm^{-1} may be attributed due to the presence of the composted-soil (organic soil) contamination in the void phase of the foam material.²⁵ The soil contamination was minimal which are in good agreement with physical, thermal and morphological properties (Figure 4c).

PU

The band of $-\text{NH}$ stretching at 3325 cm^{-1} and peak at 1588 cm^{-1} indicates the $-\text{NH}$ deformation. The stretching and bending vibrations of $-\text{NH}$ are found at 3314 and 1533 cm^{-1} , while the $\text{C}=\text{O}$ stretching frequency is noticed at 1720 cm^{-1} in spectrum.²⁶ The frequencies at 2953 cm^{-1} and 2862 cm^{-1} are corresponded to symmetric and asymmetric stretching vibration of $-\text{CH}_2$ group and its bending vibration is observed at 1402 cm^{-1} . There are no significant changes found in the

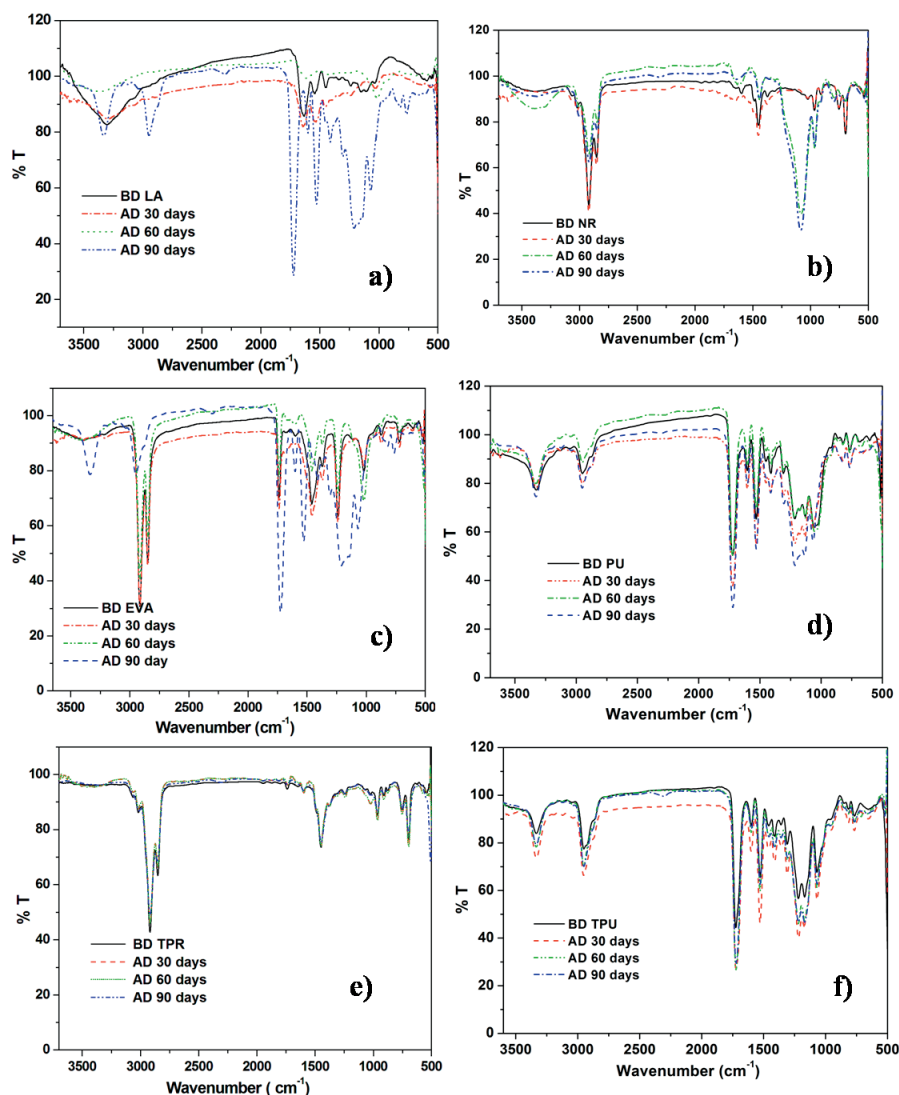


Figure 4. ATR-FTIR spectra of the sole samples before (BD), after (AD) 30, 60 and 90 days of exposure to the simulated compost environment.

$>C=O$ region even after 90 days of exposure to simulated compost environment, which implies that PU soling materials are one of the very stable polymeric materials (Figure 4d).

TPR

Thermoplastic rubber shows typical absorption of styrene $-C-H$ stretching at 3057 cm^{-1} , and butadiene $=CH_2$ and $=CH$ stretching at 3010 cm^{-1} , $-C-H$ asymmetric and symmetric stretching at 2917 and 2853 cm^{-1} respectively, $-C-H$ asymmetric bending at 1448 cm^{-1} , $=CH$ in plane bending (twisting) at 1380 cm^{-1} , and $=CH$ out of plane deformation (bending) of trans-1,4- $C=C$ at 966 cm^{-1} . Hence there are no functional changes in the ATR-IR graph of TPR after 90 days of burial, which shows the stability of the material against the nature (Figure 4e).^{27,28}

TPU

The infra-red absorbance band of hydrogen bonded urethane carbonyl appears at lower wave numbers than that of the free

urethane carbonyl group.²¹ In the order of increasing wave numbers, two $>C=O$ amide - I stretching bands are observed such as H-bonded carbonyl groups at 1600 cm^{-1} , and non H-bonded free carbonyl groups at 1723 cm^{-1} . The peak at 3336 cm^{-1} indicates $-N-H$ stretching of the urethane bond. The peaks at 2953 and 2866 cm^{-1} correspond to symmetric and asymmetric stretching vibration of $-CH_2$ group and its bending vibration is noticed at 1463 cm^{-1} .^{29,30} The infra-red spectra of thermoplastic polyurethanes before and after exposure to simulated compost environment had no changes in the urethane $>C=O$ stretching vibration in the amide -I region which is responsible for the biodegradation. Also, there are no significant structural changes in other regions. This corroborates the confirmation of the non-biodegradability and non-decomposing property of the TPU soling material even after 90 days of exposure to simulated compost environment, which are further confirmed by the TGA and DSC analysis (Figure 4f).

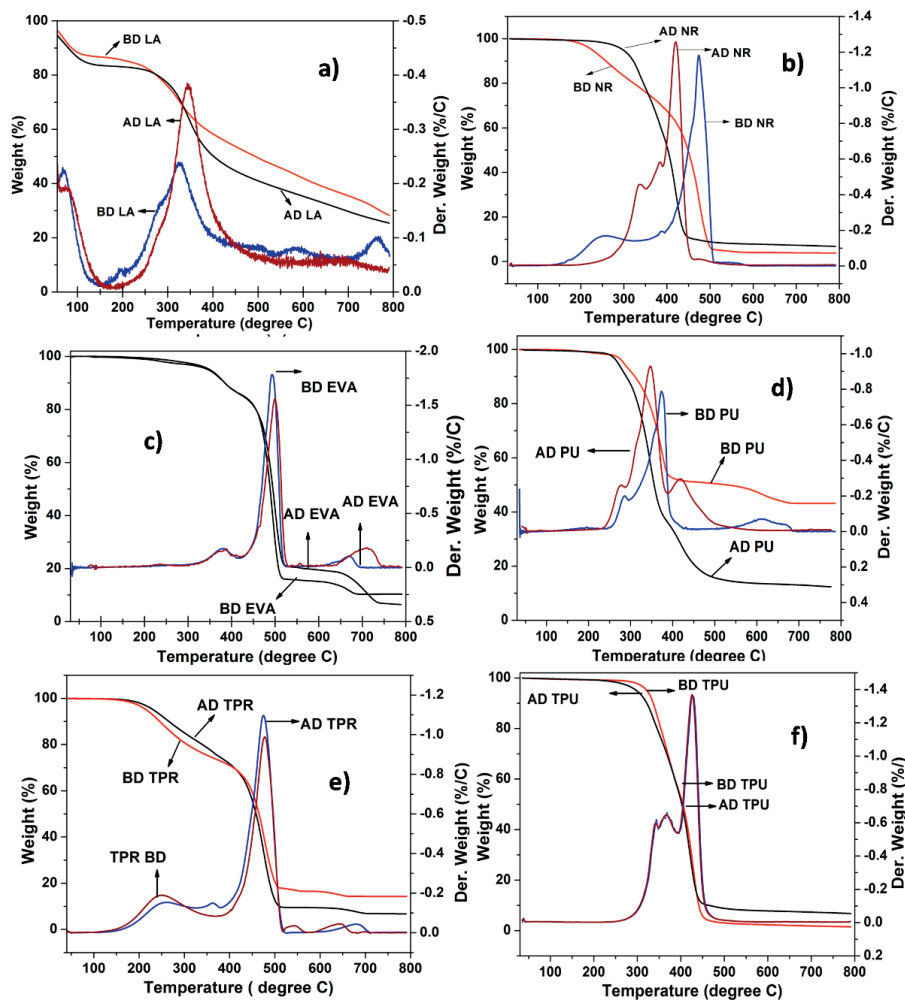


Figure 5. Thermogravimetric analysis of the sole samples before (BD) and after 90 days (AD) of exposure to the simulated compost environment.

Thermal Analysis (TGA and DSC)

The thermal characteristics of the leather samples show completely different behavior before and after the degradation study which is in good agreement with other physical characteristics.

The TGA pattern of both BD LA and AD LA are typical of vegetable tanned leather. Although no significant difference can be observed in the TGA pattern of BD LA and AD LA, few small but distinct peaks observed between 480° – 520° , 550° – 650° and 720° – 800° C in the DTG of BD LA show clear difference between these two samples. Both BD LA and AD LA show the first weight loss step below 150° C due to the evaporation of absorbed and bound water in the sample. The second major weight loss step between 250° – 400° C is primarily due to the decomposition of the collagen matrix.³¹ The small peaks observed in BD LA between 480° – 520° , 550° – 650° C provide significant hints on the complexity of the thermal decomposition of the collagen fibers, which are absent in the DTG of AD LA. The weight loss at high temperature range (600° – 800° C) in BD LA can be ascribed to the continuous pyrolysis of very stable residues, which can also be referred as passive pyrolysis region because of the very

low rate of mass loss. Nevertheless, percentage residue remained after 800° C for BD LA (28.3%) is higher than that for AD LA (25.4%). The additional weight loss and absence of DTG peaks between 480° – 520° C and 550° – 650° C in AD LA indicates degradation of some constituent of the leather after exposing them to the simulated compost environment for 90 days (Figure 5a).

The DSC curve of the leather samples before and after 90 days of exposure to simulated compost environment, display broad endothermic peak between 50° – 120° C. The thermal dehydration of the leather is observed as a broad endotherm centered at 75° C and 112° C for BD LA and AD LA respectively. The thermal denaturation of collagen matrix in leather³¹ is observed as a small endotherm at 170° C. Further, no peak is observed related to melting of the crystalline collagen zone embedded in the amorphous matrix.³¹ Due to decomposition, the crystallinity of the leather sample was lost although the collagen matrix has not degraded completely (Figure 6a).

Compared to all other polymeric soling materials, EVA samples before (BD) and after (AD) degradation show almost same trend in

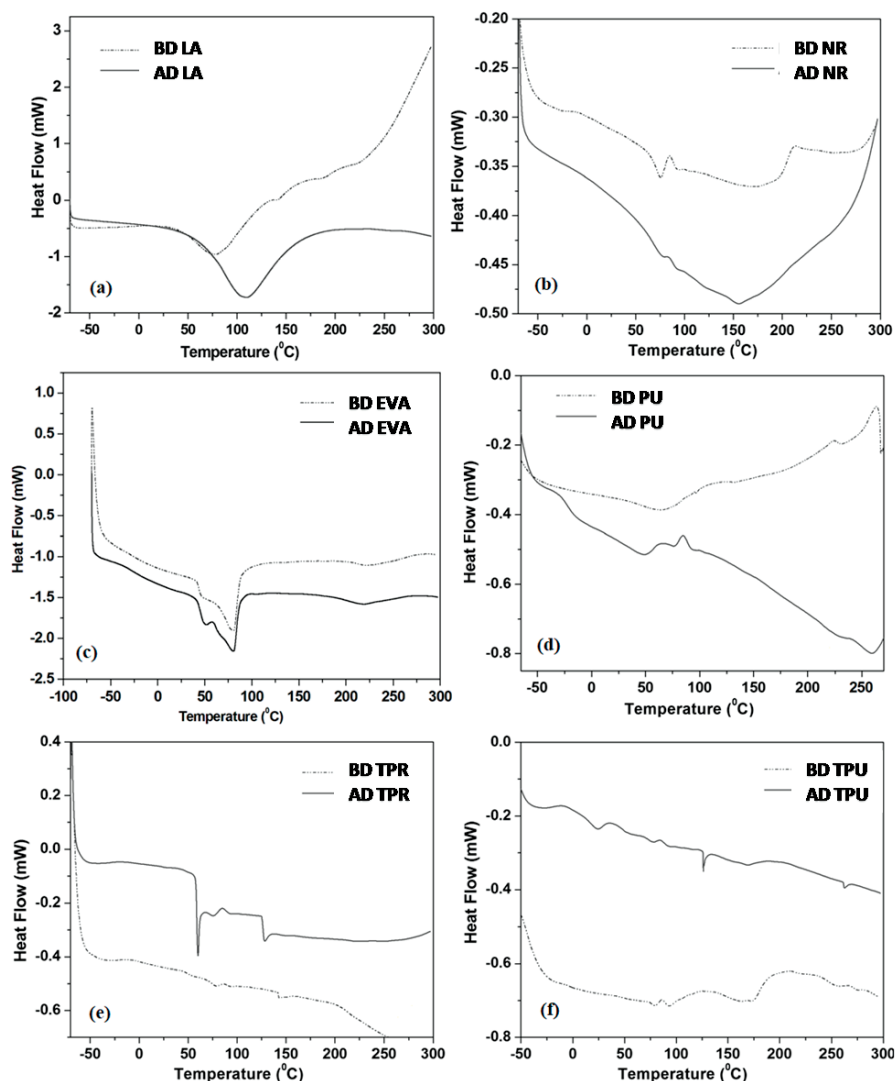


Figure 6. Differential scanning calorimetry of the sole samples before (BD) and after 90 days (AD) of exposure to the simulated compost environment.

both TGA (Figure 5 c) and DSC (Figure 6 c) studies, which is due to the high stability of the polymer backbone over aging in compost environment.

The TGA of AD PU shows a drastic weight loss as compared to the BD PU, which may be due to the hydrolysis of the ester bond that also results in poor physical properties (Figure 5d). The TGA of the TPU and TPR samples before and after exposing to degradation condition did not change, which proves that there is no alteration in the polymer content of these polymeric soling materials. This can be due to the fact that the presence of bulky rigid cyclic structures in these polymers might impede crystallization. This is in good agreement with other characterization results (Figure 5 e-f).

Although DSC shows that T_g remain same for before and after degradation samples of PU, TPR and TPU, but there is alteration in melting point which may be due to the soil contamination and also due to long exposure to compost/wet environment (Figure 6 d-f).

Morphological Analysis

The SEM images of the sole samples before and after exposure to simulated compost environment are shown in Figures 7 and 8. The surface morphology of the leather sole shows degradation/decomposition and opening of the fiber in the cross section on leather after 90 days (Figure 7d). The SEM images of PU, EVA, TPR, and TPU samples after 90 days of exposure to the simulated compost environment show significant physical and surface color change, which may be due to aging and water contamination on the soles. But there is no significant degradation/decomposition of any of these soles as shown in the SEM images (Figure 8), which is in agreement with the physical properties, ATR-FTIR and thermal analysis results. It is also seen that there are some cracks on the rubber sole samples, which may be due to the initiation of decomposition of natural rubber. This fact is also supported by the ATR-IR, mechanical and thermal characterization results.

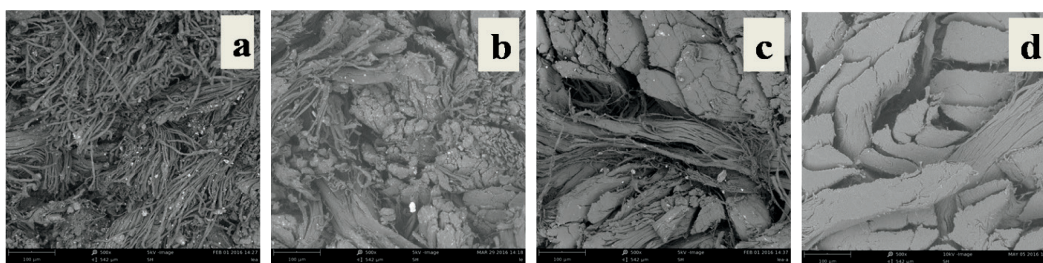


Figure 7. SEM images (100 μm scale) of the Leather sole samples a) before, b) after 30 days, c) after 60 days and d) after 90 days of exposure to the simulated compost environment.

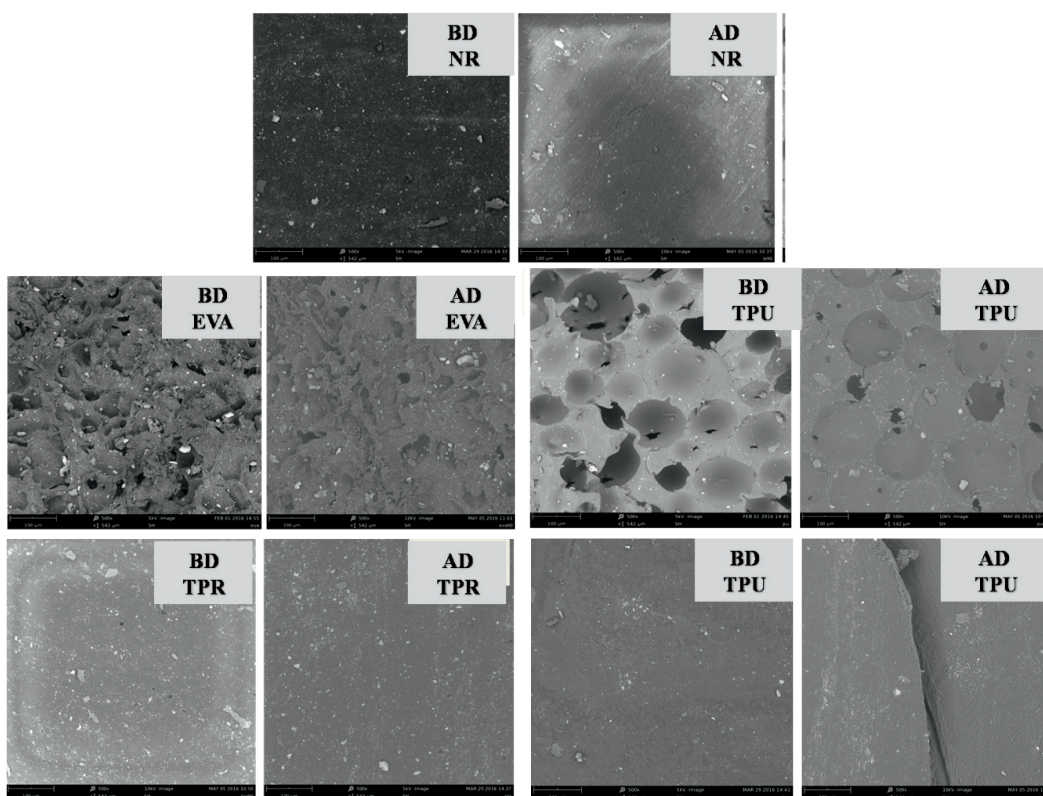


Figure 8. SEM images (100 μm scale) of the sole samples, before (BD) and after (AD) 90 days of exposure to the simulated compost environment.

Conclusions

Biodegradability and decomposing properties of the present-day footwear soling materials viz. LA, NR, PU, TPU, EVA, and TPR, were successfully investigated for a period up to 90 days and the results were compared. The weight loss recorded for the various sole samples were in the order, LA > NR > EVA > TPR > TPU > PU. The SEM images showed that the morphological characteristic of leather shoe sole (LA) was changed due to decomposition as an initiation of biodegradation. Post-degradation study of the LA and NR sole samples showed loss in weight that led to decrease in hardness and density. Further, for both the LA and NR, the tensile strength was highly reduced and the abrasion was increased. This implies that the biodegradation was started to occur in LA and NR soles. The structural conformation of LA obtained from

ATR-IR studied were in good agreement with the physical and thermal characterization results. The decomposition rate of LA sole sample was higher than the NR sole sample. In NR, along with physical properties, structural changes were also observed after 90 days of degradation study. PU and EVA sole samples showed significant changes in the physical properties, such as appearance, weight, tensile strength, hardness, density and abrasion resistance. However, no significant structural change was observed in the ATR-IR, SEM, TGA and DSC results. The TPR and TPU sole samples showed no change, except the abrasion value, which increased marginally due to soil penetration. The results proved that in terms of biodegradability, leather is the best footwear soling material and, TPR and TPU are the most stable among all the polymeric materials, till date.

The present study on the end-of-life nature of footwear materials currently used by footwear industry not only emphasized the importance of developing and using biodegradable materials in footwear manufacturing but also identified the stable polymeric soling materials, which will be helpful to establish the four 'R' system of waste management for environmental sustainability.

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