Formulating Bio-inspired antistatic NR-composite for smart tire application

A dissertation submitted in the partial fulfillment of
the requirement for the degree of
Bachelor of Science
in
Chemistry

Submitted by:
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May, 2024

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Abstract

Tires are the vital part of our transportation being deployed to fasten and sustain our daily life activities, future infrastructure development, and sustaining the supply chain especially for food and energy supply. Tires are mainly made of a composite of natural rubber (NR) and carbon black (CB). But, the fossil fuels, the primary source of CB is being depleted from the earth crust day by day. Thus, there is a need for alternative fillers. Plenty of research is going on for developing CB from different wastes particularly cellulosic or lignocellulosic biomass. However, the processing is multistep and may cause the emission of greenhouse gases which is again considered as a huge contributor for the global warming. In this work, waste human hair (HH) after its de-keratinization is investigated for its effectiveness as a green filler for the NR matrix. HH being a bio-waste and may cause several environmental issues herein the proposed work may consider the conversion of “Trash-to-Treasure” towards the production of biocompatible NR-based tire treads. In addition, the NR being a tribo-negative material and HH (because of their abundant polar functionalities enriched with electron donating groups) being a tribo-positive materials, the composite of these two may be considered to behave like an anti-static. During rolling, the friction between the road and tire tread results in production of huge static charge which causes many accidents of the carriages or automobiles. As a precaution, thus, there is a practice of keeping metal chain in the carriages to earth the developed charge. The antistatic tire, if produced, it can be considered safer. And if it is made of green fillers, it will be considered green tires. In this work, it has been observed that the static charge development is reduced with increasing the filler content (i.e., 1, 5, 10 and 20phr of HH) in comparison to the only NR. In case of 20phr HH, the composite, because of the piezoelectric property of HH, showed piezoelectric behavior that may be considered for developing green and smart tire composition. In terms of tensile and elongation, enhancement is also observed with increasing the filler content. The composite was thoroughly characterized by FTIR spectroscopy, tensile machine, optical microscope, and triboelectric measurement. Following all the characterizations, and observations it can be said that this work approach may be given immense importance for both the academia and industry towards developing a sustainable and green strategy especially in the area of composites, waste management towards our socioeconomic sustainable development.

Key words: Green filler, Smart tire, Antistatic, Triboelectricity

ACKNOWLEDGEMENT

I would like to thank my supervisor Dr. Tridib Kumar Sinha and my co-supervisor Dr. Bhawna Lamba, for their guidance and support throughout the project. Also, I would like to thank senior Ph.D. scholars to the staff of the chemistry lab, CIC lab, and HSC lab for helping in the completion of work.

Also, I would like to thank my parents Harish Singh Mehra and Deepa Mehra, and my friends for their lovable constant support without their support and encouragement I would have not done it.

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CHAPTER 1

INTRODUCTION

Automotive inventions are among the most important in modern history, and they have had a profound impact on people's lives[1]. Tires are the product of nearly a century’s worth of research and development and demand for them is predicted to rise to 3 billion units in 2019, representing an annual growth of 4% and 258 billion dollar sales[2]. The tires are no longer just pieces of rubber thanks to continuous advancement it is now sophisticated pieces of technology. Natural rubber has several advantageous elastomer qualities, including low heat hysteresis and high tensile strength, and damping also because of its remarkable elasticity, natural rubber can stretch a great deal and then regain its original shape after deformation. Because of this characteristic, it's perfect for applications like tires, rubber bands, and seals that call for flexibility and robustness. Because natural rubber conducts heat effectively in dynamic applications like tire treads, it lowers the risk of overheating and early failure. Natural rubber also has minimal heat build-up qualities permitting tires to effectively release the heat produced during operation. This guarantees tire integrity and performance throughout prolonged use and helps prevent overheating.

Moreover, in contrast to synthetic elastomers, it is a renewable product.[3] therefore, can be used in making tires, is a biodegradable and renewable material that originates from the latex sap of the rubber tree (Hevea brasiliensis). When tires are made from natural rubber instead of synthetic rubber, the environment is more sustainably managed. Overall, natural rubber's special set of qualities makes it an essential component of tires, enhancing performance, safety, and environmental sustainability in the automobile sector.

Since rubber tires are the only component of a vehicle that comes into contact with the road, they play a crucial role in both tire safety and performance. As a result, numerous studies from the perspectives of road pavement and tires have attempted to evaluate the interaction between vehicle tires and road surface to gather important data regarding vehicle stability through the developed friction [2]. The developed friction namely static electricity arises also in the silica-filled tires. As the silica tire rolls down the road and rubs against it, a static charge is built up. Car sickness, electric shocks, and radio interference are brought on by the accumulation of static electricity on the tire. These are the primary drawbacks of employing silica fillers as green fillers in tires[1]. Materials that enhance the polymer matrix's modulus and failure properties are known as reinforcing fillers, they are typically substances added to a material to improve its strength, durability, or other mechanical attributes and are sometimes referred to as reinforcing agents. In disciplines like engineering, manufacturing, and materials science, this phrase is frequently employed, for example, reinforcing chemicals are added to composite materials to reinforce the matrix material. For instance, components such as carbon fibers, glass fibers, or even nanoparticles can act as reinforcing agents in polymer composites, enhancing the material's overall mechanical properties. A reinforcing agent can also refer to something that, in psychology or behavioral sciences, strengthens or reinforces a specific behavior, this term is frequently used concerning operant conditioning. A reinforcing agent, for example, could be an incentive offered in a reward system to encourage desired actions. The most used filler in rubber companies is carbon black (CB). The structure of carbon black reinforced rubber composites determines their characteristics primarily; it can change the vulcanization of rubber's chemistry and exhibit both chemical and catalytic activity. Rubber composites benefit from CB's outstanding physical, mechanical, thermal, and barrier qualities, but they also have certain drawbacks. The incomplete combustion of heavy petroleum products produces CB. When heavy petroleum is not completely burned, hazardous waste and poisonous gasses are released. According to the International Agency for Research on Cancer's (IARC) current assessment, carbon black is classified as a Group B carcinogen and is likely harmful to humans. Through mechanical irritation, short-term exposure to high concentrations of carbon black dust can trigger pain in the upper respiratory tract. Therefore, the rubber industry must switch to sustainable filler materials in place of carbon black[4].

One of the alternatives for the rubber composite is that green filler can be a bio-based filler, bio-based composites are a type of composite material that originates from natural and renewable sources. Several works have been reported for replacing carbon black with other filler, Styrene butadiene rubber (SBR) composites made with 25 weight percent birchwood biochar and 75 weight%, carbon black have tensile strength and toughness that are nearly identical to those of the composite made with 100 weight% carbon black.[5], It was found that the use of discarded cotton to create nanocrystalline cellulose (NCC) is one method for partially substituting carbon black (CB) in NR It was also discovered that, when 10% of the CB in the composite was swapped out for NCC, its mechanical, thermal, and biodegradability qualities outperformed those of NR/CB composites[6]. It was also determined that multilayer graphene (MLG) and carbon black had a synergistic impact on chlorine isobutyl isoprene rubber (CIIR)[7].

The use of waste biomass to produce rubber composite is an effective way to reduce waste and promote sustainability. The use of sustainable sources for the production of biobased rubber composite can also contribute to the reduction of greenhouse gas emissions and with that, it promotes a circular economy. These benefits can make bio-based composite an attractive alternative to the traditional Carbon black filler(CB) rubber composite. The increasing demand for rubber and rubber-based materials has led to environmental concerns, such as deforestation, water pollution, and greenhouse emissions using our desired biobased can help mitigate these issues by reducing the reliance on non-renewable resources and promoting sustainable practices however certain benefits provided by it, it has its demerits, mainly the filler-matrix adhesion which can overcome by introducing some modifier in the filler. Commonly seen that the two most common fillers to reinforce vulcanized rubber rare silica and carbon filler among which one is a hydrophobic filler that works well with NR is carbon black while the comparison of carbon black, although silica filler has the benefit of facilitating the more environmentally friendly blending of rubber compounds during tire construction, silica filled tires have a significant issue with static electricity. This problem compromises performance, safety, durability, and fuel efficiency. As the tire rolls on the road and rubs against obstacles, silica tires accumulate a static charge. The developed static charge causes radio interference, electric shock, and car sickness.[1] and also to be noted that the silica filler is quite expensive and also has problems during the rubber compounding, including the high curing time, non-conductivity, and rigidification upon cooling. Therefore, is it needed to replace it with some other filler that can be incorporated into the tires.

One of the options for the filler can be human hair is a non-biodegradable protein fiber that has barely been explored, human hair consists of α-keratin(high sulfur content filament structure) and also it has viscoelastic behavior which helps it to sustain under external stress and it gets tougher[8]. This use of filler in the material provides an advantage over other traditional filler infused in the tires. The formulation process involves carefully selecting and mixing bio-based materials with rubber, as well as incorporating additives to enhance properties. The desired mechanical, chemical, and thermal properties can be achieved through testing and optimization. Overall, developing rubber composites with human hair infused is an important step towards creating sustainable materials for a greener future. The main problem that arises with the tires is the generation of static charge which gets stored in the tires when are in contact with the road surface which further leads to fuel consumption and other problems as well also the green filler hair will play a major role in reducing the stored charge as by looking at the triboelectricity series we will observe that rubber is below in the series which means it is tribonegative in nature which means that it will acquire a charge when coming in contact with other material and hair, in contrast, are tribopositive in nature means it loses electron while in contact therefore by nature we can assume that the charge will be neutralized. Certain works have been done by scientists in converting that static in the tires into something useful, in 2018 work was done by preparing a nanogenerator to convert that static charge in the silica based tires to electrical energy which can be further[1]. Some more notable have been in the field of the same which are the development of triboelectric nanogenerators (TENGs) allow for the harvesting of mechanical energy from a variety of sources, including vibrations, wind, and human motion. The triboelectric effect and electrostatic induction allow these devices to produce energy, which has applications in wearable technology and self-powered sensors it can also be used to power small electronic devices[9]. Integrating triboelectric materials with flexible and elastic electronics has made it feasible to create electronic skins and wearable devices sensitive to touch, strain, and other stimuli. These advancements may find use in robotics, human-computer interaction, and healthcare[10]. Adhesives that cling to surfaces via electrostatic interactions have been created using triboelectric materials. These adhesives are good for robotics, manufacturing, and medical device applications because of their reusability, controllability, and compatibility with different substrates.

Triboelectricity: phenomena and mechanism of charge accumulation

Certain materials can develop an electrical charge when they come into contact with one another and then separate, a process known as triboelectricity. Triboelectric charge, also known as the triboelectric effect, is the process by which adhesion generates energy. Through a process called contact electrification, it is when one material becomes electrically charged when it separates from the neighboring contact material, it produces electricity. Electrons go from one different material to the other when they come into touch. Friction is the cause of this charge transfer. Charges are transferred and the electrical potential of the two linked materials is balanced. The separated surfaces can acquire a positive or negative charge when one of the surfaces separates from the other material surface. An electric discharge may result from contact with a surface that is oppositely charged. Thus, triboelectricity is the production of electrical current by the collision of two distinct materials, which results in a high electron flow between them and preserves the potential difference. By rubbing the two materials up against one another, the triboelectric effect enhances surface contact between them and produces an electric charge. One can experience the sense of static electricity by moving a plastic comb through the scalp. Triboelectric electricity is the kind of static electricity we produce on a daily basis. The type of material, straining within the material, temperature of the material, surface roughness, etc., all affect the charge strength and charge polarity generated.[11] For over a decade, researchers have been working to create devices that could capture this energy and use it to power sensors, electronics, and, if produced in huge quantities, our houses as well. The accumulation of charges on dissimilar surfaces when they come into contact with one another is the basis for the triboelectric effect. A high voltage that is produced when these surfaces are separated can start an electron flow. There has been a great deal of research on this subject since TENGs were invented in 2012. Kapton and polyester served as an active layer of the first TENG device, which was created using the contact separation method.[11]

The materials in the triboelectric series are arranged according to how likely it is for them to gain or lose electrons when they come into contact with one another. In addition, triboelectric effects- which allow materials' mechanical motion to be turned into electrical energy- are being studied by researchers as potential sources of energy harvesting. The transfer of electrons between two materials during contact and separation is what produces triboelectricity. There are multiple steps to this process.

1. Contact: Based on their relative positions in the triboelectric series, the surface electrons of two materials that have differing inclinations to gain or lose electrons redistribute when they come into touch. When it comes to electrons, one material typically has a larger affinity (electron acceptor) than the other (electron donor).
2. Electron Transfer: When two materials have different electron affinities, electrons from the lower-affinity material move to the higher-affinity substance. One material gains a negative charge (extra electrons) as a result of this transfer, while the other material gains a positive charge (electron deficit).
3. Separation: The materials are separated following their interaction. Mechanical motion, like rubbing or peeling the materials apart, can help in this separation. The transferred charges on the materials' surfaces are held in place while they separate.

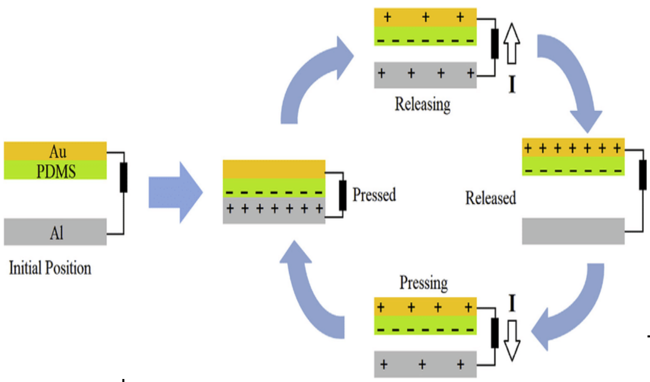


Fig.1: mechanism of triboelectricity

4. <u>Charge Accumulation</u>: The components that have been separated now have opposing charges. Regaining electrons makes a material negatively charged, while losing electrons makes a material positively charged. The potential difference is produced between the materials as a result of the charge separation. One of the most important tools for predicting the direction of electron transfer and the consequent charges on the materials is the triboelectric series, which ranks materials according to their electron affinity.[12]
This fig. is of the triboelectric series and based on this series we can confirm that our philosophy can be true and can be worked.

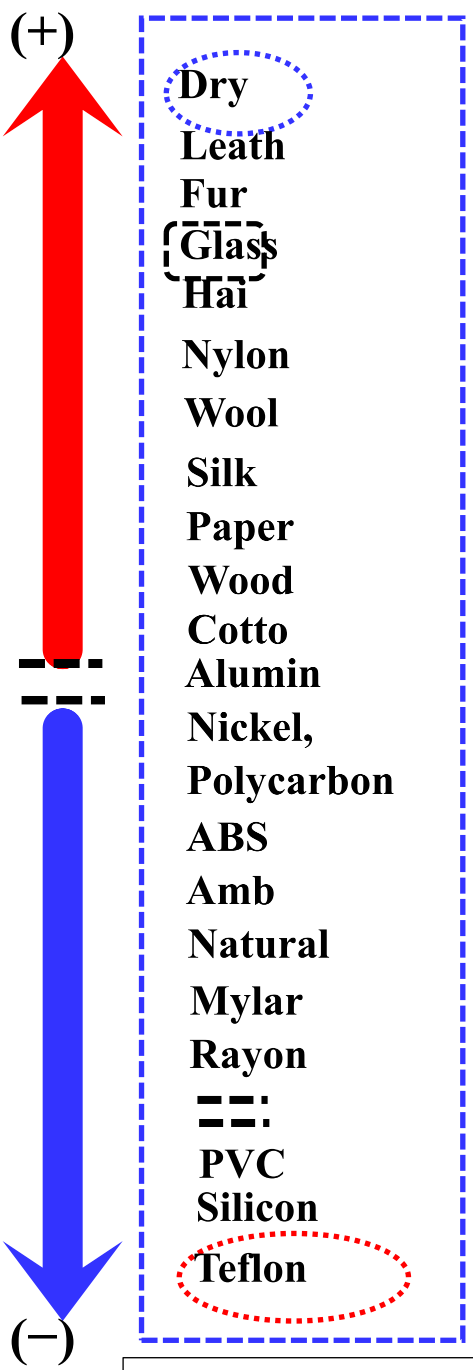


Fig2: Triboelectric series

Smart tire: "Smart tires" are tires that have been outfitted with sensors and other cutting-edge technologies to improve their efficiency, safety, and performance. Tire pressure, temperature, tread wear, and even the state of the road can all be tracked by these sensors. TPMS sensors, which track tire pressure continually, are frequently seen in retail tires. For the sake of safety, fuel economy, and tire longevity, proper tire pressure must be maintained. Tire wear is decreased and accidents are avoided when TPMS warns drivers when tire pressure is low. To track tire temperature in real-time, certain smart tires also come with temperature sensors. Drivers may be able to identify possible problems with this information, such as overloading, underinflation, or high friction, which may result in tire failure.[13,14]

Prospect of human hair in the smart tire: as per the given knowledge natural rubber is majorly sp^2 hybridized and we know that the more the "s" character of the molecule more the electronegativity of the molecule, therefore, natural rubber has an affinity towards electrons and can be said that natural rubber is tribonegative and when human hair is incorporated it is tribopositive in nature i.e. tend to lose an electron, therefore, it may be possible that when both will combine and neutralize each other also when the hair is incorporated into the matrix it may be seen that hair have some piezoelectric properties within it and may enhance the positive nature into the matrix filler sheet. However, it can be said that this triboelectric behavior depends upon external factors like temperature, humidity, and surface conditions.

CHAPTER 2

EXPERIMENTAL DETAILS

Material required

Natural rubber latex(60wt.%), Human hair(collected from different salons), Sodium sulfide solution(0.5M), Zinc Oxide, sulfur, antioxidant(tert-Butylhydroquinone), stearic acid, beaker, glass rod, $AgNO_3$ solution

<u>Instruments required for preparation and characterization </u> – Compression molding machine, Tensile strength machine, Source measurement unit(for tribovoltage measurement), Ball milling, Magnetic stirrer

Characterization tools

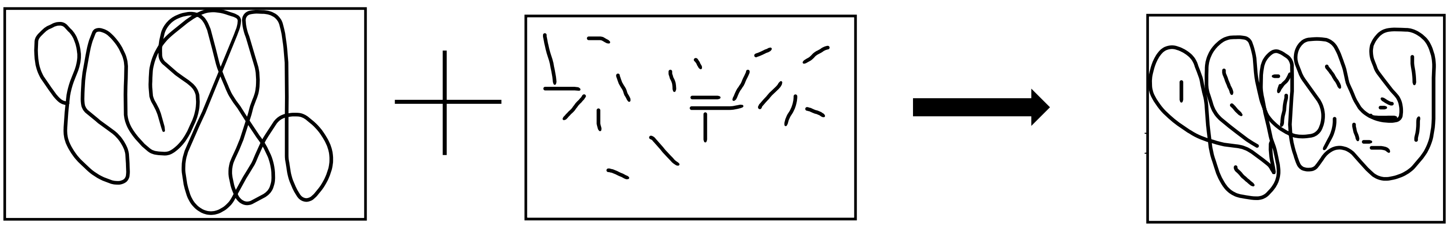
FTIR (Frontier FT-IR/FIR, Perkin Elmer)-
FTIR is used to determine functional groupings and describe the properties of covalent bonds. Organic compound vibrations: stretching and bending assistance in identifying the individual components inside a mixture of components. Provide details regarding the material's structure. recognizing the unidentified pollutants present in industrial samples.

Source measurement multimeter(Keithley)- An instrument used to detect the voltage and current, multimeters are typically utilized for measuring electrical stimuli such as resistance, voltage, and current. Electrical and electronic engineers use it on a regular basis as a diagnostic instrument that combines the functions of an ohmmeter, ammeter, and voltmeter. Etc, in any material that needs to be detected it majorly measures the value of voltage by constant tapping on the object which develops tribovoltage in the material according to the nature of that object it works in two electrodes or even single electrode method that is connected to the meter which detect the voltage can be obtained in the form of graph or even reading.

Compression molding press- A compression molding press is the equipment used in the compression molding process that molds and forms materials at high temperatures and pressures. The frame, which offers structural support, the platen, the mold cavity, the heating system, the pressure system, and the control system, which controls the press's temperature and pressure, are the main parts of the apparatus.

Procedure

Human hair samples were gathered from several salons, and thoroughly washed to remove any dirt, and the quantity of hair was measured which can be immersed in the sodium sulfide solution one at a time. Sodium sulfide solution was of 0.5 M solution, at 500ml of it was taken, and a measured amount of hair was dipped in it for two hours, with stirring for two hours at room temperature to ensure that the solution reached every hair evenly, before taking a look at the hair. Now for filtering the de-keratinized hair from the solution cotton cloth is taken, and we also washed it to ensure that there was no salt residue in the hair. We can observe that the water is clear after repeatedly washing. When this process is finished, we will take the $AgNO_3$ solution and mix it with water to observe if any black precipitate has formed, indicating that the salt has been appropriately removed from the hair. Heat the oven to 65–70°C to dry the de-keratinized hair. Crush them to the required size after they have dried so that their dispersion resembles rubber latex. Human hair and rubber latex are mixed in a magnetic stirrer for two hours while stirring continuously. Note that latex is precipitated with the help of methanol and that precipitate is washed with water till there is no smell of ammonia in that latex and dry it. After properly drying that rubber, add the necessary amounts of stearic acid and zinc oxide. Next, add the compression molding temperature of 60°C. Next, add the necessary amounts of antioxidants and sulfur at 120°C and fold that sheet again compress it in the compression molding making sure that all the additives are added properly after all these steps a sheet will be obtained. The procedure is the same when a certain other amount of human hair from 1 to 5 to 10 to 20phr will be used to create a sheet. Other than the sheet with human hair one more sheet will be prepared as a reference from the testing and characterizing composites for the same, we will now prepare samples for our testing using this prepared sheet.



NR-Matrix **hair** **NR-hair composite**

S.No.	Compounds	Quantity(phr)
1	NATURAL RUBBER(Latex)	100
2	ZINC OXIDE	6
3	STEARIC ACID	2
4	SULFUR	2.25
5	ANTIOXIDANT	1
6	HUMAN HAIR	0, 1, 5, 10, 20

Table 1: formulation of the mixes

CHAPTER 3

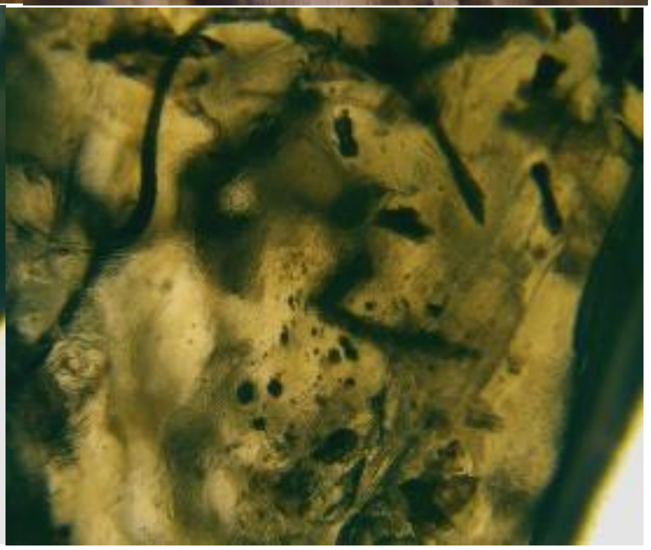
RESULT AND DISCUSSION

Microscopic view of the prepared sample

fig3:

fig4:

fig5:



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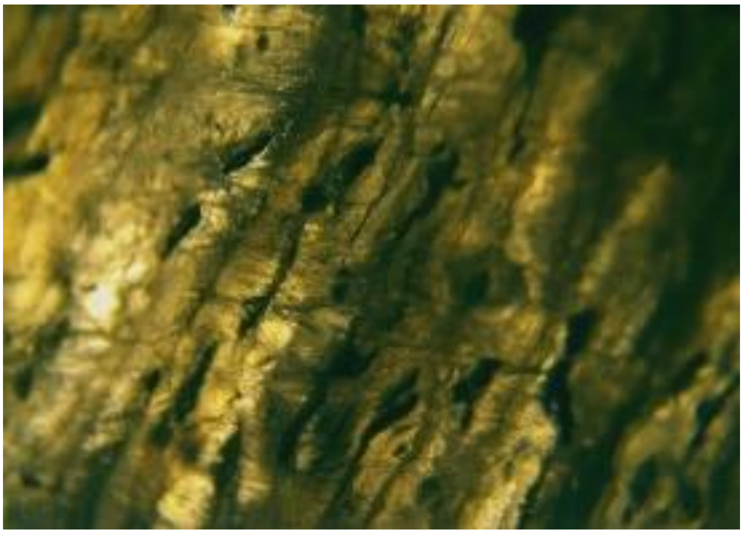
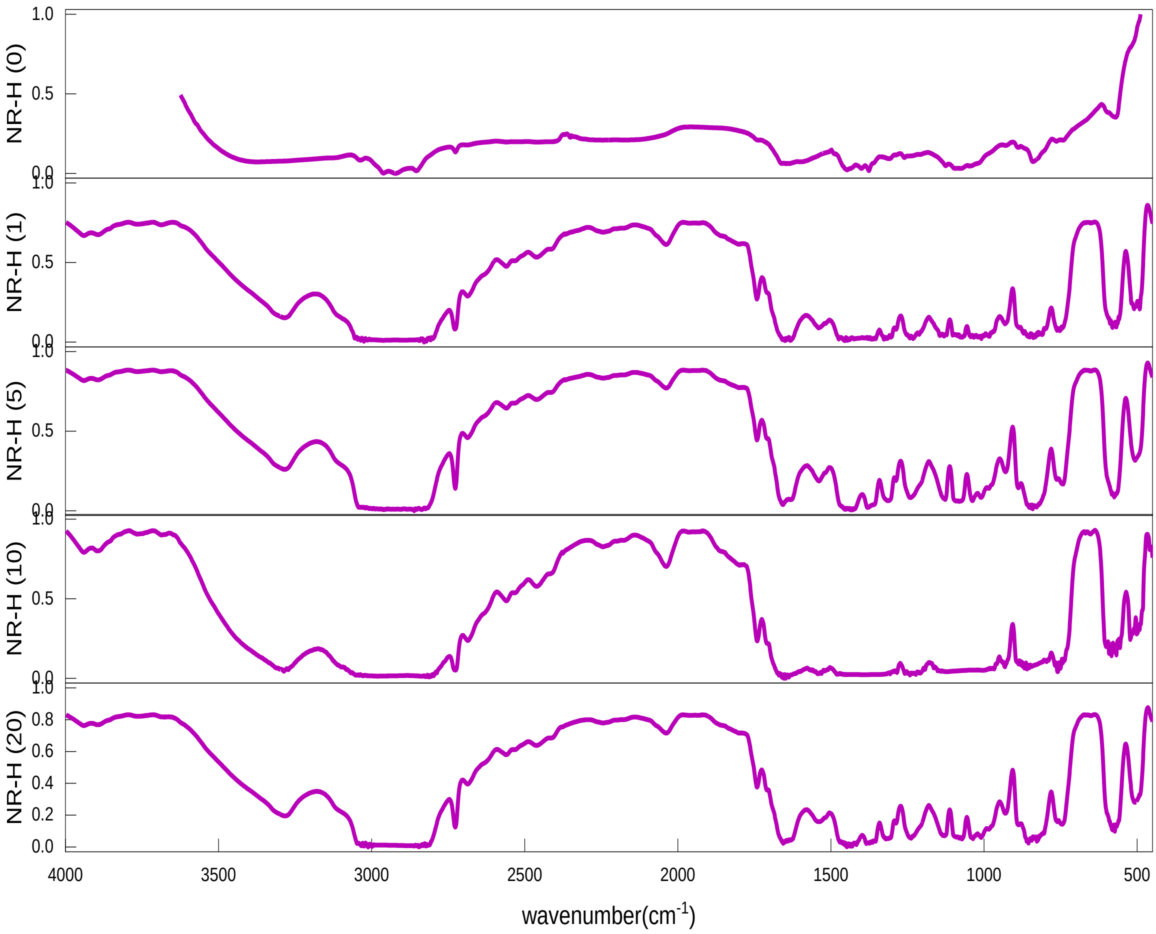


fig7:

Above is the microscopic view of NR(natural rubber)(fig3) and of the prepared composites, fig(4,5,6,7) with 1phr, 5phr, 10phr, and 20phr respectively, it can be observed that in only natural rubber there is no reinforcement added and hence is not observed, when we have started adding the filler into the matrix the rubber particle is not mixed evenly at first of the composites but as we can see at increasing the content of the filler into the natural rubber latex the interaction between the filler and matrix also increases going from 1phr to 20phr we can see in 20phr the human hair are homogenously mixed into the rubber latex due to which the properties can change and the results may vary with this mixing or the interaction of matrix and reinforcing agent but at 10phr it can be seen that the human hair is not thoroughly mixed into the latex.

FTIR of NR and NR composites



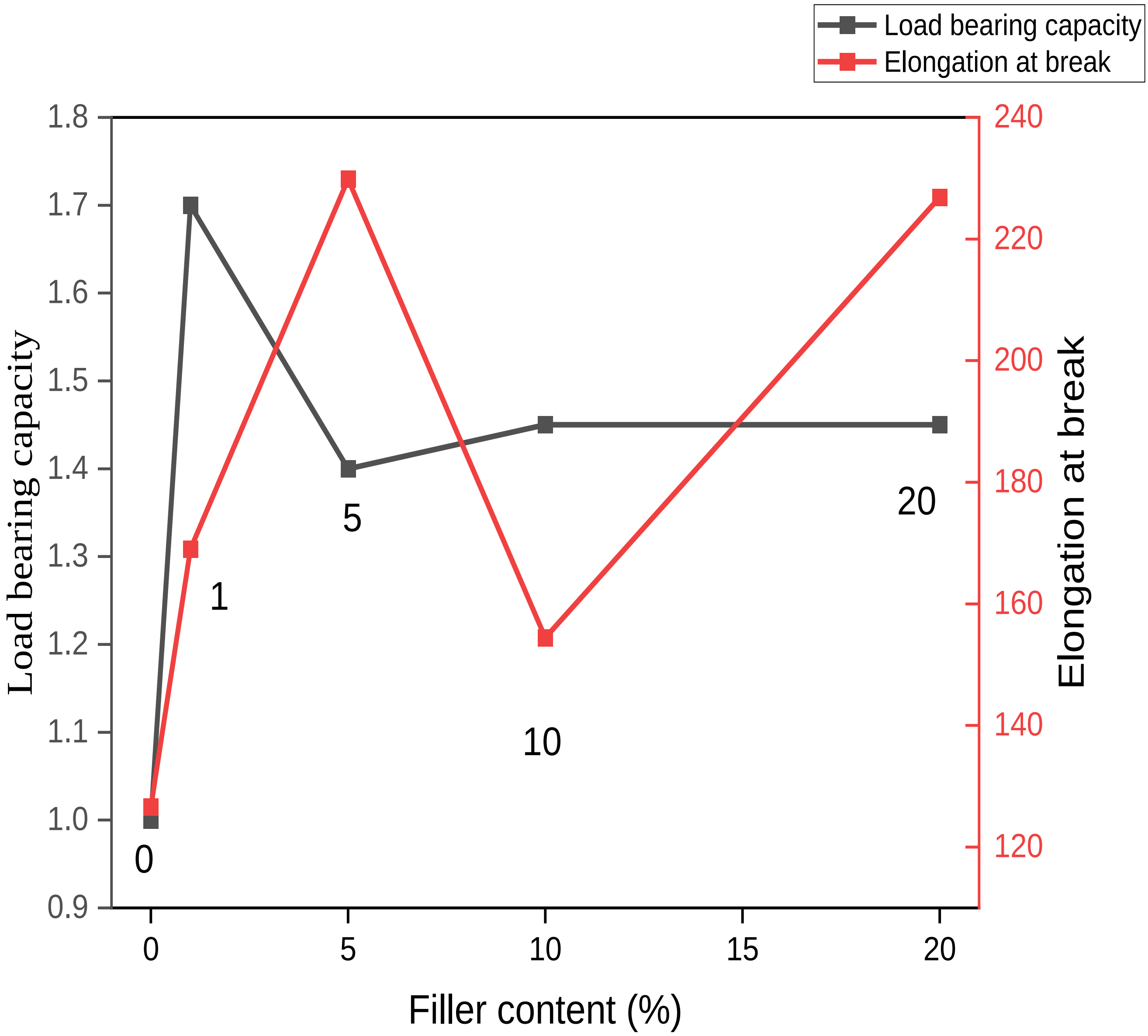
The above graph is of NR, NR-composite, the FTIR of NR and its composite shows peaks which are common in both of them, peaks observed in the above graph can be seen at 3039cm^{-1} is related to C-H stretching which is associated with the alkene, the next peak we can see at 2960cm^{-1} is of methyl (CH3) asymmetric or symmetric modes of vibrations. Next peak can see at 2725cm^{-1} which corresponds to methylene (CH2) asymmetric or symmetric vibration, next peak we can see at 1740 cm^{-1} and 1657cm-1 of C=O stretching coupled with an in-plane bending of the N–H and C–N stretching modes of amide and C=O stretching coupled with C–N stretching and bending deformation of N–H in the amide next peak at 1380 cm^{-1} is of (C-H) stretching at 840 cm^{-1} is related to bending of -C=O of carbonate.

At 2410cm^{-1} and 2552cm^{-1} peak was found in composite, not in the NR can be correlated to stretching of the (S–H) group present in hair.

TENSILE STRENGTH

Filler content	Peak load	Elongation in material
Without filler	1.1kg, 0.9kg,	113.2mm, 140mm
1% filler	1.6kg, 1.8kg	189mm, 149.4mm
5% filler	1.4kg, 1.4kg	224.3mm, 235.4mm
10% filler	1.5kg, 1.4kg	130.6mm, 178.3mm
20% filler	1.3kg,1.6kg	202.2mm, 251.5mm

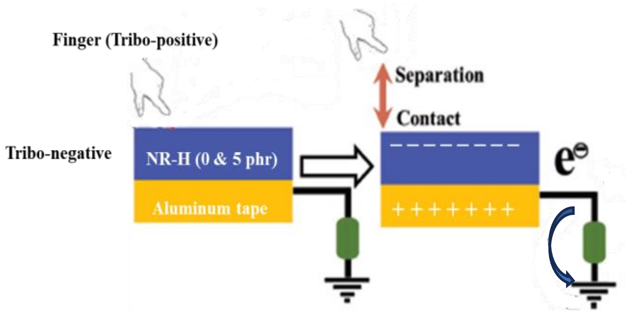
Table2: peak load and elongation of NR and NR- composite readings

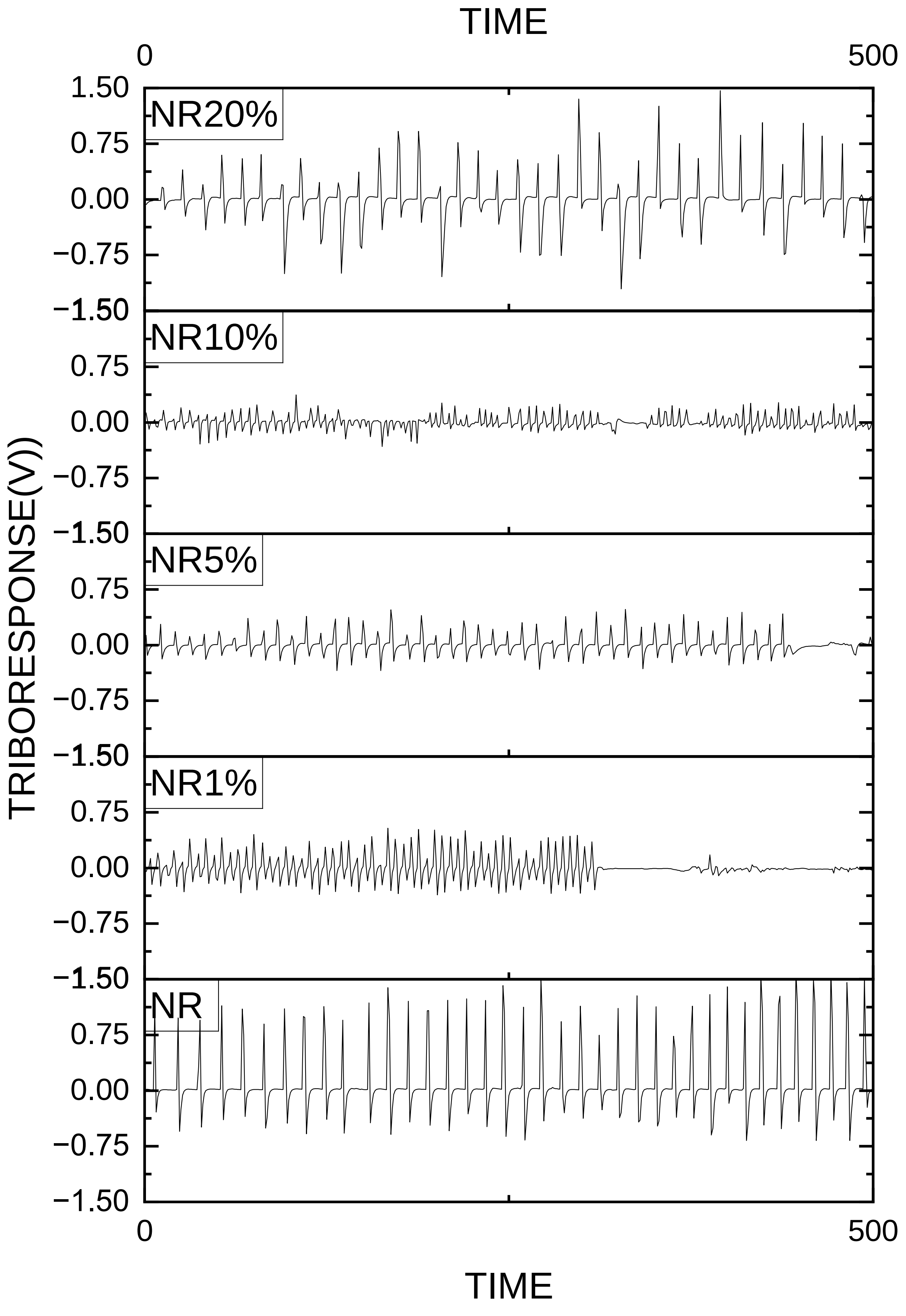


The prepared composite's load-bearing capacity, which is primarily determined by its load-bearing capacity, and the material's elongation, which aids in any material's ability to maintain its shape when subjected to external stress, are the two main factors that can be seen in the tensile strength graph. The load-bearing capacity of the prepared composite reaches its maximum at 1phr, then significantly decreases to 5phr, and then increases again at 10phr and 20phr. As a result, it can be concluded that as the filler content increases, the composite's tensile strength increases. Elongation in the material increases as the content of human hair increases elongation reaches at maximum in rubber material elongation at 5phr. It subsequently decreases at 10phr and increases significantly at 20phr. Considering these two parameters, it can be concluded that human hair is improving the tensile strength of the material.

Triboelectric properties

The triboelectric response of the composites can be measured by the source measurement unit. Since as we know that human hair is tribopositive in nature and rubber is tribonegative, measuring the tribovoltage of natural rubber alone will result in a high voltage reading on the multimeter, depicted in the graph (only NR). Additionally, it can be expected that adding human hair to rubber latex would reduce tribovoltage because it would neutralize the rubber material's charge when it comes into contact with the surface. Similar outcomes were seen as we introduced more human hair to the latex. When we raise the amount to 1phr, the charge in the composite decreases from 1.3V to 0.75V. Similarly, when we increase the amount to 5phr, the charge decreases from 0.75V to 0.5V and finally to 0.3V at 10phr of added human hair. However, there is an abrupt surge in voltage when we increase the filler to 20phr(1.4 V) this may be due to that the biomaterial in this case, human hair, is known to have piezoelectric qualities. As a result, during the separation and contact of the composite and the block, there may be an excess of hair due to which the tribovoltage and piezoelectric properties of hair combine together, resulting in an overall increase in the voltage measured. Thus, it can be concluded that adding human hair as a filler to rubber before applying tires is advantageous and can lessen the accumulated charge in the tires when they make contact with the pavement.




TIME
0
500
1.50
0.75
0.00
−0.75
−1.50
NR20%
NR10%
NR5%
NR1%
NR
TRIBORESPONSE(V))
TIME

Conclusion

From the above experiment, it can be concluded that rubber composite with human hair can be used as a good filler and it can reduce the amount of static charge developed in the NR-based tires.
However, it does not meet the desired property. As we increase the amount of the filler in the composite the developed charge reduction can be observed as well as the increase in the tensile strength is also seen but after 10% there is a significant amount of reduction in the static charge.

Future recommendations

In the future, improving matrix-filler compatibility is crucial to get better performance and the required results. To customize the surface characteristics of fillers, investigate cutting-edge surface modification methods such as chemical grafting, plasma treatment, and functionalization. By optimizing interfacial adhesion, dispersion, and matrix compatibility, these methods can improve the composite's mechanical characteristics and overall performance.

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