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# Physicochemical Modifications on Fibre Reinforced Polymer Composites for Mining Applications

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#### Abstract

Polymer composites are mainly employed as an industrial material because of their chemical and corrosion resistance, especially in mining applications. As a result of the growing demand for biodegradable, ecological, and recyclable materials, organic fibres are widely used as reinforcement in polymer composites in recent years. The challenges arising from polymer composites, like environmental impact, moisture absorption, Thermomechanical property deterioration, lower durability in mining applications are discussed in this review. This work analyses the influence of certain physicochemical modifications on the reinforcement and matrix in polymer composites for mining purpose. This investigation was to understand the effectiveness of physicochemical modifications, specifically cryogenic treatment, on reinforcements and matrix to overcome the above mentioned challenges. This study also highlights the morphological and thermal changes due to the modifications. Results show the effect of these modifications on the composite and its constituents, cryogenic treatment on the organic fibre reinforcements showed increased moisture resistance, higher cellulose composition and mechanical properties, exposing the potential of using organic fibre-reinforced polymer composite in Mining applications.

**Keywords:** Bio-Composites, Bio-Degradability, Corrosion Properties, Mining, Moisture Absorption, Physicochemical Modifications

### **1.0 Introduction**

Mining and Extraction sites conventionally use ferrous and metallic materials for working environment purposes. Interaction of these structures in a chemical environment leads to corrosive reactions and structural failures<sup>1</sup>. Breakthroughs in non-metallic materials for structural applications points out the possibility of fibre-reinforced polymer composites. Chemical-resistant piping and tanks for platinum processing, insulation cladding for chilled water transport, and ventilation ducting are some applications of composite materials in the mining and metallurgy industries<sup>2</sup>. Research communities emphasize organic materials because of the non-biodegradability and ecological challenges of conventional synthetic fibres and polymers<sup>3-5</sup>. Organic reinforcement and polymeric composite materials exhibit high moisture absorption properties, influencing the structural stability of the applications. Physicochemical modifications in the matrix and reinforcement of the composite are essential according to the requirement<sup>6-11</sup>. Adhesion between these two constituents plays a crucial part in the mechanical

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Figure 1. Images of conventional excavation and mining sites with structural components.

properties of the composites. Most structural applications encourage the hydrophobic nature of the materials to ensure the desired durability<sup>12</sup>. Resistance to chemicals and corrosion is necessary for mining and ore extraction environments.

Underground mines have a variety of unfavourable environmental circumstances, like the presence of corrosive substances incompatible with traditional materials like steel. Modern mining and construction industries use Fibre-Reinforced Polymer (FRP) rebar as an adequate substitute for steel rebar to prevent corrosion in structures<sup>13</sup>. The risk of instability after excavation at the entrance of a rock mine is a serious concern for the safety of miners in their job. Figure 1 shows the pictures of structural components in mines. The system to support the excavation wall should be strong enough to withstand loads and flexible sufficient for workability<sup>14,15</sup>. Fibre-Reinforced Shotcrete (FRS) prevents the excavation wall from collapsing because of its ease and agile spraying process<sup>16</sup>. The development of the present study was prompted by obstacles in deep excavation levels, which has resulted in a more profound knowledge of the employed FRS physicomechanical properties and their application for underground excavation works<sup>17</sup>.

Structural strengthening and restoration are critical concerns around the world. Strengthening is necessary due to a rise in the applied load. In most cases, mechanical and thermal properties required raises due to the high applied load. FRPs, because of their lightweight, noncorrosive properties, are used as strengthening systems. Cement-based adhesive allows FRP in applications with particular requirements like specific strength sufficient enough to transfer load, reinforcing fabric penetration, bonding properties for embedded fabrics, compatibility for thermal and chemical conditions, excellent thermal and fire resistance, workability, and acceptance of the environment<sup>18</sup>.

### 2.0 Physiochemical Modifications

The NaOH treatment of natural fibres is the commonly used chemical treatment to reinforce polymers<sup>19</sup>. Using



**Figure 2.** Demonstration of cryogenic treatment on a sample.



**Figure 3.** Corona discharge instrument setup. (a) Control unit. (b) Equipment head. (c) Discharging tip. (d) Treatment process.<sup>24</sup>

natural fibre modifications, chemically or physically, reduces the moisture absorption of lignocellulosic reinforcements and thus increases interface bonding. Cryogenic treatment is a technique in which fibres are treated at cryogenic temperatures (less than -150 °C)<sup>19</sup>. Materials exhibit improved thermal stability and physio-mechanical changes at these low temperatures. Figure 2 demonstrates the cryogenic treatment on a sample.

Cold plasmas are formed by the electric discharge from the mixture of charged ions, electrons, and protons, in low-pressure gases. Some device parameters heavily influence their composition and properties<sup>20</sup>. Chemical functionalization can also occur as a result of the involvement of charged groups during treatment for chemically reactive plasmas after treatment when exposed to the environment. Crosslinking of excited surface species also modifies surface structure in polymers<sup>21</sup>.

In a closed cell, positive corona discharges are ignited using plane electrodes. Tungsten and copper are used to create electrodes. The power discharge was made using a high pulsed high-voltage source<sup>22</sup>. Figure 3 shows the components required and the working of the equipment. Corona discharge plasma functions well at ambient conditions. Corona treatment is an environmentally friendly and affordable method of modifying carbonbased synthetic reinforcements from an industrial standpoint<sup>23</sup>.

### 3.0 Advances in Surface Treatment of Fiber Composites

### 3.1 Corona Discharge Treatment (CDT)

F. Oudrhiri Hassani *et al.*,<sup>25</sup> studied the influence of CDT on the surface and mechanical traits of Aloe Vera fibres. When exposed to plasma, the therapies caused alterations in the fibres. Mechanical characterizations of the treated fibres revealed a drop in tensile properties. The fibre composition and surface have been altered, resulting in this drop. The morphology changes on the surface and deterioration of fibres caused by the mechanism of etching using corona were seen in scanning electron microscopy. The lignin, hemicellulose, and moisture content of untreated and treated Aloe Vera fibres are reduced, according to FTIR transmission spectra. This research found that the modification can alter the surface morphology of fibres in more ways.

Thamirys Andrade Lopes *et al.*,<sup>26</sup> a 30-second corona treatment increased maximum moisture permeability due to the pores formation on the surface leading to increased water absorption within the films made of eucalyptus and pinus wood, as investigated here, potentially enhancing ink penetration. With increasing discharge time, corona discharge encouraged a gain in tensile strength but a significant fall in Young's modulus. Because of their greater crystalline index and nanofibril diameters, pinus nano-fibril sheets performed better than eucalyptus nano-fibril sheets in tests. Water vapour permeability of 13.1 and 14.2 g mm per unit pressure in a day for a unit sectionalarea was discovered for the eucalyptus and pinus sheets, respectively, with the optimal corona treatment time of 30 s.

Hamid Reza Gholshan Tafti *et al.*,<sup>23</sup> surface modification on the filler using Corona treatment successfully enhanced interfacial bonding between CNT and polymer, indicating that corona treatment improves interfacial interaction and improves the homogeneous distribution of the reinforcements in the polymer. The modification reduced the filler agglomeration, according to ATR-FTIR data. TGA analysis revealed that corona-modified fillers decompose at a greater temperature. Furthermore, with changed fillers, the tan d curves of CNT shifted to increased values.

Vitor Cesar Louzi *et al.*,<sup>27</sup> Corona discharge was employed to change the morphological and physicchemical properties of PP, PET, and PA-6 monofilament surfaces. Since this treatment is due to the excitement in polar groups on a filament surface, the surface free energy increased. The groups involving oxygen, such as -OH, -C=O, -COOH, and -NCO, enhanced their water absorption capacity, according to FTIR/ATR data. The surface morphologies of the surfaces changed according to SEM examination.

Xinyu Luan, Zhiqing Song *et al.*,<sup>28</sup> showed that modifying the chemical composition of alfalfa seeds treated with AC CDT can improve their hydrophilicity. With the increased discharge voltage, the epidermis of the seed degrades and fractures the coated seed surface, improving water absorption ability. The physical etching of alfalfa seeds treated with AC CDT by ion wind is successfully reduced by the petri dish cover, and the concentration of RAs is low.

### 3.2 Cold Plasma Treatment (CPT)

WU Mengjin *et al.*,<sup>29</sup> cold plasma was found to increase the surface performance of the fibres, functional group and surface roughness, stimulate fibre surface activity and significantly increase fibre-matrix interface bonding. The environmental sustainability of this treatment is advantageous and will improve the plasma treatment composite material industrial production.

Murilo J.P. Macedo *et al.*,<sup>30</sup> found that the CPT improved the wettability of the fibres. Surface erosion



**Figure 4.** The infrared spectra and some characteristic absorption band peaks.<sup>31</sup>

caused by CPT was discovered to bring out the hydrophobic groups on the fibre's surface, allowing liquids like oils to penetrate. Finally, plasma treatment was a viable method for surface activation of kapok fibres, resulting in improved matrix/filler adhesion. Changes in characteristic absorption bands were seen in Fourier-Transform Infrared (FTIR) spectra in Figure 4, showing that change in the chemical composition of the fibre. Surface roughness increased as measured by SEM. Furthermore, the ability to absorb water was considerably impacted, but the capacity to absorb oil rose. Thermo-Gravimetric Analysis (TGA) revealed that the plasma treatment affected the thermal behaviour marginally and activated the fibre surface.

S. Maraisa *et al.*,<sup>31</sup> examined the effects of CPT or autoclave treatments on the parametric characteristics of composite films. According to studies, plasma treatment of flax fibres reduces the permeability coefficient P.

With autoclave treatment, its moisture resistance is amplified. CPT promotes fibre and matrix interface bonding, whereas autoclave treatment decreases the water solubility in fibres. All of these findings support the idea of substituting glass fibres with flax fibres after this treatment because the stiffness and hydrophobic nature of the fibres is improved. It may be concluded that if the system is intended for applications with high stiffness requirements, treatments are necessary. The thermal degradation throughout the range of 20-30 % of decomposition has changed to second-order reaction at a temperature range of 280-315 °C. The plasma-treated fibres showed first-order reactions in 10% and over 40-80 % conversion.

### 3.3 Cryogenic Treatment (CT)

Lijin Thomas *et al.*,<sup>32</sup> observed CT of hemp fibres reduced its hydrophilic behaviour. The fabric's thermal stability has



Figure 5. Comparison of untreated and cryogenic treated hemp fabric using DTG graph<sup>33</sup>.

increased significantly from 436 °C to 447 °C, as shown in Figure 5. Pectin has improved physical properties due to increased extensive constituents such as cellulose and a decrease in hemicellulose. After cryogenic treatment, the enthalpy of degradation and specific heat capacity of hemp fabric was significantly decreased. Duration of 10 minutes and 300 minutes Deep CT hemp fabric outperforms untreated and 60-minute CT hemp fabric in terms of thermal properties. These findings expose hemp fabric as an environmentally friendly material with superior thermal stability and mechanical properties to conventional materials for structural applications.

Myung-GonKim et al.,33 studied the feasibility of using carbon nanotubes as the filler in CFRP composites for lowtemperature applications. The amino-functionalization process increased the interfacial bonding between the nanomaterial and the polymer. The increase in strength is primarily due to increased energy dissipation to break CNTs rather than pull out during loading. Two types of UD prepregs were created to investigate the fracture properties and functionalize effect of a composite at low temperatures for CNT-reinforcing CFRP. CFRP with FCNT exhibited the highest fracture toughness compared to other specimens at low temperatures. It was also discovered that the CFRP with FCNT AE signals had higher energy levels than the control specimens. This attributes to the release of higher strain energy used to break CNT and to propagate the crack.

YiqinShao *et al.*,<sup>34</sup> influence of CT on the properties of a CNT with FRP composite is studied using a regulated cooling process with a gradual cooling rate. Although the treatment unaffected cryo-treated fibres' mechanical properties, the Weibull distribution for CNT fibre strengths shows fewer changes. The electrical resistance measurement for the cryogenically treated sample displayed an increased rate of change in electrical resistance with strain, indicating improved interfacial fibre and matrix interaction. Furthermore, the CT Improves Interlaminar Shear Strength (ILSS) by 31% due to the differential thermal shrinkage for the CNT fibre and polymer.

### 3.4 Chemical Treatment

Shahrooz Amidi *et al.*,<sup>35</sup> investigated the influence of conditioning methods and NaOH treatment on the residual fracture toughness at the interface of FRP and



**Figure 6.** Comparison of untreated and NaOH treated hemp fabric using FTIR plot<sup>33</sup>.

concrete due to the moisture content. The link between IRH and fracture toughness of the interface is required to understand the mechanism and quantify the degradation due to moisture in FRP and concrete interface. The proposed new conditioning approach does present a new direction for improving specimen design and conditioning methods to achieve a more homogeneous water distribution along the interface. Additionally, using a silane coupling agent improves the residual fracture toughness of a water-attacked contact.

Jun-Jie Zeng et al.,36 studied durability assessment of Polyethenenaphthalate (PEN) FRP and Polyethene terephthalate (PET) FRP composites based on ageing in NaOH solution at different temperatures. This study tested the durability of FRP sheets after ageing in a NaOH solution at different temperatures. SEM was used to examine the microstructure of PEN FRP sheets. The results reveal that after ageing at various temperatures, the young modulus of FRP sheets' first and second linear components change only slightly. Based on the values of the parameters obtained from this study, the Arrhenius equation was used to analyze the long-term degradation of FRP sheets. It was found that the test parameters largely influence the failure mode. In a NaOH solution immersion environment, the durability of PEN FRP is far superior to the typical GFRP composites.

Gao Maa *et al.*,<sup>37</sup> investigated plant and mineral-based Natural Fibre-Reinforced Polymer (NFRP) as alternatives to traditional GFRP composites due to their environmental, technological, and economic benefits. Four composite specimens such as raw jute fibre reinforced with epoxy, alkali-treated jute fibre reinforced with epoxy, silanetreated jute fibre reinforced with epoxy, and natural basalt fibre reinforced with epoxy, were produced and aged for 180 days under diverse conditions. As the temperature of the water and alkali solutions increased, the tensile strength of all four types of composites decreased. The alkali solution reduced the strength of these four types of composites more than the water solution reduced the strength of the equivalent composite. Furthermore, the loss in tensile strength was greater than the reduction in Young's modulus. SEM measurements confirmed the loss of interfacial characteristics in these composites under various ageing situations. Silane solution influences the functional groups like cellulose and hemicellulose C-H bonding leading to deteriorating mechanical properties, the FTIR plot shown in Figure 6 illustrates the change in cellulose bonding in hemp fibres after silane treatment.

# 4.0 Future Scope and Challenges

Direct cryogenic treatment depleted the mechanical behaviour of most naturally Fiber Reinforced Composites. This problem can be solved by using suitable additives. Future research will focus on predicting the residual strength of environmentally aged FRP/steel joints that could benefit from the methods presented in this paper. It is accomplished by employing FE analysis techniques such as cohesive zone modelling to account for adhesive and FRP composite moisture and time-dependent fracture properties. Developing efficient test methodologies for characterizing the environmental-dependent cohesive laws of adhesives and FRPs is one of the future research needs in this area.

Researchers worldwide face several challenges in developing fully green bio-composites in which both the matrices and reinforcement are derived from organic resources. Furthermore, Poor interfacial bonding is a factor to consider when fabricating cellulose-based NFRCs due to the hydrophilic nature of plant-based natural fibres and the hydrophobicity of the polymer matrices. Because of the low interfacial interaction, NFRCs cannot provide the desired mechanical properties, despite delivering the most sought-after biodegradability properties and significantly less expensive than synthetic fibres. Other notable challenges in producing NFRCs include cellulosic natural fibres with lower thermal stability, high moisture absorption, and less wettability. Furthermore, it is not always possible to ensure that natural fibres have similar properties because their properties vary depending on weather, season, cultivation conditions, and production processing.

### 5.0 Conclusion

This work was attempted to provide insights and information that could be useful for future research to develop valuable polymer composite from organic and synthetic fibers for mining applications, following are the observations form the study.

- Surface irregularities lead to higher mechanical properties, moisture absorption in fibre due to cryogenic treatment, leading to increase in composite durability.
- Pre-alkalization allowed non-cellulosic substances to be removed and the fibril surface exposed, resulting in improved wettability, indicating higher hydrophobic behaviour.
- Influence of Chemical modifications affected the primary and secondary layers of the straw, leading to improved hydrophilic behaviour and Thermal stability has improved.
- Cold plasma may be a viable method for improving fibre-matrix adhesion in biodegradable polymer composites.
- Autoclave treatment improves water permeability, while plasma treatment improves mechanical properties in reinforced composites.
- The bulk thermal characteristics of the materials are not affected by corona discharge treatment.

Enlisted effects from physiochemical modifications shows the possibility to overcome the challenges followed by polymer composites used in mining applications, also keeping structural, biodegradable, and corrosion resistance requirements in emphasis.

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