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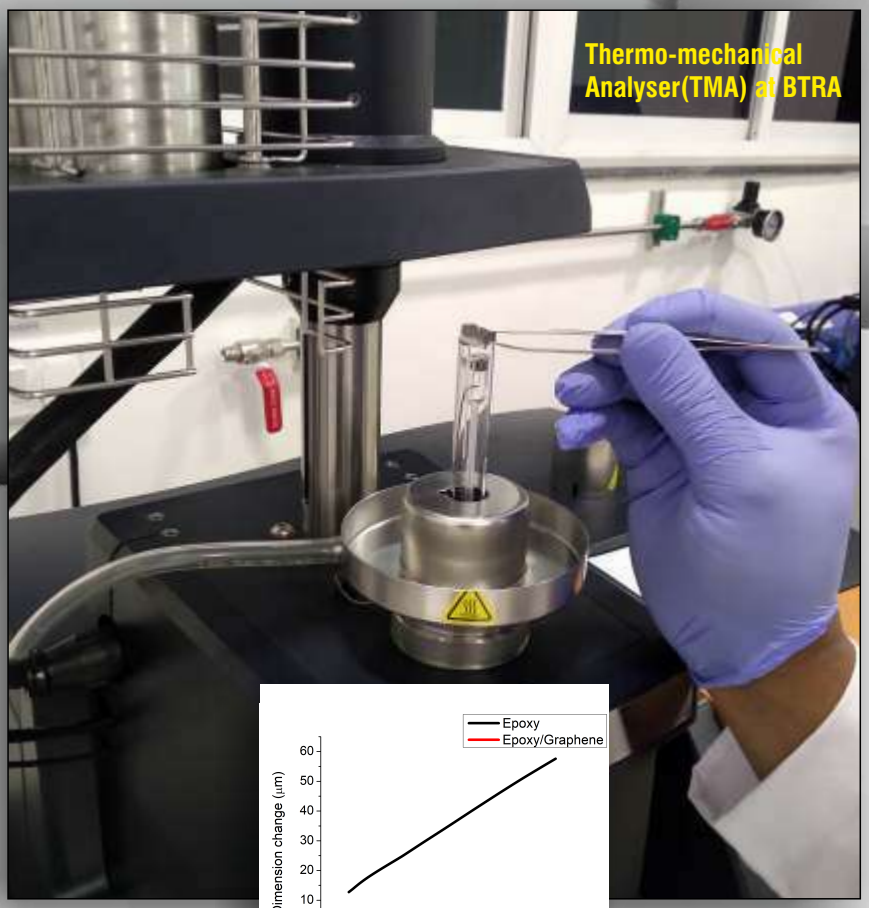

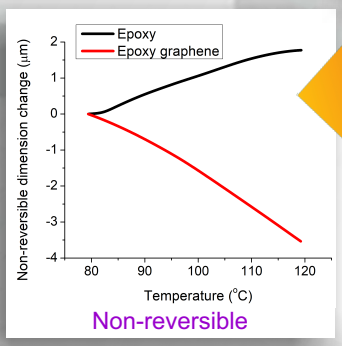

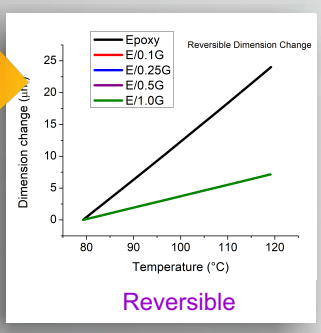

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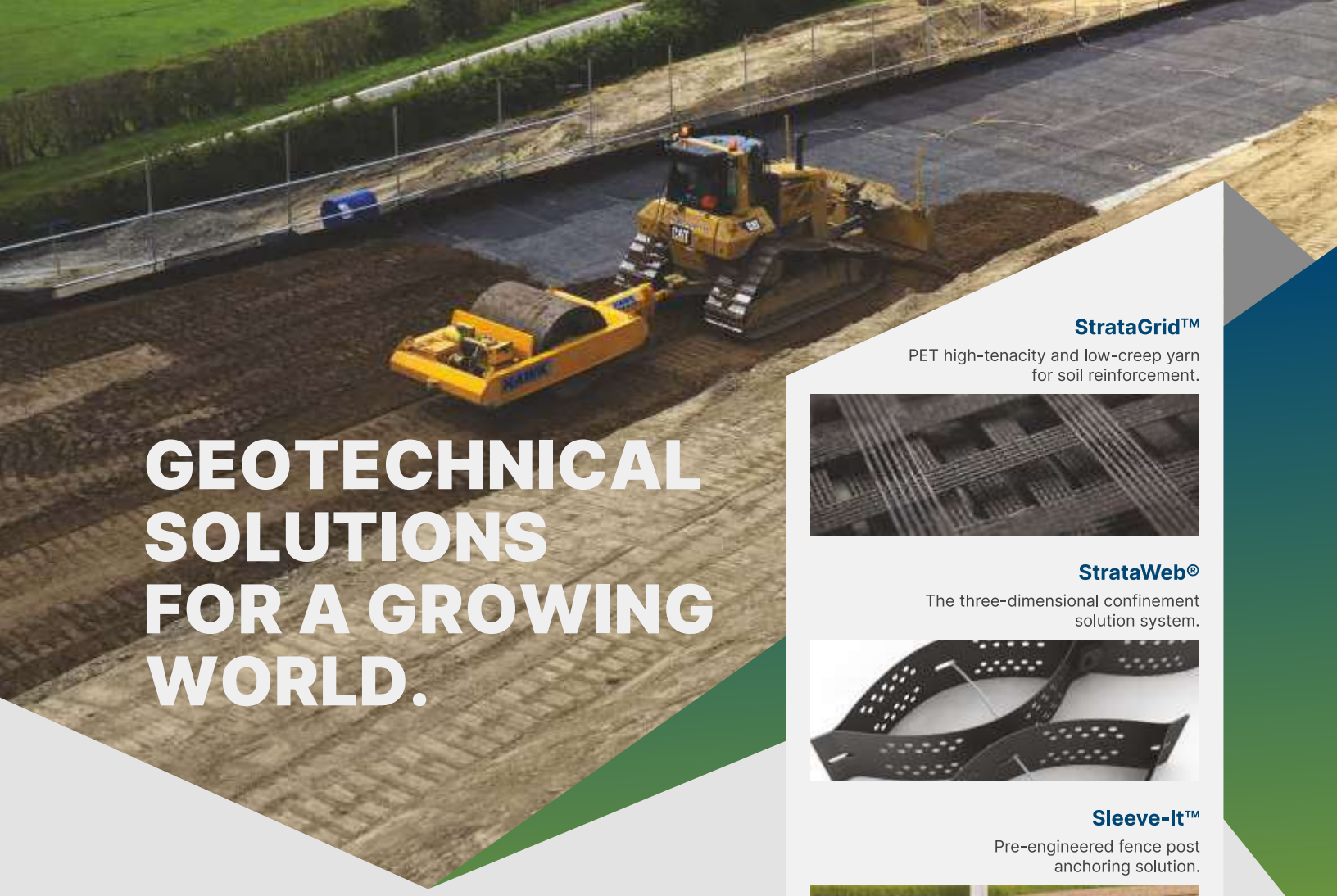

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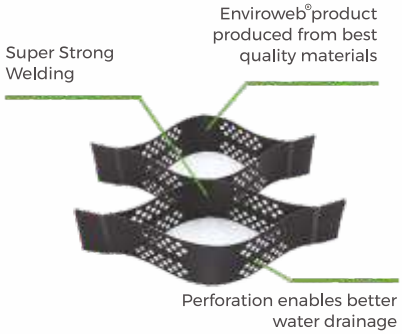

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EDITOR'S DESK

Dear Readers,

Greetings!!

Research with persistent and focused efforts lead to a positive result. Fostering research and providing a platform to publish quality research papers and related articles has been a continuous effort of BTRA Scan. We are working hard to help the journal in climbing up the ranking ladder. In continuation to this effort, I am delighted to present to our readers the 3rd issue of 52 Edition of BTRA SCAN.

This issue has papers from the different domains such as Thermal expansion behaviour of epoxy resin within graphene, Plasma assisted antistatic finish on polypropylene and sustainable flexible composite material. Now we are open for authors from outside so researchers can send their original articles, case studies, research reviews or empirical contributions for publication in our journal.

I thank my entire publishing team for all their support. Together we would work towards making the journal a truly influential publication. Comments and suggestions are always welcome.

Our sincere thanks to all the reader and contributors for their support and interest.

T V Sreekumar, PhD
Director, BTRA

Contents

01 Plasma Surface Modification of Polypropylene for Durable Antistatic Finishing
- Shital Palaskar (BTRA, Mumbai)

05 Tuning the Coefficient of Thermal Expansion of Epoxy Resin with Graphene - A Study via Modulated TMA
- Nishant Chandel, Akash C Kanse (BTRA, Mumbai)

10 Sustainable Flexible Composite: An Upcoming Development in Technical Textile
- S. Basak, D.B. Shakyawar, Kartick K Samanta, Niranjan Kumar, S. Ghosh (ICAR-National Institute of Natural Fibre Engineering and Technology, Kolkata)

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Plasma Surface Modification of Polypropylene for Durable Antistatic Finishing

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Abstract

Plasma surface modification of the polypropylene (PP) woven fabric was carried out using helium and oxygen gasses. Change in surface hydrophilicity after plasma treatment was measured by the wicking height measurement. Nano-Graphene was used to introduce antistatic functionality on the PP fabric. The effectiveness of the applied finish was studied by measurement of static charge development and half decay time. Change in surface morphology and chemistry was analyzed by SEM and FT-IR respectively. ISO 105- C10 (A 1) test method was adapted to assess the wash durability of the developed antistatic PP samples.

Keywords

Antistatic, Graphene, Plasma, Polypropylene (PP)

Citation

Shital Palaskar - "Plasma Surface Modification of Polypropylene for Durable Antistatic Finishing ", *BTRA Scan* - Vol. LII No. 3 July 2023, Page no. 1 to 4

1.0 Introduction:

The use of polypropylene is incensing in various fields like automotive, packaging, medical etc. However due to the static charge generation, low surface free energy, absence of functional groups on the polymer surface limits its application in sports and apparel next to skin garments. PP is also difficult to dye and chemical bond to any nano materials without any structural modification. Modification of the PP to conquer those problems has been tried in various ways like UV radiation grafting and electron beam irradiation[1–3], plasma surface modification and grafting[4], and application of various additives like antistatic, antioxidant, organic and inorganic fillers during melt spinning. In recent years, the use of graphene for the modification of fibre properties is gaining importance worldwide due to the extraordinary property of graphene. Graphene has found applications in electronics, data storage, supercapacitors, solar cells, wearable electronics, sensors etc [5–7.] Researchers have applied graphene on various textile fibres and studied its electrical properties. Cotton is the most studied textile fibre for graphene application followed by polyester and nylon. However, polypropylene is the least studied. Recently, modification of PP polymer with graphene oxide during met spinning has been reported. The extrusion technique is the most widely used. However, the major drawback of this technique is the aggregation and non-uniform dispersion of graphene. Therefore, there is a necessity to develop a technique to modify the PP with graphene using a suitable approach[8]. As the plasma surface treatments are known for improving the wettability or hydrophilicity of the material depending on the gas type used S. Palaskar et al. [9] have reported the change in wetting properties of the different types of PP fabric after helium plasma treatment. The surface free energy of the PP tape samples was measured by the contact angle (CA) method using different test liquids. The untreated PP tape samples showed a surface energy of 23.59 mJ/m^2 which was then increased to 33.26 mJ/m^2 after plasma exposure of 15sec at 3.5kW discharge power. Further, it was reduced to 32.87 mJ/m^2 after 28 days of ageing. It must be noted that even after 28 days of ageing the surface energy of the plasma treated sample is very high than that of the untreated samples. This shows the durability of the plasma treated samples. Likewise, other researchers have also reported the durability of the plasma modified polymeric material[10].

In the present study, we have reported the surface modification of PP woven fabric using plasma treatment and the application of nano-graphene for the development of antistatic PP fabric.

2. Materials and Methods:

2.1 Materials :

Polypropylene (PP) fabric – multifilament with 130GSM was procured from Kiran Threads Surat, Gujrat. Graphene

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nano particles were procured from Ad Nano Labs Bangalore, India. Other reagents were of laboratory grade. Plasma gasses were from INOX India Pvt. Ltd.

2.2 Plasma Treatment:

An atmospheric pressure plasma system working on the dielectric barrier discharge (DBD) principle was used for the plasma treatment of PP fabric. 50cm wide PP fabric sample was passed through the plasma zone to get treated. The plasma was generated from a mixture of helium and oxygen gasses and total plasma exposure was 30sec. at plasma generation power of 2.5kW.

2.3 Preparation of graphene solution:

Dimethylformamide (DMF) was used for making graphene solutions. 50ml of ethanol was mixed with 50ml of DMF and 0.5gm of graphene nanoparticles were added to this mixture. Dispersion of the graphene nanoparticles was done through an ultrasonication process for 60min at room temperature. The prepared solution was applied to the PP fabric by padding and curing repeated times. After the application of the graphene solution samples were washed to remove the unfixed graphene particles and prepared samples were tested for change in static charge decay using a static honestometer.

3. Results and discussion:

3.1 Wicking properties:

The wettability of the untreated and plasma treated samples was measured by the vertical capillary rise method according to ISO 9076-6:2000. Figure 1 shows the wicking heights of the untreated and plasma treated samples. As can be seen from the figure, after plasma treatment of 30sec the wicking height of the PP samples was increased from 70mm to 120mm. The increase in wetting properties can be attributed to the generation of hydrophilic functional groups after plasma treatment 11.

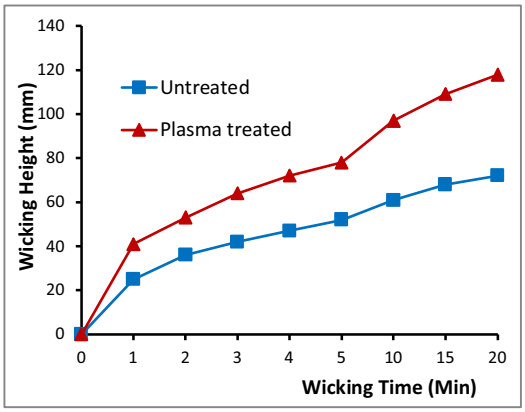

Figure 1 Wicking weight of untreated and plasma treated PP samples

3.2 Static charge measurement:

Static change developed on the untreated, graphene treated and plasma + graphene samples was measured using a static honestometer. 10kV charge was applied to the fabric and impressed peak voltage and time required for half decay was measured and shown in figure 2. As can be seen from Figure 2, the impressed peak voltage for the untreated sample was around 2500V and the time required for half decay was more than 120sec. The hydrophobic nature of the PP sample is responsible for high charge generation and holding it for a long time. However, only after plasma treatment without graphene, the impressed peak voltage was reduced to 2200V.

It was observed that for graphene treated samples the impressed peak voltage was reduced significantly. Further, it can be seen from Figure 2 that the samples treated with plasma + graphene have the lowest impressed peak voltage. This may be due to better impregnation of the graphene inside the sample.

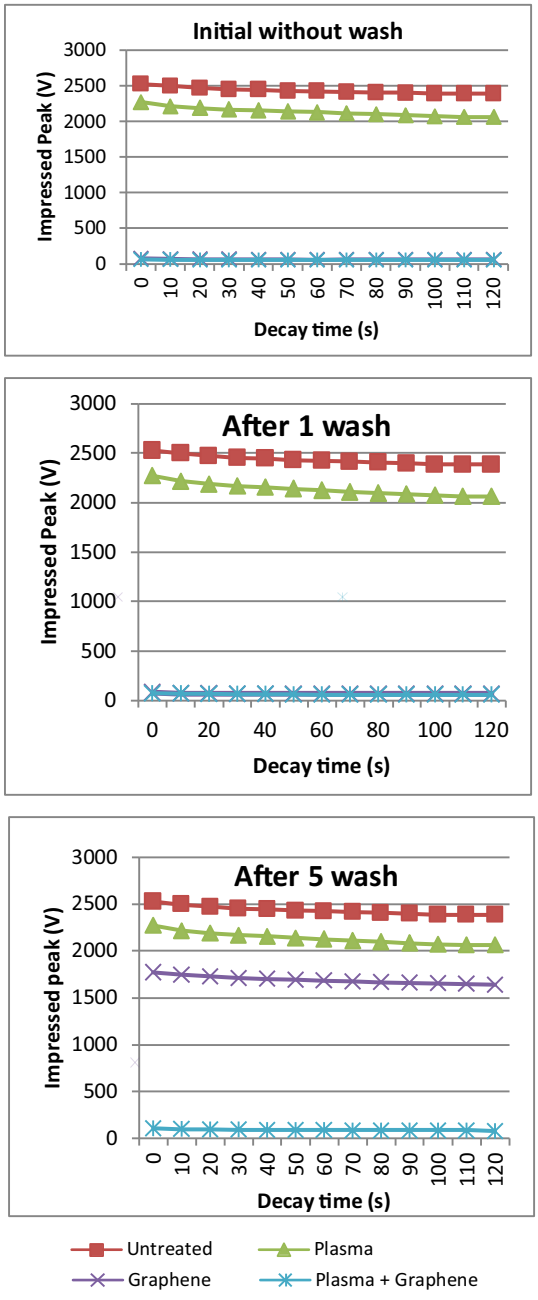

Figure 2. Static decay charge of the untreated and plasma treated PP samples. Durability to washing.

Washing of the plasma + graphene treated samples was carried out as per ISO 105 standard test method at 40°C for 30 min and after drying the samples overnight static charge was measured again. It can be seen from Figure 2, that after 1 washing graphene treated as well as plasma+ graphene treated samples are showing the same results and good resistance to washing. However, after 5 washing cycles, the graphene treated sample showed an impressed peak voltage of around 1700V and lost its antistatic properties. On the other hand, plasma+ graphene treated samples showed no change in impressed peak voltage and it was very low even after 5 washing cycles. This could be attributed to better adhesion of graphene nanoparticles on the plasma treated samples. Plasma treatment can improve the adhesion and increase the durability as reported in the published literature[12].

3.3 Surface Morphology by Scanning Electron Microscopy (SEM)

The surface morphology of the treated samples was studied by scanning electron microscopy. Figure 3 demonstrates SEM micrographs of the graphene (3-A) and Plasma+ graphene (3-B) treated PP samples. It can be observed that more graphene nanoparticles have adhered to plasma treated sample than that of the only graphene treated sample. This could be due to the improved wettability of the plasma treated samples as shown by the wicking measurements. This higher adsorption of the graphene nanoparticles is mainly responsible for reduced impressed peak voltage and improved antistatic properties.

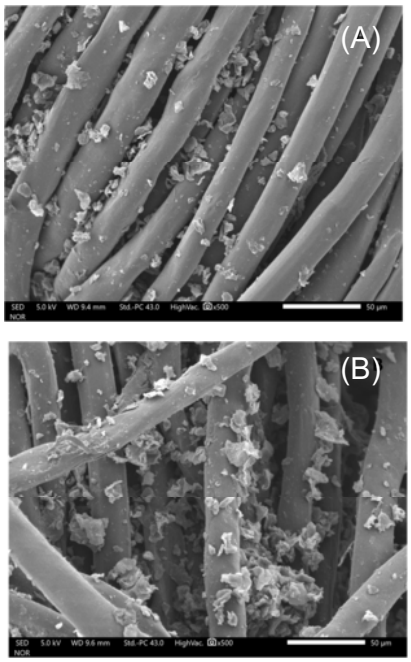

Figure 3. SEM images of the graphene (A), Plasma +Graphene (B) treated samples

3.4 Fourier transform infrared spectroscopy study (FTIR)

Perkin- Elmer FTIR spectrometer was used for recording the ATR-FTIR spectra of the untreated and plasma treated PP samples. Characteristic peaks of PP polymer can be seen at peak positions 2950, 2918, 2868,2839, 1454 and 1375 cm^{-1} for untreated as well as for plasma treated samples as depicted in Figure 4. Apart from the characteristic peaks, addition peaks at 1734 and 1103 cm^{-1} can be seen for plasma treated samples in Figure 4. Symmetrical vibrations of the C=O carbonyl group are responsible for peak at 1734cm^{-1}, which shows the surface oxidation after plasma treatment and hence improved wettability [13].

The peak at 1103cm^{-1} is attributed to ester C–O–C bond stretchings [14].

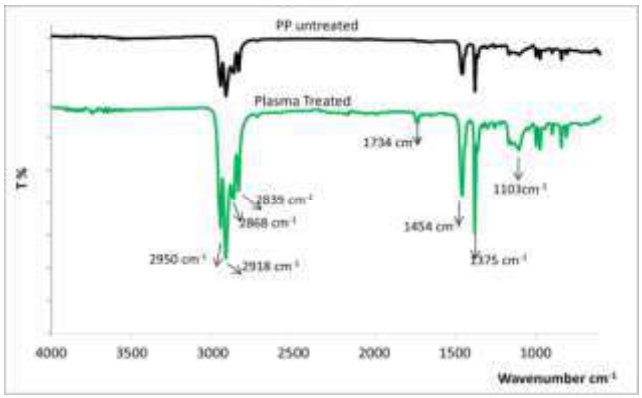

Figure 4. ATR- FTIR spectra of the untreated and plasma treated PP samples

4.0 Conclusions:

Antistatic finishing of the plasma surface modified PP fabric was carried out using graphene nanoparticles. The wettability of the PP samples was found to be increased after plasma treatment with helium and oxygen. The impressed peak voltage of the graphene treated as well as plasma + graphene treated samples was found to be reduced significantly before washing. Plasma + graphene treated samples showed durability to washing up to 5 washing cycles. Further, SEM results proved more deposition of the graphene nanoparticles on the plasma treated sample. ATR-FTIR results showed the additional peak at 1734 and 1103cm^{-1} which is mainly responsible for improved wettability and adhesion of graphene nanoparticles onto the surface of plasma treated PP sample.

Acknowledgment:

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Tuning the Coefficient of Thermal Expansion of Epoxy Resin with Graphene - A Study via Modulated TMA

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Abstract
In this study, modulated thermomechanical analysis (MT-TMA) was used to study how graphene affected the coefficient of thermal expansion (CTE) of epoxy resin. Epoxy resin nanocomposites with different graphene concentrations (0-1 wt%) were prepared by dispersing graphene in epoxy resin using an ultrasonication and probe-sonication technique. The MT-TMA results showed that graphene reduced both the dimension change and the CTE of epoxy resin. The CTE of epoxy resin dropped from 182.9 to 127.8 µm/m-°C as the graphene concentration increased from 0 to 1 wt%. The MT-TMA results could also be represented by reversible and irreversible components of dimensional changes which corresponded to the elastic thermal expansion and influence of graphene on epoxy behaviour. The reversible component showed a reduction in CTE by graphene, indicating that graphene restricted the thermal expansion of epoxy resin. The irreversible component showed a negative slope of dimension change by graphene incorporation which indicated that the negative CTE of graphene had a direct influence on the epoxy property by delaying the crosslinking reaction of epoxy resin. These results showed that graphene could effectively reduce the CTE of epoxy resin and enhance its dimensional stability.

Key words:
Graphene; Epoxy resin; Coefficient of Thermal Expansion (CTE); Modulated Thermomechanical analysis (MT-TMA)

Citation
Nishant Chandel & Akash C Kanse - "Tuning the Coefficient of Thermal Expansion of Epoxy Resin with Graphene - A Study via Modulated TMA", *BTRA Scan* - Vol. LII No. 3, July 2023, Page no. 5-9

1.0 Introduction:

Epoxy resin, a thermosetting polymer widely employed in industries such as aerospace, defence, automotive, electronics, and coatings [1], undergoes a reaction between epoxy base resin and curing agents or hardeners to form a crosslinked network structure. With desirable properties like high mechanical strength, good adhesion, chemical resistance, and thermal stability, epoxy resin fulfils the requirements of various industries. However, certain drawbacks, such as low fracture toughness, high coefficient of thermal expansion (CTE), and poor electrical conductivity, limiting its potential applications across many industries. These limitations negatively impact the performance and durability of epoxy-based composites, especially in harsh conditions like fluctuating high temperatures during processing or service [2]. Graphene, a two-dimensional carbon nanomaterial having excellent properties, like high specific surface area, aspect ratio, Young's modulus, thermal conductivity, and electrical conductivity makes it the most suitable filler for property improvement. By incorporating graphene as a nanofiller, epoxy resin can be strengthened, leading to improved mechanical, thermal, and electrical properties [3].

CTE is an important parameter affecting the properties of epoxy resins and their fibre-reinforced composites. CTE is a measure of how much a material expands or contracts when its temperature changes. CTE of epoxy resins is generally higher than that of their reinforcing fibres, which can cause thermal mismatch and residual stress during processing or service [4]. Thermal mismatch and residual stress can lead to microcracking, delamination, and reduced mechanical performance of epoxy-based composites. The CTE of epoxy resins can be influenced by several factors such as curing conditions, molecular structure, crosslink density, filler type and content. Among these factors, fillers such as graphene and graphene-based materials can significantly affect the CTE of epoxy resins by forming the network structure and changing their thermal properties [5]. CTE of these materials can be measured by sophisticated dimension change measuring instruments. Several studies have reported the

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effect of graphene-based materials on the CTE of epoxy resins using Thermomechanical analysis (TMA) and other techniques. For example, Ackermann et al. investigated the effect of amine-functionalized reduced graphene oxide (frGO) on the mechanical, thermal, and electrical properties of epoxy/carbon fibre-reinforced polymers (CFRP) [6]. They found that frGO increased CFRP's apparent interlaminar shear strength and transverse electrical conductivity, but did not affect Young's modulus, Tg, storage modulus, specific heat capacity, thermal conductivity at room temperature, and in-plane electrical conductivity. They also observed that frGO slightly increased the CTE of CFRP compared to unfunctionalized reduced graphene oxide (rGO) and neat CFRP. Domun et al. studied the effect of plasma-functionalized graphene nanoplatelets (f-GNP) on epoxy resin's fracture toughness and thermal properties [7]. They found that f-GNP improved the fracture toughness and Tg of epoxy resin at low filler content (0.25 wt%). They also reported that f-GNP increased the CTE of epoxy resin by 22% at 0.25 wt% compared to neat epoxy resin. Wang et al. synthesized triethanolamine-modified graphene oxide (TEA-GO) and used it as a nanofiller for epoxy resin-based coatings. They found that TEA-GO improved the dispersion and interfacial interaction of graphene oxide (GO) in epoxy resin. They also found that TEA-GO decreased the CTE of epoxy resin-based coatings compared to GO and neat epoxy resin [8].

The above studies show that graphene-based materials can affect the CTE of epoxy resins in different ways depending on their surface modification, dispersion state, interfacial interaction, filler content, and matrix composition. In addition to that, the difference in reported results may be occurred due to the influence of the mode of testing used for Epoxy samples. Therefore, it is important to understand how these factors influence the CTE of epoxy resins and their composites with graphene nanofillers. This study aims to investigate the effect of graphene on the thermomechanical behaviour of epoxy resin using modulated TMA (MT-TMA).

2.0 Experimental

Material: Epoxy resin of commercial grade was procured from Venus trading corporation and Graphene of ~99% purity (mentioned by the vendor) was procured from Ad-Nano Technologies Pvt Ltd.

Procedure: Suitable amount of graphene and Epoxy was weighed to obtain 4 different compositions of 0.1 wt%, 0.25wt%, 0.5 wt% and 1wt%. Graphene was mixed in epoxy and ultrasonicated in a bath sonicator for 1 hr followed by probe sonication for 15 min in pulse mode (2 sec pulse and 0.5 sec gap). After graphene dispersion, a hardener was added to the Epoxy/Graphene composite solution ((Epoxy: Hardener):: (2:1)) and samples were prepared.

Characterization: All epoxy and composite samples were tested in a Thermo-mechanical analyser instrument, TMA 450-E (TA Instruments, USA). The samples were tested for the modulated temperature of 5ºC for 300 sec, with a temperature ramp of 3ºC/min from 50ºC to 150ºC.

3.0 Results and Discussion

3.1 Difference between standard TMA and MT-TMA

As mentioned above, standard TMA is a technique that measures the dimensional changes of a material as a function of temperature under a constant load. Standard TMA can provide information such as Tg, CTE, and thermal stress for various materials but its effect on monitoring minor changes and transition has major false reports for epoxy and epoxy composites. On the other hand, Modulated temperature TMA (MT-TMA) is a variant of TMA that applies a sinusoidal temperature modulation on top of a linear heating or cooling ramp. MT-TMA can also enhance sensitivity by reducing the effects of thermal lag and drift [9]. Figure 1 represents the difference between standard TMA Vs MT-TMA of epoxy resin, where MT-TMA is better suited for conducting epoxy resin studies.

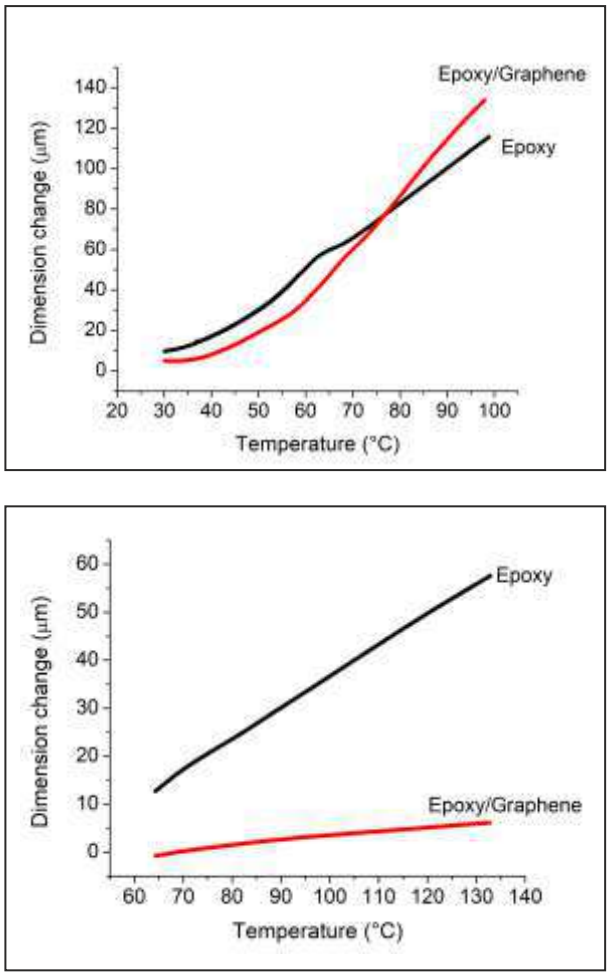

Figure 1: Standard TMA Vs Modulated TMA of Epoxy resin

As shown in the graphs, MT-TMA gave more consistent and expected values of dimension change than standard TMA, since Graphene has negative CTE and incorporation of

Graphene in epoxy should restrict dimension change than increase it. These show that MT-TMA has some advantages over TMA for testing epoxy resins and their composites, such as higher sensitivity, resolution, accuracy, and reliability.

3.2 Effect of graphene concentration on epoxy and composite properties via MT-TMA mode of testing:

As mentioned earlier, MT-TMA is a technique that measures the dimensional changes of a sample as a function of temperature, time and force in a more sensitive way by applying a sinusoidal temperature modulation on top of a linear temperature ramp and measures the linear expansion of the sample under a constant force. Figure 2 represents the MT-TMA of all composite samples.

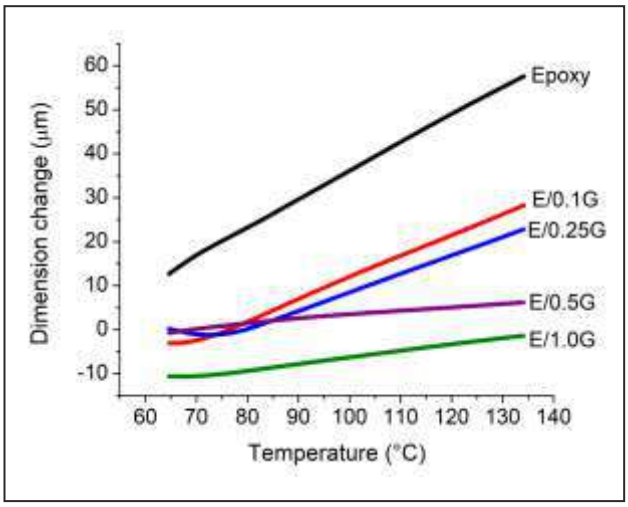

Figure 2: MT-TMA overlay of Epoxy/Graphene composite samples

Incorporating graphene into epoxy resin had a significant effect on the epoxy's dimensional stability, as represented by experimental results. The dimensional change of the epoxy resin reduced as the graphene concentration increased. This effect was more noticeable at high temperatures, where graphene improved the epoxy's viscoelastic properties. These findings can be explained by the properties of graphene, which improved the both thermal and mechanical properties of epoxy resin. To further explore the causes of this effect in more detail, we performed MT-TMA to examine both reversible and irreversible factors that contributed to this dimensional change.

MT-TMA can separate the reversible and irreversible components of the dimensional changes, which can be affected by different factors such as curing, relaxation, crystallization, and decomposition. The reversible component of the dimensional change is associated with the thermal expansion or contraction of the material, which depends on the temperature rate of change. The reversible component can be used to measure the CTE of the material, which is a measure of how much a material expands or contracts when its surrounding temperature changes. The irreversible component of the dimensional change is associated with the deformation or recovery of the material, which depends on both time and temperature. While, the irreversible component can be used to measure the stress relaxation, softening or shrinkage of the material, which are related to the molecular structure, crosslink density, filler type and content, and interfacial interaction of the material. Epoxy and the composite with various concentrations of graphene have exhibited both reversible and irreversible dimensional changes during MT-TMA. The reversible component can reflect the CTE of the epoxy matrix and filler, while the irreversible component can reflect the curing, and stress relaxation of the epoxy matrix and graphene. By separating these components, MT-TMA can provide more information on the thermomechanical behaviour of epoxy resins and their composites than standard TMA.

- Reversible dimensional change

In MT-TMA, the reversible dimensional change is calculated by analysing the amplitude of the modulated signal [9]. The modulated signal is a small sinusoidal deformation that is superimposed on a larger deformation. By analysing the amplitude of the modulated signal, it is possible to determine the reversible component of the dimensional change, which is in phase with the temperature changes. This reversible component is related to the viscoelastic properties of the material, which are affected by the addition of graphene. Figure 3 represents the comparative overlay of reversible dimensional changes observed via MT-TMA.

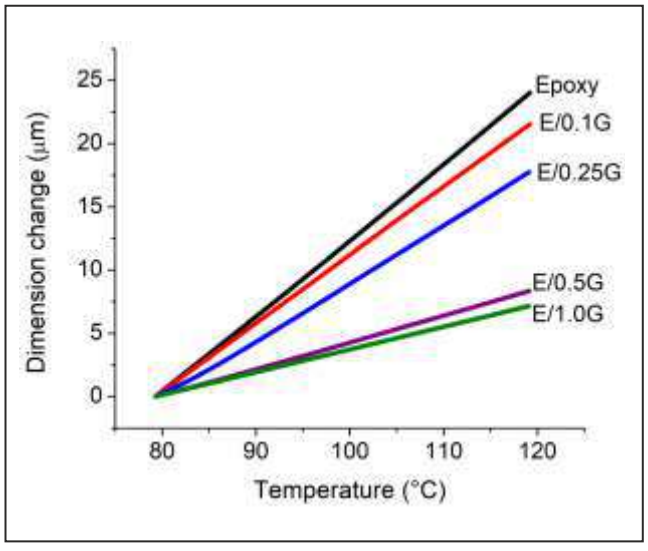

Figure3: Reversible dimension overlay of Epoxy/Graphene samples

In the case of graphene-epoxy composites, the addition of graphene showed improvement in the mechanical and thermal properties of the material, which leads to a reduction in the reversible dimensional change. This reduction in reversible dimensional change indicates that the material is more resistant to deformation and can recover its original shape more effectively (as represented in Table 1). This can

happen when the interfacial interaction between graphene and epoxy is strong or stable, which means that there is a low internal thermal resistance (ITR) between them. A low ITR means that heat can easily flow from epoxy to graphene during heating or cooling, which can reduce the thermal stress and deformation in the composite. This can also increase the molecular mobility and free volume of epoxy, which can reduce its CTE.

Table 1: Dimensional changes and CTE of epoxy and epoxy composite samples

Sample name	Graphene conc.	Dimension change (um)	CTE (㎜/m-℃)
Epoxy	0%	44.8	182.9
E/0.1%G	0.1%	31.35	172.8
E/0.25%G	0.25%	22.66	167.0
E/0.5%G	0.5%	9.22	138.6
E/1.0%G	1.0%	6.85	127.8

- Irreversible dimensional change

Thermal expansion and contraction are not the only phenomena that affect the dimension change of composites. There are also non-reversible phenomena such as stress relaxation and filler influence that depend on the applied stress and processing time of the composite. Stress relaxation is the decrease in stress over time under constant strain, while filler influence is the effect of filler on polymer composite due to interfacial bonding and inherent properties. When a composite is subjected to thermal stress or strain, it can deform both elastically and viscously. The elastic deformation is reversible and returns to its original shape when the stress or strain is removed, while the viscous deformation is irreversible and causes a permanent change in shape. Graphene has a negative coefficient of thermal expansion, which means that it contracts when heated [11]. The irreversible deformation caused by Graphene may have caused the negative non-reversible dimension changes in composites, which means that they contract due to the release of internal stresses or the rearrangement of molecular chains (as shown in Figure 4). Also, the negative slope of irreversible dimension change represents that the crosslinking reaction is slower and smooth in graphene-incorporated composite films than in their thermal expansion [12]. This also indicates that the material releases more internal stress by thermal expansion than it generates by cross-linking. This internal stress causes the material to contract irreversibly in order to balance these stresses.

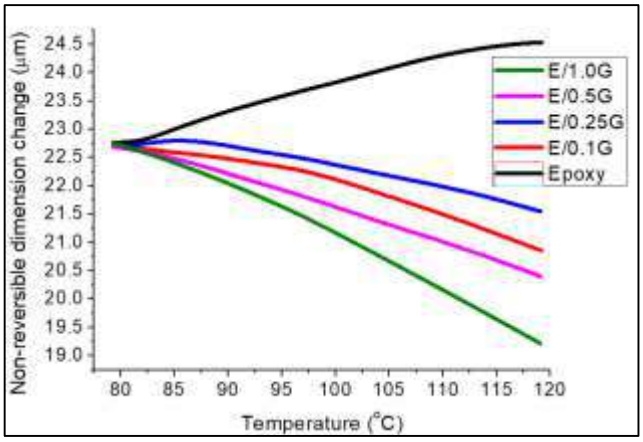

Figure 4: Irreversible dimension overlay of Epoxy/Graphene samples

4.0 Conclusion

TMA has some limitations in detecting minor changes and transitions in epoxy and epoxy composites. Modulated temperature TMA (MT-TMA) is a variant of TMA that applies a sinusoidal temperature modulation on top of a linear heating or cooling ramp which enhances the sensitivity and resolution by reducing the effects of thermal lag and drift. Graphene incorporation has affected the CTE and dimension change of epoxy composites by influencing the thermal conductivity and interfacial interaction between graphene and epoxy molecules. Graphene incorporation can reduce the CTE of epoxy composites by reducing the reversible dimension change due to thermal expansion. This can happen when the interfacial interaction between graphene and epoxy is strong or stable, which means that there is a low ITR between them. Graphene incorporation made the negative slope of irreversible dimension change in epoxy composites by influencing the crosslinking reaction and internal stress in the epoxy matrix. The strength and type of interfacial interaction can affect the heat transfer and stress transfer between graphene and epoxy, which in turn affects the crosslinking reaction and internal stress in the epoxy matrix.

ACKNOWLEDGEMENTS

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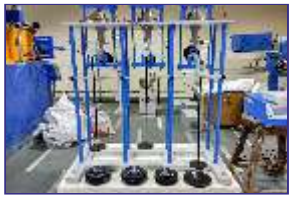
Installation Damage of Geosynthetics

The geosynthetics are prone to some amount of damage during their installation. To assess the quantity of the installation damage, a standard method was initially developed by Watts and Brady of the Transport Research Laboratory in the United Kingdom. The procedure has also discussed in the ASTM D 5818 with similar requirements. We are at BTRA doing the test following same ASTM D 5818 method followed by respective tensile strength. For the time being we are using the construction site for the sample preparation. If customer will agree, BTRA will collect the sample from site after standard procedure and provide the report.





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Sustainable Flexible Composite : An Upcoming Development in Technical Textile

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Abstract
The current review context elaborates on the engineering methods adopted by the researchers for the development of different sustainable flexible composites for use as an alternative to leather like material. This article also elaborates on the usage of different natural fibre-based cellulose, bacterial cellulose, and different plant-based compounds for the construction of leather like lifestyle products with the examination report of essential physical properties of engineered products. Besides, it elucidates the process conditions followed by the researchers for making natural fibre based flexible composite products

Key words:
Plant based flexible composite, leather, natural fibre, Cellulose

Citation
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1.0 Introduction

Generally, natural leather production and processing involved a larger quantity of toxic synthetic chemicals like sulphuric acid, sodium hydroxide, formaldehyde, heavy metal salt, chrome treatment etc. These chemicals have increased the biological oxygen demand (BOD), Chemical Oxygen demand (COD), and Total dissolved solids (TDS) level of effluent water and polluted the surrounding environment with different harmful microbes and foul chemical-based smell. In addition, the slaughtering of animals for the raw source of leather hide is another major concern. Therefore, the development of artificial leather is getting attention from industries and researchers. Artificial leather made from the elastomeric coating (mainly polyvinyl chloride, polyurethane etc.,) of synthetic fibres is also popular in different trade names into the commercial market. Major advantages of the products are high impact resistance, light weight, flexibility, high abrasion resistance, tensile strength and cheaper cost [1, 2,3,4]. However, these products are not eco-friendly and could affect the user's feet due to microbes, and fungus generation, and could generate bad odour on continuous usage due to lack of breathability and water vapor permeability [5-7]. Apart from these mentioned difficulties, now a day, the world is moving towards sustainability and as per the Animal Rights Act, the collection of leather from animal origin is also almost banned in some of the countries. Therefore, researchers and entrepreneurs are searching for suitable sustainable alternatives to leather for human beings. In this direction, natural fibre based footwear is an attractive and appropriate addition. Natural fibres from the cellulosic background are having high modulus, tensile strength and a moderately high coefficient of friction, abrasion resistance, lightweight, breathability and aristocratic eco-friendly look [8-10]. In addition, fibres from the protein background like wool are soft, thermally non-conductive and flexible and also can transmit water vapor easily into the surroundings [11-13]. In the last decade, different commercial companies are marketed natural fibre based footwear products. Different kinds of elastomeric coating (PVC, polyurethane, nitrile rubber, sterile butadiene rubber, acrylonitrile butadiene rubber, neoprene etc.,) on the natural fibre is also popular in the market. However, it is also not completely eco-friendly due to the long synthetic chain of rubber present in the coated composite material. Therefore, natural rubber is slowly getting popularity as a coated material on the natural fibre and also has been used as the sole material of footwear. In this direction, natural fibre also has been used by researchers as a reinforcing agent with rubber as the sole material of footwear [14-17]. Incorporation of the natural fibre in the rubber-based formulation has increased its toughness, tensile strength, coefficient of friction etc. In addition of it, Functionality in terms of antimicrobial (insole), anti-odour (insole), water and dust repellent (outer shell), and moisture management properties (lining material) are very important for the end users and few research works also have been accomplished on the outer textile material and also on the composite layer of the outer shell of footwear [18-22]. To the best of our knowledge, to date, no comprehensive review is

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there on the exploration of natural fibre for the engineering of footwear products and the creation of artificial leathers.

In the current context, a comprehensive review is represented on the exploration of natural fibre for making footwear materials with their important physical properties. In addition, it also systematically represents the usage and performances of rubber coated natural fibre material as the upper part, lining and sole of footwear products. Besides detailed standardized testing parameters are represented with critical discussion on the research lacuna and futuristic approaches in the domain of natural fibre based footwear materials.

1.1 Natural leather processing

Natural leather could be processed by the following technical sequence. Detail processing methods are discussing in below section [23-25]

a. Curing-Raw hides from different part of the country has come in the leather industries. Raw hides or skins must be preserved by salts or freezing, or chilling to prevent bacterial or microbe attacks [23].

b. Soaking- The main objective of this step is to rehydrate the hide, as well as to remove any excess salt or dirt from the hide.

c. Liming- This process assists to remove hair from hides.Alkali(Lime-Ca(OH)2) and sodium sulphide both are used for this purpose. This is more commonly referred to as a "pelt".

d. Fleshing- This process involves passing the pelt through a machine that removes fatty layers of the flesh side of the pelt. Pelt will also be split into layers at this stage.

e. Deliming- This step involves lowering of alkalinepH of processed leather and turning it to acidity. Normally it is done by ammonium chloride and other organic salt.

f. Bating- This process is applied to flatten or relax the pelt by the use of enzymes.

g. Pickling- Bated pelt come into the most important pickling section of the leather industry. Tanning requires pelts to be mildly acidic whereas pickling involves the application of acid and salt solution. If a pelt is not to be tanned for several months a strong solution may be applied to act as a preservative. Therefore for storage purposes of untanned leather, pickling is a necessary step.

h. De- Greasing- For tanning purposes, a pelt should be free from excess grease. It is performed by water or a mild solvent [24-25].

i. Tanning- A variety of types of tanning follow in leather industries, but the most common is chrome tanning or vegetable tanning.After chrome tanning. leather hide becomes blue and it is called "wet blue" leather in the commercial market. Vegetable tanning plant extracts may be used to produce thick, firm, and brown leather, ideal for belts, shoes, bags, and cases. This process is mainly used for the preparation of gloves or soft items.

j. Splitting- In this step, a machine is used to slice leather into two layers. One of the resulting layers will be without a grain surface. This piece can be used to produce suede or have an artificial grain surface applied to it.

k. Shaving- The grain surface stays with that piece, another machine is used to shave the non grain side. This is how leather is made to a desired level of this thickness.

l. Neutralization- This step in how leather is made is done to remove residuals from any of the previous chemical applications. Additional tanning materials may also be applied to create a particular style or texture in the finished product [24,25].

m. Dyeing- Depending upon the intended use of the finished leather, any number of colours may be applied at this stage. This is how leather is made in black, red, brown and even white varieties [25].

n. Fatliquoring- This process involves lubricating the leather with oil to ensure that it is both flexible and soft. This is especially important when producing leather for fashion etc.

o. Samming- Moisture must be taken out of the leather before it will be ready for production. Almost half of the water is removed through several different machines [24,25].

p. Setting out- The leather is now stretched and the grain surface is smoothed out. In so doing, the moisture remaining in the leather is further reduced.

q. Final drying- Leather is generally dried until less than 20% water content remains.

r. Staking & Dry Drumming- To ensure that the leather is soft and flexible, it is further massaged in a staking machine. This process separates the fibres. Once complete, the leather is placed inside a rotating drum for extensive tumbling.

s. Buffing & Brushing- The flesh surface of the leather is now totally removed through buffing to produce a softer feel, or simply to reduce the overall thickness. A thorough brushing happens thereafter to remove any dust accumulated during buffing.

t. Finishing- Finishing occurs in leather production to ensure even colour, remove any defects on the grain

surface, correct the level of gloss, and add a protective and water-resistant surface.

u. Final-Grading- Grading of the leather was performed depending on feel, softness, thickness, and texture.

1.2 Variation of the process for different types of leather material

All leather items depend on the process of manufacture(tanning process). In the gloves materials(soft material) most important factor is the usage of fat liquor chemical in a high percentage, but hard materials (bags, belts) are mainly manufactured from vegetable-tanned leather. "Nappa" leather is very soft and flexible, used normally in the car seat cover and as a furniture covering material [26-28]. Different kind of lifestyle leather articles depends on the process and percentage of chemicals. Extra polish and roller effect need to soft and flappy articles and also final coating/dying mechanical operation apply depending on the final products. In mechanical processes like the staking process, open fibres of leather are by stacked machine and resulted in softy materials [29]. Most often chemicals and mechanical operations lead to different to many kinds of leather products.

From the aforementioned part, it was quite clear that leather processing requires a huge quantity of water, chemicals, heavy metal salts etc. Especially It may cause harmful effects on the effluent as well as on the surrounding atmosphere. However, natural leather has huge demand in the commercial market for its long-term use, physical strength, flex resistance, enriched tensile properties etc.

2. Plant-based flexible composite

2.1 Plant-based and natural fibre based flexible composite products

Recently, "vegan" terminology is very much popular in the world market because it nullifies the usage of any animal-based product or by-product for using leather materials. Although there are many official issues with the usage of this terminology. Usually "vegan leather" made from plant and vegetable background are also getting popularity because of its sustainability, lower animal harm, breathability and more bio-degradability. Snap-pap is vegan leather, recently available in the market. It looks like a paper material and it is a mixture of cellulose and latex. It is available in different colours like light brown, dark brown, black etc [30]. Teak leaf leather is another example of sustainable leaf-based vegan leather. As per the literature it is made of Teak leaves, cotton non-woven fabric and a thin lamination of natural chemicals on the outside of the leaf. Thin lamination made the material waterproof, lightweight and high tear resist product [31]. Two layered cotton non-woven bind with acrylic-based binders has been placed on the back side of the leaves and the upside of the leaf was coated with a thin polyolefin layer. This leather also could be made from the leaves of some other plants like bananas, pineapple, kambucha leaves etc [32]. The physical properties of snap-pap leather have been represented in Table 1.. Velarde et al 2019 reported the use of cactus leaf for making cactus leather due to its rugged thick skin. It is a fantastic bio-mimicking approach and they have reported that initially cactus leaf has been cleaned and mashed. Thereafter it has been sundried for a particular period before dyeing with natural reagents [33]. Cactus leathers are used for producing car seats, shoes, bags and wallets from cactus leather. One London-based commercial branch has launched a leather based product from mango. They have wastage mangoes available in the commercial market. They have also revealed the technology of mashing and boiling the mangoes. However, in detail, technology has not been revealed by the researcher in the open platform [34]. Apart from it, recently, other vegan leathers from grapes, mushrooms etc., also have been launched in the market. As per reported literature, the roots of mushrooms contain mycelium and continuous dispersion of mycelium on sawdust and agricultural waste created a thick matt of natural leather and its polymeric composition is the same as the composition of the shells of crabs. However, lots of technical problems are there for the commercial viability of the mushroom leather-like product [35]. Recently, Kerelia et al 2020 have prepared bacterial cellulose from coconut water. As per the mentioned process, they have left coconuts in the sterilize water for the culture of bacteria. Jelly-like viscous materials have generated after 12-14 days of impregnation in water and they are mixed with banana fibre or gum and produced a continuous 3D sheet of natural leather like material. Finally, they have air dried and softened the sheet for further usage into different end products like footwear, bags, wallets etc., [36].

Artificial leather from bacterial cellulose, in this line, researchers have further reported that Acetobacter Xylinum, a gram-negative soil bacteria has been used for the synthesis of natural cellulose. They synthesized cellulose in the laboratory and compared its properties with natural animal leather [37]. In this direction, another research group have developed cellulose through Komagataeibacte (genre) bacteria. These bacteria engulf tea leaves and produce cellulose film. After drying, this material produced soft bovine leather and it is useful for orthopaedic footwear applications because of its soft nature [38]. According to the reported literature, this cellulosic material is very soft and could be used as the sole material for orthopaedic patients. Plant-origin-based vegan leather is quite new, promising and emerging research area in the domain of artificial leather and a lot of research opportunities are there in this direction.

Natural fibre based flexible composite

In 2004, a research patent has been filed on the application of textile based upper material for the engineering of athletic footwear. They have adopted the weft knitting process for making of the textile based upper part of the footwear. The research group claimed that the prepared upper part accepts ventilation and performs a proper cooling effect on the underlying foot on the sole. Prepared sole material has a great cushioning effect and also succeeds to provide traction or control effect during foot movement. As per their claim, they have used three-layer system of knitted structures. Exterior layer has good wear resistance, flexibility and air permeability. Intermediate layer lightweight polymer foam that provides a cushioning effect and protects the foot from objects that may contact the upper. Finally, the interior layer was made of a textile material having good moisture-wicking properties and removing perspiration from the contact area of the foot. They have joined the three layers by adhesive and also by mechanical-based stitching process [2]

Researchers have pointed out some important attributes of natural fibre for its application as footwear material. Properties like heat and moisture transference, absorption, air permeability, tension strength, weight, thickness, shape etc., are important for footwear application. Very recently Nam et al 2019 reported the engineering method of multilayer natural fibre based components as an alternative to leather. They have claimed that the material is completely sustainable. They have used cellulosic fibre mat, denim fabric and hemp fabric and compared its properties with the leather arrangement made with calf and pig leather. As per the report, both the arrangement has same properties in terms of break force and total heat loss [26]. The shoe lining is the material inside the shoe that comes in contact with the entire foot. It is composed of side, upper and heals. A research group has reported the physical and thermal comfort characteristics of the knitted fabrics used for shoe linings [12,15]. They have made spacer fabric by knitting two entirely different fabrics, having different properties and making a unique structure. Cotton and cotton/ bamboo blended yarn was used for making flat and interlock knitted spacer fabric. They have shown that the material shows excellent compression elasticity, cushioning, air permeability and breathability, high thermal insulation and temperature regulation [15]. The cotton/ rayon blend combination showed better frictional resistance whereas the cotton/ bamboo weft knitted structure showed comfort under hot weather conditions [15].

In the year of 2017, one company named Hugo Boss launched pineapple leaf fibre based footwear products in the market. It is marketed as a trade name of "Pinatex". They are claiming that the upper part of the shoe is made of pineapple leaf fibre and is dyed with natural dye [39]. Recently as per the published report, they have launched sneakers and chappal like products in the commercial market. As per their report, pineapple leaf fibre has been felted into a nonwoven structure and used for making the upper part of the footwear. They have endorsed that the waste of almost 16 pineapple plants has been used for 1 square meter of Pinatex [40]. The prepared footwear is soft, lightweight and also delivers breathability. Reports endorse that Pinatex is inherently shower resistant and dirt materials deposited could be easily wiped by moist cloth. In the mid of the year 2021, one company named Dope Kicks launched hemp fibre based water repellent footwear. They have prepared woven textiles by using strong hemp fibre and added one chemical based coating on the outer surface of the footwear for water resistance and for avoiding dust and dirt on the surface of the footwear. They have reported that the insole of the footwear has been made by using cork, a natural material that can provide antibacterial action and also deliver cushioning effect to the end users [41].

Another part of this context has mainly covered artificial leather containing natural fibre as base material. Natural rubber consists of 2000 isoprene units (C5H8) and has low tensile strength, elasticity (viscoelastic), lower resistance to crack initiation and permanent tackiness property (much less than polyester, epoxy, and thermoset resins). Vulcanization of natural rubber forms bridges between the chains of isoprene units and provides strength, elasticity, viscosity, hardness etc. Accelerator-like complex organic compound (stearic acid) has been used in vulcanizing formulation in the presence of activator like zinc oxide. This basic formulation could be used as a coating material on the natural textile surface. In addition of it, the incorporation of a particular amount of filler, cross-linker, and anti-ozone compound is also a challenging issue for rubberized formulation makers. Effective interaction between natural rubber and natural fibre is a major challenging issue. It could be solved by modification of fibre surface or by modification of matrix. Some of the researchers have reported that the graft copolymerization of natural fibre with different monomers like stearic acid, maleic anhydride etc. assists in uniform adhesion, and stress transfer of natural fibre in the rubber matrix. Silane can act as a bridging agent between natural fibre and matrix. Silane is a silicon based chemical that contains hydrophobic groups, almost like an unsaturated hydrocarbon. These groups assist to create functionality on the fibre surface and as a result, it is chemically linked with the rubber matrix and enhanced strength properties. Composite prepared by using silane as bridging material has lowered the scorch time and curing time. Acetylation of fibre surface also could be a good proposition for better fibre and matrix adhesion as it will make the surface of the natural fibre more hydrophobic. Heat treatment (make the surface hydrophobic), and plasma irradiation treatment (assist in functional group generation) of natural fibre also could be explored for making the surface more hydrophobic

[depending on polymerising gas used] and generate adhesion compatibility with natural rubber. Modified matrix like epoxidized natural rubber (more hydrophobic groups) also could be used for improving adhesion property and uniform filler dispersion [42]. These approaches already have been taken by various researchers for making rubber and natural fibre based bio-composite and artificial leather products. It shows that in the presence of a crosslinking agent, natural rubber could be linked with the polar based cellulose background.

3. Mechanism of rubber-cellulose attachment

It is reported that the artificial leather could be engineered by coating natural fibre based canvas cloth with rubber formulation. Thereafter it is coated with cellulose nitrate and has been embossed to get a leather like appearance. In the nineteenth century, Sheesley patented a useful formulation for the coating of natural fibre based textile materials for the engineering of artificial leather. He has engineered multiple wood pulp made sheets into the form of artificial leather by using a mixed formulation of 18-22% rubber solid (latex), 4-7% albumin based gum, 60-655 water, 6-8% ethyl alcohol, ethyl acetate and 1-3% formaldehyde with very minor quantity (1%) of ammonia. Ammonia has been added into the formulation for the stabilization of the latex and formaldehyde removes the odour and assists in the tanning process of the engineered product [43,44] Jeong et al 2007 proposed a method of preparation of artificial leather by using different compositions of polyester and nylon blend as nonwoven base material having g/m2 range from 180-280 and free air volume range 70-90%. They coated the said nonwoven material with polyurethane elastomer by following the wet coagulation method in the coating machine. Air pressure, temperature and humidity level are different from the outer atmosphere, inside the shoe. Therefore, they have measured important physical parameters like air permeability, water vapor permeability, thermal transport etc. for the engineered artificial leather. As per the report, the used nonwoven material showed water vapor permeability of 5000gm/m2 day and it has been decreased to 2000gm/m2 day after coating. As per the report, heat keeping rate of the nonwoven is decreased after coating with elastomeric material and they have also claimed that the heat flow rate of the coated material has been improved as compared to the nonwoven fabric and as a result, a cool feeling has been observed for the finished product [21], Wool et al 2013 has patented technology of making artificial leather from natural fibre made fabric and triglyceride based plant oil. They have prepared composite like artificial leather material from nonwoven flax and kenaf fibres and a suitable mixture of soybean oil, linseed oil and thin fatty acid and functionalized monomer (vinyl aromatic or acrylate monomer) [45]. Very recently, one innovative research idea has been reported on the preparation of fully biodegradable artificial leather by the multi layering approach of natural fibres [23]. The concerned article shows the technical direction for the production of sustainable footwear by using imitation leather made of natural fibre. As per the report, researchers have developed a multilayered cellulosic material based mat by using a tertiary layer of cellulosic mat, denim fabric and hemp fibre made fabric. They have also compared the physical properties of the multi-layered structure with the bilayeredculf and pig skins. According to a published report, there is no significant difference between the two structures in terms of breaking force and heat loss. Moreover, the air permeability and water vapor transmission rate of the natural fibre made structure is higher as compared to the real leather [23]. A joint project of NSTEDB and FICCI, in collaboration with IJIRA, has represented that impregnated composite made by jute cotton union fabric could be used as a supplement to natural leather. They have prepared toe puff, counter components, and insole material from it. Toe puff is present in the front part of the shoe in between the leather and lining. They have claimed that the engineered material is more flexible, compact and has high shape retention property as compared to natural leather. They have reported that initially jute cotton union fabric has been treated with the water based polymeric solution for the manufacturing of toe puff and counter stiffener. For further betterment and for meeting international standards, they have treated the water based emulsion treated fabric with hot melt adhesive. However, they have not mentioned the details of the chemicals explored for experimental purposes [12]. In the same year, the concerned scientist filed a patent on the engineering of footwear by using a thermoplastic composite made of jute cotton union fabric and thermoplastic emulsion based formulation. As per their report, they have used styrene monomer with talc, PVA and sterile butadiene rubber for the emulsion based treatment and followed by high temperature curing. They have used formulation based on polystyrene: 25-40%, filler (mineral powder): 10-20%, plasticizer (dioctyl phthalate): 1-3% and solvent (benzene/toluene/acetone) for the preparation of hot melt adhesive required for the engineering of toe puffs. As mentioned in the earlier part, Initially, they treated the jute and jute cotton union fabric with the emulsion and cured the sample. Thereafter they made it into the desired shape of the sole and finished it with the hot melt coating of the adhesive before final use in footwear products [46]. “Noani” is an example of artificial leather based on composite construction. It consists of three layers composed of polyester microfiber material (upper layer), leather fibre board (core layer), and coated textile with foamed PVC and textile carrier (backside layer) [47]. Table 1 shows the comparison of the physical properties of different sustainable leather alternatives in contrast with natural leather.

Table 1 Summary of the Basic structures and important properties of the footwear products made from natural fibre

Natural leather	Important physical properties of natural leather			
	Tensile strength (N/mm^2)	Max elongation (%)	GSM (g/cm^2) & thickness (mm)	Air permeability (cc/s/cm2)
Natural double layer leather (cow skin and pig skin combination) [8]	14-15	54.9	439 & 2.25	0.006
Natural goat leather [6-7]	12-13	55.61	523 & 1.93	4.6
Synthetic leather	**Physical properties of synthetic leather**			
Polyester coated with polyurethane [29]	3-4	80-100	550 & 1.4	Less than 1
Sustainable leather alternatives	**Important physical properties of leather alternatives**			
Cellulosic mat (outer shell), denim fabric and hemp fabric (inner shell) [18,41]	5-7	5-10	641-650 & 2.26	10-15
Jute-cotton mat coated with rubber [45]	4-5	4-5	650 & 2.2	15-20
Linen/flax fibre based leather [35]	12-13	10-14	420-450 & 1.2	10-12
Pineapple fibre based leather [43]	4.5-5.5	15-20	500 & 1.43	8-10
Snap pap leather [30]	3-4	4-5	350-400 & 0.57mm	2-3
Teak leaf leather [31]	2-3	7-10	300-400 & 0.57-1	5-7
Muskin leather [35]	1-1.5	10-15	600-625 & 6-7	10-15
Natural fibre based rubberized flexible composites				
Natural fibre and rubber composite	Important physical properties (Various physical properties)			
Bagasse fibre (30%) +natural rubber [14]	6-7	25-30	Composite hardness: 60shore A	No permeability
Silane modified bamboo fibre+ natural rubber [15] (use in frozen land)	12-13	20-25	700 & 3	Less than 1
5% bleached jute fibre+ natural rubber based formulation [16]	11-12	9-10	600-650 & 4	4-5
Alkali modified pineapple fibre+ natural rubber based formulation [41-43]	5-7	5-10	550-650 & 4-5	1-2

4. Conclusion

The main advantages of natural fibre based flexible composite products are bio-degradable, renewable, soft to skin and also breathable. Comfort and lifetime of the said products are very much important. Different research works are already going on the natural fibre (jute, wool, cotton, pineapple, hemp) based flexible composites. In all cases, natural fibre based woven or non-woven fabric has been used for the engineering of shoe upper part, and lining and for the preparation of insole and other lifestyle products like wallets, belts, jackets, seat covers etc. However, applications of those products usually are in very limited areas (mainly in-house applications and in dry atmospheres) and the technology is not up to mark as most of them are damaged in moist conditions, easily attacked by microbes, moths (only for woollen footwear) and generate bad odour on continuous usage. In addition of it, the footwear material needs to be more resilient, moldable, lightweight and have adequate

anti-slip (frictional resistance) and impact resistance properties as per the end usage of the concerned product. Moreover, the abrasion resistance property of the natural fibre based footwear (upper part and insole) also needs to be improved by using suitable chemicals or by changing the basic construction parameters of yarn and textile. Some of the natural lignocellulosic fibres like ramie, flax etc., or suitable blends of them could be used for making nonwoven and for engineering upper shoe parts and insole material of footwear products. These ligno-cellulosic fibres have high ply ability, modulus, bendability, fineness etc. Therefore, the exploration of newer domains of natural fibres could be one important future thrust of this area.

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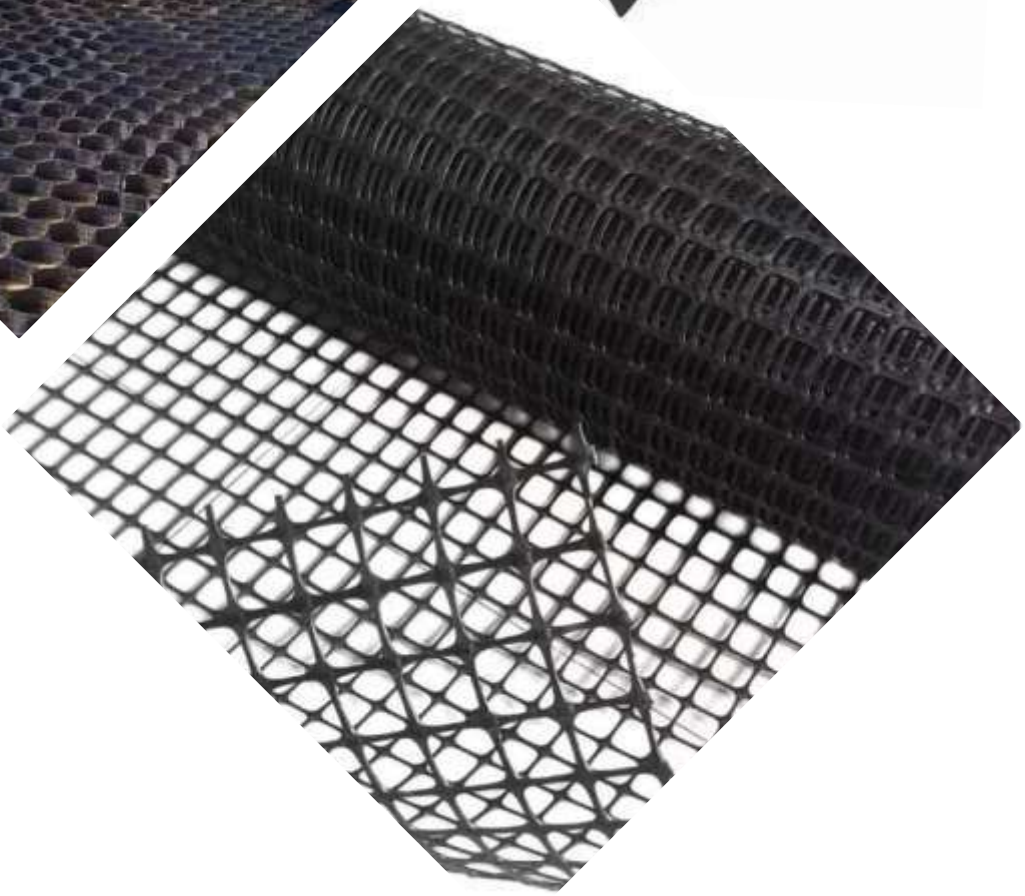

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