

A STUDY OF THE EFFECT OF ACETYLATION ON HEMP FIBRES WITH VINYL ACETATE

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Chemical modifications of hemp fibers were performed with acetic anhydride (AA) and vinyl acetate (VA) in the presence of pyridine or potassium carbonate as catalysts. Hemp fibers (*Cannabis sativa*) were successfully acetylated by VA in the presence of potassium carbonate (15% WPG), but no weight gain was obtained when pyridine was used as catalyst. Hemp fibers were also modified with acetic anhydride (AA) in the presence of potassium carbonate and pyridine as catalyst (14% and 16% WPG, respectively) under identical conditions, and the results were compared with those obtained using the VA technique. AA-modified, VA-modified, and control hemp fibers were characterized by Infrared (FTIR), ¹³C CP MAS NMR and thermo gravimetric analysis (TGA).

Keywords: Acetylation; Acetic anhydride; Vinyl acetate; Hemp fibers; Chemical modification

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INTRODUCTION

There is an increasing interest in the use of lignocellulosic fillers as reinforcement for composites. Utilization of lignocellulosic fibers such as wood, hemp, flax, *etc.*, have a number of advantages such as low cost, low density, and non-toxicity. They are renewable resources with high specific properties, and they do not cause any abrasion to the processing machines. Unfortunately, some of the properties of lignocellulosic fibers, such as dimensional instability, biodegradability, flammability, as well as degradation caused by acids, bases, and ultraviolet radiation limit the utilization areas (Fengel and Wegener 1989). There are some drawbacks to using lignocellulosic compounds as reinforcement in the thermoplastic composites. A first drawback is the low compatibility between the hydrophilic lignocellulosics and the hydrophobic polymer; this leads to decreased strength and impact properties. A second drawback is the low thermal stability of lignocellulose.

When lignocellulosic fibers are used as reinforcement in the thermoplastic composites, they are exposed to high temperatures (180°C and above) during the manufacturing process. It is essential to improve the interface between the matrix and the hydrophilic lignocellulosic fibers, as well as the thermal stability of lignocellulosic fibers. The methods for improving the compatibility of lignocellulosic materials that are used as fillers include esterification, silane treatment, use of coupling agent, and treatment with other chemicals (Raj *et al.* 1989; Felix and Gatenholm 1991; Bledzki *et al.* 1996). It was reported that promoting the interfacial compatibility between hydrophobic matrix of the

polymers and hydrophilic lignocellulosic fibers improves the physical and mechanical properties of the composites.

Chemical modification can be observed by the chemical reaction between reactive parts of the lignocellulosic cell wall polymers (hydroxyl groups generally) and a chemical reagent, with or without catalyst, to form a covalent bond between these two. All of the methods investigated to date have involved the chemical reaction of a reagent with the cell wall polymer hydroxyl groups. The chemical modification of lignocellulosic fibers with various reagents including anhydrides (such as acetic, succinic, maleic, propionic, butyric, hexanoic, crotonic and methacrylic anhydrides), isocyanates, formaldehyde, acetaldehyde, or epoxides (such as ethylene or propylene oxide, glycidyl methacrylate, allyl glycidyl ether *etc.*) has been the subject of research for many decades (Rowell 1983; Rowell *et al.* 1991; Banks and Lawther 1994; Kumar 1994; Hon 1996; Rowell 2006; Çetin 2000; Çetin and Özmen 2001; Hill 2006).

Recently, maritime pine sapwood blocks have been successfully acetylated to different weight gains by vinyl acetate reactions with potassium carbonate as a catalyst (Jebrane and Sebe 2008; Jebrane *et al.* 2011a). The reactivity of wood components, namely cellulose and lignin, was also investigated with vinyl acetate reaction (Jebrane *et al.* 2011b). Scots pine sapwood has recently been successfully acetylated with a new transesterification reaction using vinyl acetate in the presence of various catalysts such as potassium acetate, potassium carbonate, and sodium carbonate (Çetin *et al.* 2011). The main advantages of this new technique are that acetaldehyde is produced as a byproduct. Acetaldehyde is a non-acidic, low boiling point (b.p.= 21°C) compound that is easily removed from modified wood after reaction. However, when the acetylation method is used, a weaker acid (acetic acid) is liberated with acetic anhydride. So this compound is hard to remove from wood after reaction, imparting an undesirable odour to the wood and causing strength losses or the corrosion of metal fasteners (Li *et al.* 2000; Larsson Breliid 2002; Jebrane *et al.* 2011b).

In this study, classical acetylation of hemp fibers (*Cannabis sativa*) with acetic anhydride was compared with the new acetylation method using vinyl acetate. As far as the author is aware, there have been no reports of vinyl acetate being used in the acetylation of hemp fiber. The reactions were performed on hemp fibers with dimethyl formamide as a solvent. Modified samples were characterized by weight percent gain (WPG) calculations. FTIR and ¹³C CP-MAS NMR spectroscopy on both acetylation methods of the modification of hemp fibers were also determined. The thermal degradation of hemp fibers and acetylated hemp fibers were investigated using thermogravimetric analysis between room temperature and 800°C.

EXPERIMENTAL

Acetylation of Hemp Fibers

Hemp fibers were extracted with deionised water for 6 hours, then with a toluene:acetone:ethanol mixture (4/1/1, v/v/v) for an additional 6 hours using a Soxhlet extractor and then oven-dried at 103°C overnight and transferred to a desiccator containing phosphorus pentoxide, and allowed to cool to room temperature. The

extracted hemp fibers were transferred to a round-bottom flask containing DMF solution with acetic anhydride (AA) or vinyl acetate. The reaction protocol was adopted from an earlier publication (Çetin *et al.* 2011). In the acetic anhydride (AA) and vinyl acetate (VA) acetylation tests, two different catalysts, namely pyridine (10 mmol/g of dry hemp fibers) and potassium carbonate (K_2CO_3) (1.1 mmol/g of dry hemp fibers), were used. All reactions were performed at 100°C with various reaction times (15 minutes to 24 hours). For each reaction, 1 g of hemp fibers containing 20 mmol of VA or AA and 50 mL of DMF were used, and each set of conditions was repeated three times. At the end of the reaction, all modified samples were extracted with deionized water for 6 hours, followed by a mixture of toluene:acetone:ethanol mixture (4/1/1, v/v/v) for 6 hours. This was done to remove excess unreacted chemicals and by-products. The Soxhlet thimble and contents were oven-dried overnight at 103°C and then transferred to a desiccator containing phosphorus pentoxide until cool. Lastly, weight gain levels were calculated.

The weight percentage gain (WPG) was calculated according to Equation 1,

$$WPG(\%) = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

where W_1 is the sample weight before treatment, and W_2 is the sample weight after treatment.

Infrared Spectroscopy

Infrared absorption spectra of acetylated and unmodified hemp fibers were obtained with the KBr (potassium bromide) technique, using a Shimadzu 8400s FT-IR spectrometer, Kyoto, Japan, at a resolution of 4 cm^{-1} (40 scans). In each case, 1% w/w of oven-dry hemp fibers was dispersed in a matrix of KBr and pressed to form pellets.

^{13}C -CP-MAS NMR Analysis

Solid state ^{13}C CP-MAS (Cross Polarization-Magic Angle Spinning) NMR spectra of hemp fibers were obtained at room temperature on a Bruker DPX-400 NMR spectrometer (Bruker, Hanau, Germany), using MAS rates of 4 and 8 kHz, a frequency of 100.61 MHz for ^{13}C NMR.

Thermogravimetric (TGA) Analysis

The thermogravimetric analyses of control and acetylated hemp fibers were performed by thermal gravimetric analyzer (Shimadzu TA60, Kyoto, Japan). The sample weight was 20 mg. The measurements were carried out at a heating rate of 10°C/min in an inert nitrogen atmosphere with a flow rate of 20 mL/min. Weight loss amounts versus temperature were recorded.

RESULTS AND DISCUSSION

The reaction mechanism between hydroxyl groups of hemp fibers with acetic anhydride (AA) or vinyl acetate (VA) is shown in Fig. 1. In order to compare the

classical AA modification with the new VA technique, the same reaction protocols were applied to both methods. There was no weight gain without solvent (DMF) or with pyridine catalyst when VA was used. As seen from Fig. 2, approximately 16%, 14%, and 15% WPG levels were ultimately achieved for 24 hours reaction with pyridine-catalyzed acetic anhydride (pAA), K_2CO_3 -catalyzed acetic anhydride (AA), and vinyl acetate (VA), respectively. According to a previous study, the weight percent value of acetylated hemp fibres was found to be about 5.8% after acetylation with acetic anhydride without catalyst at 100°C for 3 hours. It is reported that the reason for this low weight gain value is the lower reactivity of cellulose in the absence of a suitable catalyst (Tserki *et al.* 2005).

The hydroxyl groups on the hemp fibers react with acetic anhydride to form an ester bond, with acetic acid produced as a by-product (Fig. 1a). When potassium carbonate, which is a base, was used as a catalyst, it resulted in acid-base interactions with the acetic acid produced in the acetylation reaction. The initial pH value of reaction medium was measured as 10.3, and at the end of the reaction, the pH value was measured as 8.2 at 22°C. The reaction medium was therefore still basic.

Pyridine is an effective catalyst, since it serves not only to swell the wood structure, thereby permitting effective ingress of reagent, but it also catalyses the reaction via nucleophilic mediated catalysis. In the case of pyridine, the pyridinium ion is created in the reaction environment, as shown in Fig. 3. The pH value was measured 7.9 at the beginning of the reaction, and the final pH was 6.6 at the end of the reaction.

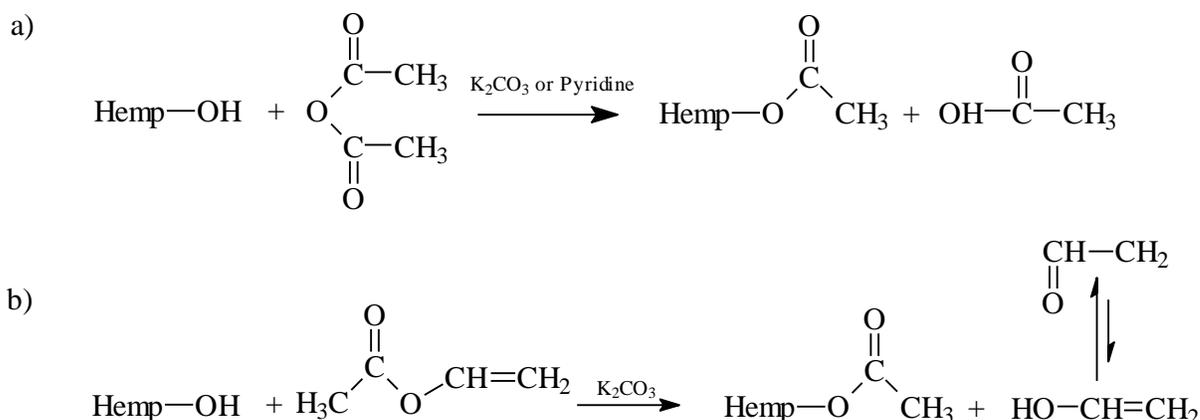


Fig. 1. The reaction between (a) acetic anhydride or (b) vinyl acetate and hemp fiber

Proof of the reactions between AA or VA with hemp fibers was obtained by FTIR spectroscopy (Fig. 4). In general, the spectrum of the acetylated hemp fiber with vinyl acetate was similar to that of acetylated hemp with acetic anhydride. The peak at around 1750 cm^{-1} is due to the carbonyl stretching vibration ($\nu\text{C}=\text{O}$) and confirmed the formation of ester bonds after reactions with AA and VA (Çetin *et al.* 2005; 2011). The esterification reaction is also confirmed by the appearance of a new peak at 1240 cm^{-1} , attributed to the C-O stretching vibration ($\nu\text{C}-\text{O}$) of the acetyl moieties. The band in the spectra of acetylated fibers located at 1380 cm^{-1} is assigned to the C-H bending ($\delta\text{s C}-\text{H}$)

vibrations of the methyl groups introduced. The intensity of the band at 605 cm^{-1} also increased and was associated to some vibrations of the grafted methyl groups.

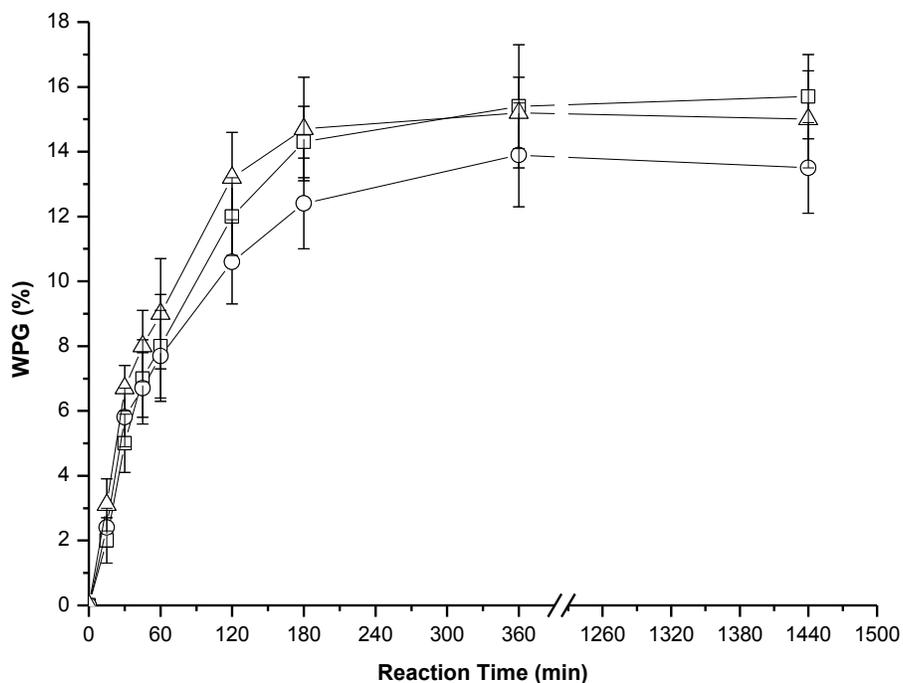


Fig. 2. Effect of reaction time on WPG (weight percent gain) values of acetylated hemp fibers with acetic anhydride (with K_2CO_3 (circle) or pyridine catalysts (square)) or vinyl acetate (with K_2CO_3 triangle) at 100°C

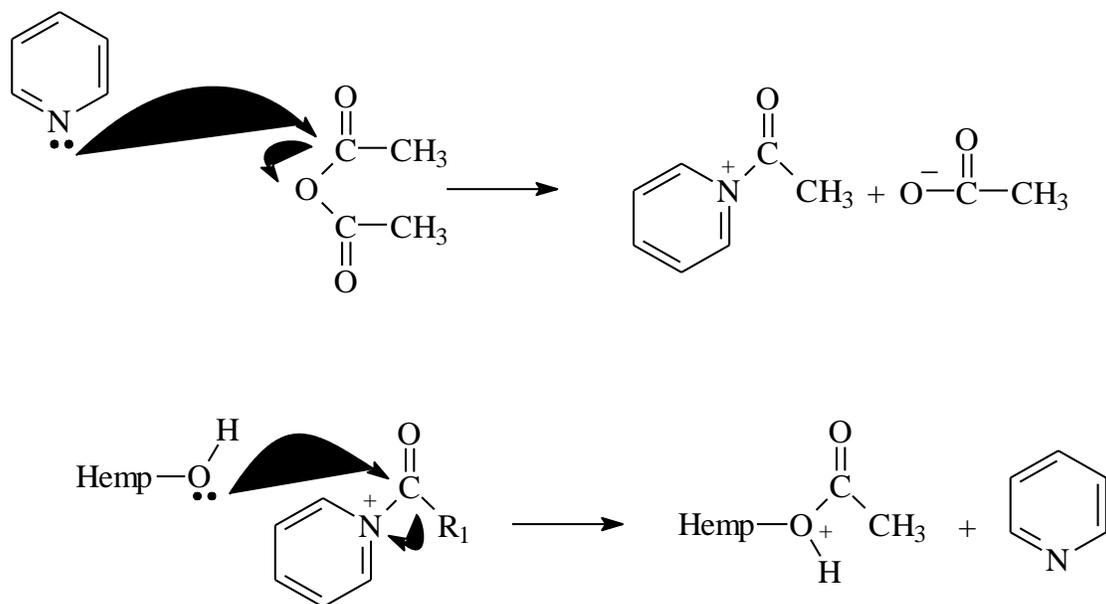


Fig. 3. Acetylation mechanism when pyridine is used as catalyst

In addition to the FTIR observation, acetylation reactions were confirmed by the ^{13}C NMR spectra. The ^{13}C NMR spectrum of unmodified hemp fibers is shown in Fig. 5 (H). Figure 5 shows a dominant pattern in the ^{13}C NMR spectra attributable to carbohydrates, namely C1 (105 ppm), C4 crystalline (89 ppm), C4 amorphous (84 ppm), C2 (75 ppm), C3/C5 (73 ppm), C6 crystalline (65 ppm), and C6 amorphous (62 ppm) (Boonstra *et al.* 1996, Çetin *et al.* 2005). The methoxy and aromatic groups of the lignin normally appear at 59 and 150 ppm, respectively, but with hemp fibers, these peaks were not clearly observed due to the low lignin content of hemp fiber (4%).

After acetylation of hemp fibers with pAA, AA, or VA, the methyl band of the acetyl group at 21 ppm (Fig. 5 assigned as b) and the carboxylic group at 171 ppm (Fig. 5 assigned as a) show the acetyl groups on the wood components. There was no difference between the pAA-, AA-, or VA-modified hemp fibers' NMR spectra.

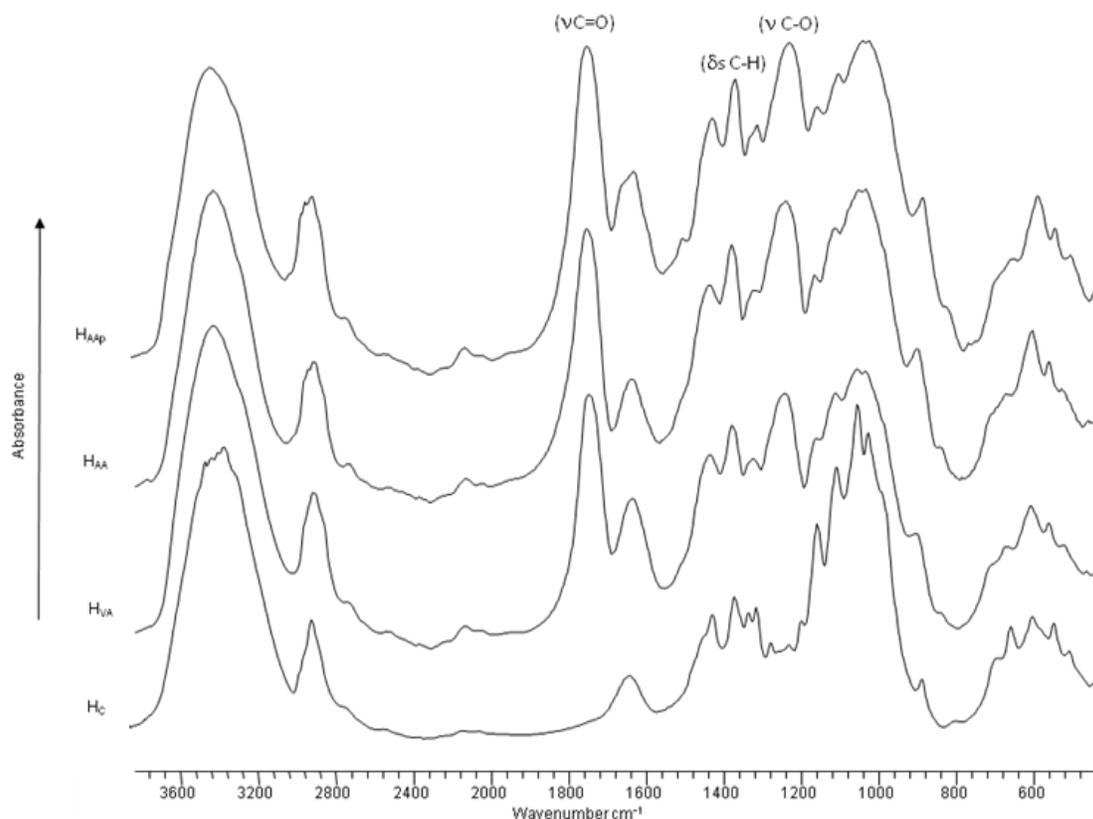


Fig. 4. FTIR spectra of untreated (HC), acetic anhydride modified with K_2CO_3 catalyst (13% WPG) (HAA), acetic anhydride modified with pyridine catalyst (16% WPG) (pHAA), vinyl acetate modified (15% WPG) (HVA) hemp fiber

Thermogravimetry is one of the most widely used techniques to monitor the composition and structural dependence of thermal degradation on natural cellulose fibers. The thermal degradation of the control and the acetylated hemp fibers was investigated using the techniques of thermogravimetric analysis between room temperature and 800°C , and results are shown in Fig. 6.

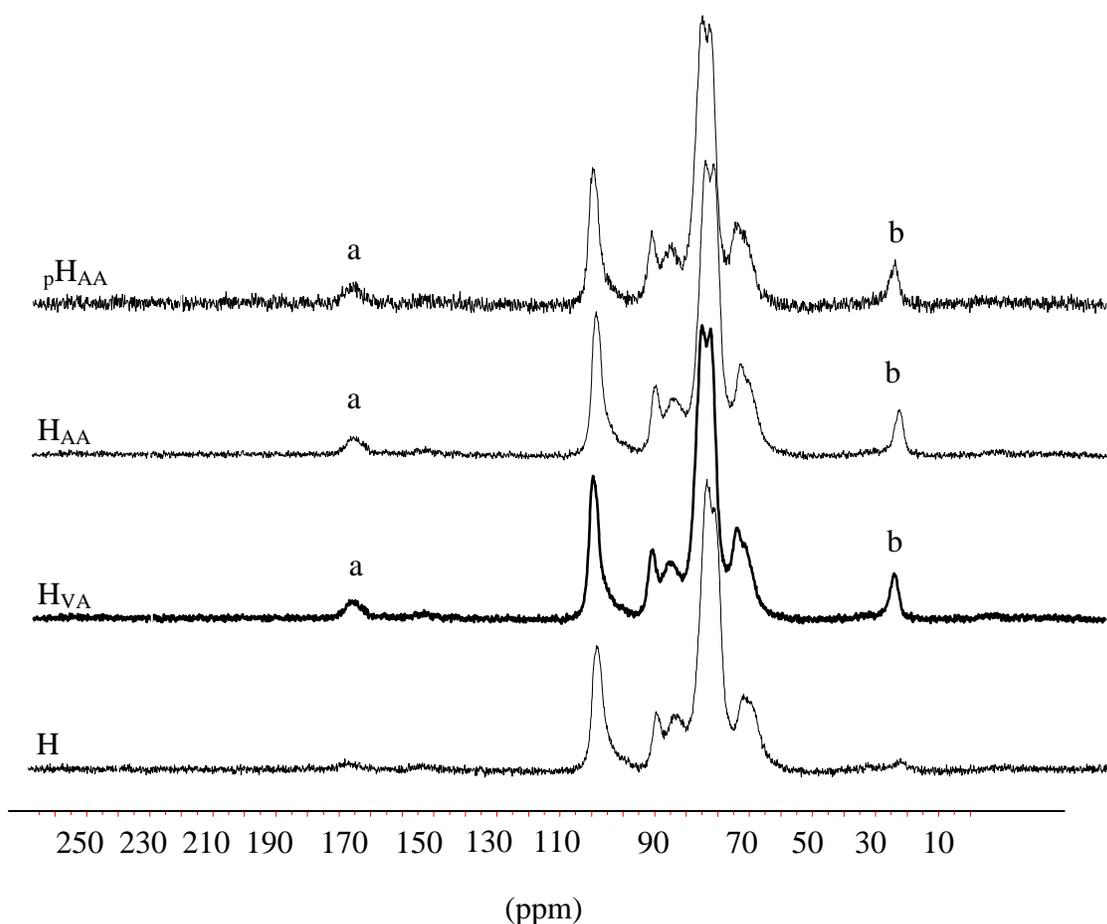


Fig. 5. ^{13}C CP-MAS NMR spectra of unmodified (H), acetic anhydride modified with K_2CO_3 catalyst (13% WPG) (HAA), acetic anhydride modified with pyridine catalyst (16% WPG) (pHAA), vinyl acetate modified (15% WPG) (HVA) hemp fiber

For the control hemp fibers (Fig. 6a), three regions of thermal decomposition were noticed between 25 to 150°C, 150°C to 420°C, and 425 to 670°C, which were denoted region I, region II, and region III, respectively. Complete decomposition of the fiber occurred at 670°C. The first region is related to the release of water or moisture. The second region is related to the degradation of the main components of fibers namely hemicelluloses, lignin, and cellulose. Hemicelluloses are generally thought to degrade first, followed by cellulose and then lignin (Mwaikambo and Ansell 1999). It was reported that the hemp fibers contain large amounts of pectins (18%) and hemicelluloses (16%) (Ouajai and Shanks 2005). These chemicals are not thermally stable and tend to degrade at an early stage of heating. The third region is related to degradation of the char.

Similar behavior was also observed with acetylated samples (Fig. 6b, c, d). As the temperature was increased, decomposition of the fibers occurred. On pyrolysis of the control hemp fibers, the active temperature of decomposition was determined as 376°C, after acetylation of hemp fibers with VA (Fig. 6b), the main decomposition temperatures shifted to higher value which was 392°C.

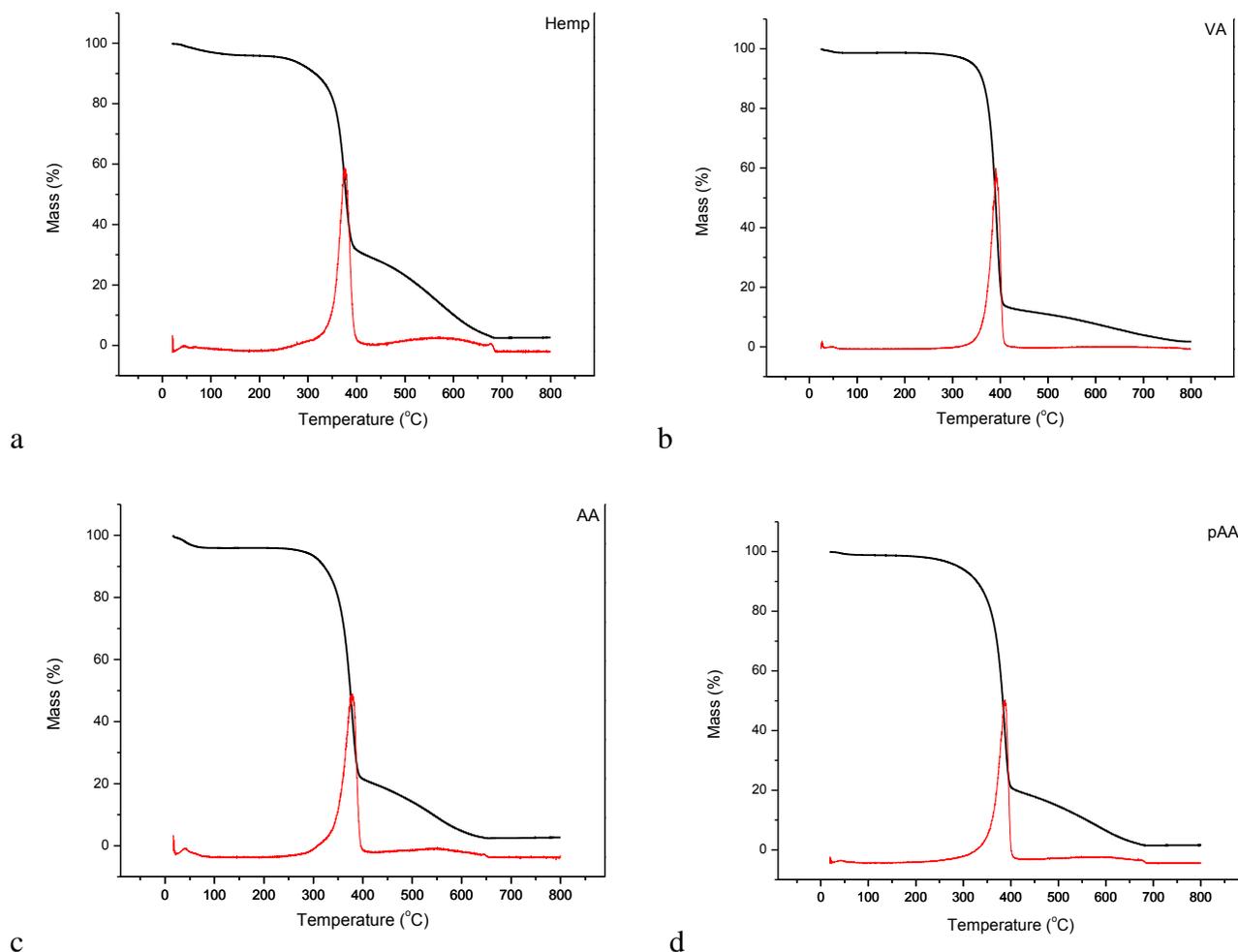


Fig. 6. TGA curves of (a) hemp, (b) VA (15% WPG), (c) AA (13% WPG) and (d) pAA (16% WPG) modified hemp fibers

Control hemp fibers showed char formation (about 33% of the total weight) at around 400°C, whereas the VA-modified sample showed 14% char formation at 410°C. AA- and pAA-modified samples showed around 22% and 21% char formation at 400°C, respectively. Therefore the acetylation process reduced the char formation, but VA acetylation appears to give the best result from those tested. All studied samples gave around 2.5% final ash content.

CONCLUSIONS

1. The WPG value did not exceed 15% with pyridine (13% with K_2CO_3) catalyzed acetylation with AA, even after 24 h reaction time. In VA modification, a maximum of 15% WPG value was obtained using K_2CO_3 -catalyzed transesterification reactions.

2. Results of AA and VA modification yielded similar WPG values (*ca.* 15%), which were obtained with AA and VA modification under the same reaction conditions.
3. With chemical modification, the maximum weight loss temperature was increased by *ca.* 15°C when compared with untreated hemp fibers.

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