4.2 Thermal studies

4.2.1 Thermogravimetric Analysis (TGA)

Pure samples (PVA, starches and fibers)

The TG analysis of pure PVA was carried out at a heating rate of 10°C/min, and the TG curves for the degradation of PVA in nitrogen atmosphere are shown in Figure 4.93.

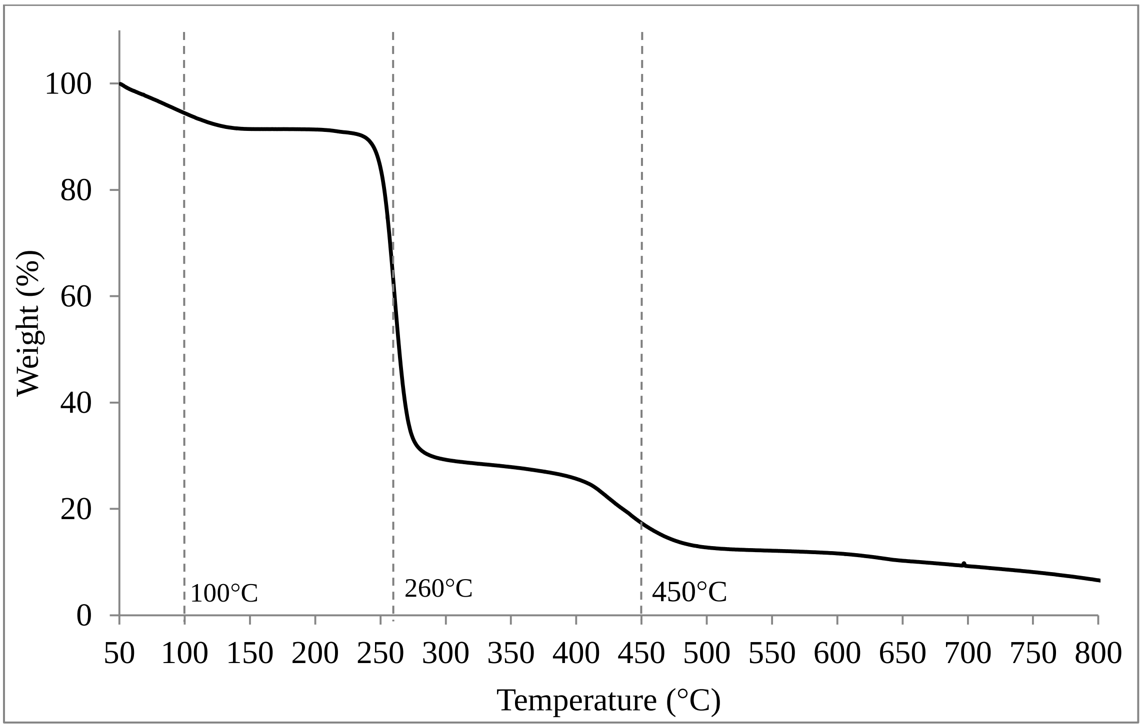

Fig. 4.93 TG curves for the degradation of PVA in nitrogen atmosphere at 10°C/min.

The shape of the mass loss curve is consistent with the generally accepted two-step mechanism for the degradation of PVA (Maruyama, Takeuchi, & Tanizaki, 1989) (Anders & Zimmermann, 1987). Basically the decomposition of pure PVA occurred in 2 stages and began at 200°C. Below 200°C; the weight loss is attributed to the evaporation of water and the release of hydrolysis residue volatiles such as methanol and methyl acetate (Marten & Zvanut, 1992). In between 200-500°C, the decomposition forms volatile organic compounds which subsequently produced conjugated unsaturated polyene structures. The volatiles organic compounds formed were due to the scissioning of carbon-carbon bonds of the polymer backbone which led to the generation of carbonyl functional group products (Rahman, Lee, Rahmat, & Samad, 2010). For the second stage, decomposition that occurs at temperature as high as 450°C, remains of PVA would start to produce small amounts of hydrocarbon products such as alkenes, alkanes, and aromatics and finally all the mass losses with becomes constant at temperature above 700°C and this feature indicates that stable carbonaceous residues were formed at this level (Tubbs & Ting, 1973) (Thomas, Guerbois, Russell, & Briscoe, 2001). Figure 4.94 shows the TG curves for the decomposition of different starches between the temperatures of 50-900°C.

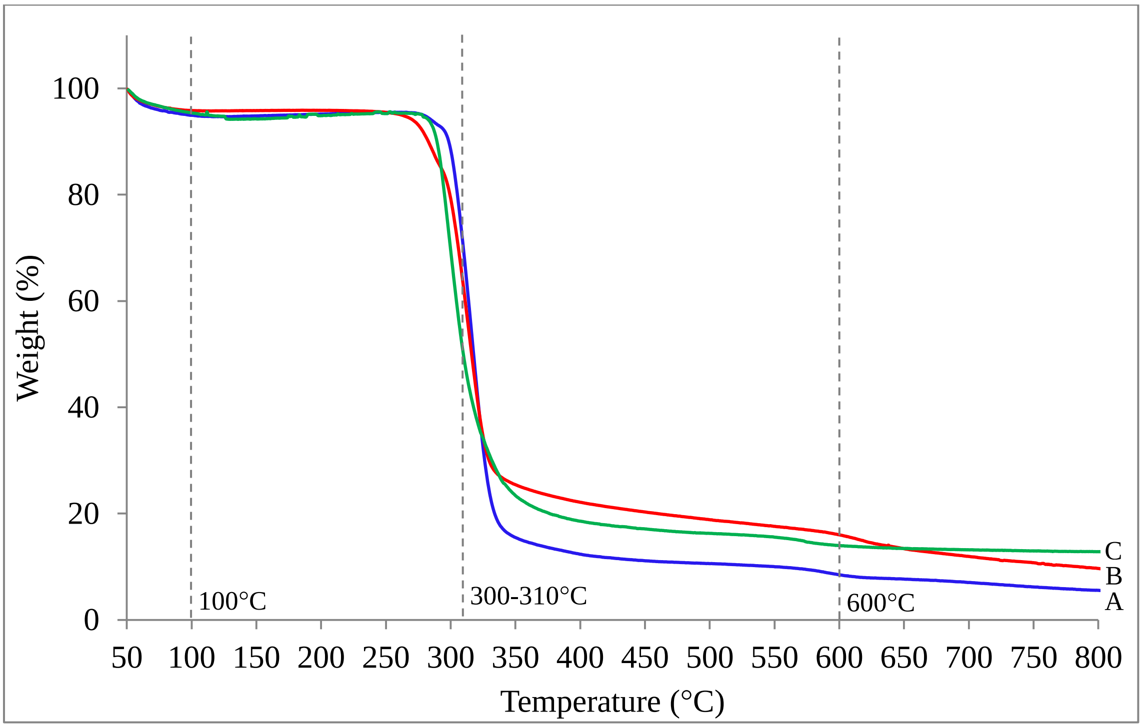

Fig. 4.94 TG curves for the degradation of tapioca (A), rice (B) and sago (C) starch in nitrogen atmosphere at 10°C/min.

According to the TG curves for different starches, one common feature that can be observed is that major degradation of the starches occurs at 300-310°C. This is due to the depolymerisation and degradation of the starches into non-oxidative process. The starches pass through a series of irreversible alterations where the altered structural form of starch leads to the formation of polydextrins (Lacerda, et al., 2008). The product polydextrin is soluble in cold water and is used as industrial gums (Aggarwal & Dollimore, 1998) (Aggarwal & Dollimore, 1996). For decomposition below 200°C, evaporation and dehydration occurs in the starches where the moisture content of the starch was totally released during this stage. At higher temperature (> 450°C), depolymerisation of the macromolecules takes place with the formation of β-(1,6) anhydro D-glucopyranose (levoglucosan), 2-furaldehyde (furfural) and a range of low molecular weight volatile and gaseous fragmentation products (Aggarwal & Dollimore, 1998). At temperatures higher than 600°C all mass losses became stabilized and this is indicated by the inert carbonaceous residues that were formed. From the TG curves it can be observed that there is no significant difference in the thermograms of starches from different botanical origin except for a slight difference in the char yield of the carbonaceous residue.

Figure 4.95 shows the TG curves for the decomposition of treated bamboo, kenaf, roselle and napier fibers between the temperatures of 50-800°C.

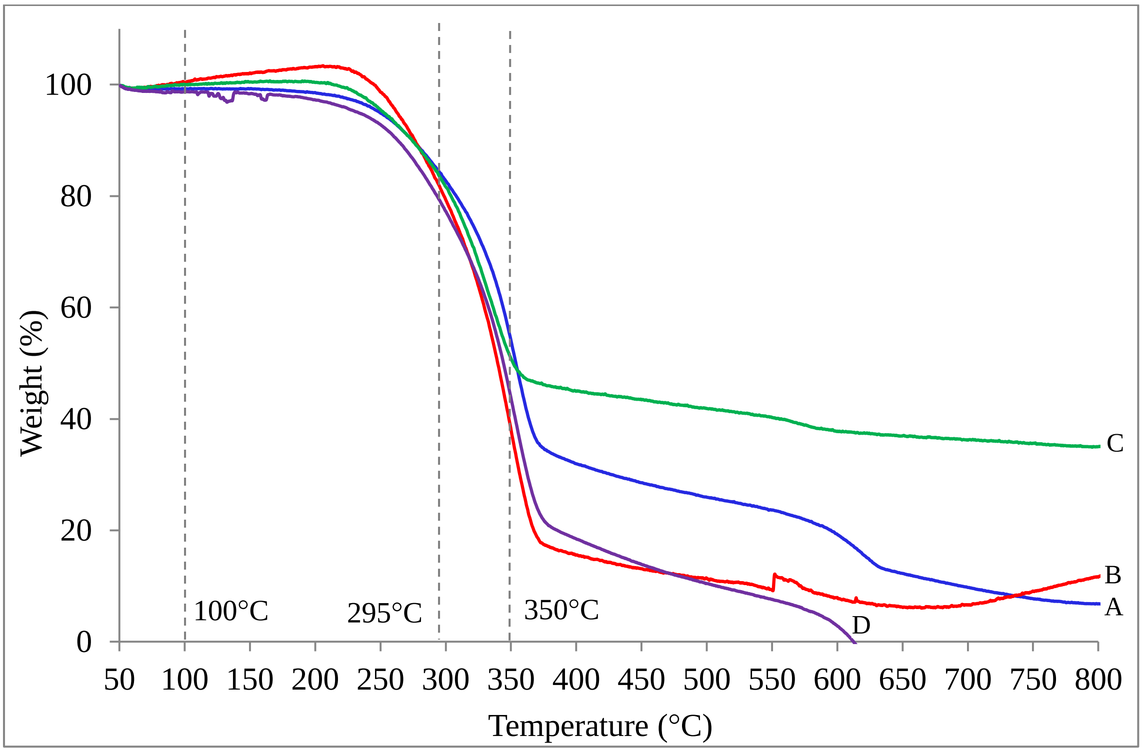

Fig. 4.95 TG curves for the degradation of bamboo (A), kenaf (B), roselle (C) and Napier (D) fibers in nitrogen atmosphere at 10°C/min.

As illustrated in Figure 4.95, the TG curves for the different treated natural fibers were similar in the way they decompose. The main decomposition range of temperature for all the fibers is between 295°C and 350°C. For temperatures below 200°C, water and other low molecular weight compounds remaining after the alkali treatment process vaporized. From the thermograms of the different treated fibers, it can be observed that the curves represents two decomposition steps that overlap each other that is the thermal degradation of cellulose and lignin that occurs at temperatures 300-350°C and 280-500°C, respectively (Rosa, et al., 2009) (Lee, Rahman, Rahmat, & Mokhtar, 2011). In between the temperature range of 295°C and 350°C, the crystalline structure of the treated fibers starts to destruct resulting in the increase of amorphous structure such as L-glucose. At temperature higher than 400°C, the crystalline region of the fibers totally destruct and the cellulose decomposed into the monomer of D-glucopyranose, which could be further decomposed into free radical and eventually these free radicals are converted into volatiles and tar (Yang, Xu, Ma, & Wang, 2008). The difference between the TG curves of the different treated fibers can be seen in the char yield at temperatures higher than 700°C. Higher amounts of char yield can be seen from the TG curves of the treated bamboo and roselle fibers. This may be caused by the presence of small amounts of lignin that withstood the cellulose extracting procedure (bleaching and alkali treatment) (Morain, Alvarez, Cyras, & Vacquez, 2008). As mentioned before in Chapter 3, the lignin content of the different fiber used in this study differs, bamboo and roselle has the highest value of lignin naturally (John & Anandjiwala, 2007) (Dutt, Upadhyay, Singh, & Tyagi, 2009). According to literature, among the three main components of natural fiber, lignin was the most difficult one to decompose. Lignin is full of aromatic rings with various branches (as can be seen in Figure 2.6); the activity of the chemical bonds in lignin covered an extremely wide range, which leads to the degradation of lignin occurring in a wide temperature range. Its decomposition happened slowly under the temperature range of 200°C to 700°C but at a very low mass loss rate. Generally the solid residue left from lignin pyrolysis was the highest among the three main components of natural fibers (Yang, Yan, Chen, Lee, & Zheng, 2007).

PVA/different starches composites

Figure 4.96, 4.97 and 4.98 show the TG decomposition curves for PVA blended with different concentration of starches.

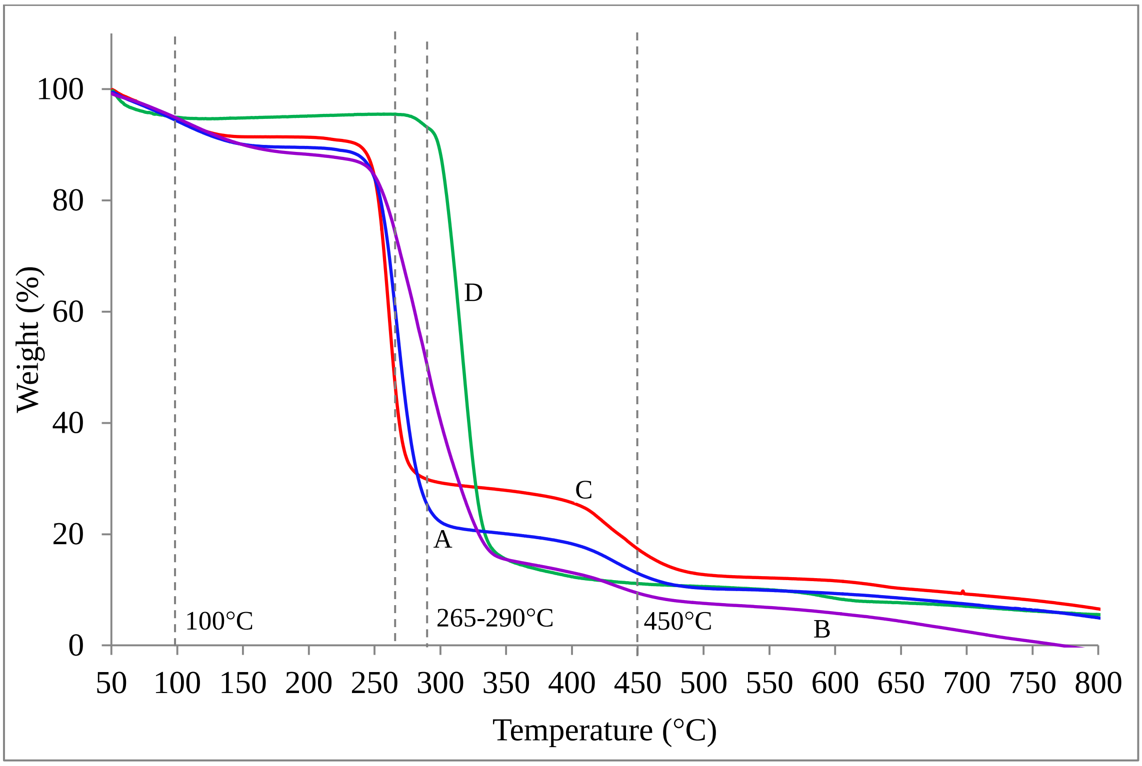

Fig. 4.96 TG curves for the degradation of PVA/1TS (A) and PVA/3TS (B) composites. The curves were compared with the TG curves of pure PVA (C) and pure tapioca starch (D).

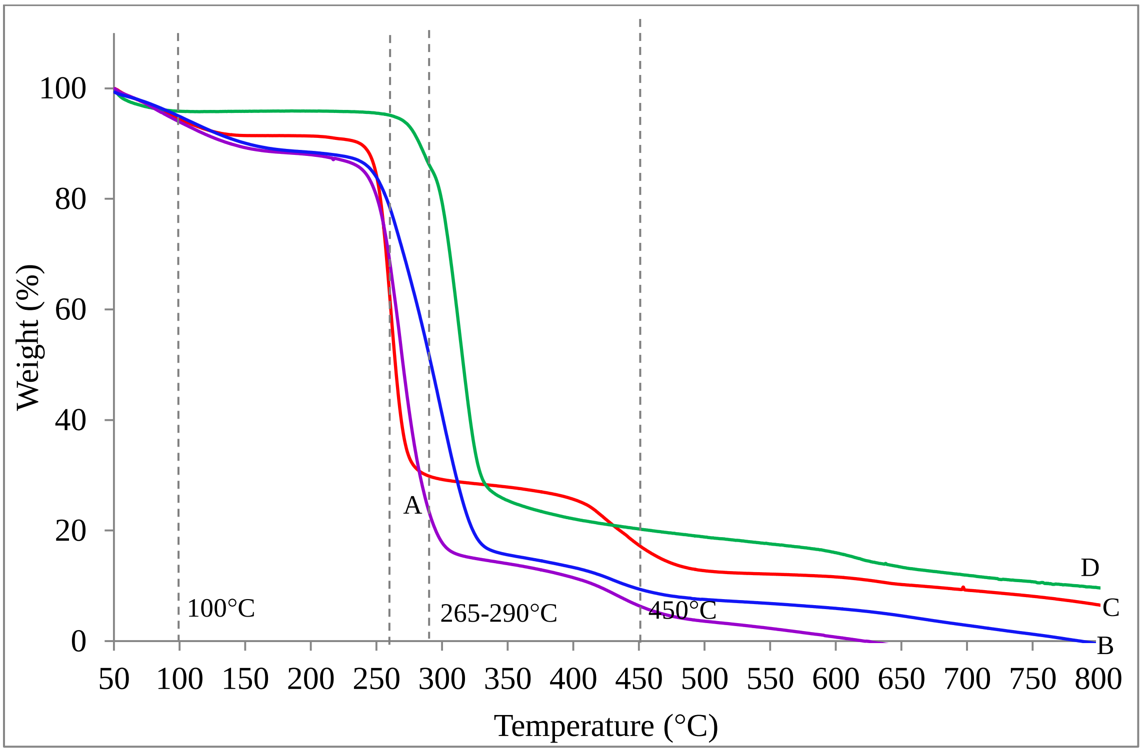

Fig. 4.97 TG curves for the degradation of PVA/1RS (A) and PVA/3RS (B) composites. The curves were compared with the TG curves of pure PVA (C) and pure rice starch (D).

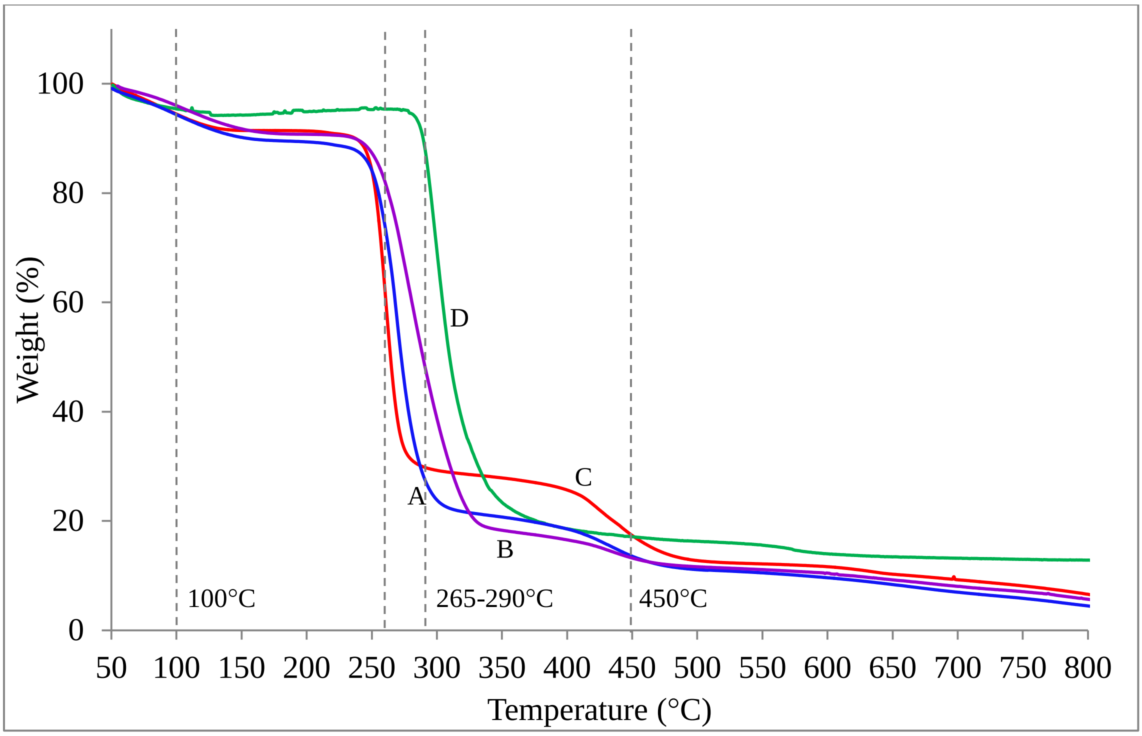

Fig. 4.98 TG curves for the degradation of PVA/1SS (A) and PVA/3SS (B) composites. The curves were compared with the TG curves of pure PVA (C) and pure sago starch (D).

According to the TG curves, pure PVA and starch show similar trends of degradation. This is because starch and PVA mainly consists of hydroxyl functional groups (Lee, Rahman, Rahmat, & Mokhtar, 2011). It can also be concluded from the thermograms that starches from different botanical origins are more thermally stable than pure PVA. Starches tend to exhibit higher degradation temperature compared to PVA due to the presence of thermal resistive cyclic hemiacetal of its starch structure. The five- or six-membered cyclic ring is very stable in terms of its chemical structure. The cyclic form of D-glucose unit arrangement has dense structure with good shielding effect against thermal attack and thus higher energy is required to break the bonding (Wade, 1999). For the blended films of PVA and different starches, the overall decomposition can be divided into three different temperature ranges. For temperatures below 200°C, evaporation of moisture occurs. Blended films of PVA/different starches have the greatest mass loss at this stage because starches in the blended films are more prone to absorb moisture (Gordon, Imam, & Greene, 1996). In the temperature range between 265°C and 290°C, PVA degrades more rapidly than starch. The decomposition of PVA forms volatile organic compounds as well as generation of conjugated unsaturated polyene structure. At higher temperatures (> 450°C), small quantities of hydrocarbon related products such as alkenes, alkanes and aromatics dominates the decomposition. When there is an increase of starch in the blended films, the degradation temperatures of the films were higher in the temperature range of 265°C to 290°C. This proves that the blended film of PVA and starch are molecularly compatible and contributes towards forming a more thermally stable composite with high thermal energy stability.

PVA/different starches/different fibers composites

Figure 4.99 to 4.102 shows the TG thermograms for PVA blended with 1g of tapioca starch and mix with different concentration of different treated fibers between the temperature ranges of 50 to 900°C.

Figure 4.103 to 4.106 shows the TG thermograms for PVA blended with 1g of rice starch and mix with different concentration of different treated fibers between the temperature ranges of 50 to 900°C.

Figure 4.107 to 4.110 shows the TG thermograms for PVA blended with 1g of sago starch and mix with different concentration of different treated fibers between the temperature ranges of 50 to 900°C.

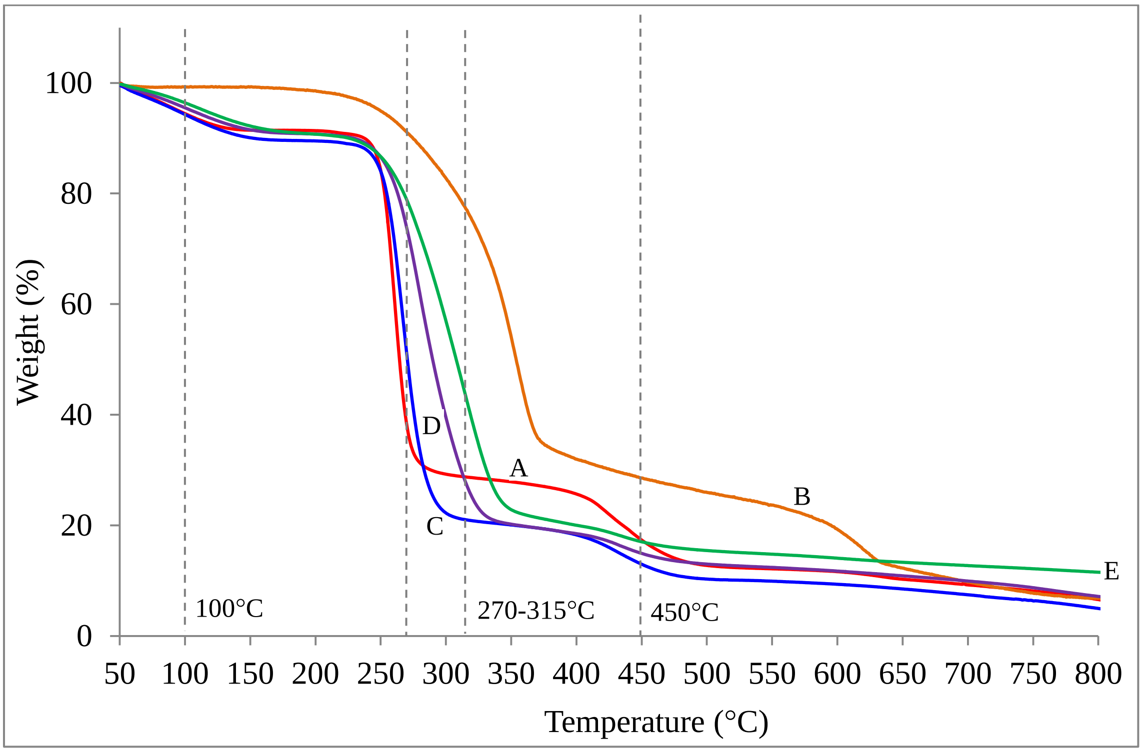

Fig. 4.99 TG thermograms of pure PVA (A), treated bamboo fiber (B), PVA/1TS (C), PVA/1TS/1BB (D) and PVA/1TS/3BB (E) between the temperature range of 50°C to 900°C.

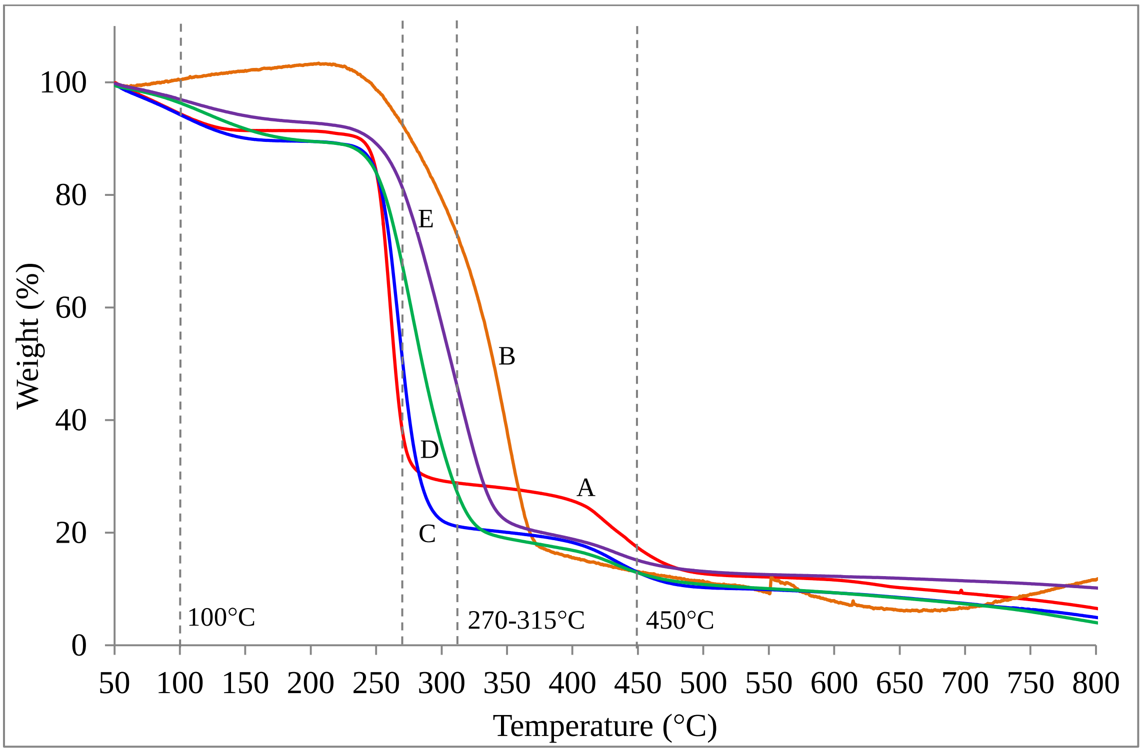

Fig. 4.100 TG thermograms of pure PVA (A), treated kenaf fiber (B), PVA/1TS (C), PVA/1TS/1KF (D) and PVA/1TS/3KF (E) between the temperature range of 50°C to 900°C.

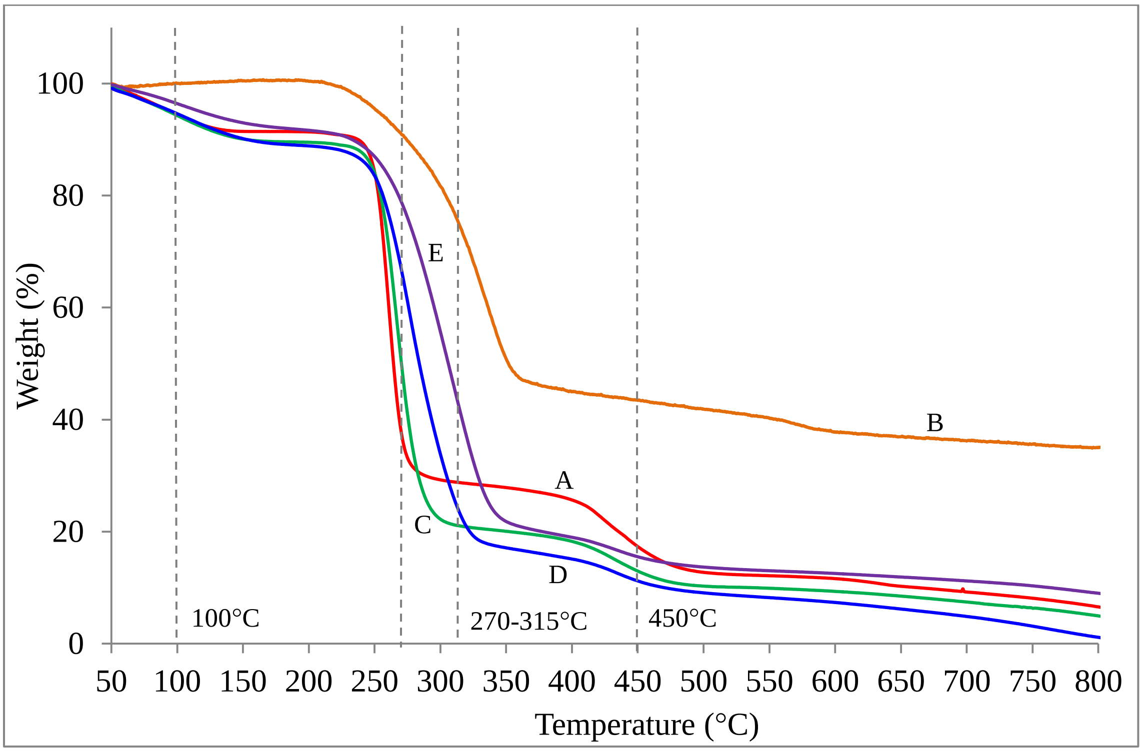

Fig. 4.101 TG thermograms of pure PVA (A), treated roselle fiber (B), PVA/1TS (C), PVA/1TS/1ROS (D) and PVA/1TS/3ROS (E) between the temperature range of 50°C to 900°C.

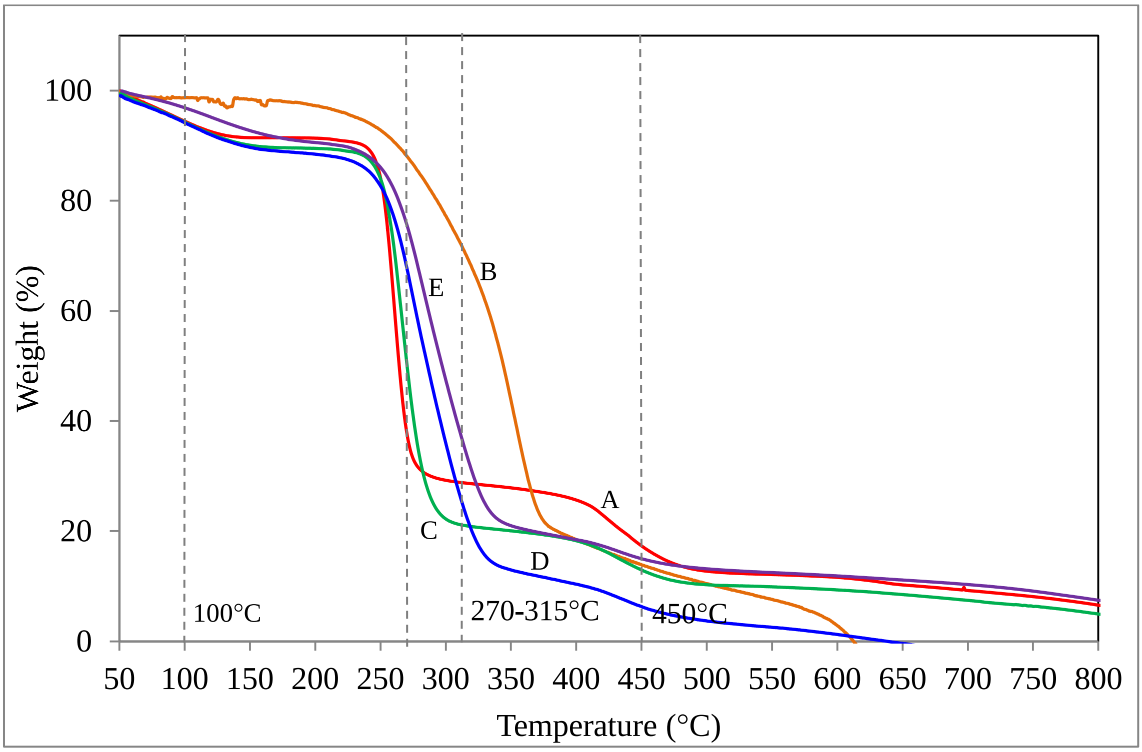

Fig. 4.102 TG thermograms of pure PVA (A), treated napier fiber (B), PVA/1TS (C), PVA/1TS/1NP (D) and PVA/1TS/3NP (E) between the temperature range of 50°C to 900°C.

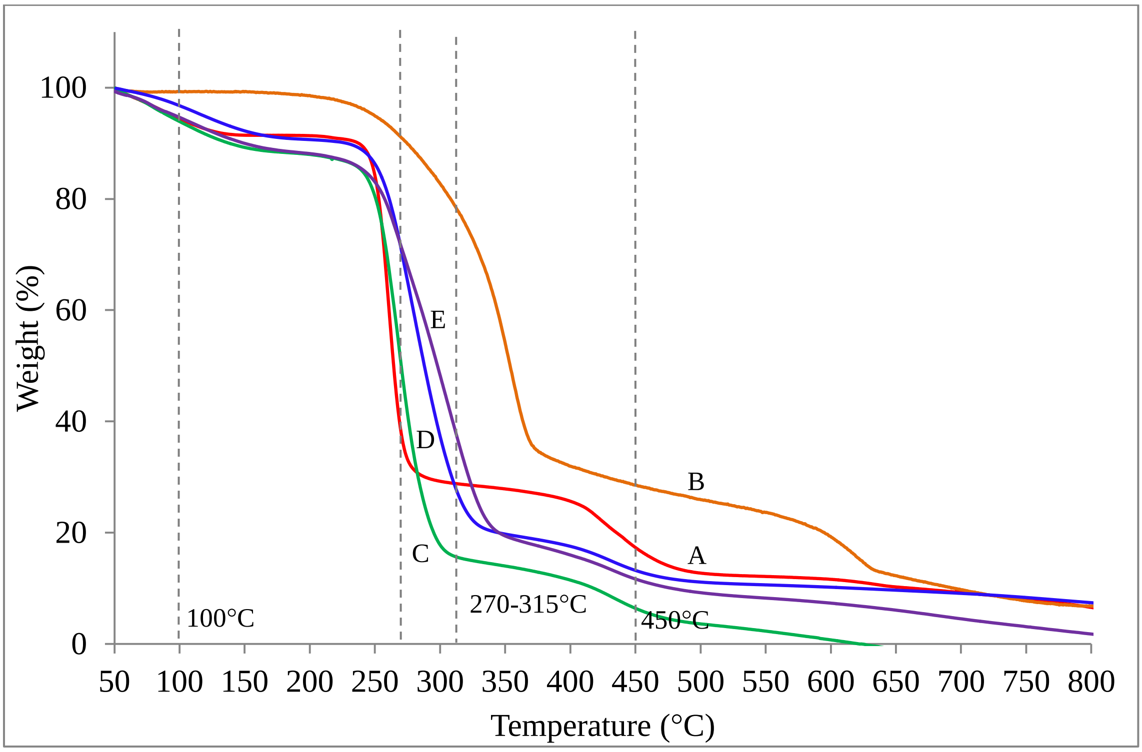

Fig. 4.103 TG thermograms of pure PVA (A), treated bamboo fiber (B), PVA/1RS (C), PVA/1RS/1BB (D) and PVA/1RS/3BB (E) between the temperature range of 50°C to 900°C.

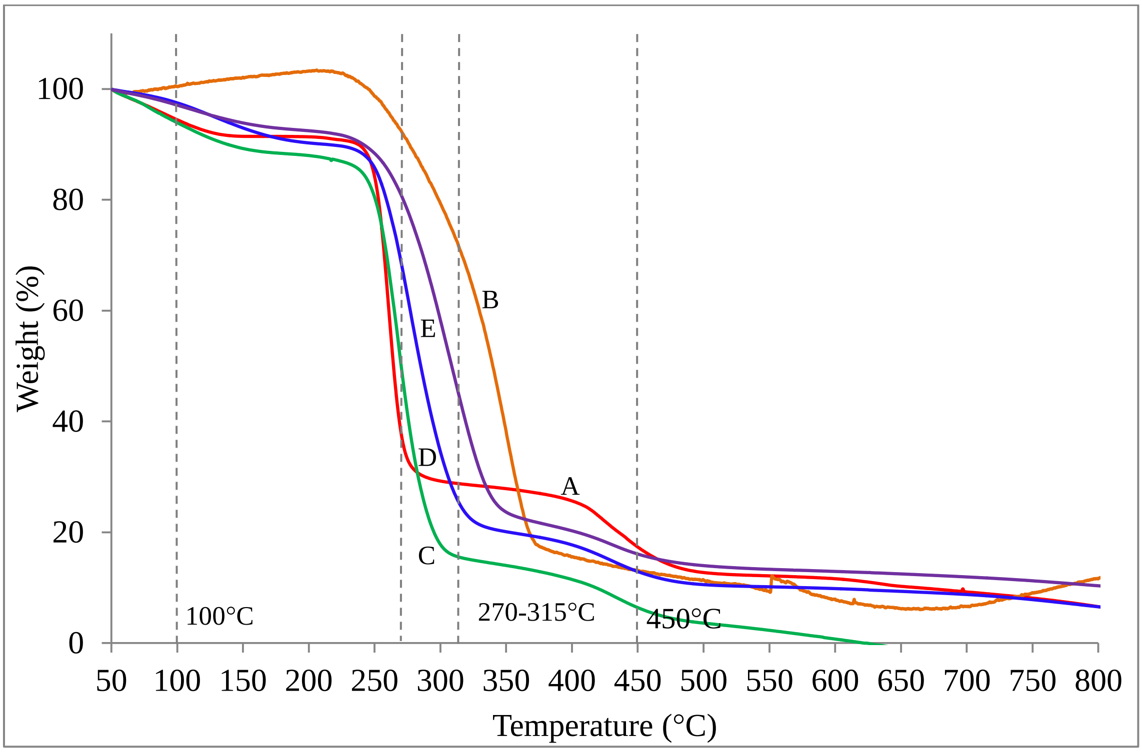

Fig. 4.104 TG thermograms of pure PVA (A), treated kenaf fiber (B), PVA/1RS (C), PVA/1RS/1KF (D) and PVA/1RS/3KF (E) between the temperature range of 50°C to 900°C.

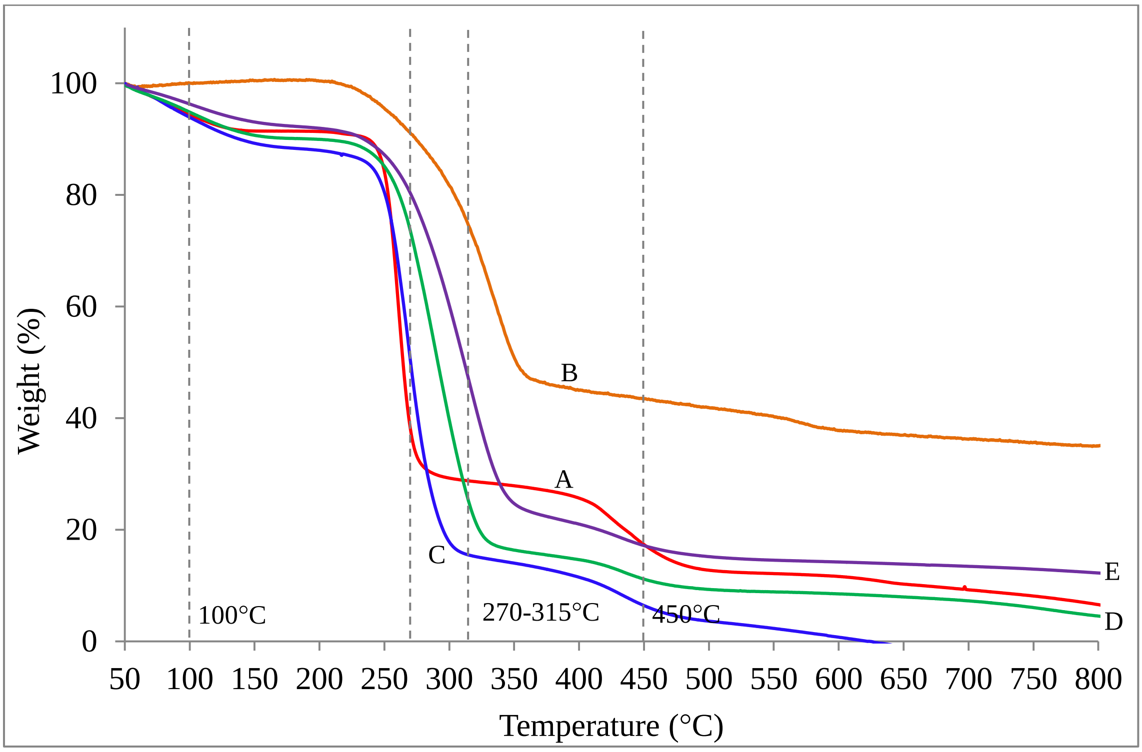

Fig. 4.105 TG thermograms of pure PVA (A), treated roselle fiber (B), PVA/1RS (C), PVA/1RS/1ROS (D) and PVA/1RS/3ROS (E) between the temperature range of 50°C to 900°C.

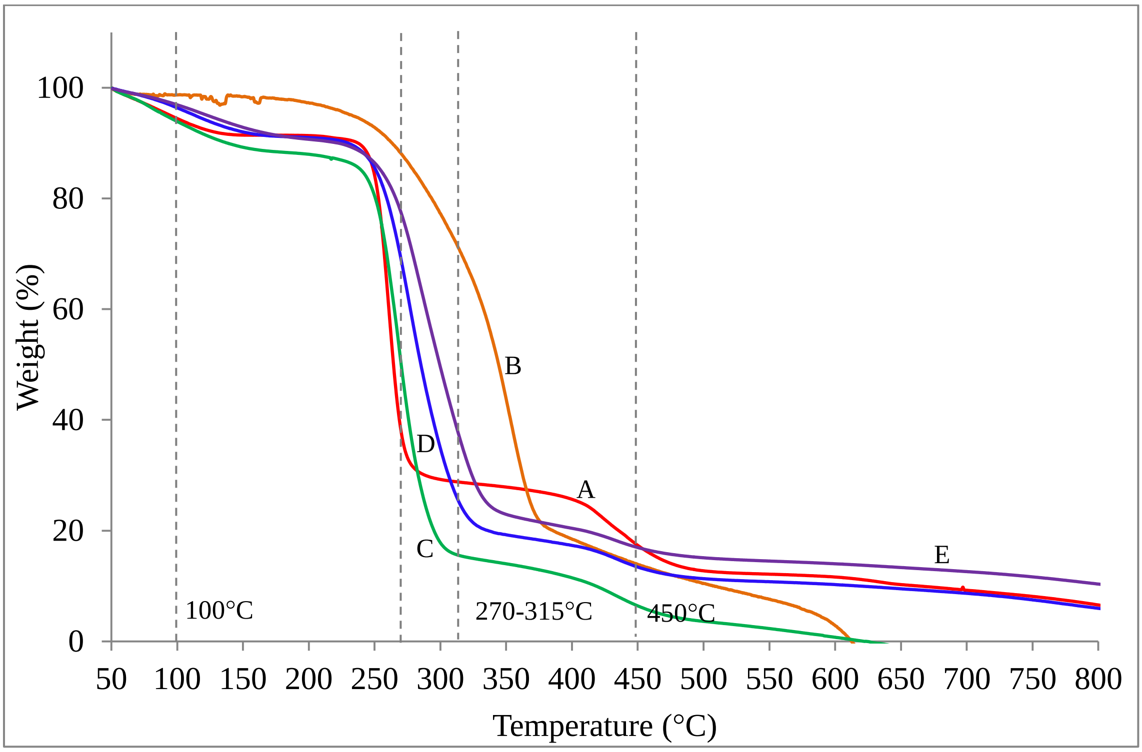

Fig. 4.106 TG thermograms of pure PVA (A), treated napier fiber (B), PVA/1RS (C), PVA/1RS/1NP (D) and PVA/1RS/3NP (E) between the temperature range of 50°C to 900°C.

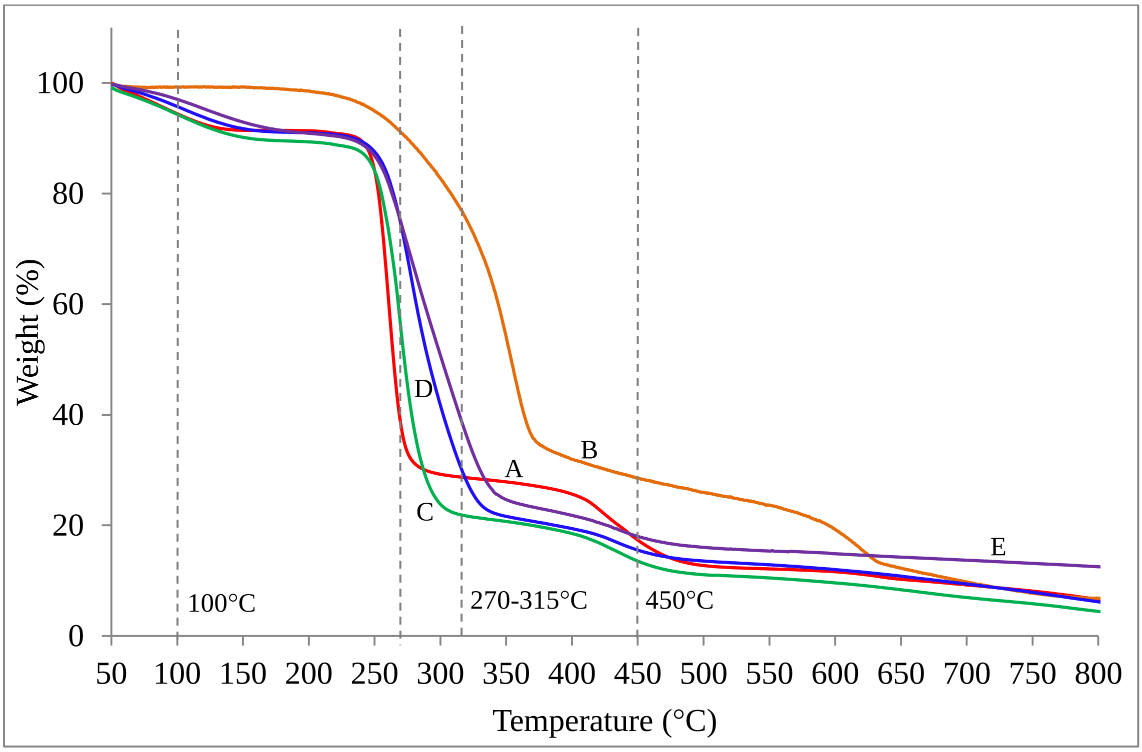

Fig. 4.107 TG thermograms of pure PVA (A), treated bamboo fiber (B), PVA/1SS (C), PVA/1SS/1BB (D) and PVA/1SS/3BB (E) between the temperature range of 50°C to 900°C.

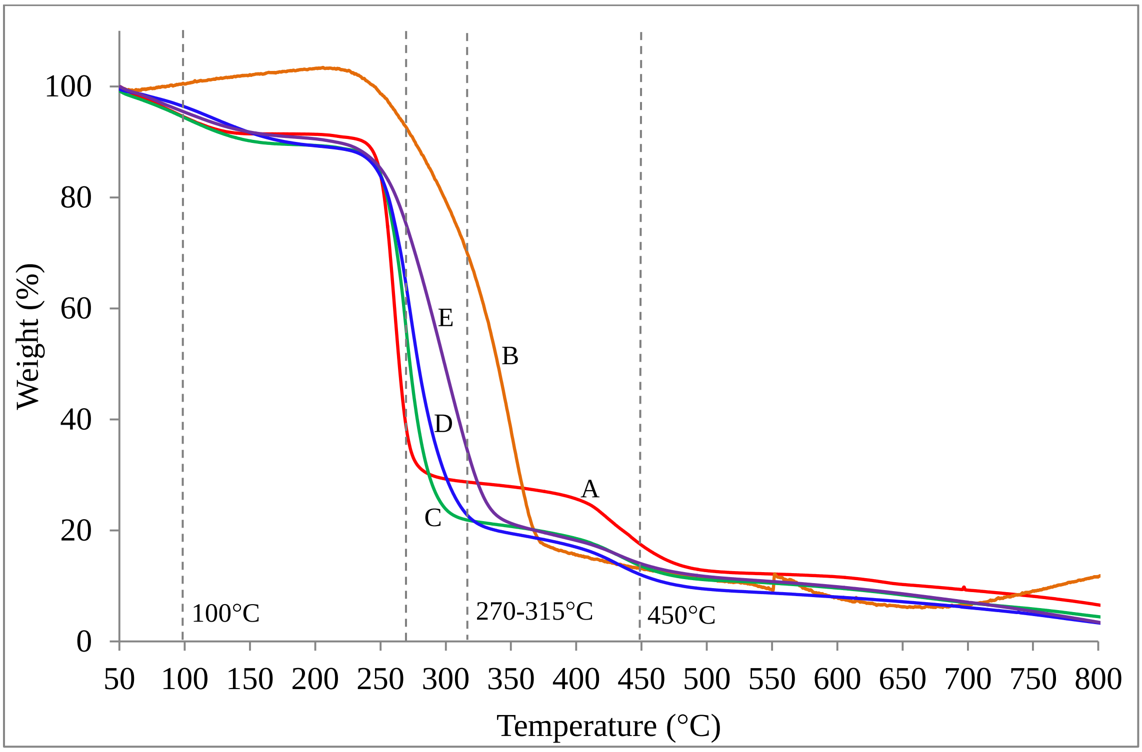

Fig. 4.108 TG thermograms of pure PVA (A), treated kenaf fiber (B), PVA/1SS (C), PVA/1SS/1KF (D) and PVA/1SS/3KF (E) between the temperature range of 50°C to 900°C.

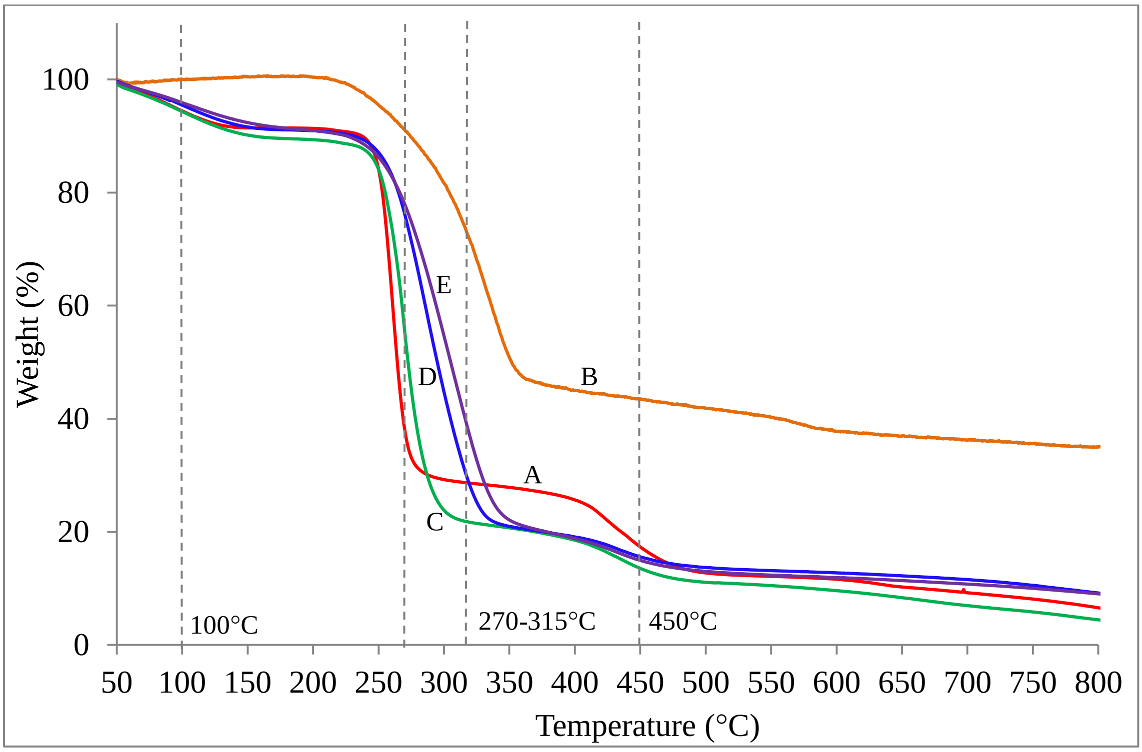

Fig. 4.109 TG thermograms of pure PVA (A), treated roselle fiber (B), PVA/1SS (C), PVA/1SS/1ROS (D) and PVA/1SS/3ROS (E) between the temperature range of 50°C to 900°C.

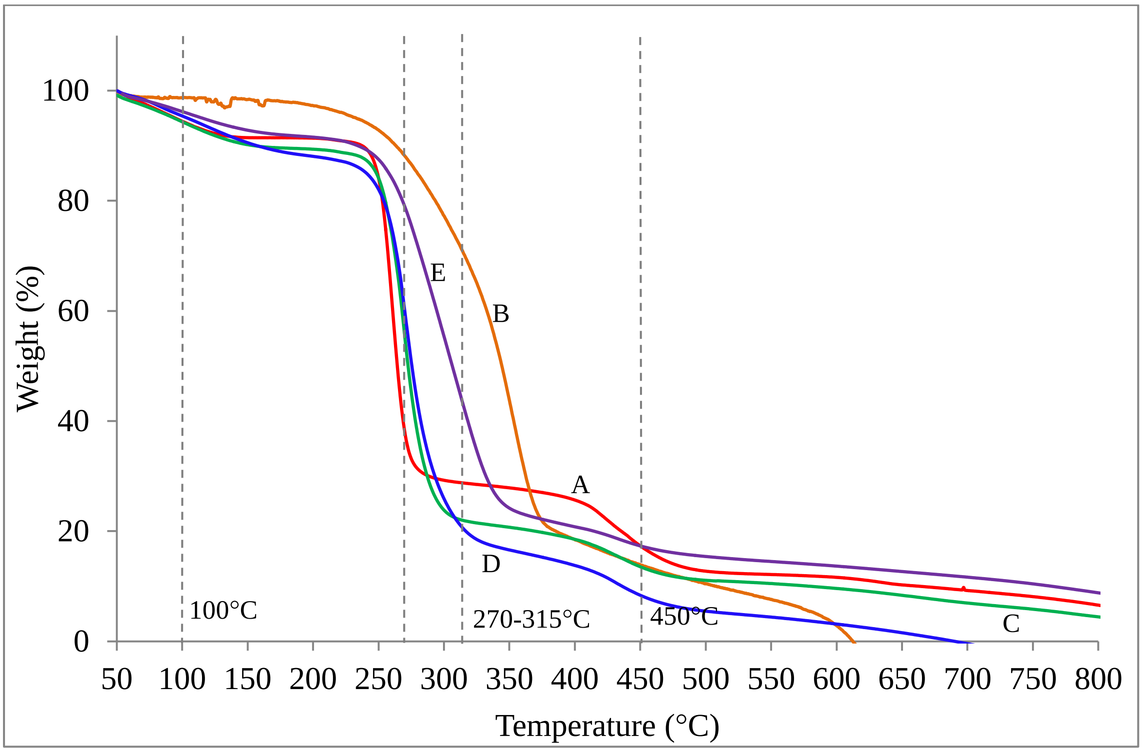

Fig. 4.110 TG thermograms of pure PVA (A), treated napier fiber (B), PVA/1SS (C), PVA/1SS/1NP (D) and PVA/1SS/3NP (E) between the temperature range of 50°C to 900°C.

The TG curves for all the biocomposite films of PVA blended with different starches and different treated fibers also show a similar trend of decomposition. Observations indicate three decomposition steps recognizable in the curves for the blended films. The presence of such multiple decomposition temperature range is not surprising as it is much in accordance with the composite characteristics of the materials. Additionally, pure PVA, different treated fibers and PVA blended with starch were individually analyzed and compared with the blend of PVA/starch/fibers for their thermal stability, as the thermal decomposition of the prepared blends will ultimately be influenced by the stability of each component present in the mixtures. After the evaporation of moistures and other low molecular compounds at around 100°C, for PVA the decomposition mostly occurred in two steps, the temperature range of 270-300°C and at around 450°C. According to the analysis done on starch, it exhibits a single decomposition at around

300°C. The treated fiber that are mainly composed of cellulose and small amounts of lignin exhibits decomposition at around 295-315°C (for cellulose) (Alvarez & Vacquez, 2004). These decomposition temperatures ranges of all the components that make up the blended films overlap one another on the TG curves. It can also be observed from the TG curves that the solid residues formed after total decomposition of the PVA/starch blend was lesser than the PVA/starch blend reinforced with treated fibers. This may be attributed from the greater thermal stability of the treated fiber mainly because the main composition of the treated fibers is cellulose. Cellulose has a strong and stable chemical structure and high energy is required to break its molecular bonding. Therefore, addition of the fibers into the PVA/starch blend films can improve the stability of the biocomposite films (Rosa M. F., et al., 2009) (Corradini, Imam, Agnelli, & Mattoso, 2009). It is also observed that the solid residues of the PVA/starch/fiber films were enhanced as the wattage of fiber content added was increased. By incorporating fiber fillers of 1g and 3g to the PVA/starch blends, the thermal stability shifts to slightly higher temperature. This may result from strong interfacial interactions through inter- and intramolecular hydrogen bonding between the large specific surface are of the treated fiber and starch and PVA matrix (Phattaraporn, Waranyou, Fazilah, & Thawien, 2010).