Thermal properties of kenaf fiber-based nanocellulose reinforced polyurethane composites

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Abstract. Natural fibers made into cellulose have attracted interest in the research and development of composite materials in recent years. One of them is Kenaf fiber from Sumberejo, East Java. The Kenaf fiber nanocellulose reinforced polyurethane (NC-PU) composites were prepared via in-situ polymerization. The purpose of this research is to analyze the thermal properties and morphology of PU and NC-PU composites. Then, TGA (thermogravimetric analysis), DTG (differential thermogravimetric analysis), DSC (differential scanning analysis) and SEM (scanning electron microscope) are applied to characterize PU and NC-PU composites. The addition of nanocellulose up to 7 wt.% in polyurethane was found to decrease the melting temperature of NC-PU composites and decrease the rate of decomposition. The lowest decomposition rate is attributed to the composite material of 10 wt.% NC-PU, which has a decomposition rate of 1.7 %/min, and the highest residual decomposition rate of 67 %. The addition of nanocellulose to PU also decreases the average pore size of NC-PU composites.

Keywords: Sumberejo’s kenaf fiber, nanocellulose, polyurethane, composite, thermal properties

1. Introduction
Polymer composites were made from natural fibers and bio-polymers referred to as green composites. Some natural fibers are coir, flax, sisal fiber, hemp fiber, pineapple fiber, and kenaf fiber. Whereas, examples of polymers including starch, polylactic acid (PLA), CNSL and furans [1]. In recent years, several studies have investigated the advantages of natural fibers as alternatives synthetic fibers. Among them are used for automotive and furniture because natural fibers have excellent trait than synthetic fibers. One of the natural fibers that has the potential to make composite materials is kenaf fiber [2]. The chemically treated kenaf fiber can be cleaned fiber surface, the process of surface absorption of air, and increase the surface roughness. The treated kenaf fiber can fill the gaps in composite materials. Kenaf fiber can also reduce the porosity of the core in the sandwich composite. The raw materials of kenaf are also cheaper than hemp, flax, and jute. Kenaf fibers contain cellulose from 45.0–70.6 %, and 8–13 % lignin, while for their mechanical properties, kenaf fibers have tensile strength up to 223 MPa and a modulus young at 14.50 GPa [3].

PU are polymeric materials containing various urethane (-NH-CO-O-) resulting from the reaction between polyols and isocyanates. PU can be formed with different characteristics. For example, this PU foam can form as open cell and closed cell which can affect thermal properties [4].
Some research in the development of composite materials have shown an interest in cellulose in recent years, as it can improve the properties of composite materials. This nanocellulose have some interesting advantages, such as, they have nano meter size, non-toxic, biodegradable, and biocompatible. Nanocellulose can be applied for biomedicine, energy, environment, polymer composite reinforcement [5].

In this study, the nanocellulose obtained from kenaf fiber that was provided from Balai Penelitian Tanaman Pemanis dan Serat (Balittas), Malang, Jawa Timur. Nanocellulose was extracted mechanically using an Ultra Fine Grinder at Balai Besar Pasca Panen, Bogor. This research utilizes TGA (thermogravimetric analysis), DTG (differential thermogravimetric analysis), DSC (differential scanning analysis) to characterize polyurethane foam reinforced with kenaf fiber nanocellulose, in which the composition of nanocellulose is 0, 3, 5, 7 and 10 wt.%. The purpose of this research is to analyze the thermal and morphological properties of the nanocellulose-reinforced polyurethane composite material from kenaf fibers with variations of nanocelluloses. From previous studies, the thermal properties of East Java kenaf fiber and NC-PU composites have not been studied. In this study, the in-situ polymerization method was used to characterize the thermal properties of kenaf fiber and NC-PU composite.

2. Materials and method

Figure 1 shows the research outline of this study. Starting from the alkalization process of kenaf fiber, lignin and hemicellulose are mainly removed because they interfere the interface bond between the substrate and the natural fiber [6]. The kenaf fiber used was obtained from Sumberejo, East Java and PU were purchased from PT Justus Kimia. After the cellulose obtained, the structure made into a nano size by using ultra-fine grinder. The ultra-fine grinder process was carried out at Balai Pasca Panen, Bogor. The nanocellulose mixed with polyurethane using the in-situ polymerization method. After the composite was formed, the samples were characterized with TGA (thermogravimetric analysis), DTG (differential thermogravimetric analysis), DSC (differential scanning calorimetry). Then, continued with SEM (scanning electron microscope) observations. Characterization was carried out at BPPT Material Technology Center, Serpong. The names of PU samples and kenaf fiber nanocellulose reinforced polyurethane composites were identified as PU, 3 NC-PU, 5 NC-PU, 7 NC-PU, and 10 NC-PU.

![Figure 1. Research outline](image-url)
The process of alkalizing kenaf fiber and making nanocellulose were started from treating the kenaf fiber using 5% NaOH. The kenaf fiber was soaked in NaOH solution for 24 hours to remove lignin, hemicellulose, and other impurities. The kenaf fiber was then rinsed 7 times using aquabidest until the water was clear. The fiber was then left for 24 hours at room temperature. After that, the drying process at room temperature was performed continued by heating the fibers in the oven for 24 hours at a temperature of 65°C [7].

The fiber was removed from the oven and was cut in 1 cm long to turn into nanocellulose. The fiber that had been treated with alkalization was mashed in a mixer grinder to obtain powdered cellulose. Then, the powdered cellulose was dissolved in 10% NaOH solution and stirred using a stirrer 60–80°C of temperature. After the powder dissolved, the cellulose was rinsed and dried using an autoclave at high temperature until the water content was removed. After that, the cellulose powder was bleached 7 times with acetate buffer solution and 1.5% NaClO₂. After the bleaching process was complete, the powdered cellulose was suspended using an ultra-fine grinder with 1440–1500 rpm of speed. This process was carried out, so the cellulose powder was fibrillated into nanocellulose.

The next process was to manufacture nanocellulose (NC) -Polyurethane (PU) composites with in-situ polymerization method. The 14 grams of the polyol solution was prepared in two containers with each container contains 7 grams of polyol solution. In addition, 3, 5, 7, and 10 wt.% of NC suspension was added to 7 grams of polyol solution. Those solutions were stirred at 600 rpm for one minute at 70°C. After that, the 7g of remained polyol solution was added to the previous mixture at a speed of 600 rpm for 4 minutes at room temperature. Then, the 21 g isocyanate solution was mixed into the NC + polyol solution and stirred manually for 20 seconds. Further, the mixture was poured into a mold that was prepared before and let stand for about 60 minutes during the in-situ polymerization process. After the mold was opened, the NC-PU composites were stored at room temperature before being tested.

After the manufacture of nanocellulose (NC) -Polyurethane (PU) composites with in-situ polymerization method were completed, the TGA, DTG, and DSC testing step were performed. The polyurethane and NC-PU composites were tested using the TGA, DTG, and DSC analysis methods. Furthermore, the TGA, DTG, and DSC tests were started from 30°C to 800°C with 10°C/minute adjustable temperature increased under argon gas conditions. After the test was complete, the obtained data was processed into a graphic with the OriginPro 8.5 software. The last activity of this research was the use of SEM (Scanning Electron Microscope) for observation, in which SEM was used to observe the surface of PU samples and NC-PU composite materials, and Image J was used to process the SEM images, thus according to ASTM E1730 -19 got the aperture. The observations were conducted at a magnification of 400µm. SEM image observations were carried out on PU samples, 3 NC-PU, and 5 NC-PU samples.

3. Results and discussion

3.1. Results of TGA and DTG of PU and NC-PU composites

Figure 2 reveals the results of TGA measurements for PU and NC-PU composites. Whereas figure 3 presents the measurement results of the polyurethane DTG and NC-PU composites. $T_{\text{onset}}$ is the temperature at which the degradation has decreased by 5% of 100% of the material. The $T_{\text{onset}}$ temperature degradation appears in the range of 234.1°C to 244.8°C. For all of the samples, there was a decrease in temperature $T_{\text{onset}}$ in the composite 3 NC-PU but it increased again to 244.8°C at 7 NC-PU then decreased again in the 10 NC-PU composite of 234.1°C. Compared to PU, the $T_{\text{onset}}$ temperature composite of 7 NC-PU has a better value slightly. Figure 3 also shows the final degradation that occurs in PU and NC-PU composites. The final degradation in PU was remain 20%, 3 NC-PU composite had 17% remaining, 5 NC-PU composite had 16% remaining, 7 NC-PU composite had 27% remaining, and 10 NC-PU composite had 36% remaining. Compared to PU samples, the NC-PU composite material had higher residual decomposition. This shows the role of NC in
reducing the rate of decomposition in certain compositions. The composition that produces the best thermal conductivity of the nanocellulose-enhanced polyurethane composite is a composition of 0.4 % by weight of nanocellulose [8].

Figure 2 and figure 3 describe three degradation patterns that occur in PU and NC-PU composites. The first stage of degradation occurred at 246 °C to 260 °C. The degradation of NC-PU composites has decreased, along with the addition of NC composition to PU. This shows the role of nanocellulose in thermal stability. The first degradation is due to the separation between the urethane bonds and the separation of NC with these urethane bonds [9]. The second stage of degradation occurred at temperatures of 344.2 °C to 350 °C. In the second stage, the degradation of NC-PU and PU composites did not change significantly, but compared with the PU at 344.2 °C, the composition of 7 NC-PU and 10 NC-PU increased to 349 °C and 350 °C. This happens because when 7 NC-PUs and 10 NC-PUs are formed, there are still NCs remaining in the PU.

![Figure 2. TGA results of PU and NC-PU composites](image)

![Figure 3. DTG results of PU and NC-PU composites](image)
Table 1. Characteristics of PU degradation and NC-PU composite

| Sample  | $T_{\text{onset}}$ (°C) | Final decomposition (%) | $T_{\text{max}}$ (°C) | $W_{\text{max}}$ (%/minute) |
|---------|-------------------------|-------------------------|------------------------|-----------------------------|
| PU      | 243.9                   | 80                      | 246                    | 344.2                       | 387 | -2.44 | -5.0 | -2.8 |
| 3 NC-PU | 242.6                   | 83                      | 251                    | 345                         | 390 | -2.40 | -5.1 | -3.0 |
| 5 NC-PU | 237.8                   | 84                      | 257                    | 345.2                       | 392 | -2.35 | -5.1 | -3.1 |
| 7 NC-PU | 244.8                   | 73                      | 258                    | 349                         | 435 | -1.73 | -4.9 | -2.33|
| 10 NC-PU| 234.1                   | 64                      | 260                    | 350                         | -   | -1.7  | -4.7 | -    |

Liu explained that the second step of degradation is due to the degradation that occurred in polyols. Furthermore, the third step of degradation occurs at temperatures of 387 °C to 410 °C. The third step of degradation was different from the 3 NC-PU and 5 NC-PU composites by ± 5 °C when compared to PU but increased to 435 °C in the 7 NC-PU composites. It is also showed that nanocellulose remains were trapped in PU [10]. Meanwhile, Członka gave an explanation that the third stage of degradation occurred due to isocyanates and several compounds that could not be decomposed in the previous stage which could be said to be residues [11].

The DTG curves for PU and NC-PU composites show the decomposition rate. The figure shows that as the content of nanocellulose in PU increases, it will slow down the decomposition rate in the sample. This shows that nanocellulose can prevent the heat propagation that occurs in PU, because the pore size in figure 7 is getting smaller. Nazeran et al. explained that heat transfer occurs through the cell rilene, and the smaller cell size can reduce the thermal conductivity that occurs [12]. Meanwhile, Liu argued that adding nanoparticles can effectively improve the thermal stability of hybrid materials [9].

3.2. Results of DSC PU and NC-PU composites

Figure 4 to figure 8 show the results of DSC measurements for PU and NC-PU composites. Figure 4 reveals the DSC graph of the PU sample. The figure shows an exothermic pattern of PU, which includes two endothermic peaks and one Tm melting point in figure 4. Two endothermic peaks were detected at 270 °C and 350 °C. While the melting point temperature occurs at 450 °C. Due to the limitations of operating equipment at low temperatures, the DSC measurement performed in this study could not discover the detected glass transition temperature (Tg) value. From Wang's research, it was found that the Tg PU value was in the range of -36.42 °C to 1.2 °C [13].

Figure 5 shows the DSC graphic of the 3 NC-PU composite sample. Figure 5 shows the exothermic pattern in the 3 NC-PU composites, which has one endothermic peak and one melting point. Endothermic peaks were detected at about 350 °C and melting point at 420 °C. In Somdee's research, it was found that the Tg temperature for the soft segment was around 64 °C, while the hard segment was for the temperature range 58–70 °C [14].

Figure 6 shows a DSC graphic of a 5 NC-PU composite sample. Figure 6 shows the exothermic pattern of the 5 NC-PU composites, which has one endothermic peak and one melting point. The endothermic peak was detected at a temperature around 330 °C and melting point at 400 °C. The Tg value on the 5 NC-PU composite material could not be detected by the DSC measurements that had been carried out. In Wang's research, it was found that the temperature of Tg was at -36.42 °C to 1.2 °C with variations in the ratio of [NCO]/[OH] [13].

Figure 7 shows the DSC pattern of the NC-PU composite. Figure 7 shows the exothermic pattern of the 7 NC-PU composites, with one endothermic peak and one melting point on the graphic. The endothermic peak was detected around 340 °C and melting point at 440 °C.
Figure 4 shows a DSC graphic of a 10 NC-PU composite sample. The figure shows an exothermic pattern on the 10 NC-PU composites, which shows melting point on graphic. The melting point detected was at 450 °C.

In this study, as shown in table 2, there are endothermic peaks and melting point temperatures in PU and NC-PU composite materials. The presence of nanocellulose eliminates the endothermic temperature 1, and 10 NC-PU in the composite material eliminates the endothermic temperature 2. This mechanism cannot be determined in detail. Compared to the melting point PU, the presence of NC reduces melting point but significant for composite 3 NC-PU. The 10 wt.% NC content in PU increases the melting point value to the melting point PU value, which is 450 °C. Figure 8 shows a DSC graphic of a 10 NC-PU composite sample. The figure shows an exothermic pattern on the 10 NC-PU composites, which shows melting point on graphic. The melting point detected was at 450 °C.

3.3. SEM observation on PU and NC-PU composites

Figure 9 (a-i) shows SEM images of PU and NC-PU composites with three magnifications, such as 1 mm, 400 µm, and 10 µm. Samples surface observations by SEM carried out on polyurethane and NC-PU composites showed differences from the structure in figure 9 (a-i). Compared to PU, 3 NC-PU and 5 NC-PU composite materials have different PU pore sizes. The average size of the PU pore was approximately (48.17 ± 33.37) µm, while the 3 NC-PU and 5 NC-PU composite pores were approximately (30.9 ± 19) µm and (37.6 ± 12.76) µm. Observation by SEM showed that the average pore size of NC-PU composites was smaller than of PU pore size.
Figure 8. Graphics of 10 NC-PU DSC composite

Table 2. $T_m$ temperature value

| Sample   | $T_{endotermic1}$ | $T_{endotermic2}$ | Melting point |
|----------|-------------------|-------------------|---------------|
| PU       | 270               | 350               | 450           |
| 3 NC-PU  | -                 | 350               | 420           |
| 5 NC-PU  | -                 | 330               | 440           |
| 7 NC-PU  | -                 | 340               | 440           |
| 10 NC-PU | -                 | -                 | 450           |

Figure 9. SEM imagery of PU with (a-c) 1 mm, 400 µm and 10 µm scales, (d-f) 3 composite of NC-PU with 1 mm, 400 µm, and 10 µm scales, (g-i) 5 composite of NC-PU with 1 mm, 400 µm and 10 µm scales.
Figure 9 (continued). SEM imagery of PU with (a-c) 1 mm, 400 µm and 10 µm scales, (d-f) 3 composite of NC-PU with 1 mm, 400 µm, and 10 µm scales, (g-i) 5 composite of NC-PU with 1 mm, 400 µm and 10 µm scales.

This indicates that the presence of NC affects the pore size of PU. It is possible that the viscosity of NC-PU composites increases with the addition of NC. The increase in viscosity will make it difficult for the PU and NC mixture to rise during the swelling process and inflict a smaller pore size [15]. From thermal testing and observations by SEM it can be said in general that the addition of NC changes the degradation temperature and melting point, as well as changes the pore size of NC-PU composites.

4. Conclusion

The highest degradation temperature was obtained by 7 NC-PU composites at the temperature of 244.8 °C. Figure 8 shows a DSC graphic of a 10 NC-PU composite sample. The figure shows an exothermic pattern on the 10 NC-PU composites, which shows melting point on graphic. The melting point detected was at 450 °C. Meanwhile, the highest material decomposition rate was 10 NC-PU, which has 67 % remain. T\text{onset} temperature indicated the higher temperature is applied, the more heat resistant is observed. The results of DTG measurements of PU samples and NC-PU composites decreased the rate of decomposition as the composition of the nanocellulose increased. The lowest decomposition rate was found in 10 NCPU composites at 1.7 %/minute. SEM observations of PU samples and NC-PU composites showed a decrease in average pore size along with the addition of nanocellulose to PU.

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