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Modification of Footwear PVC Outsoles into Graphene Oxide-Based PVC (PVC/GO) Soling Composites for the Enhancement of Better Physical Properties

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Article

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ABSTRACT

Outsole is a crucial component of a shoe's bottom that directly contacts the ground. Comfort and durability are the most expected characteristics of outsoles. Various nanocomposites are utilized to increase the thermal stability, light weightiness, microporosity, and durability of polymeric materials. In this research, PVC soling composites were prepared using synthesized graphene oxide (GO) from a modified Hummer method. The goal is to improve physical properties like thermal stability or durability, lightweight, tensile strength, and hardness. The GO content in developed soling composites ranged from 0.1% to 0.4% by the colloidal blending method. FTIR, TGA, XRD, and SEM characterized GO and GO/PVC soling composites. The presence of the functional groups C=C, C-O-C, -C=O, and -OH was confirmed by the FTIR spectra of GO, while oxygen-holding functional groups to the layered structure caused the separation of the interlayer space to grow from 0.34 nm to 0.86 nm, according to GO XRD data. XRD results revealed that the GO layers were uniformly distributed in the polymeric matrix of composites. TGA results exhibited that the percentage of mass loss for GO was 81.96% at 800 °C and for soling composites it decreased continuously with an increase in the content of GO, respectively. SEM analysis revealed that the composites with GO showed a homogeneous composite with significantly porous surface morphology. Proportional improvement of tensile strength and hardness for GO-based soling materials were in an increased proportion and density were in a decreased proportion, making the outsole lightweight and durable. Finally, the results suggest that GO/PVC soling composites can improve the durability, mechanical and thermal stability, light weightiness, and microporosity of PVC soles, while the best performance was found for PVC/GO-0.4% soling composites.

KEYWORDS

composites, GO, PVC/GO, soling materials, synthesis, characteristics

INTRODUCTION

Wearing footwear helps protect the foot from the environment by reducing risk and enabling pain-free movement on different walking surfaces [1]. Outsole is the essential part of footwear that saves the bottom portion of the human foot from heat, cold, and surface abrasion. The permanent requirements of an outsole will rely on the environment and tasks selected for the individual shoe [2,3]. Durability can be a selling characteristic for a shoe but may come at the expense of additional

weight or lessened flexibility. A reduction in the weightiness of soles facilitates better walking. Heavy bottoming materials are unfavourable because of the lack of balance between uppers and bottoms [4]. The lightweight soles should not be liable to stretch out the shape and lose their ground insulation as well as foot comfort properties [5].

Various auxiliary ingredients such as stabilizers, plasticizers, blowing agents, fillers, and pigments are used to produce the lightweight sole without compromising desirable properties [6]. Blowing agents are used to make porosity by generating nitrogen (N_2) gas and carbon dioxide (CO_2) gas. Thus resulting in the reduction of the weightiness and decreased stability or strength of the soles. The outsoles undergo various temperatures in different environments to enable them to fit in a range of temperatures. Due to thermal degradation, the durability of outsoles decreases. For maintaining stability, various types of stabilizers are incorporated with soling materials [4].

The advancement of technology has paved the path of increased demand for sophisticated polymeric composite materials. However, without plasticizing or filling, PVC is frequently fragile and unsuitable for use in different fields [4]. Various soling nanocomposites are used to upgrade the properties of the soling material. Graphene oxide (GO) is a useful material as a filler and stabilizer. GO-based Polystyrene composites are lightweight, thermally stable, and durable [7]. Previous research showed that graphene oxide base polymeric-composite materials are more microporous, lightweight, and firm in thermal heat. Due to its intriguing physical and chemical properties, wide surface area, hydrophilic qualities, cost-effectiveness, and simple manufacturing processes, graphene oxide (GO) has recently attracted more interest than other stabilizers and reinforcing agents [8-12]. According to Guiying Wu et al. (2018), the nanocomposites with one weight per cent GO content in the PU matrix (PU-1) showed exceptional all-around qualities. The glass transition temperature (T_g) and commencing disintegration temperature of the PU-1 composites were raised by 14.1°C and 31.8°C , respectively, in contrast to unadulterated PU. Additionally, Young's modulus and tensile strength were enhanced by 102% and 126%, respectively. The remarkable improvement in the mechanical and thermal stability of PU/GO composites has been ascribed to high compatibility and the uniform distribution of GO with the PU matrix. The robust interfacial contact between the strengthening agent and the PU matrix may be responsible for the characteristics' enhancement with the addition of GO [11]. GO has been an engrossing choice as an anchoring site to form GO-based nanocomposites [12].

In addition, Mindivan reported varied concentrations of 0.1, 0.3, 0.5, and 1 wt.% of polyvinylchloride/graphene oxide (PVC/GO) composites to evaluate the structural and thermal changes [13]. The X-ray Diffractometer (XRD) measurements of most composites showed that the GO layers spread evenly throughout the polymer matrix. The composites with 0.1 and 0.5 weight per cent GO filler shown by Scanning Electronic Microscope (SEM) analysis revealed a homogeneous composite with tremendously porous and microporous morphology, respectively. Less GO in PVC materials did not

profoundly progress the thermal stability of the investigated composites, according to TGA (Thermogravimetric Analysis) and DSC (Differential Scanning Calorimetry) reports [13]. Deshmukh and Joshi prepared PVC/GO composite films with an organized linkage of macro-pores morphology via the colloidal blending process, and stated that the durable collaboration among PVC and GO amplified the thermal strength of the composite films. They also reported that the dipole-dipole interaction of hydrogen and chlorine atoms makes the polymer backbone stiffen and GO interacts with the chlorine atoms by covalent bond [14]. Mindivan and Göktaş reported the improvement of thermal and mechanical properties (tensile strength and hardness) by altering the loading amount of reduced GO which plays the role of filler in composites [15]. However, studies on the PVC/GO composite are still scarce.

Despite the abundance of research on graphene oxide-based polymer composites to improve thermal stability, light weightiness, and microporous materials, no research has been done yet to investigate the existence of soling composites, especially PVC soling composites. To the best knowledge, this was the first study about the composite of GO and PVC soling materials. This research has explored their performance in the improvement of thermal stability, mechanical stability, and microporosity in soling materials to make them lightweight.

EXPERIMENTAL

Materials

All of the experimental procedures used reagents and substances were of analytical grade. Loba Chemie Pvt. Ltd. provided the graphite powder that was 98% extra pure. The other chemicals were granules of PVC soles (Sarla Multiplast Pvt. Ltd, black grade, moulding purposes, and extrusion purposes), Tetra Hydro Furan ($(\text{CH}_2)_4\text{O}$), hydrochloric acid (HCl), Hydrogen peroxide (H_2O_2), sodium nitrate (NaNO_3), potassium permanganate (KMnO_4), sulphuric acid (H_2SO_4), deionized water, and distilled water. The composition of PVC granules was presented in Table 1.

Table 1. Composition of PVC granules

Name of the composition	Proportion (parts per weight)
PVC polymer	100
Sulphur	3.5
Zinc Oxide	3.5
China clay	30
Blowing agent	3
Paraffin wax	2.5
Petroleum jelly	2.5
Accelerators	2
Antioxidant	1

Instruments and Accessories

To make and analyze GO and GO-based soling composites utilized instruments and supplies were: a hot air oven, a pH meter (HANNA instruments), a digital balance (XB 220A, Precisa), filter papers (pore size 20 micrometres), and digital balance, Ice bath, Petri dish plate, X-ray diffractometer (Ultima 4, XRD), Scanning Electron Microscope (SEM, JSM-6490LA, JEOL), hotplate, a magnetic digital stirrer (PA 1180, LK LAB Korea), Thermo-gravimetric Analyzer (TGA-50, Shimadzu), Fourier Transform Infrared Spectrophotometer (FTIR) (Model IR Prestige 21, Shimadzu Corporation, Kyoto, Japan), SATRA thickness gauge (Model: STD-495), Abrasion resistance tester, Tensile testing machine (Model: STD-172, Serial No. 9167, England), Durometer, Density measuring instruments.

Synthesis of Graphene oxide (GO)

GO was prepared from the fine graphite powder of natural raw materials (98% extremely pure) according to modified Hummer's Method [16]. Each graphite powder and NaNO_3 was added 4 g to 200 mL of H_2SO_4 . The mixture was constantly agitated (at 60 rpm) in an ice bath with a temperature range of 0 to 5 °C for four hours. Then, it was chilled in an ice bath (10-15 °C) while being stirred and KMnO_4 (24 g) was slowly added to the medium. The addition rate was closely monitored by keeping it below 15 °C. After removing the ice bath, the solution was agitated at 35 °C until it took on a pasty brown colour. The combination transformed into a pasty brownish state, signalling the end of the reaction. A gentle 200 mL addition of water diluted the solution. The temperature was abruptly raised to 98 °C, changing its tint to brown. Further dilution was done with 400 mL of water while stirring constantly after the heating unit was switched off to cool. The reaction was finally stopped by adding 40 mL of 30% H_2O_2 to the mixture and noticing the formation of a yellow tint. The solution was rinsed with 10% HCl and deionized (DI) water numerous times for refinement. After filtering and dehydrating in an oven at 60 °C temperature, the GO was visible in a solid state.

Synthesis of Graphene Oxide based soling composites

Synthesis of PVC soling composites

PVC (10 g) was first added in 50 mL Tetrahydrofuran (THF) at 70 °C to dissolve and then the mixture was stirred for two hours at 60 °C. The subsequent uniform distribution was put onto a glass petri dish and placed in a 60 °C oven to allow the solvent to evaporate slowly, producing a PVC composite. The label read sample (a) PVC/GO-0%.

Synthesis of PVC/GO soling composites

With the help of the colloidal blending method, PVC/GO composites were produced [13,15]. Before being cooled to room temperature, PVC (10 g) was added first to 50 mL of THF to dissolve at 70 °C. Then, GO powder was dissolved independently in THF at 25 °C. At 60 °C, the two solutions were agitated for two hours. To create a PVC/GO composite, the homogeneous dispersion of the result was placed onto a glass petri dish and stored in a 60 °C oven for the solvent to evaporate slowly. The GO content in the PVC/GO soling composite was amplified from 0.1–0.4 wt.% (Table 2).

Table 2. GO content in the PVC/GO composites

SL.	Sample Name	GO content (in weight %)
1	PVC/GO-0.1%	0.1
2	PVC/GO-0.2%	0.2
3	PVC/GO-0.3%	0.3
4	PVC/GO-0.4%	0.4

Characterization of synthesized GO and GO-based soling composites

The Thermo-gravimetric analysis of the GO, PVC soling composites, and GO-based soling composites was analyzed with a TGA within the temperature range from 50 °C to 800 °C. The FTIR analysis of GO ranged from 600 cm⁻¹ to 4000 cm⁻¹ wavenumbers. Again, the XRD analysis of GO, GO-based soling composites, and soling composites without GO was carried out with an XRD. The morphological surface of the composite materials was investigated with SEM. Evaluation of tensile strength and percentage of elongation of soling composites were carried out according to SATRA PM-136 [17]. Hardness, abrasion resistance, and density also were measured according to ISO-868, SATRA TM 174, and SATRA TM 138, respectively by durometer, abrasion resistance tester, and density measurement machine for evaluation of physical properties of soling composites [18].

RESULTS AND DISCUSSION

Characterization of synthesized GO

The FTIR spectra of GO displayed in Figure 1a revealed the existence of several functional groups with oxygen on its outward. The significant broad peak of the stretching vibration of the O-H bonded at 3200 cm^{-1} included water molecules as well as alcohol and carboxylic acid groups [19]. The features of GO have hydroxyl, carboxyl, and epoxy functional groups [20]. The C=O group found in GO was at 1719 cm^{-1} [21]. In addition to the influence after the bending vibration of the O-H bond, which resulted in increased intensity, the peak at 1600 cm^{-1} corroborated the stretching vibration of the C=C bond, suggesting the presence of sp^2 hybridized carbon [20]. The peaks of the C-O bond's stretching measured at 1400 cm^{-1} and 1028 cm^{-1} indicated the presence of the epoxy group [21]. Therefore, every peak examined in the figure met the theoretical peak values for graphene oxide.

The XRD pattern of synthesized GO was displayed in Figure 1b and showed one main 2θ at 10.3° . The transformation of graphite to GO was verified by the diffraction peak at $2\theta = 11^\circ$ approximately [22]. In addition, the XRD pattern's characteristics showed that the produced GO was in crystalline form. Graphite's XRD pattern was revealed at 26.4° in Figure 1b which remained unreacted. It was revealed that the matching interlayer distance was 0.34 nm. After oxidation, the interlayer gap expanded to 0.86 nm, as indicated by the diffraction peak's shift to 10.3° [23]. Because oxygen-holding functional groups were interpolated in the layered configuration [24], the interlayer space augmented from 0.34 nm to 0.86 nm.

Thermal gravity analysis was used to examine the proportions of weightiness loss by rising the temperature for GO. The TGA and derivative curve were presented in Figure 1c. Owing to the elimination of outward moisture and inter-layer engrossed H_2O , the graph showed a weight loss of 18.47% between 50°C and 205°C [13]. Weight loss increased with temperature and was about 77.74% between 205.57°C and 547.45°C due to the decomposition of CO_2 , CO, COOH, and O_2 [13]. Finally, it reached to mass loss of 81.96% at 600°C .

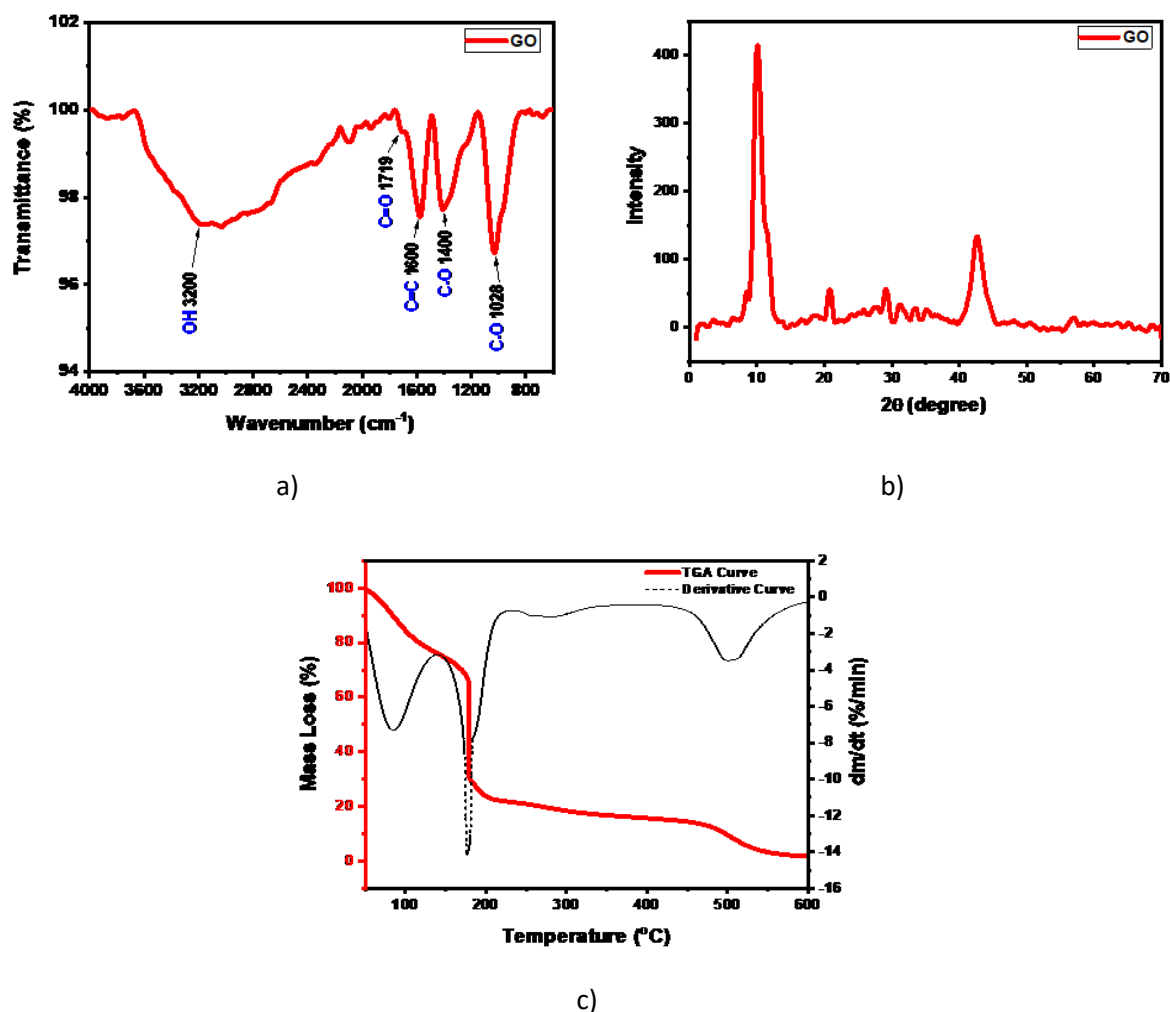


Figure 1. a) FTIR spectra, b) XRD, and c) TGA graph of GO

SEM was used to examine the graphene oxide's surface morphology. Figure 2 depicted the SEM image of (a) at low magnification (X1,000) (b) at medium (X2,000) and (c) at high magnification (X5,000) of GO sample. The first image shows that the particles were visible with defined borders at low magnification. Additionally, worm-like structures that were randomly collected on the surface were observed [25]. High-magnification samples were acquired to see the morphological surface.

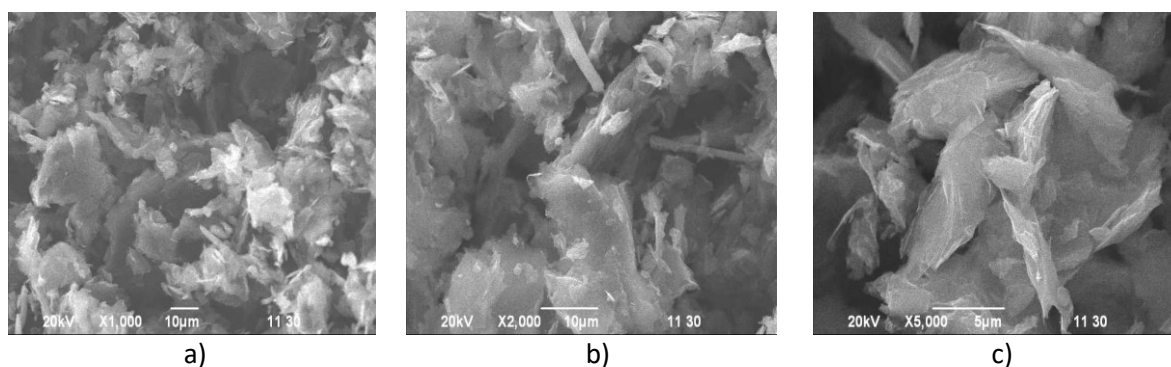


Figure 2. SEM image of GO: a) low magnification (X1,000) b) medium magnification (X2,000) c) high magnification (X5,000)

Characterization GO-based Soling composites

TGA Analysis of GO-based PVC soling composites

Decomposition behaviours of GO-based PVC soling composites have been conducted by thermal gravimetric analysis. The graph in Figure 3 showed that the decomposition of the PVC and PVC composite occurred in two stages. Firstly, it was visible at 200 – 300 °C due to the probable dehydrochlorination of virgin PVC [26] and the exclusion of oxygen-bearing active groups of GO for PVC/GO composites. Secondly, the decomposition in the range of 400 – 500 °C can be assumed for the loss of alternate lone and dual carbon bonds [14].

After 700 °C, the mass loss for PVC composite without GO was 89.34%. But, with the addition of GO in PVC composite, the mass loss percentage was reduced to a little extent. The mass loss percentage of PVC/GO for 0.1%, 0.2%, 0.3%, and 0.4% at 700 °C was 88.14%, 82.29%, 76.10%, and 75.21%, respectively. The amount of mass loss reduced due to the application of GO in PVC was 14.13%, as shown in Figure 3. Therefore, the thermal stability of the PVC/GO soling composites increased with the increase of GO content. This indicates a resilient interfacial interaction between GO and PVC [14].

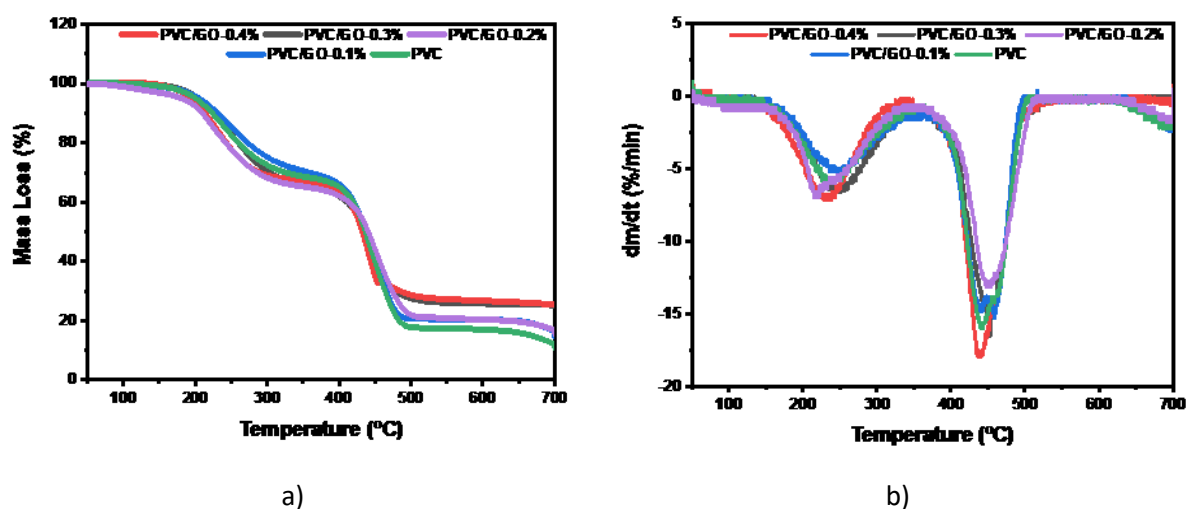


Figure 3. TGA Analysis of GO-based PVC soling composites: a) TGA curve, b) derivative TG curve

XRD analysis of GO-based PVC soling composites

Due to the short X-ray diffraction intensity of PVC and the small extents of added GO, the outcomes demonstrated that the reflection profile of PVC/GO composites was nearly identical. PVC's diffraction angle was approximately 12.33°, while GO's was 10.3°, and the small amount of GO to the PVC composites was left unreacted. With increasing the amount of GO, the intensity at a diffraction angle of 10.3° increased gradually. These findings across all composites showed that some GO layers were not evenly distributed throughout the polymer matrix, as shown in Figure 4.

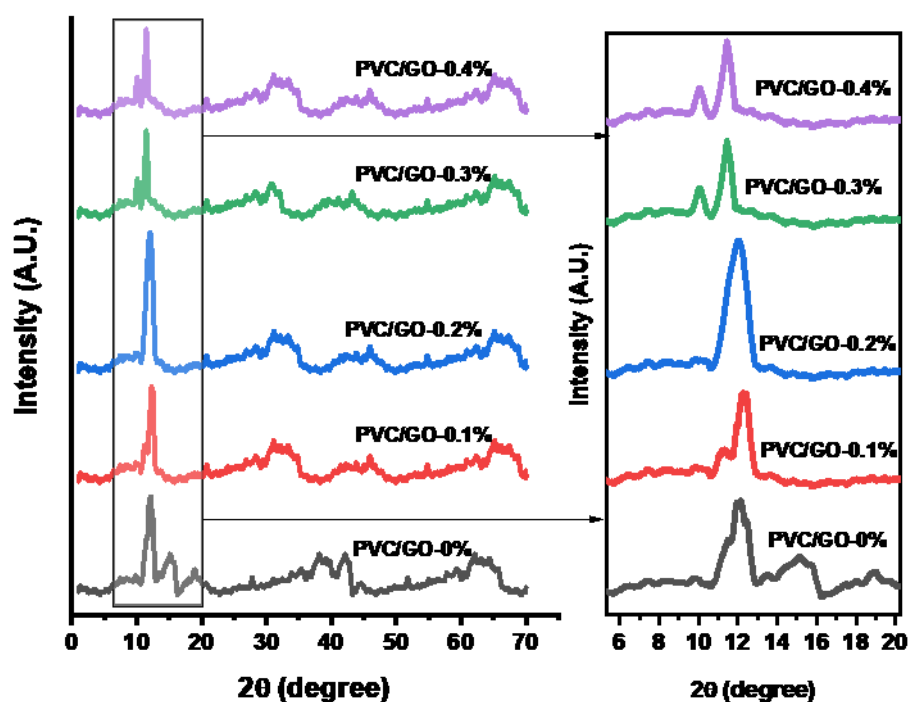
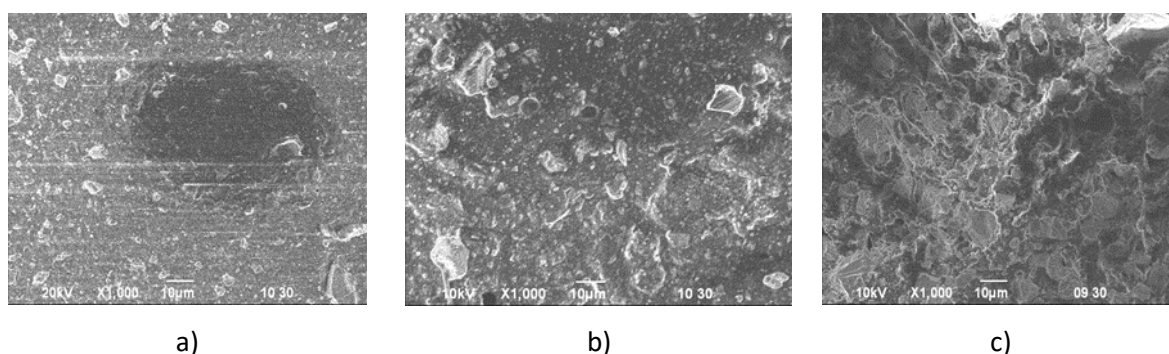


Figure 4. XRD Analysis of GO-based PVC soling composites

SEM Analysis of PVC/GO soling composites

The SEM images of PVC/GO soling composites were shown in Figure 5 at X1000 magnification. PVC/GO-0.4% composites with modest doping amounts of 0.4% of GO demonstrated an unbroken and dense arrangement with vastly porous as matched to the conventional surface of PVC granules. In Figure 5, the PVC/GO-0.4% composites' SEM picture revealed a randomly arranged crumpled structure in the shape of thin sheets that were tightly related to one another. The PVC/GO-0.4% composite showed pores and cavities due to the polymer development in the GO pores and galleries [14]. In Figure 5 (a), (b), and (c), the SEM appearance of PVC/GO-0% composite specified a minor porosity, but in the image of PVC/GO-0.4%, the size of the porosity was larger than PVC/GO-0%. Therefore, PVC and GO caused uniform composites by filling PVC in between GO nanosheets outputs a microporous morphology.



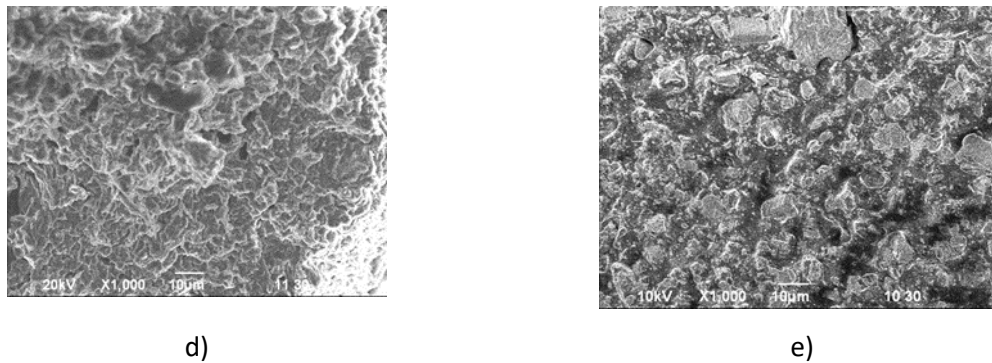


Figure 5. SEM analysis of a) PVC/GO -0%, b) PVC/GO -0.1%, c) PVC/GO -0.2% d) PVC/GO -0.3%, and e) PVC/GO-0.4%

Physical properties of GO-based PVC soling composites

The experimental results for the Physical properties of GO-based PVC soling composites were enlisted in Table 3. From the results, it was revealed that with increasing the amount of GO as composites, the physical properties of GO-based PVC soling composites were increased, excluding elongation and abrasion resistance without considering density. Among five samples, PVC/GO-0.4% gave the best result for tensile strength and hardness. The percentage of elongation, abrasion resistance, and density were cut down with increasing GO into PVC soling materials but based on equal density, the mass loss due to abrasion for all samples was near to the equivalent. Mindivan and Göktaş reported the increment of hardness and reduction of elongation with the increase of GO loading on PVC [15]. In addition, Deshmukh and Joshi reported the augmentation of tensile strength for the GO content increment in PVC composites [14].

Table 3. Physical-mechanical properties of GO-based PVC soling composites

Sample name	Tensile strength (Kg/cm ²)	Elongation (%)	Hardness (Shore A)	Density (gm/cc)	Abrasion Resistance (mm ³)
PVC/GO- 0%	105.5±7.2	230.1±8.0	64±4.7	1.10±0.01	184.5±4.7
PVC/GO-0.1%	117.7±4.8	225.4±6.5	70±6.6	0.99±0.006	189.5±5.3
PVC/GO-0.2%	128.6±3.75	220.1±5.3	71±8.1	0.99±0.008	193.7±6.1
PVC/GO-0.3%	135.5±3.1	218.6±5.0	73±4.0	0.94±0.004	193.9±4.5
PVC/GO-0.4%	140.3±4.2	218.1±2.8	75±3.7	0.96±0.005	194.6±3.3
Standard [18]	Max 140	Min 300	60-80	1.20-1.27	Max. 350

CONCLUSION

Sole is an integral part of footwear that protects the foot from the environment by lowering the chance of injury and allowing for pain-free movement on a variety of walking surfaces. The study suggested that GO-based PVC soling composites were thermally more stable, durable, and lightweight. Due to the addition of blowing agents only, the stability and strength are reduced that hampers the durability of soles. In the case of graphene oxide with the presence of a blowing agent, it made the soling material more stable and lightweight with compare to conventional PVC soles. The scope of application of the output from this research is very prospective in the footwear industry. If the sole of PVC is incorporated with GO, it will be better than the existing PVC sole and thus the quality of footwear will be increased.

Author Contributions

Conceptualization – Hossain MD; methodology – Hossain MD; formal analysis – Hossain MD, Hossain MM and Deb AK; investigation – Hossain MD and Bin Azam FA; resources – Chowdhury M; writing-original draft preparation – Hossain MD; writing-review and editing – Deb AK and Hossain MM; visualization – Hossain MD and Hossain MM; supervision – Chowdhury M. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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