CHAPTER 4: RESULTS AND DISCUSSION

4.1 Structural and morphological studies

4.1.1 Fourier Transforms Infrared Spectroscopy (FTIR)

The scanning of the samples was categorized into three division that is the pure samples (PVA, starches, and treated fibers), blends of PVA with different starches and blends of PVA with different starches and fibers. The samples of the biocomposite films were measured using the attenuated total reflectance (ATR) scanning method, which provided the scanning with less emphasis on the sample preparation. This method was considered quite useful in order to avoid any reaction that might affect the samples composition or structure during the sample preparation.

Pure samples (PVA, different starches and different fibers)

Figure 4.1 shows the spectra for pure PVA between the wavenumbers of 650 cm^{-1} and 4000 cm^{-1}. The major absorption peaks obtained from this spectrum are given in Table 4.1 and these are identified with the functional groups that are responsible for the different modes of vibrations.

Table 4.1 Infrared characteristics modes of vibrations and their wavenumbers for pure PVA.

(Chen, Cao, Chang, & Huneault, 2008) (Jayasekara, Harding, Bowater, Christie, & Lonergan, 2004) (Ibrahim, El-Zawawy, & Nassar, 2010) (Das, et al., 2010) (Mansur, Orefice, & Mansur, 2004) (Han, Chen, & Hu, 2009)

Wavenumbers (cm^{-1})	**Functional groups**
3290	O-H stretching (presence of intramolecularly hydrogen bonded hydroxyl groups in single bridge compounds)
2942	C-H stretching (presence of hydrocarbon chromophore in PVA)
2912	CH_2 symmetric and asymmetric stretching
1713	C=O stretching
1654	O-H bending (water absorption band)
1327	C-H bending
1240	C=O vibration
1142	C-O stretching
1091	C-O stretching in C-O-H group
920	C-C stretching
843	C-O stretching

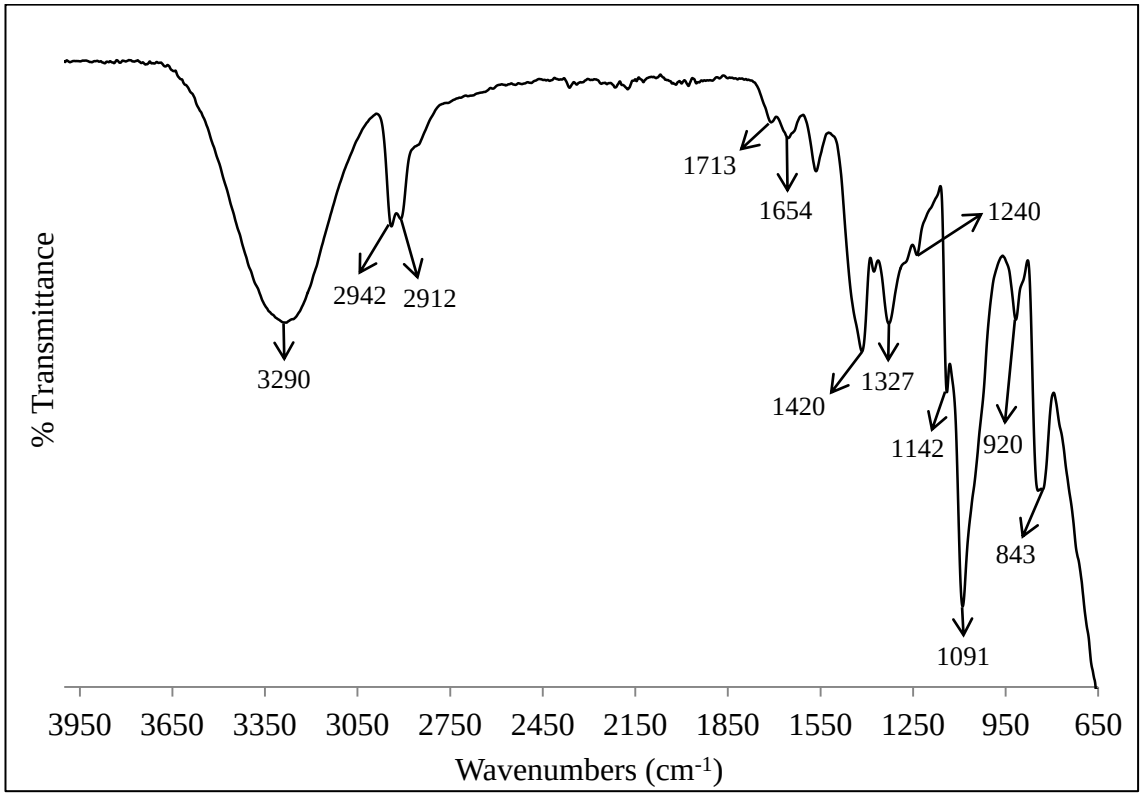

Fig. 4.1 FTIR spectra of pure PVA in the frequency range of 650 - 4000 cm^{-1}

A particular major reflection peak in the pure PVA spectra that identifies with the crystallinity of the PVA is the band 1142 cm^{-1} that corresponds to the C-O stretching band. This absorption band has been used as an assessment tool of PVA crystalline structure (Mansur, Orefice, & Mansur, 2004) (Han, Chen, & Hu, 2009). The band 1713 cm^{-1} is the characteristic carbonyl (C=O) functional group vibration due to residual acetate groups remaining after the manufacture of PVA from the hydrolysis of polyvinyl acetate (PVAc) or from the oxidation during manufacturing or processing. Figure 4.2 gives the spectrum for rice, tapioca and sago, respectively. Table 4.2 shows the major absorption peaks for starch in general.

Table 4.2 Infrared characteristic modes of vibrations and their wavenumbers for starch in general

(Chen, Cao, Chang, & Huneault, 2008) (Jayasekara, Harding, Bowater, Christie, & Lonergan, 2004) (Pal, Banthia, & Majumdar, 2006) (Xiong, Tang, Tang, & Zhou, 2008)

Wavenumbers (cm^{-1})	**Functional Groups**
3295	O-H stretching
2933	C-H stretching of CH_2
1630	O-H bending (water absorption band)
1455	CH_2 bending in plane
1340	C-O-H bending
1388	CH bending in plane
1150	C-O stretching of C-O-C
1100	C-O-H stretching
1030	C-O stretching in C-O-H and C-O-C in the anhydrous glucose ring
930	C-O-C ring vibration
851	C(1)-H(α) bending
760	C-O-C ring vibration

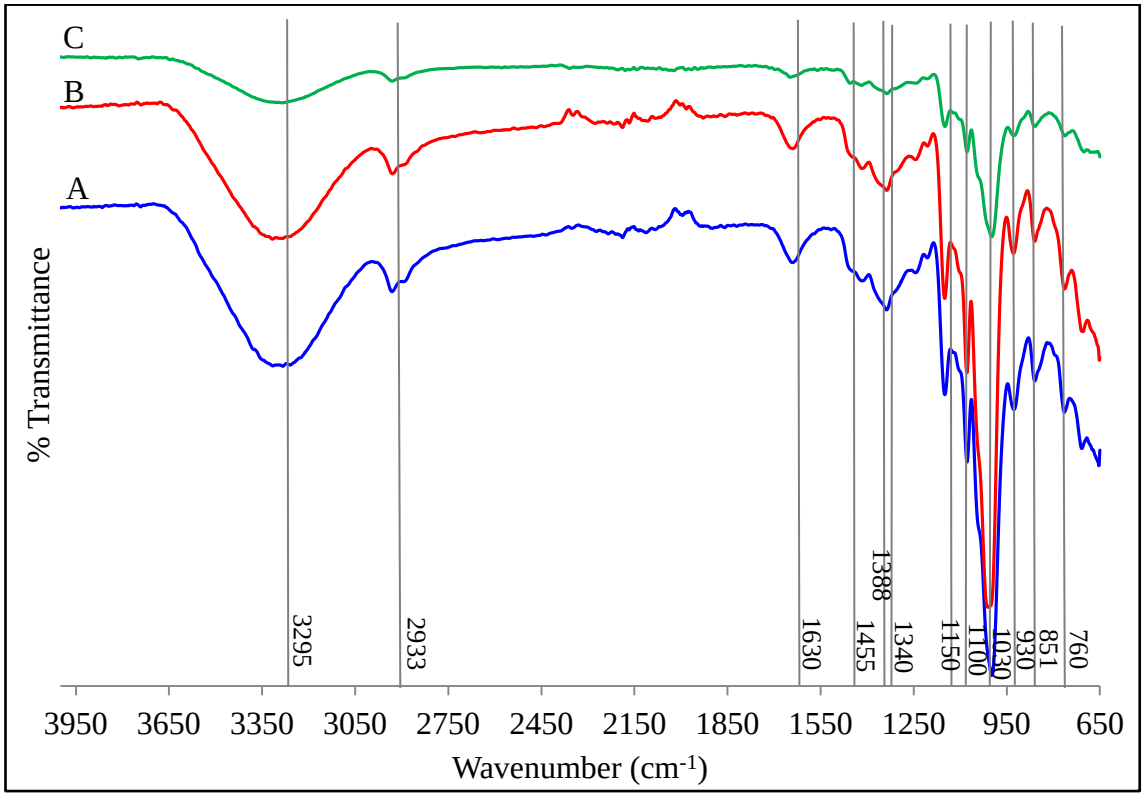

Fig. 4.2 FTIR spectrum of tapioca (A), rice (B) and sago (C) starch powder in the frequency range of 650-4000 cm^{-1}

The spectrum of starches shows nearly identical major reflection peaks that correspond to different functional groups vibration. The absorption peak at 1455 cm^{-1}, 1388 cm^{-1}, 851 cm^{-1} and 760 cm^{-1} are characteristic absorption peaks of starch (Xiong, Tang, Tang, & Zhou, 2008). The peak at 760 cm^{-1} is especially important because it is solely attributed to starch and it is an ideal reference frequency to monitor starch content in the biocomposite films.

Figure 4.3 shows the spectrum of alkaline treated bamboo, kenaf, roselle and napier grass, respectively. Table 4.3 shows the major absorption peaks for treated natural fibers in general.

Table 4.3 Infrared characteristic modes of vibrations and their wavenumbers for alkaline treated natural fibers in general

(Xiao, Sun, & Sun, 2001) (Morain, Alvarez, Cyras, & Vacquez, 2008) (Liu, Mohanty, Drzal, Askel, & Misra, 2004) (Yang, Yan, Chen, Lee, & Zheng, 2007) (Yang, Xu, Ma, & Wang, 2008).

Wavenumbers (cm^{-1})	**Functional Groups**
3350	O-H stretching
2890	C-H stretching and bending (cellulose)
2360	atmospheric carbon dioxide
1650	O-H bending
1608	C=C stretching (lignin)
1515	benzene ring vibration (lignin)
1465	C-H deformation (lignin)
1430	CH_2 bending (cellulose)
1360	C-O stretching of acetyl ring
1320	C-O stretching of acetyl ring
1240	C-O-C stretching (cellulose)
1158	C=O=C stretching (pyranose skeletal ring)
1109	O-H association (cellulose)
1025	C-O or C=C stretching (cellulose)
895	rotation of glucose residue around the glucosidic band (C_1-H deformation of glucose rings)

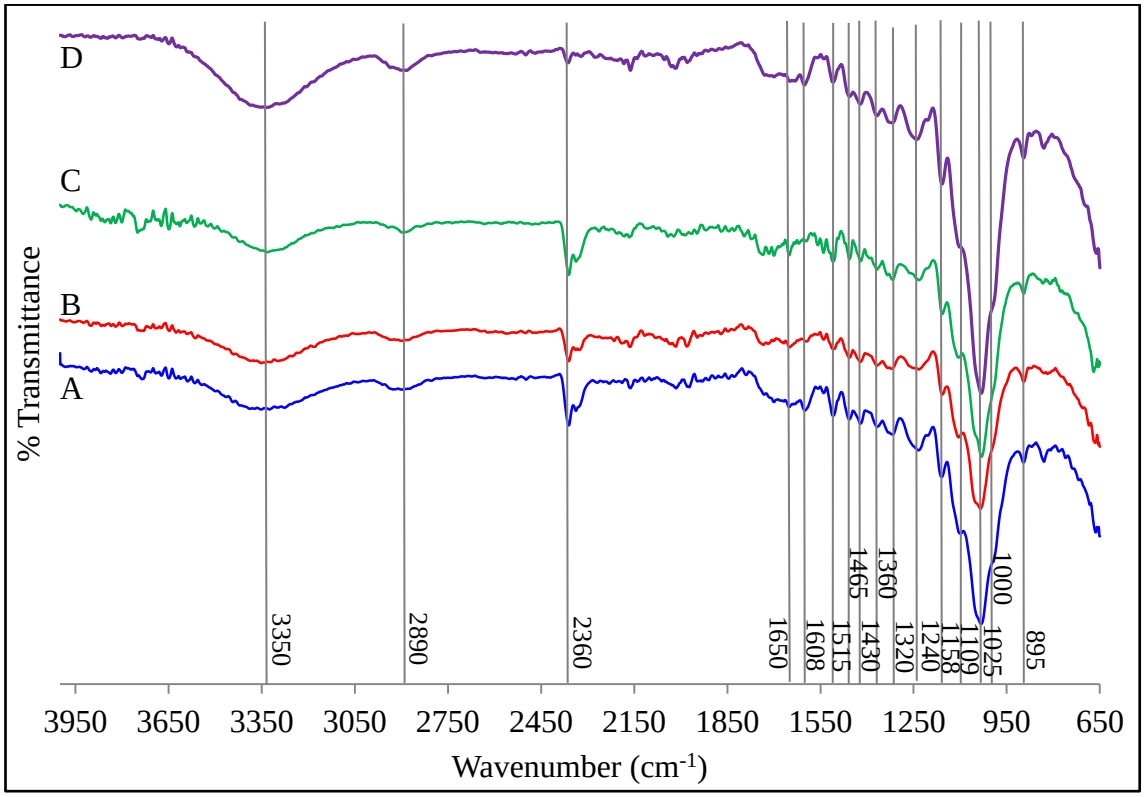

Fig. 4.3 FTIR spectrum of alkali treated bamboo (A), kenaf (B), roselle (C) and Napier (D) fibers in the frequency range of 650-4000 cm^{-1}

The spectrum of the alkali treated natural fibers also show nearly identical major reflection peaks that correspond to different vibrational groups vibrations. The hydrophilic tendency of alkali treated natural fibers is reflected in the broad absorption band in the 3700-3100 cm^{-1} region, which is related to the O-H groups present in their main components. There are generally five vibrational peaks that depicts the typical structure of cellulose and they are 2890 cm^{-1} for the stretching and bending of C-H bonds, 1430 cm^{-1} for the bending vibration of CH_2, 1240 and 1025 cm^{-1} for the C-O and C=C stretching and 895 cm^{-1} for β-glucosidic linkage (Yang, Xu, Ma, & Wang, 2008). The peak of 895 cm^{-1} is important when analyzing the conformational changes of cellulose occurring during the alkali treatment of natural fibers because it relates to the

rotation of glucose residue around the glucosidic band (Das & Chakraborty, 2006) (Rosa, et al., 2010). Alkali treatment done on different types of fibers changes their supermolecular structure and morphology but there is not much changes between the chemical structures of the different fibers.

PVA/starches composites

Figure 4.4, 4.5 and 4.6 show the spectrum of PVA with different concentration of tapioca, rice and sago starch, respectively. The spectra are compared with pure PVA and pure starch to determine the interaction between PVA and starch in the blended composites.

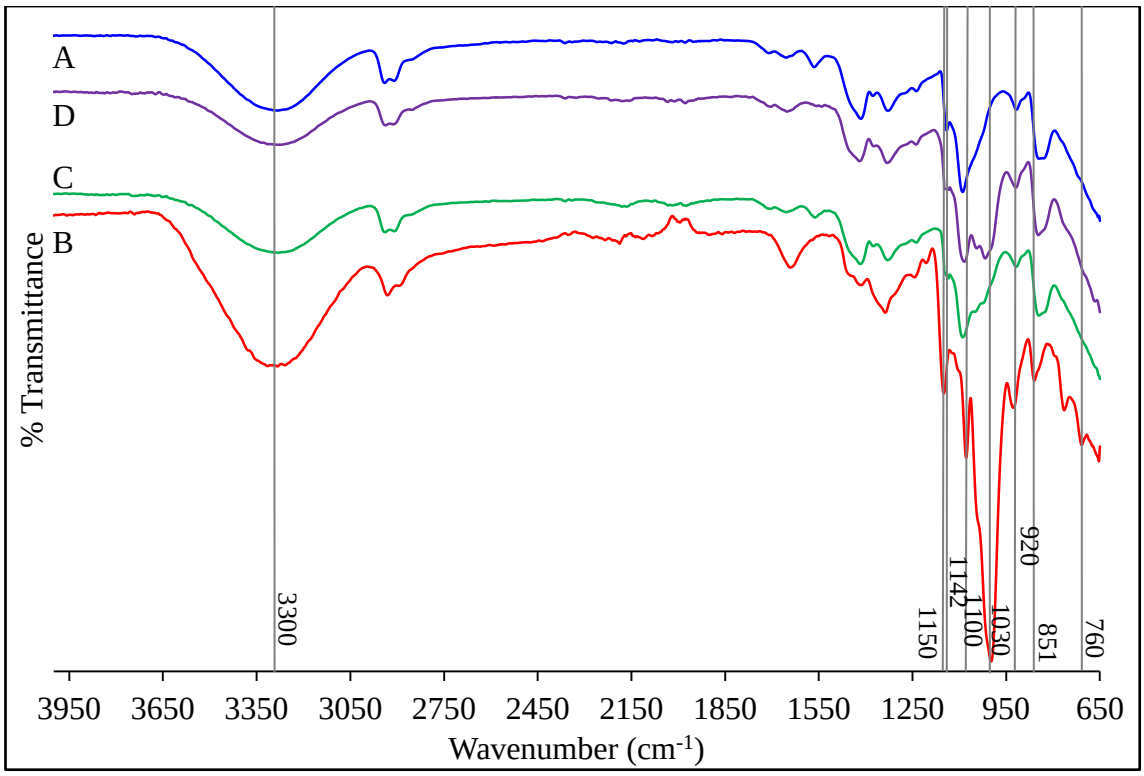

Fig. 4.4 FTIR spectrum of pure PVA (A), pure tapioca starch (B), PVA/1TS (C) and PVA/3TS (D) in the frequency range of 650-4000 cm^{-1}

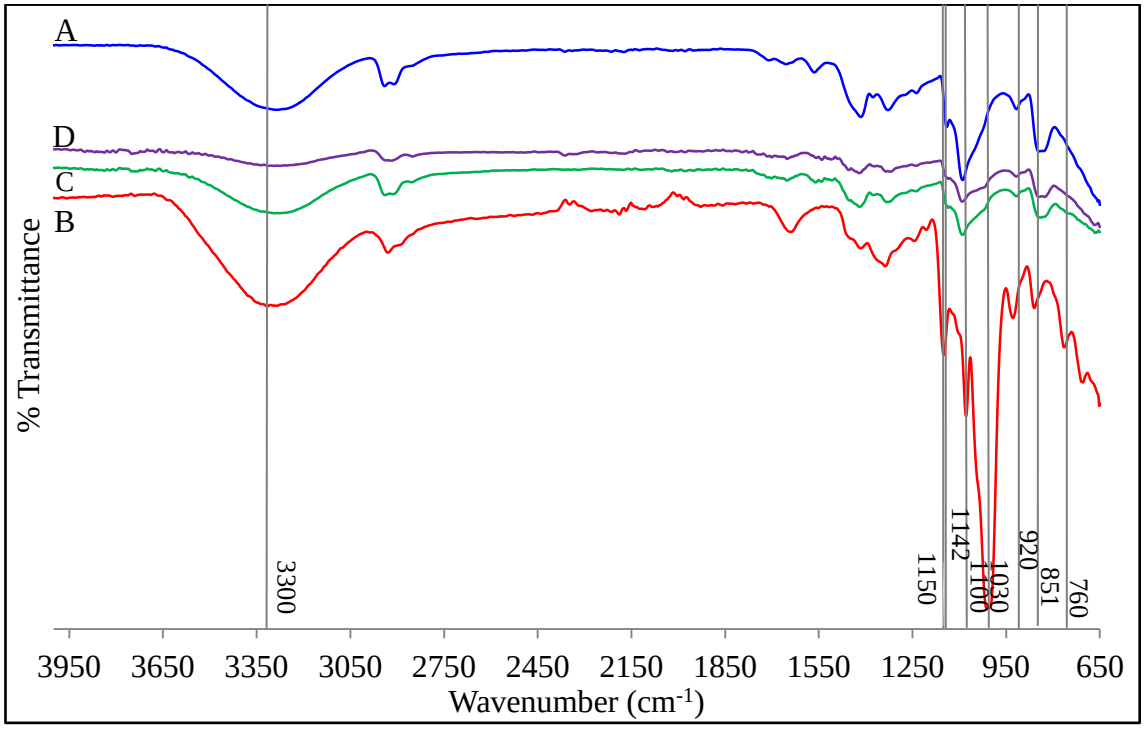

Fig. 4.5 FTIR spectrum of pure PVA (A), pure rice starch (B), PVA/1RS (C) and PVA/3RS (D) in the frequency range of 650-4000 cm^{-1}

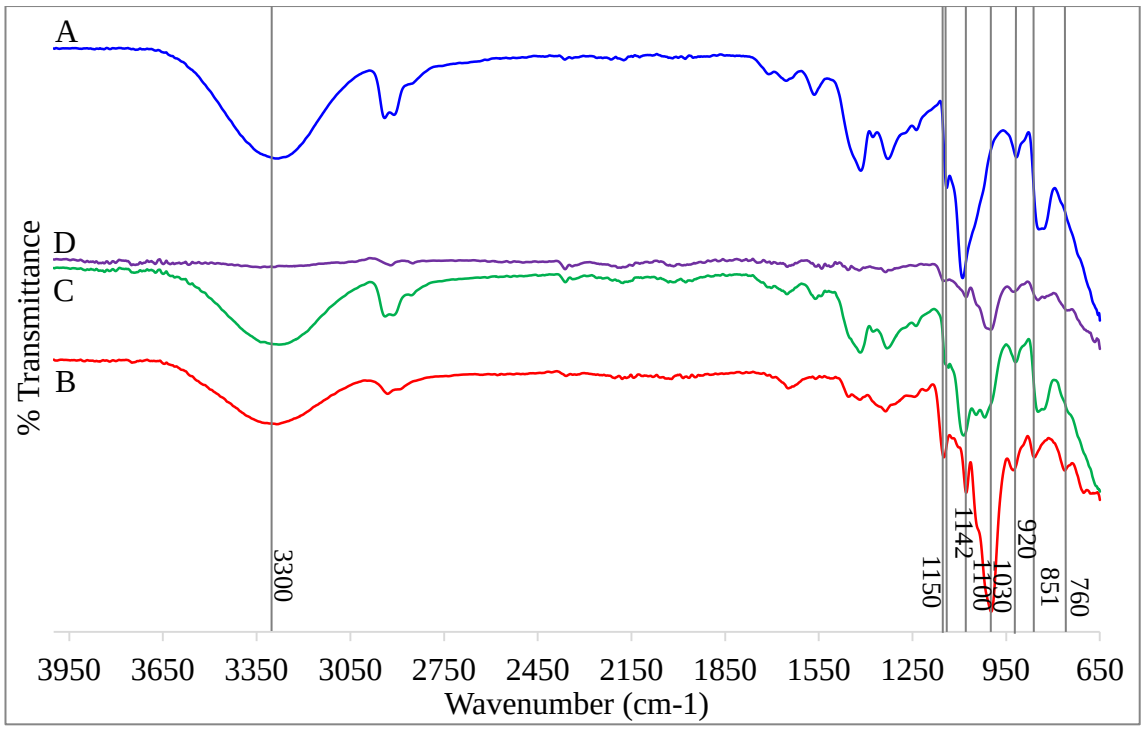

Fig. 4.6 FTIR spectrum of pure PVA (A), pure sago starch (B), PVA/1SS (C) and PVA/3SS (D) in the frequency range of 650-4000 cm^{-1}

The spectrum of PVA blended with different concentration of different starches shows nearly all of the major absorption peaks of its different blended component. In the blended films, the peak 760 cm^{-1} which relates to the stretching of the C-O-C bond weakened and shifted slightly to higher wavenumber. This peak is solely attributed by starch and is not overlap by any other component's absorption peaks. This weakening and shifting may be due to the interaction of PVA and starch molecules in the blending and film forming process (Jayasekara, Harding, Bowater, Christie, & Lonergan, 2004). The peak 1030 cm^{-1} (symmetrical stretching of the ether bond C-O-C) weakened as the starches were mixed with PVA and this change in the band's intensity indicates that the α-glucosidic linkage between the sugar units in the starch were modified by the blending reaction (Van Soest, Tournois, de Wit, & Vliegenthart, 1995). The absorption band 3300 cm^{-1} which represents stretching of the -OH groups becomes wide and the intensity of the band decreases. This indicates that all of the hydroxyl groups in the PVA molecular chain and starch are involved in the film forming process (Han, Chen, & Hu, 2009). The absorption band for starch that is 851 cm^{-1} weakened as the starch content in the film is increased from 10% to 30%. This band is sensitive to changes in the crystallinity of starch and the weakening of the band may be due to decreased crystallinity of the starch component cause by its interactions with the PVA molecules (van Soest, Tournois, de Wit, & Vliegenthart, 1994). The crystallinity dependent band of PVA, 1142 cm^{-1}, weakened in the PVA/starch blends. The decreased in intensity may indicate that the crystal structure of PVA was changed and that the crystallinity of PVA decreased (Mansur, Orefice, & Mansur, 2004). When forming the blended films, the interface bonding formed between starch and PVA may result in a decrease in the

number of hydrogen bonds and this indirectly lessened PVA crystallinity indicating that there is interaction present between the starch and PVA polymer chains. In the spectrums, the band 1100 cm^{-1} associated with the stretching of the C-O bond in C-O-H and C-O-C groups of the anhydrous glucose ring weakened and shifted to lower wavenumber. This indicates that the intra- and intermolecular hydrogen bonding of starch molecules has significantly changed due to the mixing process with PVA (Van Soest, Tournois, de Wit, & Vliegenthart, 1995) (van Soest, Tournois, de Wit, & Vliegenthart, 1994). The band of 920 cm^{-1} assigned to the C-C stretching of PVA molecular chain shifted to a higher wavenumber and decreased in intensity. Even though there are characteristic peaks of starch and PVA in the spectrum of PVA blended with different concentration of starches, it is worth noting that the shape and location of the main peaks of the blended films were closer to those of PVA. This suggests that interactions of PVA-PVA molecules dominated and were stronger than that of PVA-starch molecules and starch-starch molecules in the blending system. The magnified version of the spectra PVA blended with 1g and 3g of different starches is attached to Appendix A.

PVA/starches/fibers composites

Figure 4.7, 4.8, 4.9 and 4.10 show the spectrum of PVA blended with 1g of tapioca starch (TS) and mix with different concentration of different alkali treated fibers (bamboo (BB), kenaf (KF), roselle (ROS) and Napier (NP)). Figure 4.11, 4.12, 4.13 and 4.14 show the spectrum of PVA blended with 1g of rice starch (RS) and mix with different concentration of different alkali treated fibers (bamboo (BB), kenaf (KF), roselle (ROS), and Napier (NP)). Figure 4.15, 4.16, 4.17, and 4.18 show the spectrum of PVA blended with 1g of sago starch (SS) and mix with different concentration of different alkali treated fibers (bamboo (BB), kenaf (KF), roselle (ROS), and Napier (NP)).

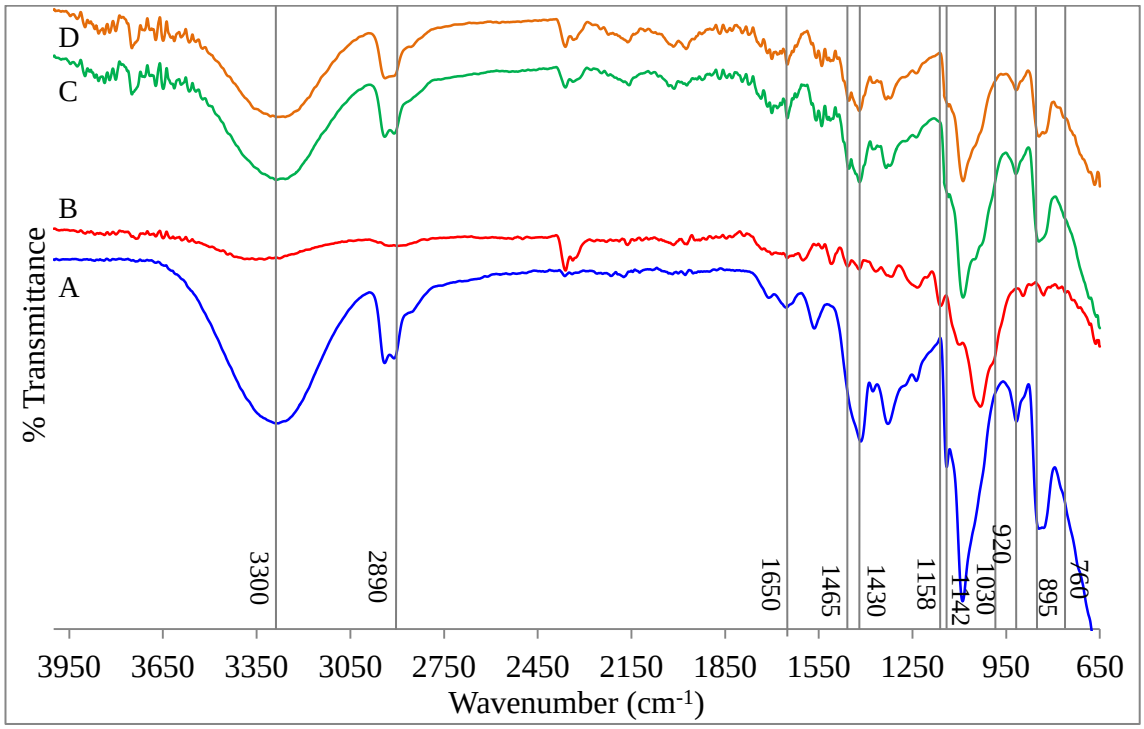

Fig. 4.7 FTIR spectrum of pure PVA (A), treated bamboo fiber (B), PVA/1TS/1BB (C) and PVA/1TS/3BB (D) in the frequency range of 650-4000 cm^{-1}

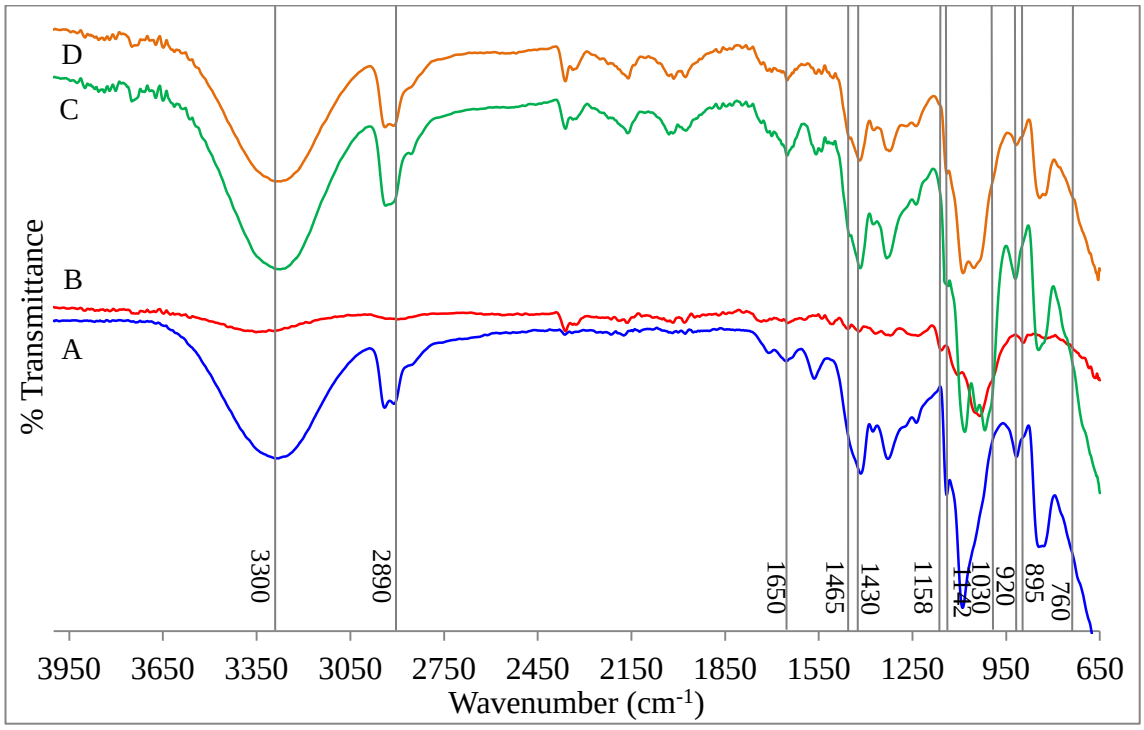

Fig. 4.8 FTIR spectrum of pure PVA (A), treated kenaf fiber (B), PVA/1TS/1KF (C) and PVA/1TS/3KF (D) in the frequency range of 650-4000 cm^{-1}

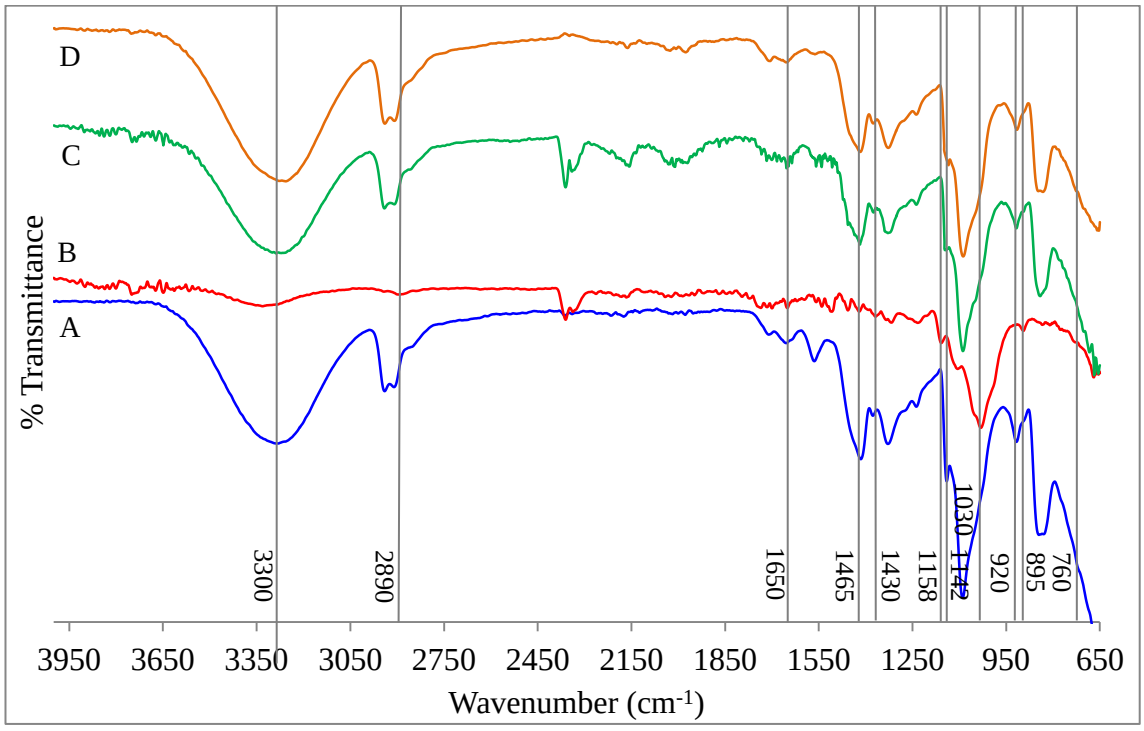

Fig. 4.9 FTIR spectrum of pure PVA (A), treated roselle fiber (B), PVA/1TS/1ROS (C) and PVA/1TS/3ROS (D) in the frequency range of 650-4000 cm^{-1}

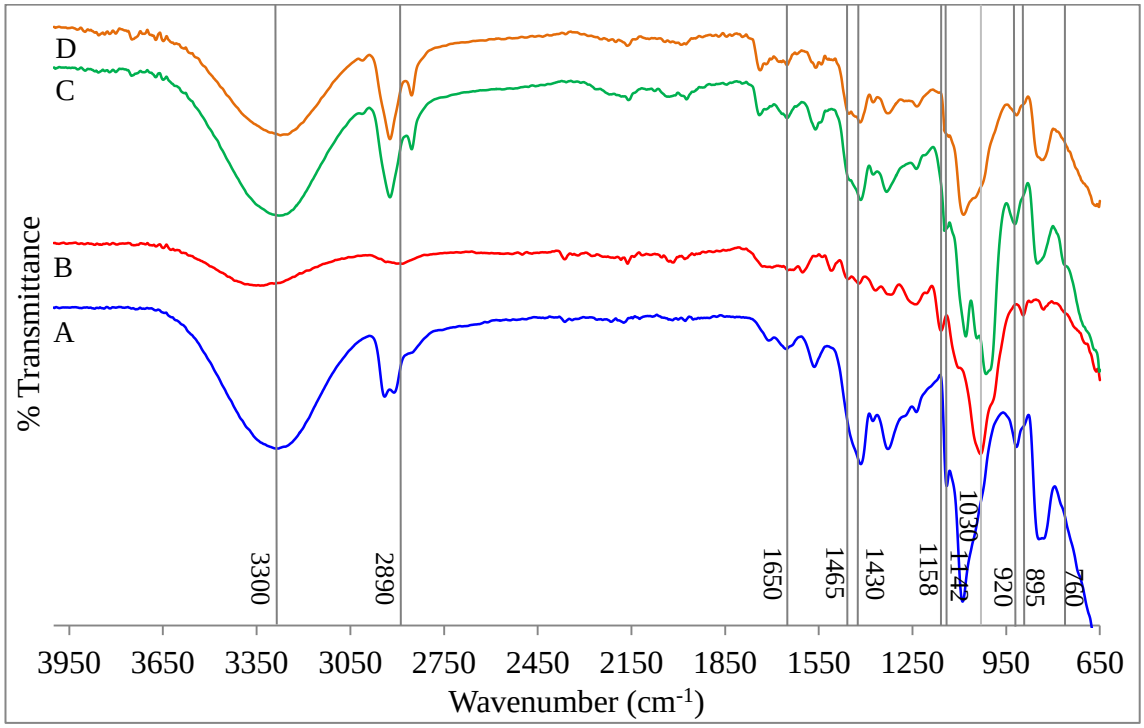

Fig. 4.10 FTIR spectrum of pure PVA (A), treated Napier fiber (B), PVA/1TS/1NP (C) and PVA/1TS/3NP (D) in the frequency range of 650-4000 cm^{-1}

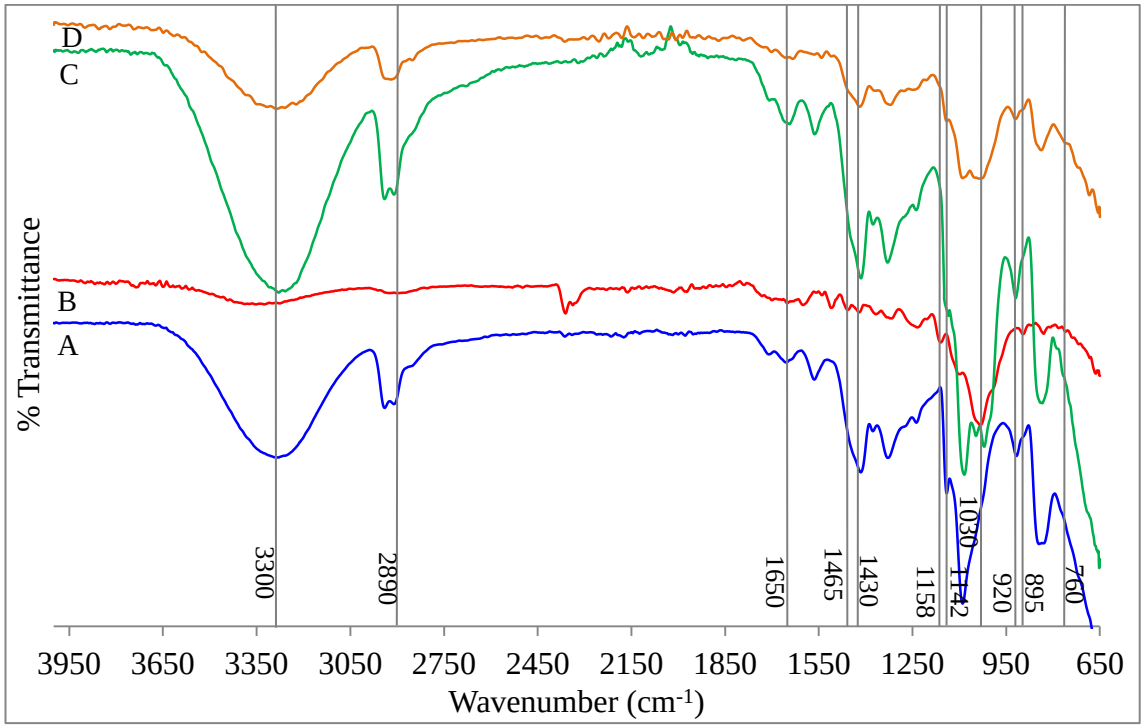

Fig. 4.11 FTIR spectrum of pure PVA (A), treated bamboo fiber (B), PVA/1RS/1BB(C) and PVA/1RS/3BB (D) in the frequency range of 650-4000 cm^{-1}

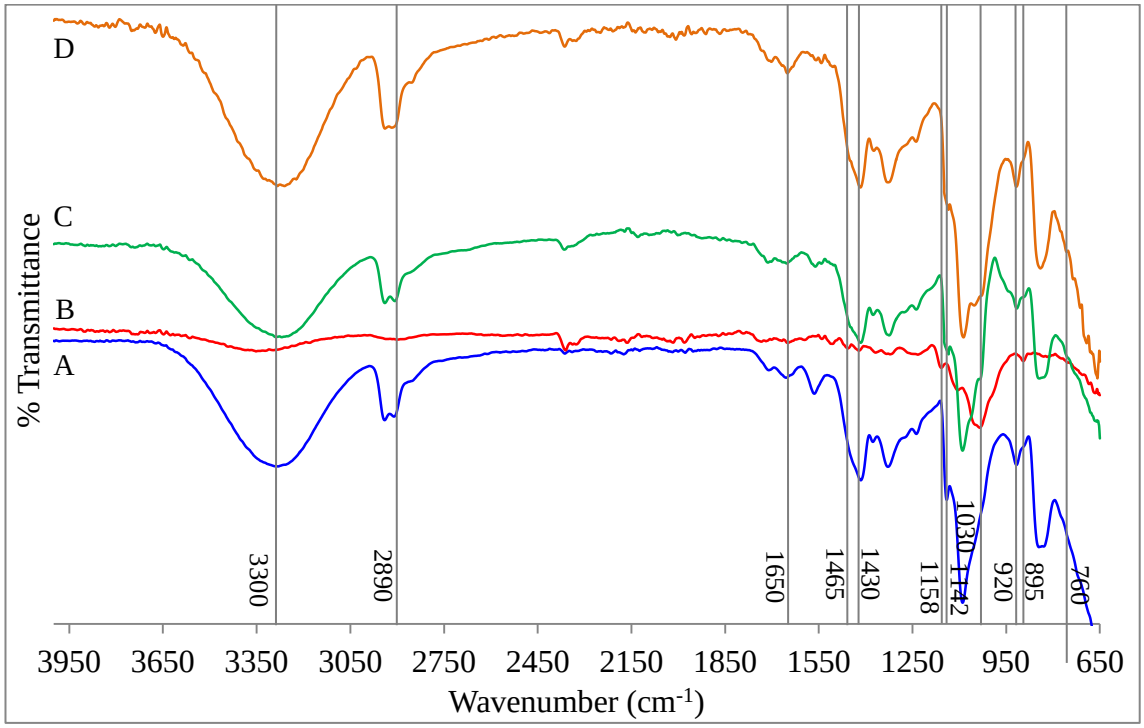

Fig. 4.12 FTIR spectrum of pure PVA (A), treated kenaf fiber (B), PVA/1RS/1KF (C) and PVA/1RS/3KF (D) in the frequency range of 650-4000 cm^{-1}

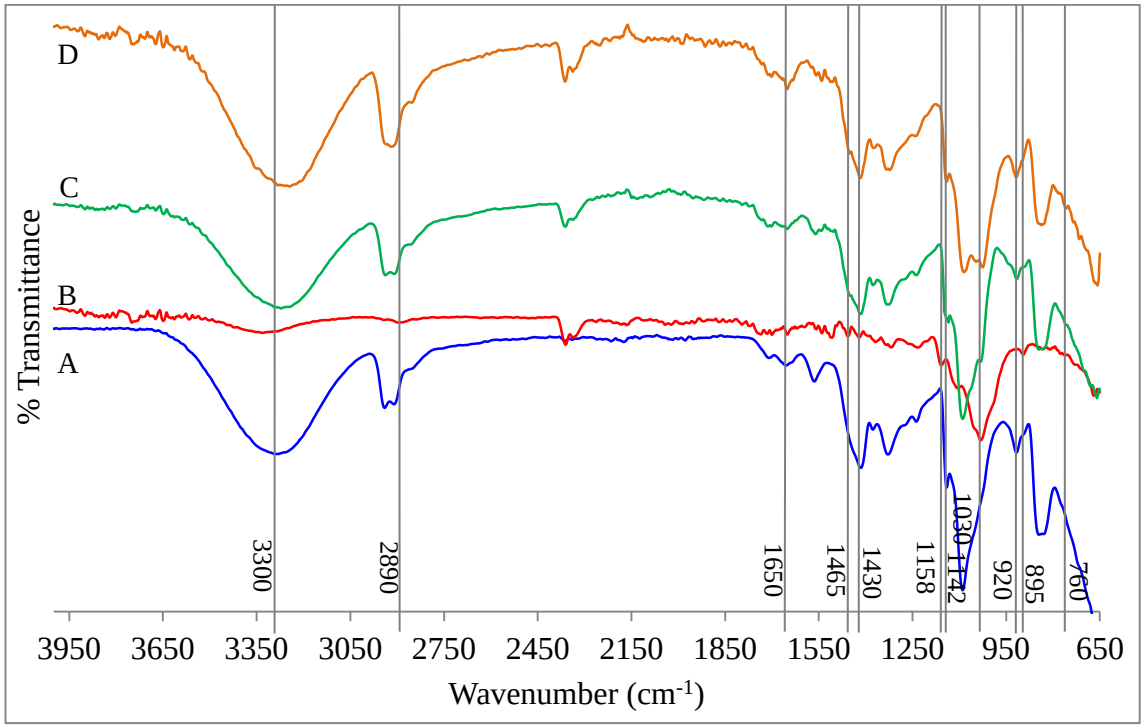

Fig. 4.13 FTIR spectrum of pure PVA (A), treated roselle fiber (B), PVA/1RS/1ROS (C) and PVA/1RS/3ROS (D) in the frequency range of 650-4000 cm^{-1}

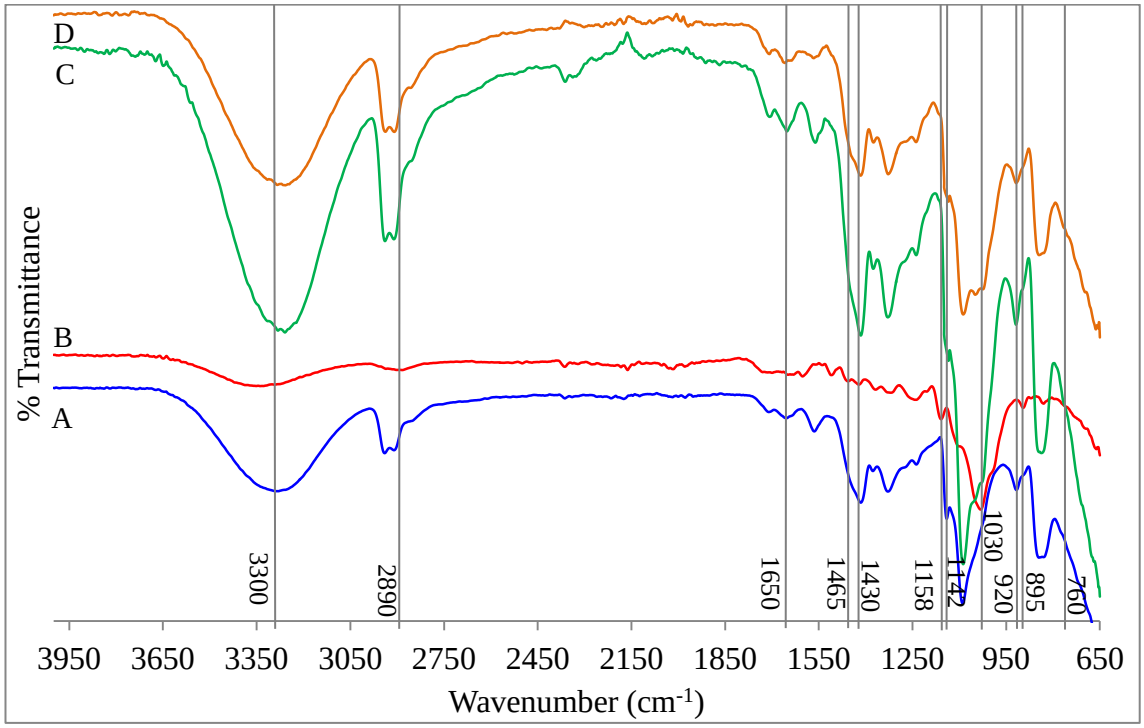

Fig. 4.14 FTIR spectrum of pure PVA (A), treated Napier fiber (B), PVA/1RS/1NP (C) and PVA/1RS/3NP (D) in the frequency range of 650-4000 cm^{-1}

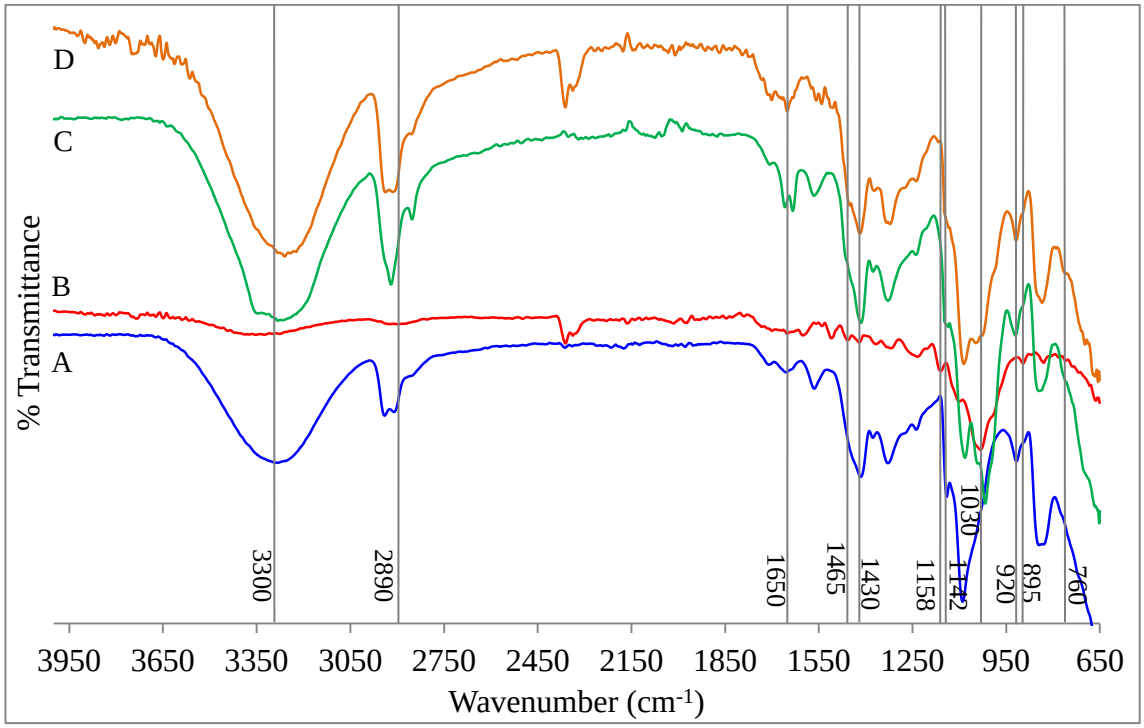

Fig. 4.15 FTIR spectrum of pure PVA (A), treated bamboo fiber (B), PVA/1SS/1BB (C) and PVA/1SS/3BB (D) in the frequency range of 650-4000 cm^{-1}

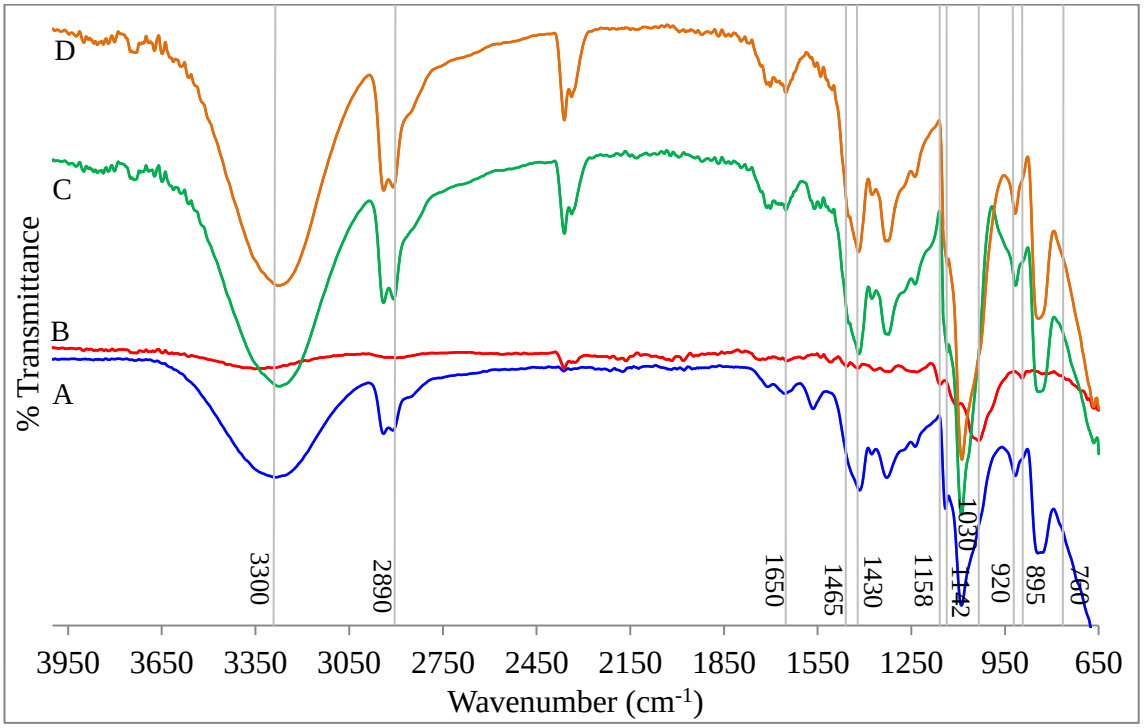

Fig. 4.16 FTIR spectrum of pure PVA (A), treated kenaf fiber (B), PVA/1SS/1KF (C) and PVA/1SS/3KF (D) in the frequency range of 650-4000 cm^{-1}

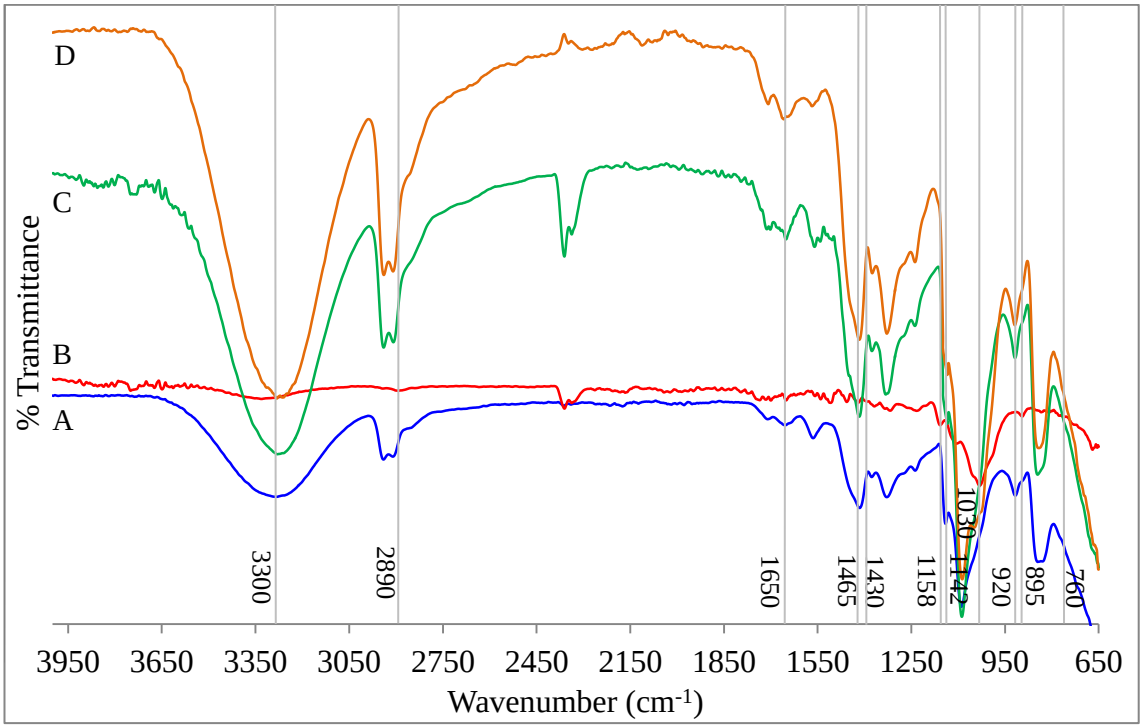

Fig. 4.17 FTIR spectrum of pure PVA (A), treated roselle fiber (B), PVA/1SS/1ROS (C) and PVA/1SS/3ROS (D) in the frequency range of 650-4000 cm^{-1}

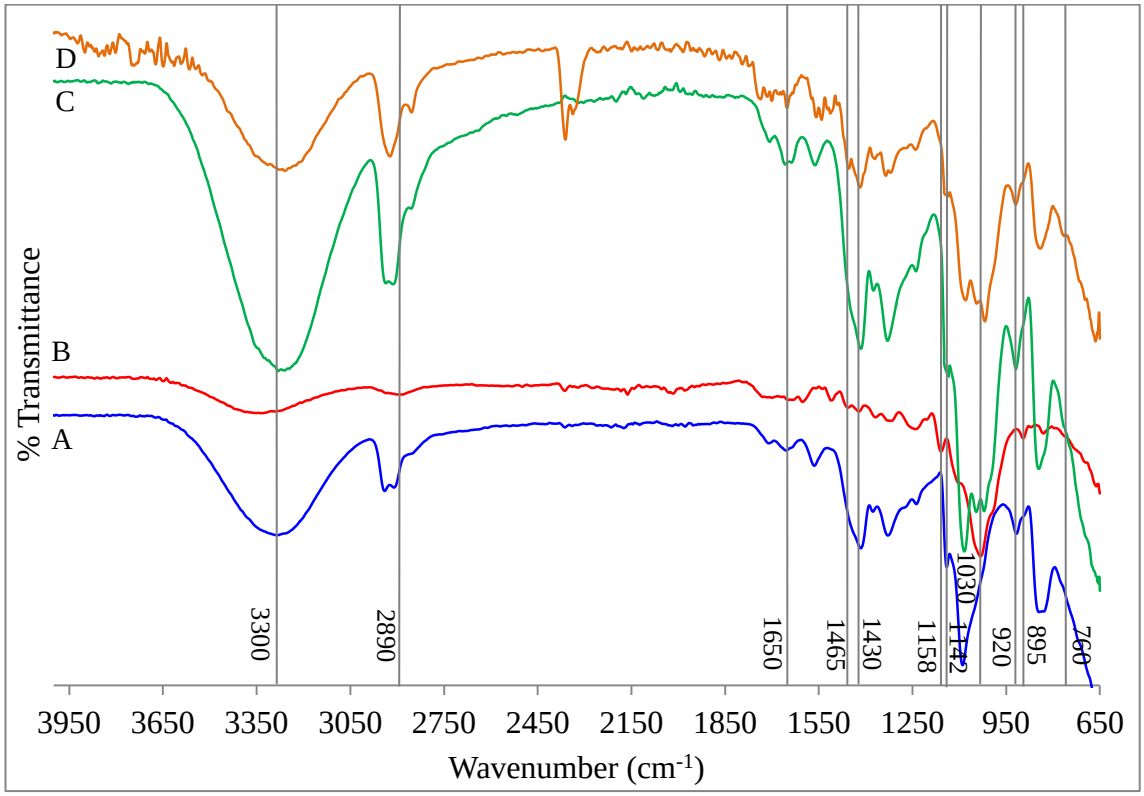

Fig. 4.18 FTIR spectrum of pure PVA (A), treated Napier fiber (B), PVA/1SS/1NP (C) and PVA/1SS/3NP (D) in the frequency range of 650-4000 cm^{-1}

From all the figures (4.7 to 4.18) that show the FTIR spectrum of PVA blended with 1g of different starches and mix with different concentration (1g and 3g) of different chemically treated natural fibers, it can be concluded that majority of the spectrum shows nearly identical absorption peaks. The vibrational peaks are contributed by the three different components that make up the biocomposite films. In the biocomposite films, the broad band at 3300 cm^{-1} that is assigned to the -OH group stretching increases in intensity and shifted slightly to lower wavenumbers. This can be attributed to the presence of inter- and intramolecular hydrogen bonded hydroxyl groups having form association between the three different blended components (Han, Chen, & Hu, 2009). It also indicates the presence of increased number of -OH groups arising in the blended

films. This may be partly contributed by the alkali treatment process of the natural fibers that cleaves through alkali sensitive bonds producing more -OH groups (Alvarez & Vacquez, 2006). The band 2890 cm^{-1}, 1430 cm^{-1}, 1158 cm^{-1} and 895 cm^{-1} are typical absorption peaks for cellulose. In the blended films, most of these peaks decrease in intensity when compared with the peaks from the spectra of the alkali treated natural fibers. The forming of intermolecular hydrogen bonded hydroxyl groups between PVA, starch and cellulose may cause the breaking down of extensive hydrogen bonding network in the cellulose molecular chains itself causing their crystalline structure to be changed (Cao, Sakamoto, & Goda). As the fiber content in the blended film increases, the absorption peaks becomes more prominent. This may be due to the increased concentration of cellulose present in the blended films. The absorption peaks that are typical of starch are 760 cm^{-1} and 1030 cm^{-1}. Both of these peaks are not clearly seen partly because of the dominant polymer matrix, PVA and the high percentage of alkali treated fibers that are composed mainly of cellulose. Both peaks, the 920 cm^{-1} assigned to the C-C stretching and the crystalline dependent, 1142 cm^{-1} that represents the polymer matrix, PVA decreases in intensity. For the crystalline dependent peak of 1142 cm^{-1} that is contributed by the C-O stretching band, the decrease in intensity may indicate that the crystal structure of PVA was changed and that the crystallinity of PVA decreased (Mansur, Orefice, & Mansur, 2004). For the same reason as stated before, when forming the blended films, the interface bonding formed between PVA, starch and fiber may result in a decrease in the number of hydrogen bonds and this indirectly lessened PVA crystallinity indicating that there is interaction present between the PVA, starch and fiber molecular chains. From all the observations, it can be concluded that

there are no peaks in the spectrum of the biocomposite films other than peaks corresponding to its individual components that make up the blend and so the FTIR analyses has shown no evidence of strong chemical interaction changing the nature of the functional groups on the surface of the biocomposite films.