Thermal properties of thermoplastic natural rubber reinforced by microfibrillar cellulose

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Abstract. Thermoplastic natural rubbers (TPNR) based on natural rubber (NR) and polypropylene (PP) blends had been successfully prepared using dynamic vulcanization. The blends were reinforced with microfibrillar cellulose (MFC). The study aimed to evaluate the thermal properties of TPNR using thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses. MFC was derived from pineapple leaf fiber (PALF) through several treatments. Dynamic vulcanization was carried out using an internal mixer. PP was previously melt-mixed with MFC, then blended with NR compound. The ratio of NR/PP blend was maintained at 60/40, while MFC concentrations were varied ranging from 0, 1, 5, 10, 15 and 20 phr. The results showed that the degradation of TPNR samples occurred in two simultaneous stages. The onset of the degradation of TPNR started ranging from 346 °C to 361 °C. MFC concentration affected the thermal stability of the samples. The highest thermal stability was achieved by incorporating 1 phr MFC. DSC studies revealed that melting temperature (Tm) and heat of fusion (ΔHf) were independent of MFC concentration. Tm was in the 161-165 °C range, while ΔHf was around 24-31 J/mol. Keywords: thermoplastic elastomer, natural rubber, polypropylene, thermal properties, cellulose.

1. Introduction
Elastomer often blends with thermoplastics, resulting in a new material with outstanding properties. This blend is known as thermoplastic elastomer (TPE). The unique properties of TPEs are centered in the combination of the processing characteristic of thermoplastics with the wide range mechanical properties of elastomer [1]. The demand for TPEs is presently growing because they provide higher output rates than conventional elastomers. Conventional processing machines of thermoplastics, such as injection molding and extruder, can be used in product manufacturing line. Thus, the production cost will automatically be reduced. Moreover, TPEs offer better material utilization since they are recyclable [2]. These advantages make the TPEs find its market substituting the traditionally used vulcanized elastomer [3]. Thermoplastic vulcanizates (TPV) belongs to the family of TPE, but has different morphology. TPV contains finely dispersed crosslinked elastomer in the continuous thermoplastic matrix and typically produced by dynamic vulcanization [4]. Commercial TPVs are mostly produced based on synthetic rubber rather than natural rubber (NR). When NR is used as elastomer phase, then the generic term of TPV turns into thermoplastic natural rubber (TPNR). Research on the TPNR development is attracting much attention recently. NR is widely known to have outstanding mechanical properties, but when blended with thermoplastics, it results in low technical specification [5]. One possible way for achieving improvement on the technical specification is by addition of fillers. The level
of the improvement is affected by many factors, i.e. the nature of the filler (natural or synthetic), particle size, surface area, shape, filler loading, and active functional groups present on the filler surface. These factors determine the interaction between filler and polymer matrix [6], and in turn the final product properties.

Fibers are widely accepted to impart reinforcement of polymer matrix. Recently, natural fiber-based fillers are paid much attention because of environmental issues and the sustainability of feedstock. Natural fibers are lignocellulosic material that are mainly composed of cellulose. Cellulose has excellent mechanical behaviors that are closely comparable to those of synthetic fiber [7]. Moreover, natural fibers are lightweight and renewable resources that are guaranteed the sustainability of the stock. The cellulosic fiber source is abundant in tropical countries. Most of them could be wastes from agricultural activities that are not well-utilized yet. Depending on the preparation method and sources, many types of cellulose-based fiber can be derived from raw cellulose. They include nanocrystalline cellulose (NCC), microfibrillated cellulose (MFC) or nanofibrillated cellulose (NFC) [8]. Nevertheless, the hydrophilic nature of natural fiber could be the major drawback of their application in hydrophobic polymer matrices [9]. This will result in poor interfacial bonding between the fiber and matrix. Surface treatment of the natural fiber should be performed to improve the fiber-matrix adhesion. Pineapple leaf fiber (PALF) is an attractive natural fiber source because of its tremendous mechanical properties due to higher cellulose content and lower microfibrillar angle [10]. Several studies have been conducted on utilization of cellulosic fiber derived from PALF in polyurethane [9], polyamide 6 [11], propylene [12] and nitrile butadiene rubber matrix [13]. Kalapakdee and Amornsakchai [14] and Yuakkul et al. [15] have successfully applied PALF in TPE matrix. The results showed that the mechanical properties are improved by fiber addition. However, those studies employed untreated or alkali-treated PALF. Application of MFC in the polymer matrix is limited. In addition, the studies conducted by Yuanita et al. [16] and Thanomchat and Srikulkit [17] have revealed that cellulose possibly act as nucleating agent for PP.

Natural fibers are organic matter that may have lower thermal stability than other components in the polymer matrix. One should consider their thermal properties for the application at elevated temperature. Kaewpirom and Worrarat [18] studied the thermal properties of PALF-reinforced poly lactic acid (PLA). They concluded that the thermal stability was governed by the amount of PALF, in which lower amount of PALF showed higher thermal stability. Other study reported that incorporating rattan nanoparticle into polypropylene matrix lead to an increase in the thermal stability of composites [7]. In this present study, the thermal characteristics of MFC-reinforced TPNR were studied. The TPNR is prepared by blending the natural rubber, polypropylene and MFC in an internal mixer. A fixed ratio of NR/PP blends of 60/40 was taken with various loading of MFC. The thermal properties were analyzed using thermogravimetric analysis and differential scanning calorimetry. Both analyses were conducted in oxygen atmosphere in order to approach real application condition.

2. Experimental method

2.1. Materials

Natural rubber grade SIR 10 was supplied by local estate. Polypropylene Trilene grade HI10HO (injection molding grade, MFI (230 °C/2.16 kg) 10 g/min). The NR compound additives included ZnO (Bracthem), Aflux 42M processing promoter (Rhein Chemie), carbon black N-330 (OCI Korea) and GPF black N-660 (OCI Korea), 2,2,4-Trimethyl-1,2-Dihydroquinoline (TMQ) (Kemai), N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) (Northeast), N-Cyclohexylbenzothiazole-2-Sulfenamide (CBS) (Northeast), Sulfur SP-325 (Miwon), Pilgard PVI Pre-Vulcanization Inhibitor. Maleated castor oil (MACO) was used as plasticizer which synthesized in our previous work [19]. Additives of TPNR preparation were antioxidant Irganox 1010 (BASF), stearic acid (purchased from CV. Indrasari Semarang) and compatibilizer PP-g-MA (Sigma Aldrich). The raw PALF was supplied in the form of 0.5 cm-cut by local producer (Subang, West Java Province). Chemical reagents needed
for MFC preparation included sodium hydroxide (NaOH), sodium hypochlorite (NaOCl), sulfuric acid (H₂SO₄) 98% and acetic acid glacial (CH₃COOH) 96%. All reagents were industrial grade.

2.2. Microfibrillar cellulose (MFC) preparation
Microfibrillar cellulose (MFC) derived from Pineapple leaves Fiber (PALF) were prepared through several processing steps including alkali treatment, bleaching, hydrolysis and mechanical treatment. Before treatments, the raw PALF was grinded using crusher. Alkali treatment was performed by mercerization using 10% (w/w) aqueous sodium hydroxide (NaOH) at ambient temperature for 18 h. The fiber to liquor (FL) ratio was maintained to 1:30. The treated-fiber (TF) were filtered, and washed with water several times until the alkali was completely removed (pH reach normal), and air-dried overnight. Bleaching process was conducted using 1% (v/v) sodium hypochlorite (NaOCl) at 70 °C for 4 h under mechanical stirring 300 rpm. The FL ratio was kept at 1:70. After finished, the fibers were filtered and washed with water for 3 times to remove excess bleaching agent. The TF is then left to dry overnight in room temperature. Hydrolysis was performed using 20% (v/v) sulfuric acid (H₂SO₄) at 80 °C for 2 h under mechanical stirring 500 rpm. The FL ratio was maintained at 1:50. Immediately following the hydrolysis, the suspension was filtered to remove the liquid. Solid fraction was washed with cold water to stop the reaction, and followed by air-dried overnight. After this treatment, the TF was undergo mechanical treatment which performed by ball-milling in acidic solution (1% acetic acid glacial). The suspension was ball-milled at room temperature for 2 h. The surface speed of the ball mill was maintained to 60 rpm. Ceramic balls with various diameter were used as grinding media. After milling, the suspension was then centrifuged for 10 minutes at 3000 rpm. Solid fraction (MFC) was removed from suspension and then washed three times to remove excess acetic acid. Finally, the solid was let to dry overnight at ambient temperature.

2.3. Thermoplastic natural rubber (TPNR) preparation
TPNR samples were prepared in two processes. First, NR and the compound ingredients were compounded in a two roll mill according to the formulation on Table 1. The resulted compound was stored in a conditioned room at 25 °C minimum for 24 h. Second, the NR compound was blended with PP and MFC by dynamic vulcanization in Rheomix Polylab 3000 OS with 300 cm³ mixing chamber (fill factor 80%). The blends were made in a fixed NR/PP ratio of 60/40 with various MFC concentration as detailed on Table 2. The mixing was carried out at 160 °C with rotor running at 90 rpm. The mixing process was run in three stages. First, PP was melted the torque remained stable. Second, MFC was added into the mix and was processed until the torque stable. The last stage was NR compound incorporation. One cycle of mixing process took at least 17 minutes. The resulted blends were pelleted and store in a sealed container.

| Ingredients | Concentration (phr) |
|-------------|---------------------|
| SIR         | 100                 |
| ZnO         | 5                   |
| Aflux 42    | 1.5                 |
| N-330       | 20                  |
| N-660       | 15                  |
| MACO        | 5                   |
| TMQ         | 2                   |
| 6PPD        | 1                   |
| CBS         | 1.2                 |
| Sulfur      | 1                   |
| PVI         | 0.1                 |

| Ingredients | Composition (PHR) |
|-------------|-------------------|
| NR compound | PN0 60 PN1 60 PN2 60 PN3 60 PN4 60 PN5 60 |
| PP          | 40 40 40 40 40   |
| MFC         | 0 1 5 10 15 20  |
| Stearic acid| 1 1 1 1 1     |
| PP-g-MA     | 1 1 1 1 1   |
| Irganox 1010| 0.5 0.5 0.5 0.5 0.5 |
2.4. Thermal analysis
Thermogravimetric (TG) and differential scanning calorimetry (DSC) were used to analyze the thermal properties of TPNR samples. Thermogravimetric analyses were carried out using simultaneous DTA-TG Shimadzu DTG-60 H equipped with TA 60 WS software. Sample was placed in alumina crucible and subjected to a temperature in the range 30 °C to 600 °C with a heating rate of 10 °C/min in oxygen atmosphere. DSC studies were performed using Perkin Elmer DSC 4000. The sample was heated from ambient temperature to 445 °C with a heating rate of 5 °C/min in oxygen atmosphere. The peak of maximum endotherm peak was considered to be the melting point of the sample, while the melting enthalpy was determined from the area of the melting peak.

3. Results and discussion

3.1. Thermogravimetric analysis
Thermogravimetric (TG) data describe a number of thermal degradation stages, material weight loss in each stage, threshold temperature etc. The TG and its derivative (DTG) tell about the information of the nature and extent of material degradation. While in DSC, the heat flow rate associated with the thermal event that can be measured as a function of time and temperature. This will provide valuable information related to melting and phase transitions of the samples [20].

Figure 1(a, b) depicts the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of MFC, neat PP and NR compound. The onset degradation temperature (T_{onset}), maximum decomposition temperature (T_{max}), maximum rate of decomposition (R_{max}) and weight loss are tabulated in Table 3. The DTG curve (Figure 1(b)) clearly indicates that the degradation of NR compound is occurred in single stage since one single peak is found. The main degradation of NR compound occurs between 356 and 410 °C. The onset degradation starts at 356 °C, and the maximum degradation is occurred at 379 °C. Similar to NR compound, neat PP shows one major degradation peak with the main degradation takes place in the range 278-311 °C. The decomposition reaches the maximum mass loss at 292 °C, and showing 7% solid residual at the end of the measurement (400 °C).

| Sample ID | Stage-1 | Stage-2 | DSC |
|-----------|---------|---------|-----|
|           | T_{onset} (°C) | T_{max} (°C) | R_{max} (mg/sec) | Weight Loss (%) | T_{onset} (°C) | T_{max} (°C) | R_{max} (mg/sec) | Weight Loss (%) | T_m (°C) | ΔH_f (J/mol) |
| MFC       | 199     | 236     | 0.0086 | 43.16 | 285 | 305 | 0.0057 | 36.63 | - | - |
| NR-comp.  | 356     | 380     | 0.0113 | 71.88 | - | - | - | - | - | - |
| Neat PP   | 278     | 293     | 0.0306 | 92.90 | - | - | - | - | 165.16 | - |
| N0        | 346     | 378     | 0.0493 | 53.88 | 420 | 519 | 0.0002 | 41.62 | 162.39 | 30.28 |
| N1        | 361     | 371     | 0.0662 | 58.42 | 410 | 414 | 0.0231 | 22.40 | 162.71 | 27.45 |
| N2        | 353     | 380     | 0.0115 | 43.25 | 447 | 464 | 0.0148 | 38.97 | 162.71 | 31.65 |
| N3        | 347     | 378     | 0.0065 | 41.53 | 413 | 450 | 0.0066 | 33.84 | 162.58 | 29.28 |
| N4        | 354     | 383     | 0.0076 | 40.20 | 449 | 467 | 0.0105 | 36.76 | 161.54 | 27.90 |
| N5        | 355     | 381     | 0.0065 | 41.51 | 449 | 467 | 0.0089 | 32.97 | 161.25 | 24.75 |

MFC degrades in two stages indicated by two major peaks on DTG curve. The first degradation occurs at the range of 199-250 °C with T_{max} at 236 °C. This is associated with hemicellulose and cellulose degradation. According to Yuakkul et al. [15], hemicellulose starts to decompose at lower temperature (150-350 °C), while decomposition of cellulose takes place at 270-350 °C. The second stage degradation is associated to lignin decomposition. The 2-stage degradation of MFC indicates impure MFC. Therefore, the isolation procedures should be improved so that it provides pure cellulose.
Figure 1. TG (a) and DTG (b) curves of the NR compound, MFC and PP.

Degradation of TPNR samples take place in two stages simultaneously as shown at Figure 2(a). Two major endothermic peaks on DTG curve (Figure 2(b)) clearly indicates this degradation mode. This result is agreed to previous studies [4, 20, 21]. The first degradation corresponds to PP degradation. NR enhances the thermal stability of PP since the onset degradation temperature of TPNR is higher than neat PP. Crosslinked-NR that finely dispersed within continuous PP matrix as a result of dynamic vulcanization acts like a great barrier (Figure 3) thus prevents the volatile PP degradation products [22]. At the second stage, the degradation starts at higher temperature corresponding to the existence of crosslinks formed during dynamic vulcanization [20]. Thus, more energy is needed to break the bonds. It is interesting here that no degradation occurred below 300 °C which is associated to MFC degradation. Perhaps, the decomposition of MFC substituents are prevented by the crosslinked rubber phase and they start to decompose at higher temperature.

Figure 2. TG (a) and DTG (b) curves of the TPNR samples.

At the first stage degradation, the addition of 1 phr MFC causes an increase in onset degradation temperature to some degree. However, further addition tends to decrease it. Also, the degradation rate significantly reduced to a lower rate by the addition of MFC. Increasing MFC concentration does not give a big influence to the degradation rate. This findings are not in agreement with Yuakkul et al. [15] that reported the more rapid degradation rate upon increasing fiber loading caused by lower thermal stability of PALF. Further studies are needed to evaluate the role of MFC in this case. Perhaps, MFC plays a role as nucleating agent for PP that increase the crystallinity of TPNR samples. Therefore, the
thermal stability is increased. Overall, the TPNR samples are thermally stable in the range of 345-360 °C, means that they may be safely processed or applied without any degradation.

![Figure 3. Barrier mechanism of volatile substances in PP matrix by crosslinked NR.](image)

3.2. Differential scanning calorimetry (DSC) analysis
Differential scanning calorimetry (DSC) study is carried out to understand the phase inversion behavior (crystallization and melting) of a material when subjected to heat [23]. This study only discusses the melting behavior of TPNR samples. The DSC thermograms of neat PP and TPNR sample are depicted on Figure 4(a, b), while the melting temperature ($T_m$) and heat of fusion ($\Delta H_f$) are tabulated on Table 3.

![Figure 4. DSC thermogram of a) Neat PP, b) TPNR samples.](image)

Both, neat PP and TPNR, samples reveal single endothermic peak that is corresponded to melting temperature ($T_m$). It is clearly seen that MFC loading is independent to $T_m$ since no significant increase is found after MFC incorporation (Figure 4b). Melting point of TPNR samples were also similar to neat PP. From Table 3 it is evidence that MFC concentration does not alter $\Delta H_f$. It is a positive indication that the energy required to process the TPNR is quite similar to neat PP.

4. Conclusion
Thermoplastic natural rubber (TPNR) made of NR/PP blend reinforced with MFC had been successfully prepared. The MFC was derived from local pineapple leaf fiber (PALF) through several chemical and mechanical treatments. TG analysis exhibited that the degradation modes of NR compound and neat PP
were occurred in single step showed by single peak in DTG curve, while MFC degraded in two steps indicating impurity of the resultant MFC. TPNR samples showed two stages degradation. The onset degradation of TPNR started at 346-361 °C which is higher than its single component. Incorporating rubber phase into PP matrix could enhanced its thermal stability to some extent degree. Melting temperature of TPNR samples did not significantly differ from neat PP, and the heat of fusion was remaining unchanged upon increasing MFC concentration. Overall, the TPNR samples were thermally stable in the range of 345-360 °C, which mean that the samples would be safely processed without any degradation caused by heat. The similarity of melting temperature to those of neat PP gives advantages not only to the processing means but also reducing cost.

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References
[1] Mondal M Gohs U Wagenknecht U and Heinrich G 2013 Mater. Chem. Phys. 143(1) 360–6
[2] Pechurai W Nakason C and Sahakaro K T 2008 Polym. Test. 27(5) 621–31
[3] Varghese S Alex R and Kuriakose B 2004 J. Appl. Polym. Sci. 92(4) 2063–8
[4] Lopattanon N Tanglakwaraskul S Kaesanm A Seadan M and akai T 2013 Adv. Mater. Res. 747 230–3
[5] Bahrudin Ahmad A Prayitno A and Satoto R 2012 Int. Conf. Innov. Polym. Sci. Tech. 4 146–53
[6] Bendjaouahdou C and Bensaad S 2013 Energy Procedia. 36 574–90
[7] Nikmatin S Syafiuddin A Hong Kueh A B and Maddu A 2017 J. Appl. Res. Tech. 15(4) 386–95
[8] Jia X Chen Y Shi C Ye Y Wang P Zeng X and Wu T 2013 J. Agric. Food Chem. 61(50) 12405–14
[9] Cherian B M Leão A L de Souza S F Costa L M M de Olyveira G M Kottaisamy M Nagarajan E R and Thomas S 2011 Carbohydr. Polym. 86(4) 1790–8
[10] Asim M Abdan K Jawaid M Nasir M Dashtizadeh Z Ishak M R and Hoque M E 2015 Int. J. Polym. Sci. 2015 1–17
[11] Panyasart K Chaiyut N Amornsakchai T and Santawitee O 2014 Energy Proc. 56(C) 406–13
[12] Ummartoyin S and Pechyen C 2016 Carbohydr. Polym. 142 133–40
[13] Wisittananawat U Thanawan S and Amornsakchai T 2014 Polym. Test. 35 20–7
[14] Kalapakdee A and Amornsakchai T 2014 Polym. Test. 37 36–44
[15] Yuakkul D Amornsakchai T and Saikrasun S 2015 Int. J. Plast. Tech. 9(2) 388–411
[16] Yuanita E Pratama J N and Chalid M 2017 Macromol. Symp. 371(1) 61–8
[17] Thanomchat S Srikulkit K 2015 Adv. Mater. Sci. Eng. 2015 1–9
[18] Kaewpirom S Worrarat C 2014 Fibers Polym. 15(7) 1469–77
[19] Indrajati I N Dewi I R 2017 IOP Conf. Ser. Mater. Sci. Eng. 223
[20] Joseph P V Joseph K Thomas S Pillai C K S Prasad V S Groeninckx G Sarkissova M 2003 Compos. Part A Appl. Sci. Manuf. 34(3) 253–66
[21] Hernández M Albano C González J Ichazo M N 2006 Polym. Bull. 56(2–3) 285–91
[22] Roy Choudhury N Chaki T K Bhownick A K 1991 Thermochim. Acta 176(C) 149–61
[23] Benmesli S Riahi F 2014 Polym. Test. 36 54–61