ABSTRACT

Natural fibres have received vast attention because of their combustible, non-toxic, low cost, hydrophilic and biodegradable properties. In this study, functionalization of cannabis indica fibre has been carried out by its grafting with acrylic acid (AAc) using a Ce³⁺-HNO₃ redox initiator in an aqueous medium. Different reaction parameters such as reaction time, pH, reaction temperature, concentrations of initiator, monomer and nitric acid were optimized to achieve the maximum percentage of grafting (21.08%). The low graft yield obtained with acrylic acid was because of its high affinity towards water. A suitable mechanism to explain initiation, propagation and termination of graft copolymerization has also been proposed. The kinetics of the graft copolymerization of acrylic acid onto cannabis indica fibre has also been studied. It has been found that the rate expression for graft polymerization is \( R_g = k[I]^{0.63}[AAc]^{1.22} \). The overall activation energy for the graft copolymerization of AAc onto cannabis indica fibre was found to be 15.25 kJ/mol within the temperature range of 25-45°C. Besides kinetic study the grafted samples were also evaluated for their physicochemical properties such as swelling behaviour in different polar and non-polar solvents along with resistance towards acid and base. Graft copolymerized samples have been found to show less resistance towards chemicals as compared to the raw fibre. Furthermore, the grafted samples were characterized by different techniques such as Fourier transform infrared (FTIR), scanning electron microscope (SEM), thermogravimetric analysis (TGA) and X-ray diffraction (XRD) studies. Thermal stability of the fibre has been found to decrease after graft copolymerization which is also supported by activation energy \( (E_a) \) values calculated both for raw and grafted fibres.

INTRODUCTION

Today, graft copolymerization of vinyl monomers onto cellulosic fibres is a subject of intense studies. A remarkable change in the physicochemical properties of the grafted fibres has been demonstrated by various workers [1,2]. Grafting of acrylic acid (AAc) onto cellulosic fibres enhances their water absorbability [3,4], cation exchange property [5] and dyeability with the basic dyes without adversely affecting their intrinsic properties. The products can be used as superabsorbents and ion-exchange composites, etc. Superabsorbents are cross-linked networks of hydrophilic polymers that can absorb water and retain a high volume of aqueous fluids.
and thus these materials can be used in many fields such as horticulture, gel actuators, drug-delivery system, water purifier and coal dewatering [6-8], etc. Extensive attention has been given by various workers towards superabsorbent polymers prepared under different conditions through graft copolymerization of vinyl monomers onto natural polymers [9-11].

Grafting of vinyl monomers onto cellulose and its derivatives using UV-radiation has been reported by Geacintov et al. [12]. The change in rayon fibres properties for their surface grafting with AAc by chemical reactions and γ-radiation method has been reported by Kaur et al. [13]. They reported that the graft copolymerization through γ-radiation method is a better method of grafting in comparison to chemical method in leading to higher thermal stability. Kinetic study of graft copolymerization of AAc and methacrylate onto starch using a ceric ion initiator has been studied by Taghizadeh et al. [14]. Sun et al. prepared and characterized the graft copolymers of carboxymethyl chitosan with methacrylic acid by FTIR and 1H NMR spectroscopy and elemental analysis [15]. Chauhan et al. have used ceric ammonium nitrate as a redox initiator for the graft copolymerization of MMA onto the cannabis indica fibres [16]. They have also studied the effect of grafting on the thermal stability of the cannabis indica fibres. Different authors have made kinetic studies for the graft copolymerization of AAc onto starch using ceric ammonium nitrate (CAN) as an initiator [17-19]. Pourjavadi et al. synthesized a novel biopolymer-based superabsorbent hydrogel through chemically cross-linked graft copolymers of κ-carrageenan and acrylic acid. Recently Lyocell fibre grafted with thermosensitive poly-isopropylacrylamide using CAN was studied for their thermal and swelling behaviour by Carrillo et al. [20]. Khan synthesized photo-induced graft copolymer of methacrylic acid onto natural biodegradable lignocellulosic fibre and reported 42% increase in hydrophilic character [21].

Cannabis indica fibres collected from higher reaches of the Himalayan region have been found to contain approximately 68% cellulose. Cannabis indica is a short plant, usually less than 6 ft in height but rarely over 8 ft and found in India, Pakistan, Afghanistan and other surrounding areas. Cannabis indica fibre (a high molecular weight polysaccharide) contains reactive OH groups which are convenient for graft polymerization of hydrophilic vinyl monomers in order to achieve superabsorbent like properties. Since not much work has been reported on the surface modification of cannabis indica fibre through graft copolymerization method [22,23], therefore it is considered worthwhile to graft copolymerize AAc onto cannabis indica fibre using CAN as a redox initiator and study its different physical and chemical properties such as moisture resistance, swelling behaviour, thermal stability, surface morphology, chemical resistance behaviour and percent crystallinity. The present study also investigates the kinetics of the graft copolymerization of the acrylic acid onto cannabis indica fibre. The main aim of the kinetic study was to determine the relationship between the rates of grafting with acrylic acid/ceric ammonium nitrate concentration and to correlate some kinetic parameters with grafting percentage.

**EXPERIMENTAL**

Cannabis indica fibres were collected from higher reaches of Himalayan region in Himachal Pradesh. The fibres were first washed thoroughly with 2% detergent solution and then dried in hot air oven at 70°C for 24 h. The dried fibres were designated as untreated fibres. Then cannabis indica fibres were subjected to Soxhlet extraction with acetone for 72 h at 50°C followed by washing with double distilled water and air drying to remove waxes and other water soluble impurities prior to graft copolymerization.

**Materials**

Acrylic acid (AAc) was purified by distillation under reduced pressure at 40°C and the middle fraction of distillate was used for further studies after drying over anhydrous calcium chloride. Ceric ammonium nitrate (CAN) obtained from Merck Chemicals (Germany) was used as an initiator. Weighing of the samples was done on Libror AEG-220 (Shimadzu, Japan) electronic balance. Humidity chamber of Swastika made was used to study the moisture absorbance behaviour of the graft copolymers.
Synthesis of Cannabis indica-g-poly(AAc)

Activation of the cannabis indica fibre was done by its immersion in 100 mL of distilled water at room temperature for 24 h prior to graft copolymerization process. After the activation of the active sites on the polymeric backbone the fibre samples were transferred into a reaction kettle containing 100 mL of distilled water used as a solvent in the grafting reaction. A definite amount of CAN and nitric acid was added to the reaction flask followed by dropwise addition of monomer with continuous stirring of the reaction mixture. The reaction was carried out at definite reaction time and temperature. Optimum conditions of time, temperature, pH, CAN, nitric acid and monomer concentration were worked out so as to acquire maximum graft yield. Homopolymer formed during the graft copolymerization was removed by extraction with hot water. The grafted samples were then dried in hot air oven at 60°C to a constant weight. The amount of graft added onto the fibre was determined gravimetrically. The grafting percentage (P_g), efficiency percentage (P_e) and rate of grafting (R_g) were calculated as per the following methods [24].

\[ \text{Grafting} \ P_g(\%) = \frac{w_g - w}{w} \times 100 \]

\[ \text{Efficiency} \ P_e(\%) = \frac{w_g - w}{w_m} \times 100 \]

\[ \text{Rate of grafting} \ (R_g) = \frac{P_g \times 100 \times 100}{1000 \times V \times M} \times 100 \text{ (mol/Ls)} \]

where \( w \) is the weight of raw fibre, \( w_g \) is the weight of grafted fibre, \( w_m \) is weight of monomer, \( V \) is the volume of the reaction mixture, \( t \) is the reaction time and \( M \) is the molecular weight of the monomer.

Chemical Resistance Behaviour

The chemical resistance of the grafted fibre was studied as a function of percentage weight loss of fibre when treated with different chemicals. A known amount (\( w_i \)) of the raw and grafted fibres was separately treated with a fixed volume of hydrochloric acid and sodium hydroxide of different strengths for a time interval of 24 h. The fibres were then washed 2-3 times with distilled water and finally dried in an oven at 70°C to a constant weight. The samples were weighed again to obtain the final weight (\( w_f \)). The percentage of weight loss was determined using the following formula [24]:

\[ \text{Weight loss} \ (%) = \frac{w_f - w_i}{w_i} \times 100 \]

Swelling Behaviour

The swelling behaviour of the raw and surface modified samples of cannabis indica fibre was studied in polar and non-polar solvents such as water, butanol, dimethylformamide and carbon tetrachloride. Dry samples of grafted fibre as well as raw fibres were subjected to the evaluation of swelling behaviour by immersing the known weights of the fibres in certain amounts of different solvents for 24 h. The samples were then removed and excess solvent was removed by being pressed between the folds of the filter paper. The samples were weighed again to obtain the final weight. The degree of swelling was calculated by using the following relationship [24]:

\[ \text{Swelling} \ (%) = \frac{w_f - w_i}{w_i} \times 100 \]

where \( w_i \) is the initial weight of the dried fibre and \( w_f \) is the final weight after the swelling.

Moisture Absorbance Study

The moisture absorbance study of the grafted and raw fibres was performed at different humidity levels ranging from 20% to 80% in humidity chamber. Percentage of humidity level during moisture absorbance studies was maintained by controlling the temperature. Each sample was subjected to a particular humidity level for a fixed time interval of 2 h. The percent moisture absorbance was studied as a function of weight gain and was calculated using the following formula [24]:

\[ \text{Moisture absorbance} \ (M_{abs}, \%) = \frac{w_f - w_i}{w_i} \times 100 \]

where \( W_f \) is the final weight of the sample removed from the humidity chamber and \( W_i \) is the weight of the dried samples.
Infrared Spectroscopy
Infrared (IR) spectra of the graft copolymerized and the raw fibre were recorded with KBr pellets on a Perkin Elmer RXI Spectrophotometer (USA).

Scanning Electron Microscopy
Scanning electron microscopic (SEM) studies of raw/surface modified cannabis indica fibres were carried out on a Leo 435 VP electron microscope Thornwood, NY). All the samples were gold plated to become conducting. Scanning was synchronized with microscopic beam for the maintenance of small size over large distance relative to the specimen. All the images were taken at a resolution of 1000X.

Thermal Analysis
Thermogravimetric analysis (TGA) of the raw and graft copolymerized cannabis indica fibres was conducted on a TGA with an auto sampling (Mettler Toledo, Switzerland) analyzer at a heating rate of 15°C/min. The thermograms were recorded over a temperature range of 0°C to 900°C in presence of nitrogen atmosphere at a flow rate of 20 mL/min.

X-Ray Diffraction Studies
X-Ray diffraction studies were performed on a Brucker X-ray diffractometer (D8 Advance, Germany), using CuKα (1.5418 Å) radiation, a Ni-Filter and a scintillation counter as a detector at 40 kV and 40 mA on rotation from 5° to 60° at 2θ scale. Each sample was finely powdered into a small particle size and homogeneously mixed before subjected to X-ray exposure. The finely powdered sample was distributed in the cavity of the sample holder with the help of glass slide. The randomly oriented powdered sample with uniform surface was exposed to X-rays from all possible planes. The angle of scattering of diffracted beam was measured with respect to incident beam of X-rays and the relative intensity was obtained.

Crystallinity index (CI) was determined by using the wide angle X-ray diffraction counts at 2θ angle close to 22° and 15°. The counter reading of peak intensity close to 22° and 15° is said to represent the crystalline and amorphous materials in cellulose, respectively. The crystallinity percentage and crystallinity index (CI) were calculated using the following formula [25]:

\[ C_r(\%) = \frac{I_C}{I_C + I_A} \times 100 \]

\[ CI = \frac{I_C - I_A}{I_C} \]

where \( I_C \) and \( I_A \) are the crystalline and amorphous intensities at 2θ scale close to 22° and 15° angles.

RESULTS AND DISCUSSION

Reaction Mechanism
C2, C3 and C6 hydroxyls and C-H groups are the active sites for the incorporation onto polymeric chains through grafting with cellulosic fibres like cannabis indica fibre. Grafting reaction proceeds through redox mechanism in which Ce(IV) ions are reduced to Ce(III) ions by the transfer of electron from the cellulose molecules, and hence active sites are generated on the polymeric backbone at which monomer radicals can attack to form graft copolymers. The breaking of C2-C3 bonds of glucose molecules in cellulose chain results in the formation of free radical sites on the polymeric backbone. The grafting of acrylic acid onto cannabis indica (CI) backbone is supposed to take place through the mechanism [26,27] shown in Scheme I.

Ceric ions form complexes with the carbon chain of polymer backbone as well as with monomer and generate free radicals (eqns 1 and 2). Monomer free radicals then result in the formation of graft copolymer [CIC-g-poly(AAc)] by reacting at the active sites of the polymeric backbone (eqns 3 and 4). Monomer may also combine with CIC-g-poly(AAc) macro-radical to form graft copolymer (eqn 5). While, the ceric ions and poly(AAc) free radicals combine with CIC-g-poly(AAc) free radicals and CH-free radicals, respectively, leading into termination reactions (eqns 6 and 7).

Effect of Time
The graft copolymerization has been recorded at
**Chain initiation**

1. **Cl cellulose** + Ce⁴⁺ \( \rightarrow \) Complex(Cl cellulose-Ce⁴⁺)
   \[ \cdot \text{H} \rightarrow \text{Cl cellulose free radical} \]

2. AAc + Ce⁴⁺ \( \rightarrow \) AAc free radical

**Chain propagation**

3. Cl cellulose free radical + AAc \( \rightarrow \) AAc free radical

4. continued
different stages ranging from 60 to 180 min at fixed concentration of ceric ammonium nitrate, AAc and nitric acid at 45°C (Figure 1). With increase in reaction time, $P_g$ increased rapidly and maximum grafting was observed at 120 min and then decreased again with further increase in the reaction time. This probably happens due to generation of increasingly monomer radicals with extended time which interacts

Scheme I. A possible mechanism for graft copolymerization of acrylic acid onto cannabis indica fibre.
with the active sites on the polymeric backbone resulting in increased $P_g$. Beyond the optimized point, at higher reaction time, $P_g$ decreases due to irreversible termination by radical coupling reactions. This may also be due to the mutual destruction of growing polymeric chains [13] leading to homopolymerization of the reaction monomer radicals and backbiting by the active radicals (Scheme II).

**Effect of Temperature**

The effect of temperature on graft copolymerization is depicted in Figure 2. It can be seen that both $P_g$ and $P_e$ show an increasing trend up to 45°C as the temperature enhancement can increase the dynamic energy of the monomer molecules, which in turn increases the diffusion of monomer molecules onto the polymeric backbone resulting in increased $P_g$ and $P_e$. On further increase in temperature, $P_g$ and $P_e$ decreased, which may be due to increased chain termination reactions between monomer molecules and grafted chains. Combination of free monomer radicals at higher temperature may also result in decreased grafting yield [28].

**Effect of Initiator**

The effect of initiator concentration on graft copolymerization of polymeric backbone has been depicted in Figure 3. It can be established from the figure that $P_g$ increases with the increase in CAN concentration.

![Scheme II. Chain cleavage leads to lower degree of grafting.](image)
up to $1.82 \times 10^{-2}$ mol.L$^{-1}$ at constant concentration of monomer and nitric acid, and after that $P_g$ shows a downward trend. This behaviour can be easily understood in terms of increase in CAN concentration which results in more free radical active sites on the polymeric backbone, which may lead to greater $P_g$. However, with further increase in CAN concentration, it accelerates the dissociation rate of Ce(IV), which reduces the concentration of CAN participating in graft copolymerization.

**Effect of Nitric Acid Concentration**

In aqueous medium CAN exists as Ce$^{4+}$, [Ce(OH)]$^{3+}$ and [Ce-O-Ce]$^{6+}$ ions (eqns 8 and 9). Due to their large size, these ions are not able to form complexes with polymer backbone. However, in the presence of HNO$_3$, equilibrium shifts further towards Ce$^{4+}$ ions, therefore graft copolymerization increases with increase in nitric acid concentration.

\begin{equation}
Ce^{4+} + H_2O \leftrightarrow [Ce(OH)]^{3+} + H^+ \tag{8}
\end{equation}

\begin{equation}
2[Ce(OH)]^{3+} \leftrightarrow [Ce-O-Ce]^{6+} + H_2O \tag{9}
\end{equation}

Figure 4 shows the effect of nitric acid concentration on grafting parameters. It can be seen that $P_g$ increases significantly with the increase in nitric acid concentration, and $P_e$ also follows a similar trend. However, $P_g$ decreases with further increase in the nitric acid concentration beyond an optimum value.

**Scheme III.** Hydrolysis of the cellulosic fibre due to increased HNO$_3$ concentration.
Effect of pH

With increase in pH of the reaction medium, $P_g$ increases up to pH 7, but beyond pH 7 there is a decrease in the graft yield as depicted in Figure 5. This may be due to the fact that at higher pH the OH radicals are generated in basic medium which combine with the backbone free radicals to terminate the chain reaction (Scheme IV) [13].

**Effect of Monomer Concentration**

The effect of monomer concentration on graft copolymerization onto polymeric backbone at constant concentrations of CAN and nitric acid at temperature of 45°C is depicted in Figure 6. It can be established from the figure that $P_g$ increases with increase in AAc concentration up to $2.91 \times 10^{-1}$ mol.L$^{-1}$ beyond which $P_g$ shows a downward trend. The above behaviour of the monomer concentration may be explained on the basis of greater free radicals which reach polymeric backbone, resulting in increased $P_g$. The decrease in $P_g$ beyond optimum value of AAc was probably due to preferential homopolymerization over graft copolymerization as well as due to restricted movement of free radicals onto polymer backbone because of increased viscosity. Needless to say, the increase in the chain transfer to monomer molecules may be another possible reason for the diminished grafting at
Kinetics of Graft Copolymerization

The mechanism of graft copolymerization is quite complex as it involves various stages like propagation, termination, homopolymerization and copolymerization reactions. However, kinetically, the rate of the graft copolymerization \( R_g \) with respect to monomer and initiator concentrations can be written as follows [29]:

\[
R_g = k[\text{initiator}]^m[\text{monomer}]^n
\]  

(10)

Here, \( m \) and \( n \) can be experimentally determined by the logarithmic form of the equation given above:

\[
\log R_g = \log k + \log[\text{initiator}]^m + \log[\text{monomer}]^n \]  

(11)

The experimental results show a change in the rate of grafting with the changes in concentration of the CAN keeping the concentration of the acrylic acid constant (Table 1).

The slope of the \( \log R_g \) vs. \( \log [\text{CAN}] \) graph plotted by the data given in Table 1 showed that the rate of grafting was proportional to 0.63 power of the CAN concentration.

Likewise the initial rates of grafting were determined by changing the concentration of acrylic acid from 1.75 to 2.91 mol/L and keeping the CAN concentration constant (Table 2).

The slope of the \( \log R_g \) vs. \( \log [\text{AAc}] \) graph plotted using the data in Table 2 showed that the rate of grafting was proportional to the 1.22 power of the acrylic acid concentration.

<table>
<thead>
<tr>
<th>[CAN] ( \times 10^{-2} ) (mol.L(^{-1} ))</th>
<th>( P_g )</th>
<th>Log [CAN] + 3</th>
<th>( R_g \times 10^{-5} ) (mol.L(^{-1}.s(^{-1} ))</th>
<th>Log ( R_g ) + 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.91</td>
<td>10.76</td>
<td>0.95</td>
<td>1.03</td>
<td>0.015</td>
</tr>
<tr>
<td>1.36</td>
<td>14.56</td>
<td>1.13</td>
<td>1.40</td>
<td>0.140</td>
</tr>
<tr>
<td>1.82</td>
<td>16.68</td>
<td>1.26</td>
<td>1.60</td>
<td>0.200</td>
</tr>
</tbody>
</table>

[AAc]: 0.29 mol.L\(^{-1} \), T: 45°C, t: 120 min, HNO\(_3\): 1.2 mL, pH: 7.0.
Therefore:

\[ R_g = k[J]^{0.63}[AAc]^{1.22} \]

Kinetics of graft copolymerization of ethyl acrylate onto cellulose by using ceric ammonium nitrate as an initiator have also been studied by Gupta et al. [30]. They found that the grafting rate is proportional to 1.5 power of ceric ion and activation energy was found to be 28.9 kJ/mol. Graczyk et al. have reported grafting rate is proportional to the powers 0.5 and 1 of their respective ceric ion and monomer concentrations at low concentration of CAN [31].

Since grafting reaction was carried out at different temperatures and other conditions remaining constant therefore we may equalize the reaction rate with grafting rate. Substitution of the Arrhenius relation by general rate equation yields the following equation:

\[ R_g = A[CAN]^m[AAc]^n e^{-Ea/RT} \]

where A, Ea and T indicate collision parameter in the Arrhenius equation, activation energy and absolute temperature, respectively. The final equation may be written as:

\[ \log R_g = \log k - \frac{Ea}{RT} \quad (12) \]

This implies that when the plot of \( \log R_g \) vs. 1/T (K\(^{-1}\)) is a straight line, the activation energies of the reaction can be evaluated. The result is depicted in Figure 7 which shows that plot of \( \log R_g \) vs. 1/T is a straight line. Thus, the overall activation energy for the graft copolymerization of AAc onto cannabis indica fibre is found to be 15.25 kJ/mol. The results obtained in our laboratory are consistent with other studies reported [32,33].

### Swelling Behaviour

The swelling percentage of raw and grafted cannabis indica fibres in different solvents such as water, methanol, dimethylformamide (DMF) and carbon tetrachloride was studied as a function of the percentage of grafting at 35°C and the results are shown in Figure 8. The following swelling order in different solvents has been observed both with grafted as well as raw fibres.

\[ H_2O > C_2H_5OH > DMF > CCl_4 \]

A high swelling percentage in water is expected because water enters into hydrogen bonding with hydroxyl group of the cannabis indica fibre. Amorphous region of the fibre is generally responsible for H-bonding where hydroxyl groups

### Table 2. Dependence of rate of grafting (Rg) on acrylic acid concentration.

<table>
<thead>
<tr>
<th>[AAc] (mol.L(^{-1}))</th>
<th>Pg</th>
<th>Log [CAN] + 1</th>
<th>Rg (\times 10^{-5}) (mol.L(^{-1}).s(^{-1}))</th>
<th>Log Rg + 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.17</td>
<td>11.20</td>
<td>0.24</td>
<td>1.07</td>
<td>0.03</td>
</tr>
<tr>
<td>0.23</td>
<td>14.66</td>
<td>0.36</td>
<td>1.41</td>
<td>0.15</td>
</tr>
<tr>
<td>0.29</td>
<td>21.08</td>
<td>0.46</td>
<td>2.03</td>
<td>0.30</td>
</tr>
</tbody>
</table>

[CAN]: 1.82 \(\times 10^{-2}\) mol.L\(^{-1}\), T: 45°C, t: 120 min, HNO\(_3\): 1.2 mL, pH: 7.0.
are exposed for such interactions. Further dielectric constant values of different solvents also have great effect on the swelling behaviour of the fibre. As regards the dielectric constants, the order of the solvents studied is as follows:

\[H_2O > C_2H_5OH > DMF > CCl_4\]

\((\varepsilon = 78.35) \quad (\varepsilon = 24.30) \quad (\varepsilon = 36.71) \quad (\varepsilon = 2.24)\)

Water, having a higher \(\varepsilon\) value easily enters into H-bonding with the fibre leading to maximum swelling. DMF, as an aprotic solvent, is a polar molecule with high \(\varepsilon\) which interacts with the hydroxyl group of the fibre leading to a substantial degree of swelling. In case of carbon tetrachloride which has low dielectric constant \((\varepsilon = 2.24)\) a lower degree of swelling has been observed. It is also observed in Figure 8 that percent swelling of the acrylic acid grafted \textit{cannabis indica} fibre in water is higher than the raw fibre. The maximum degree of swelling is observed at 17.24\% graft level. The degree of swelling in butanol and DMF for 17.24\% graft level is also higher, while in carbon tetrachloride it is less than that of raw \textit{cannabis indica} fibre.

It was further observed that the degree of swelling decreases with increased \(P_g\). This may be due to the formation of inter and intramolecular hydrogen-bonded structures between the pendant carboxyl groups that are not affected by the presence of the added solvent (Figure 9).

The lower swelling of acrylic acid graft copolymerized fibres in carbon tetrachloride was due to lower interaction of CCl\(_4\) with carboxyl groups in comparison to hydroxyl groups of the raw fibre.

**Acid/Base Resistance**

The chemical resistance has been studied in terms of a weight loss of the fibre with dilute solutions of strong acids and bases. The effects of acid (HCl) and the base (NaOH) were studied by keeping the raw and \textit{cannabis indica}-g-poly(AAc) fibres in basic and acid solutions for a period of 24 h and the result obtained are shown in Figures 10 and 11. From these figures it is clear that chemical resistance of grafted fibres decreases with increases in degree of grafting both with acid and base. The maximum weight loss was found at high \(P_g\) (21.08\%). This probably could
be due to the formation of acrylic acid sodium salts and to some extent due to the solubility of polyacrylic acid chain. However, at lower $P_g$ the grafted samples showed little resistance towards bases or acids.

**Moisture Absorbance**

Raw *cannabis indica* fibres have been found to show 1.91, 2.45, 3.21 and 3.75% moisture absorbance at 20%, 40%, 60% and 80% humidity levels in the given order (Figure 12). From the figure, it is also clear that *cannabis indica*-g-poly(AAc) fibre showed higher moisture absorption which increases with increases in $P_g$. This could be due to the fact that with increase in the graft yield, more carboxyl groups are available for formation of the hydrogen bond with the water molecules.

**FTIR Analysis**

FTIR Spectrum of raw *cannabis indica* fibre showed a broad peak at 612.6 cm$^{-1}$ (due to out-of-plane -OH bending), 897.6 cm$^{-1}$ (due to β-glycosidic linkage), 1252.1 cm$^{-1}$ (due to -C-O-C- and -C=O stretchings in xylan side substituent and lignin aromatic C=O stretching), smaller peaks at 1376.2-1429.3 cm$^{-1}$ (due to -CH, -CH$2$ and -CH$_3$ bending), 1635.0 cm$^{-1}$ (due to H-O-H bending of absorbed water and for lignin C-H deformation), 2143.2 cm$^{-1}$ (due to O-H stretching of absorbed moisture), 2335.5 cm$^{-1}$ (due to C-H stretching in polysaccharide chains), 2922.3 cm$^{-1}$ (for C-H stretching vibration of aliphatic methylene group) and an intense broad peak ranging from 3024 to 3691 cm$^{-1}$ (due to the hydrogen bonded -OH vibration of the cellulose structure fibre). However, in FTIR spectra of the *cannabis indica*-g-poly(AAc), characteristic absorption bands at 1729.9 cm$^{-1}$ and 1570 cm$^{-1}$ were obtained due to carbonyl stretching of pendant carboxylic acid group and unsaturated group, respectively.

**Morphological Studies**

Surface morphology of both treated and untreated *cannabis indica* fibres was studied through scanning electron microscopy and the results are shown in Figure 13. The comparison of SEM micrographs of the raw and acrylic acid grafted *cannabis indica* fibres showed that the morphology of the fibre changes upon grafting, indicating that the chains of polymeric AAc have been incorporated onto *cannabis indica* fibre.

**Thermal Stability**

The TGA analysis of the raw and *cannabis indica*-g-poly(AAc) fibres is shown in Figure 14 and the corresponding thermal characteristics are given in Table 3. Thermal behaviour of both raw and grafted fibres was studied as a function of weight percentage residue with increase in temperature. In the case of raw *cannabis indica* fibre, at the beginning, depolymerization, dehydration and glucosan formation took place between the temperature range of 25.0°C and
250.0°C followed by the cleavage of C-H, C-C and C-O bonds [25,34]. For the raw fibre, the initial decomposition temperature (IDT) has been found to be 256.33°C (6.91% weight loss) and final decomposition temperature (FDT) to be 383.25°C (61.12% weight loss). In the case of AAc grafted cannabis indica fibre, the IDT has been found to be 236.9°C (7.88% weight loss) and FDT to be 388.68°C (54.85% weight loss). Decrease in IDT of grafted fibre could be due to decomposition of anhydride (formed due to dehydration of carboxylic acid groups) of poly(AAc) chains to carbon dioxide and intermediate species such as ketones, ketenes and unsaturated compounds in the temperature range of 200-275°C, accompanied by an overall decrease in the acrylic acid content [35]. However if we take decomposition temperature (DT) at 20% and 60% weight losses for both raw and grafted fibres as a standard of comparison then it has been observed that at higher temperature cannabis indica-g-poly(AAc) fibres are thermally more stable than the raw fibres. Analysis of the activation energy also supports the above trend (Figure 15). The activation energy has been calculated within the temperature range of 250-400°C by using Broido equation as given below:

$$\ln \left[ \ln \left( \frac{1}{y} \right) \right] = -\frac{E}{R} \left( \frac{1}{T} \right) + K$$  \hspace{1cm} (13)

![Figure 14. Thermogravimetric analysis of the raw and cannabis indica-g-poly(AAc) fibres.](image)

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample designation</th>
<th>IDT (°C)</th>
<th>FDT (°C)</th>
<th>DT (°C) at 20% (by weight) loss</th>
<th>DT (°C) at 60% (by weight) loss</th>
<th>Residual weight (%) at 600°C</th>
<th>Activation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Raw cannabis indica fibre</td>
<td>250.33</td>
<td>383.25</td>
<td>329.61</td>
<td>383.25</td>
<td>27.04</td>
<td>56.12</td>
</tr>
<tr>
<td>2</td>
<td>Cannabis indica-g-poly(AAc)</td>
<td>236.90</td>
<td>388.68</td>
<td>329.18</td>
<td>447.00</td>
<td>27.84</td>
<td>43.94</td>
</tr>
</tbody>
</table>

Table 3. TGA and activation energy analyses of the raw cannabis fibre and cannabis indica-g-poly(AAc) fibres.
Figure 15. Variation of $\ln[\ln(1/y)]$ for raw and grafted cannabis indica fibres.

where $R$ is gas constant, $T$ is temperature in Kelvin, $K$ is a constant, $y$ is a normalized weight ($w_t/w_0$), $w_t$ denotes the weight of the samples at any time $t$, while $w_0$ denotes the initial weight of the samples. From Figure 15, it is clear that the value of activation energy was higher for raw fibres, for which the thermal stability has also been found higher than grafted fibre.

XRD Study
The polymorphism of cannabis indica fibre was studied before and after graft copolymerization, using X-ray diffraction. For the raw fibre, two responses were noticed at $2\theta = 15^\circ$ and $22^\circ$ which indicate that cannabis indica fibre is a semi-crystalline material. The same responses appeared in case of the cannabis indica-g-poly(AAc) fibre but with different intensities (Figure 16). The relative degree of crystallinity of both fibres was calculated and it is given in Table 4. As shown in this table an increase in degree of grafting was accompanied by a decrease in the relative degree of crystallinity. This could be explained on the basis that grafting causes disturbance in the crystalline region of the fibre by creating amorphous region. Thus, as the degree of grafting increases, the amorphous regions become predominant and overshadow the crystalline feature of the fibres.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>$I_{22}$</th>
<th>$I_{15}$</th>
<th>Crystallinity (%)</th>
<th>Crystallinity index (CI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Raw</td>
<td>709.00</td>
<td>348.00</td>
<td>67.07</td>
<td>0.509</td>
</tr>
<tr>
<td>2</td>
<td>Cannabis indica-g-poly(AAc)</td>
<td>603.65</td>
<td>314.89</td>
<td>65.71</td>
<td>0.478</td>
</tr>
</tbody>
</table>

Table 4. Degree of crystallinity (%) and crystallinity index (CI) of raw and cannabis indica-g-poly(AAc) fibre.

CONCLUSION
Cannabis indica fibres have been successfully modified through grafting in air by free radical polymerization. The optimum conditions for the maximum degree of grafting (21.08%) onto cannabis indica fibres have been found to be: time: 120 min, temperature: 45°C, [CAN]: $1.82 \times 10^{-2}$ mol.L$^{-1}$, [HNO$_3$]: $2.88 \times 10^{-1}$ mol.L$^{-1}$ and [AAc]: $2.91 \times 10^{-1}$ mol.L$^{-1}$. The rate of grafting has been found to be more dependent upon monomer concentration. The degree of swelling of grafted samples in polar and dipolar aprotic solvents has been found to be better.
than that of the raw fibres. The grafted fibres have been found to have high FDT compared to that of raw fibre which ensures their high temperature applications. Due to high moisture absorbance behaviour of the grafted fibres these can be used as water superabsorbent as well as for the removal of harmful ion like Pb, As and etc. from the water sources.

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REFERENCES


17. Taghizadeh MT, Khostravy M, Kinetics and mechanism of graft copolymerization of vinyl monomers (acrylamide, acrylic acid, and methacrylate) onto starch by potassium dichromate as redox initiator, Iran Polym J, 12, 497-505, 2003.