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Influence of cryogenic and chemical treatment on thermal and physical properties of hemp fabric

Lijin Thomas^{1,2,4}, M Mubarak Ali^{1,2}, V N Aju Kumar^{1,2} and Sabu Thomas³

¹APJ Abdul Kalam Technological University, Kerala, India

²Department of Mechanical Engineering, TKM College of Engineering, Kollam, Kerala - 691005, India

²School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala - 686560, India

⁴E-mail: lijinthomas3@tkmce.ac.in

Abstract. Conventional synthetic materials in engineering applications are imprinting our ecosystem with non-biodegradable wastes. Environmental awareness throughout the world has influenced materials design and selection, which is leading to orientation from synthetic to biodegradable materials. Efforts are put to improve the properties of existing natural materials for engineering applications. In this study hemp fabric was subjected to alkalization, maleic anhydride treatment and cryogenic treatment, to improve the fabric's physiochemical properties. Differential scanning calorimetry (DSC), Thermo gravimetric analysis (TGA), and Differential Thermo gravimetric Analysis (DTG) were used to investigate the changes in thermal behaviour of untreated and treated fabric. Physical properties such as functional groups of fabrics were studied and compared with Fourier Transform Infrared Spectroscopy (FTIR). Alkalization and maleic anhydride treatment on fabric have substantially increased the number of hydrogen bonding in cellulose, which lead to increase in stiffness of the fabric. Thermal stability of hemp fabric has increased significantly with cryogenic treatment. An increase in the cellulose composition after the cryogenic treatment shows better physical properties. These observations give hemp fibbers wide range of opportunity to be part of engineering applications with thermal stability, stiffness, and eco-friendly requirements.

1. Introduction

Natural fibres have gained popularity within the structural manufacturing industries, especially as a popular reinforcement for (FRP) fiber reinforced polymer composite. Because of its properties like low cost, considerable mechanical properties, non-abrasive, high specific strength, bio-degradable, and eco-friendly characteristics. Advanced materials like natural composites are introduced with recyclability, ease of manufacturing makes it a better choice than the conventional synthetic composites[1]. Environmental awareness within the engineering community have changed the approach on material selection and application[2]. Hemp fibres are mostly found in northern hemisphere, many species of cannabis sativa plant are cultivated for industrial applications. The advantage of this material is its rate of growth across the world, hence this fibre is predominantly used in textile industries and is cost effective compared to synthetic fibres[3]. In natural fibres, cellulose constitute as a major structural component. Characteristic properties of the fibres are determined by the composition of cellulose, lignin and hemicellulose. There are 6 main components within hemp fibres which are as follows cellulose, hemicellulose, lignin, pectin, waxes and minerals [4].



The physiochemical modifications of natural fibres are by chemical and thermal treatments. It can enhance the hydrophobic nature in lingo-cellulosic fibres, improve adhesion by increase in interface bonding and enhance thermal properties[5]. Most commonly used chemical treatment on lingo-cellulosic fibre is the alkaline treatments[6]. Due to alkalization swelling of these fibres occurs and the crystalline structure of the cellulose relaxes. Native cellulose that shows a monoclinic crystalline lattice of cellulose-I, will change to different polymorphic forms, i.e. alkaline cellulose and cellulose II[7]. Researchers points out improved thermal stability with long-term resistance to moisture in natural fibres with alkaline treatment. Anhydrous treatment comprises of drenching the fibres in a solution of maleic anhydride in toluene or xylene to impregnate and react with hydroxyl groups on the fibre surface[8]. It has been appeared that maleic anhydride (MA) can be utilized as an additive during processing or grafting the fibre. It improves the tensile strength, bending strength, stiffness, and impact strength of the composites[9]. A cryogenic treatment is a method of treating fibres at cryogenic temperatures (below $-150\text{ }^{\circ}\text{C}$). At this low temperature conditions, materials showcase increased surface roughness, thermal stability, and some physiochemical changes. This paper investigates the impact of chemical and cryogenic treatment on physiochemical properties of hemp fabric.

2. Methodology

The hemp fabric was subjected to alkalization and maleic anhydrous treatment. Untreated and treated fabric was analyzed with Fourier Transform Infrared Spectroscopy (FTIR) for physical characteristics. Secondly the hemp fabric is treated with cryogenic liquid for different time durations. Thermal analysis was conducted with Differential scanning calorimetry (DSC), Thermo gravimetric analysis (TGA), and Differential Thermo gravimetric Analysis (DTG). Results of cryogenic treatment of untreated and treated hemp fabric were analyzed and compared.

2.1 Pre alkalization and maleic anhydrous treatment

Hemp fabric was dipped into NaOH (5% wt.) solution for 2 hours at ambient temperature. Then the fabric was washed with distilled water and dried in an air oven at $70\text{ }^{\circ}\text{C}$. Pre-alkalized fabric was soaked in a solution of maleic anhydride (10% wt.) in acetone for 2 hours at $60\text{ }^{\circ}\text{C}$. The treated fabric was washed with fresh water (ph-7). At last, the fabric was dried in an air oven at $70\text{ }^{\circ}\text{C}$.

2.2 Cryogenic treatment

Hemp fabric is cut into $10*10\text{cm}^2$ sheets for the treatment. Deep cryogenic treatment is conducted on 3 samples with different immersion time duration i.e. 10, 60 and 300 minutes. Liquid nitrogen (N_2) is the liquid coolant used for the treatment. The coolant is stored at 77K inside a partially thermal insulated Thermocol box.

3. Results and Analysis

Physiochemical characterization of chemical and cryogenic treated hemp fabric was conducted with Differential scanning calorimetry (DSC), Thermo gravimetric analysis (TGA), Differential Thermo gravimetric Analysis (DTG), and Fourier Transform Infrared Spectroscopy (FTIR) analysis. The experimental results of treated with untreated fabric were compared.

3.1 Comparison of untreated and alkalized hemp fabric

FTIR spectroscopic analysis on hemp fabric with Alkali pre-treatment is represented in Figure 1. Increased hydrogen bonding is observed due to addition of the hydroxyl groups, from reaction with sodium hydroxide. This is evident by the increase in the absorbance peaks between the range 3000 and 3600 cm^{-1} according to Beer–Lambert law. The two peaks at 2900 and 2968 cm^{-1} were due to the presence of asymmetric and symmetric methyl and methylene stretching groups, which has increased with NaOH treatment. Absorbance peaks near 1707 cm^{-1} in the FTIR spectrum, which corresponds to the wave numbers of carboxylic ester ($\text{C}=\text{O}$) in pectin and waxes, spectrum indicates reduction of these constituents due to NaOH treatment. The absorption peaks from 1050 to 1090 cm^{-1} was due to

C=O stretching vibration in hemicellulose [10]. Figure 1 shows the broadening of this band and increase in vibration absorbance for treated hemp fabric compared to untreated fabric.

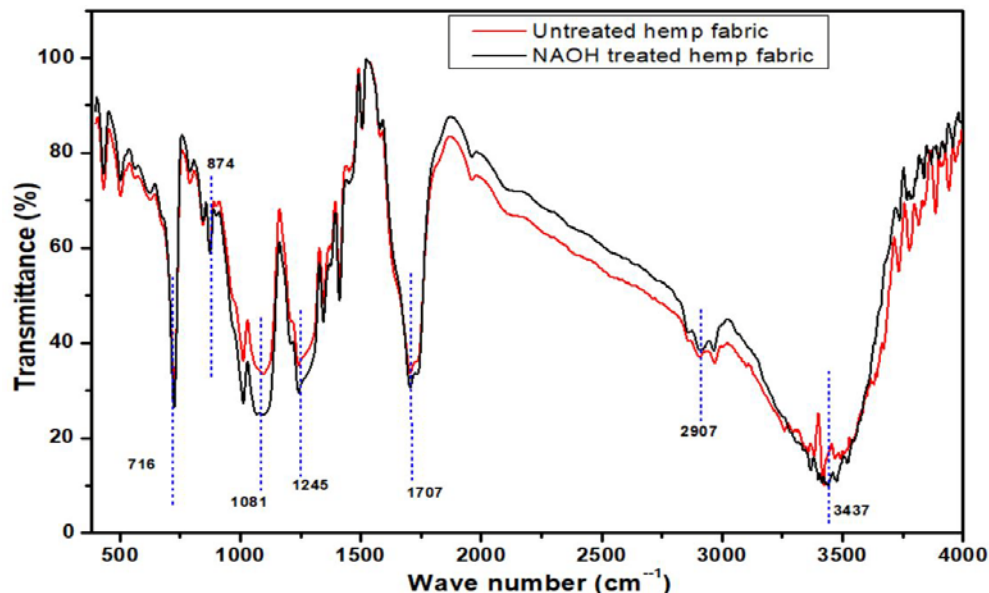


Figure 1. FTIR spectrum of untreated hemp fabric and NaOH treated hemp fabric

3.2 Comparison of untreated and maleic anhydrous treated hemp fabric

Absorbance band in treated material is higher than untreated material, indicating the increase in number of hydrogen bonds due to maleic anhydrous treatment, according to Beer–Lambert law. Wave number from 3000 cm^{-1} to 3700 cm^{-1} represents OH stretching vibration regions in the cellulose [11]. Vibration absorption peak at 2904 cm^{-1} were related to asymmetric and symmetric methyl and methylene stretching groups, it also shows the presence of lignin in the fabric [12]. This peak in Figure 2 was shifted to 2918 cm^{-1} , after maleic anhydrous treatment, which indicates higher degree of hydrogen bonding for treated fabric. Peak at 1592 cm^{-1} of untreated fabric shows the presence of C=C aromatic symmetrical stretching, which is not observed with treated hemp fabric. Peak at 1445 cm^{-1} shows HCH and OCH in-plane bending vibration and CH_2 symmetric bending of cellulose and hemicellulose. Broadening of this band reflect more disordered structure which is not visible in treated fabric. Absorption band at 608 cm^{-1} of treated fabric represent C-OH out-of-plane bending and OH out-of-phase bending of cellulose while no peak in untreated fabric at 608 cm^{-1} .

Two curves in Figure 3 trace the same path, which indicates both the specimens possess similar decomposition with increase in temperature. Decomposition of the material occurred in four distinct stages [13]. In the primary stage of degradation, the moisture in the fabric was evaporated at $50\text{--}150^\circ\text{C}$, which leads to a mass degradation of approximately 1.12% and 2.43% for untreated hemp fabric and chemical treated hemp fabric respectively. Increase in degradation mass, results due to the decrease in hydrophobicity due to chemical treatment in hemp fabric. Secondary stage shows the loss of hemicellulose and pectin at $250\text{--}380^\circ\text{C}$, with corresponding degradation of 27.3% and 26.2% for untreated and chemical treated hemp fabric respectively. Tertiary stage lies between $380\text{--}480^\circ\text{C}$, this represents comprehensive decomposition of the constituent's cellulose and lignin in the fabric. The TGA curve dropped sharply with a mass degradation is 52.7% and 53.7% for untreated and chemical treated hemp fabric respectively. Fourth stage which is above 380°C is from the residual burning with oxidative decomposition.

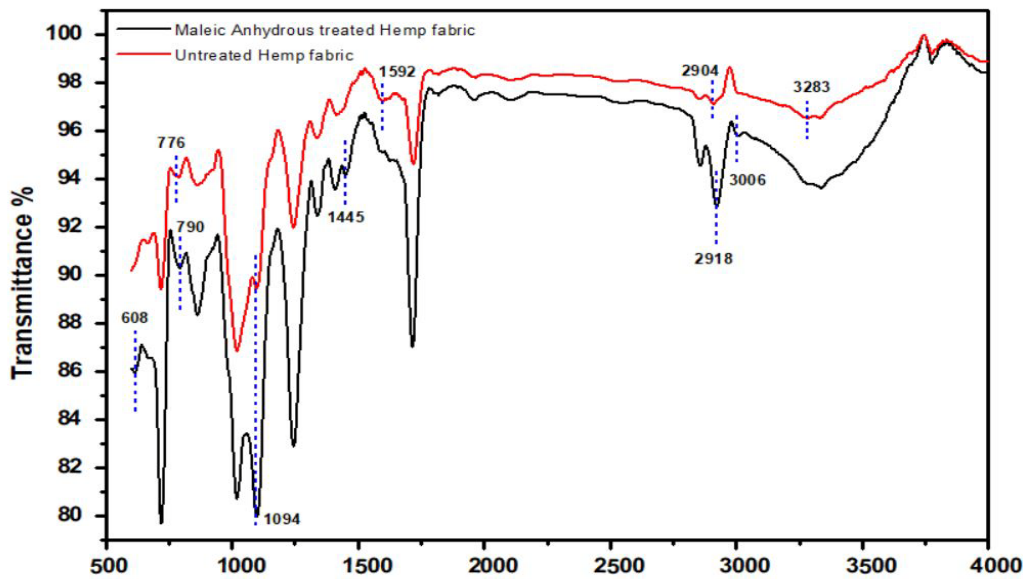


Figure 2. FTIR spectrum of untreated and maleic anhydrous treated hemp fabric

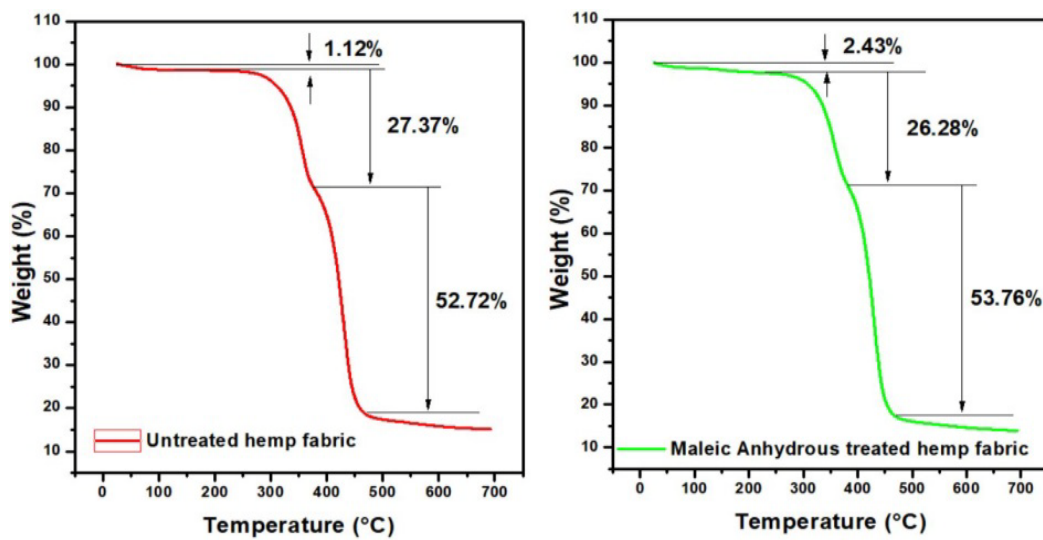


Figure 3. TGA curves of untreated and Maleic Anhydrous treated hemp fabric

The peaks in the curve from Figure 4 represent the maximum degradation of the material at the shown temperature range. Secondary temperature peak shows the degradation of hemicellulose and pectin. Chemical treated hemp fabric shows peak at 358°C which is higher than untreated hemp fabric. Indicating chemical treatment on the fabric is increasing the stability of hemicellulose or pectin [14]. Secondary stage degradation of chemical treated hemp fabric shows less derivative weight compared to the raw hemp fabric which corresponds to an increase in derivative weight for chemical treated hemp fabric compared to raw hemp fabric at tertiary stage degradation. This plot confirms that Maleic anhydrous treatment in hemp fabric results in reduced hemicellulose and lignin content, which leads to increase in cellulose content [15].

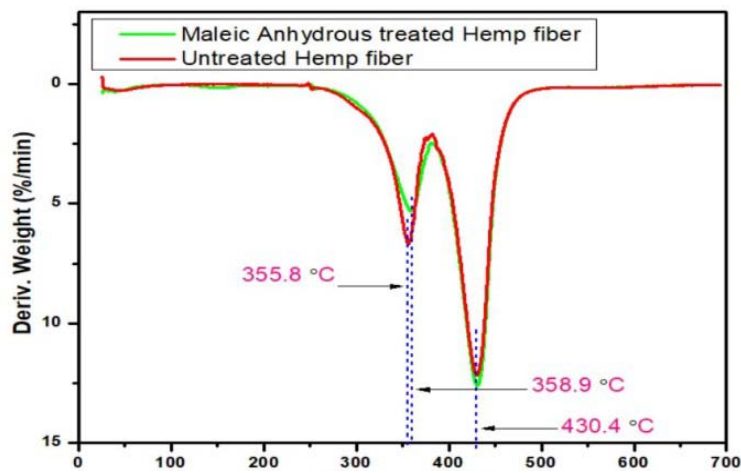


Figure 4. DTG curves of untreated and Maleic Anhydrous Treated hemp fabric

3.3 Comparison of untreated and cryogenic treated hemp fabric

Thermal stability has improved significantly with cryogenic treatment on hemp fabric as shown in Figure 5. The secondary stage derivative weight of untreated hemp fabric 31.19% is higher than 10 minute, 60 minute, and 300 minute cryogenic treated hemp fabric which is 28%, 24%, and 26% respectively. Untreated hemp fabric shows tertiary stage mass loss of 54.11% which is smaller than 10 minute, 60 minute, and 300 minute cryogenic treated hemp fabric mass loss which is 55.16%, 57.6%, and 54.38% respectively. This represents decrease in hemicellulose and lignin with increase in cellulose content due to cryogenic treatment on hemp fabric [10].

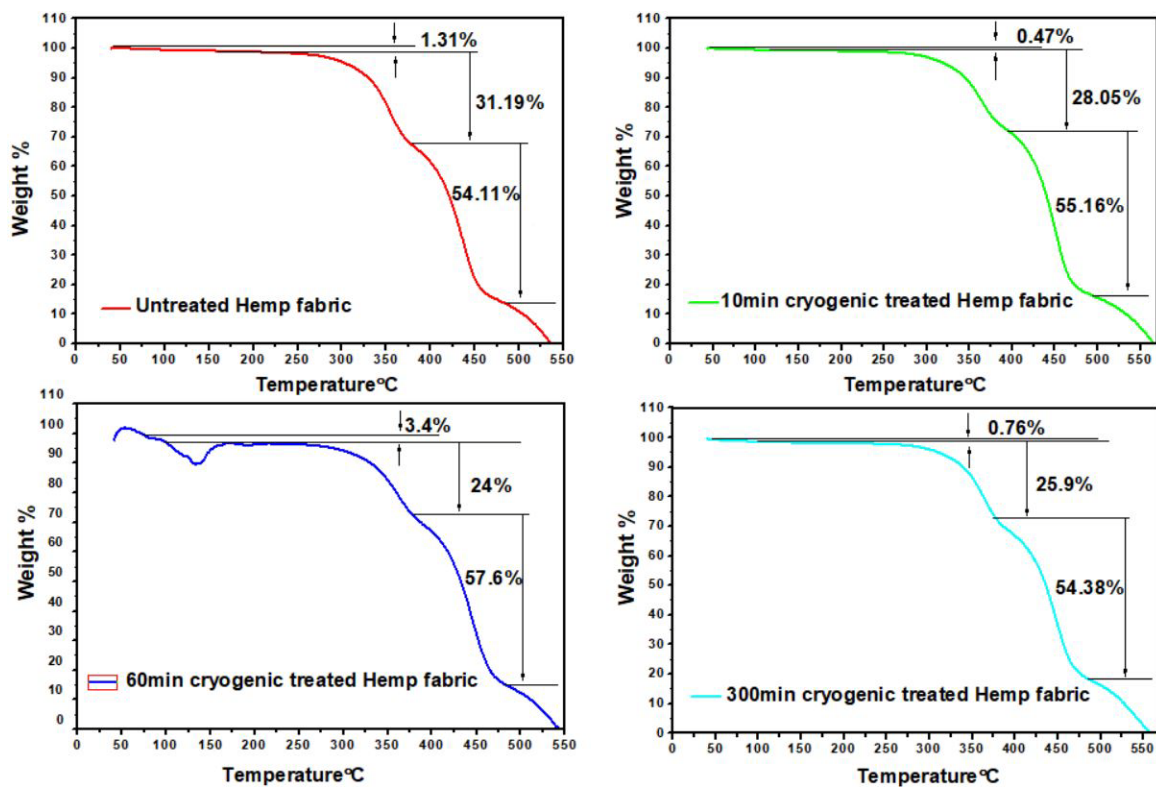


Figure 5. TGA curves of untreated and cryogenic treated hemp fabric

Untreated hemp fabric shows a tertiary stage peak at 435.9°C, while the cryogenic treated fabric's tertiary stage peaks were at 44°C, 445.4°C, and 447°C for 10, 60, and 300 minutes respectively as shown in Figure 6. Secondary stage peak also had a significant increase due to the cryogenic treatment on the fabric. These two stages help understand significant thermal behaviour of a material. Decomposition of core constituents (Hemicellulose, Cellulose, Lignin etc.) of a natural fabric happened at these stages. Decomposition temperature of cryogenic treated fabric is higher compared to untreated fabric, hence the thermal stability of hemp fabric has improved by cryogenic treatment at 77°K [14].

At initial stage of degradation i.e. below 100°C the moisture gets evaporated, evaporation of water is an endothermic process [16]. Studies have observed that, constituent like lignin in natural fibres degrades at temperature near 200°C whereas hemicellulose and α -cellulose degrade at higher temperatures[17]. Untreated hemp fabric showed, degradation of lignin, hemicelluloses and α -cellulose at temperature range of 350-450°C, the exothermic peak which is observed in DSC curve (Figure 7) for untreated fabric at this temperature range represents the degradation. Whereas all cryogenic treated fabrics displayed exothermic peak at temperature range 360-475°C. This was probably due to the partial removal of lignin, and hemicelluloses from the fabric. As a result, thermal stability of the treated fabric was improved when compared to the untreated fabric. Heat flow from the sample to sink for increasing the temperature of the sample and reference with constant temperature difference, has significantly reduced in cryogenic treated hemp fabric. While leading to lower exothermic reaction which shows improved thermal stability. Calculated values of enthalpy and specific heat capacity from untreated and cryogenic treated hemp fabric DSC is enlisted in the Table 1. Experimental data shows lower enthalpy for cryogenic treated hemp fabric compared to untreated hemp fabric.

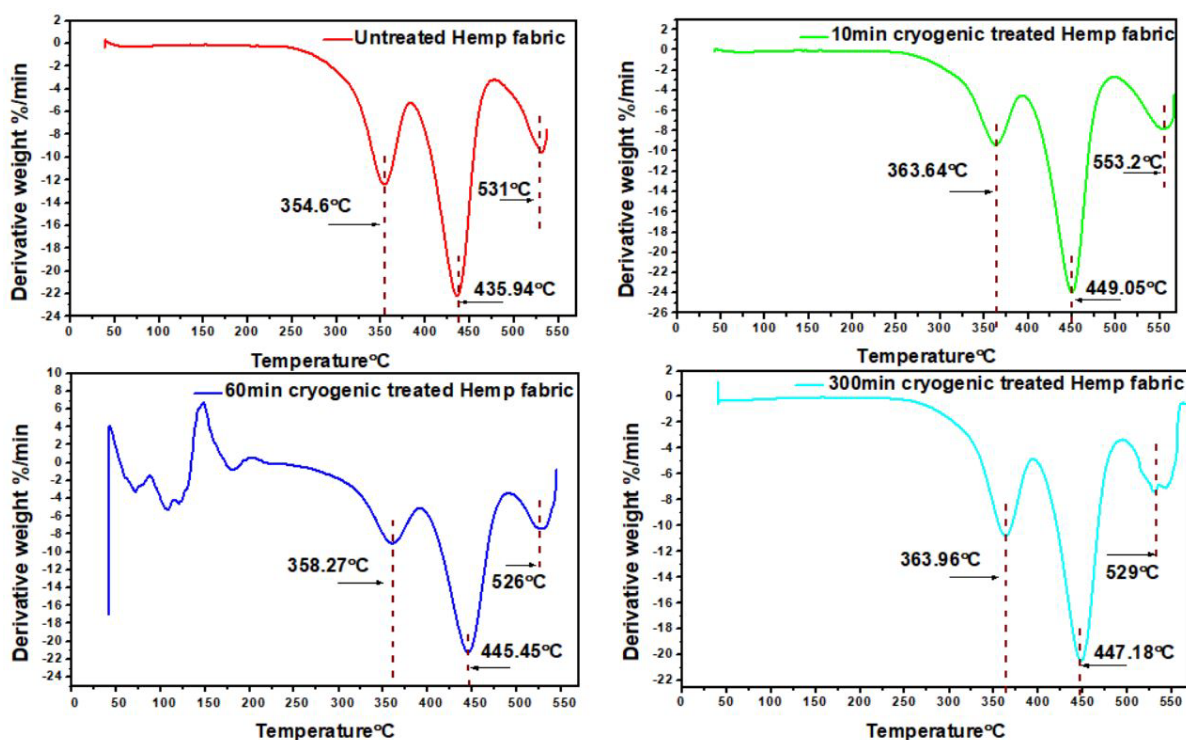


Figure 6. DTG curves of untreated and Cryogenic treated hemp fabric

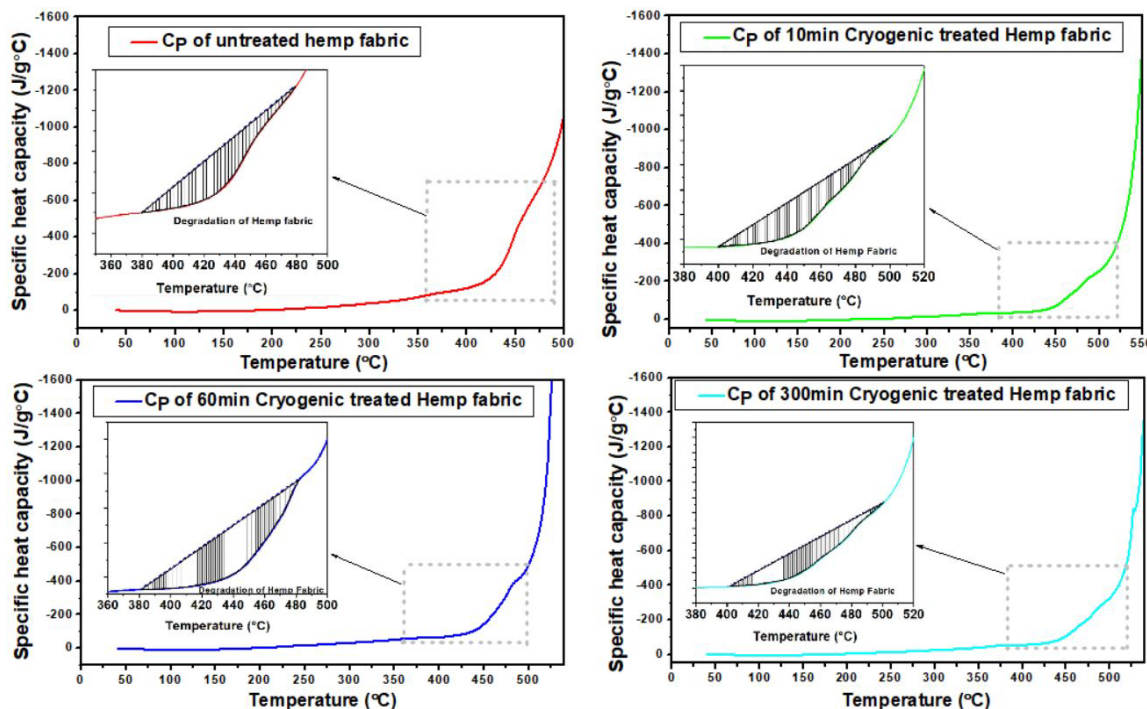


Figure 7. DSC curves of untreated and Cryogenic treated hemp fabric

Table 1. Thermal properties of Untreated and Cryogenic Treated hemp fabric from DSC data

Samples	Degradation range of hemp fabric		Enthalpy of degradation $\Delta H_{\text{degradation}}$ (kJ/g)	Specific heat capacity at T_i C_{pi} (J/g °C)	Specific heat capacity at T_f C_{pf} (J/g °C)
	T_i (°C)	T_f (°C)			
Untreated hemp fabric	380	480	12.88	99	714
10min cryogenic treated hemp fabric	400	501	4.19	35.4	258.7
60min cryogenic treated hemp fabric	382	483	8.88	60.3	386.8
300min cryogenic treated hemp fabric	402	502	4.78	54.4	337.3

T_i (°C) – Temperature at which tertiary peak start, T_f (°C) – Temperature at tertiary peak finishes.

4. Conclusion

In summary, alkalization and maleic anhydrous treatment on hemp fabric has improved its physical behaviour with an increase in number of hydrogen bonding within cellulose. Removal of waxes and pectin from the lignocellulosic fabric provided more space for cellulose OH covalent bonding, which lead to improvement in fabric stiffness. Hydrophobic behaviour declined due to the reaction with OH groups from the treatment. Cryogenic treatment on hemp fabric has improved its hydrophobic behaviour, which is evident with lower derivative weight at initial stage of degradation. Thermal stability of the fabric has significant increased from 436°C to 447°C. Increase in extensive constituent like cellulose and decrease in hemicellulose, pectin shows better physical properties. Enthalpy of degradation and specific heat capacity of hemp fabric have reduced significantly after cryogenic treatment. It reduces the energy available for fabric degradation. 10minutes and 300minutes duration

deep cryogenic treated hemp fabric shows better thermal properties than untreated and 60minutes cryogenic treated hemp fabric. These results support hemp fabric, as alternate bio-degradable material with thermal stability and better physical properties over synthetic materials for engineering applications.

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