Thermal degradation and swelling behaviour of acrylonitrile butadiene styrene rubber reinforced by carbon black

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Abstract. Acrylonitrile butadiene styrene rubber (NBR) has been widely applied in the automotive industry. However, unfilled NBR has poor properties. The purpose of this publication was to study the effects of carbon black (CB) variations on the thermal degradation and swelling resistance of NBR blends. The CB used in this study were HAF, SRF, and the combination of HAF and SRF. NBR samples with different carbon black fillers were prepared by a two-roll mill. The thermal stability and swelling resistance were studied by TGA (heated in oxygen with heating rates of 10, 15, and 20 °C/min at 30-600 °C) and immersed by IRM 903 for 72 h. The degradation of NBR composites occurs in two stages. The kinetic parameters of the degradation process were studied by applying Coats and Redfern method. The filled NBR composites have better thermal and swelling resistance than unfilled NBR composite. The swelling percentage and percentage of mass decomposed at 600 °C were 6.3% and 53.34% for HAF-composite, 6.9% and 56.05% for SRF-composite, and 2.1% and 57.17% for HAF/SRF-composite. Unfilled NBR gives swelling percentage and percentage of mass decomposed of 27.1% and 78.56%. HAF is the proper filler for NBR composite to reach a good thermal and swelling resistance.

1. Introduction

Acrylonitrile butadiene rubber (NBR) is a synthetic rubber that is mostly used in automotive applications. It has a generally excellent resistance towards oil, abrasion, water, and alcohols. However, it has poor resistance to ozone because the butadiene has an unsaturated chain backbone. Unfilled NBR vulcanizate has poor mechanical properties because of the absence of strain-induced crystallization [1]. The addition of filler can improve the properties of elastomers significantly [2, 3]. One of the most commonly used filler is carbon black (CB) that plays an important role as reinforcing filler. This conductive composite material is a low cost and has high flexibility and also good mechanical properties [4-7].

As a filler, CB has various types. Based on its manufacturing process, the common CB are furnace black that has a size from 8 nanometers and thermal blacks that has a size from 200 nanometers. The common CB in the market divided into some type based on its particle size, i.e. N110 SAF (Super Abrasion Furnace), N220 ISAF (Intermediate Super Abrasion Furnace), N330 HAF (High Abrasion Furnace), N550 FEF (Fast Extrusion Furnace), N660 GPF (General Purpose Furnace), N774 SRF (Semi Reinforcing Furnace), and N990 MT (Medium Thermal) with particle sizes of 11-19, 20-25, 26-35, 40-48, 49-60, 61-100, and 200-500 nm. The different types of CB give different characteristics and CB-rubber. The important properties of CB are the structure, the particle size, and the surface activity of

CB. The lower particle size of CB, the better dispersion in the rubber molecules. The structure and surface activity of CB also related with the interaction between rubber molecules and filler [8-10].

The use of rubber products in a certain time can decrease the properties of the rubber material called degradation. The degradation of rubber material is caused by time and temperature. The rate of degradation depends on the polymer type, storage, and the application. Oil-resistant polymeric materials are also essential for the automotive application and industry. The degradation and swelling resistance analyses can give valuable information about the performance of materials and the suitable conditions of using and storage [11, 12].

Some related study about NBR composite had been done by some researcher. Khaled studied the effect of curing system on mechanic and psycho-chemical of NBR [2]. Nabil *et al.* studied the effect curing system on the thermogravimetry and swelling of NBR [13]. De Sousa *et al.* studied NBR with different clays on morphology and mechanical properties [14]. Jovanovic *et al.* found that 80 phr HAF gave the best aging resistance on NBR composite [5]. Salehi *et al.* found that HAF can improve thermal stability in fluoroelastomer composites, but not any differences with GPF and MT [9]. Manoj *et al.* found that ISAF carbon black give the better mechanical and swelling resistance than HAF and SRF on EPDM/NBR blend [15]. It is known that each type of CB has the different effect on the elastomer. However, NBR reinforcement by different types of CB has not yet been studied in detail, especially in the thermal degradation and swelling properties. In this study, the thermal decomposition and swelling of NBR blends will be studied by using thermogravimetric analysis (TGA) and by immersed the NBR composites in IRM 903 oil. The purpose of this publication was to study the effect of CB variations on thermal degradation and swelling resistance on NBR composites. So that it can optimize the use of fillers to get the required product. The fillers used were HAF (High Abrasion Furnace)/ CB N330, SRF (Semi-reinforcing Furnace)/ N774, and the combination of HAF and SRF. The degradation and swelling resistance analyses are very important to know the suitable conditions of using and storage. This is the second publication from the previous study by Yuniari *et al.* [16]. Previous publication evaluated the kinetic vulcanization and the mechanical properties of NBR composites.

2. Experimental method

2.1. Material
NBR composites were made with the formulations described in the previous publication [16] with NBR kraynac 4975 F, ML (1+4) 100 °C (75±5), ACN content of 48,5 ± 1,5%, carbon black HAF (OCI) with a particle size of 26-30 nm and SRF (OCI) with a particle size of 60-70 nm, paraffin wax (Antilux 654 A), paraffinic oil (Indrasari), zinc oxide (ZnO, Indoxide), stearic acid (Aflux 42M Rhein Chemie), 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ, Kemai), n-(1,3-dimethylbutyl)-n'-phenyl-p-phenylenediamine (6PPD, Starchem), thiuram disulfide (TMTD) and 2,2-dithiobis(benzothiazole) (MBTS) (Shandong), and sulfur (Miwon).

2.2. Method
The composites were made according to the method and formulations described in the prior publication [16]. The ingredients for NBR compound as shown in table 1 were accurately weighed and mixed by a laboratory-size two-roll mill. Compounds were mixed by the sequence: NBR, ZnO and stearic acid, paraffinic oil and CB, then 6PPD, TMQ and paraffin wax, MBTS and TMTD, and the last is sulfur. After reach a homogeneous compound, approximately 25 min, the compound were stored in 23±2 °C for 24 h. Then, the curing time of the compound was tested by rheometer (Gotech 3000 A). The compounds were vulcanized in a hydraulic press (Toyoseiki A-652) at 160 °C with a pressure of 150 kg/cm^2 with time-based on the rheometer.

Table 1. NBR compound formulation.

Material	Amount, phr (per hundred rubber)			
	NBR1	NBR2	NBR3	NBR4
NBR	100	100	100	100
ZnO	5	5	5	5
Stearic acid	1	1	1	1
Paraffinic oil	10	10	10	10
HAF	0	40	0	20
SRF	0	0	40	20
6 PPD	2	2	2	2
TMQ	2	2	2	2
Paraffin wax	0.5	0.5	0.5	0.5
MBTS	1.5	1.5	1.5	1.5
TMTD	0.5	0.5	0.5	0.5
Sulfur	1.5	1.5	1.5	1.5

2.3. Thermogravimetric study

The thermogravimetric analysis was observed using Shimadzu DTG 60. The oxygen gas flowed at a rate of 30 ml/min at 30-600 °C using an alumina pan with 5-8 mg of NBR powder sample with a heating rate of 5, 10, and 15 °C/minute.

2.3.1. Kinetic parameter. This study used the Redfern Coats equation to calculate the kinetic parameters as some previous study [17,18]. TG is determined by measurement of degradation rate and fractional mass loss according to temperature change. The fraction of conversion x is defined as:

$$x = \frac{W_0 - W_t}{W_0 - W_f} \tag{1}$$

where W_t is the actual mass at any degradation time, W_0 is the initial mass, and W_f is the final mass at the end of the thermal degradation process. The rate of degradation, $\frac{dx}{dt}$, can be expressed as the product of the function of temperature and the function of conversion:

$$\frac{dx}{dt} = k(T) f(x) \tag{2}$$

where $k(T)$ is the rate constant and $f(x)$ is the reaction model which describes the dependence of reaction rate on the extent of reactions. If thermal degradation behavior follows the Arrhenius equation, then $k(T)$ is expressed as:

$$k = A exp(-\frac{E}{RT}) \tag{3}$$

$$f(x) = 1 - x \tag{4}$$

For constant heating rate, $\beta = \frac{dT}{dt}$, equation (2) can be arranged:

$$\frac{dx}{dT} = \frac{A}{\beta}(1 - x)\exp(-\frac{E}{RT}) \tag{5}$$

An integration from equation (5) leads to the equation (6)

$$\ln\left[-\frac{\ln(1-x)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{6}$$

In equation (6), $\ln\left[-\frac{\ln(1-x)}{T^2}\right]$ is linear with $\frac{1}{T}$ with the slope as $-\frac{E}{R}$ to calculate the activation energy. Whereas intercepts can be used to calculate the pre-exponential factor. In this study, it is assumed to take a first order reaction.

2.4. Swelling study
Swelling test was performed for 72 h at 23±2 °C according to ISO 1817 by immersed the NBR composites in IRM 903. The lower swelling percentage indicates the higher solvent resistance of the composite. The change in mass was calculated by equation (7).
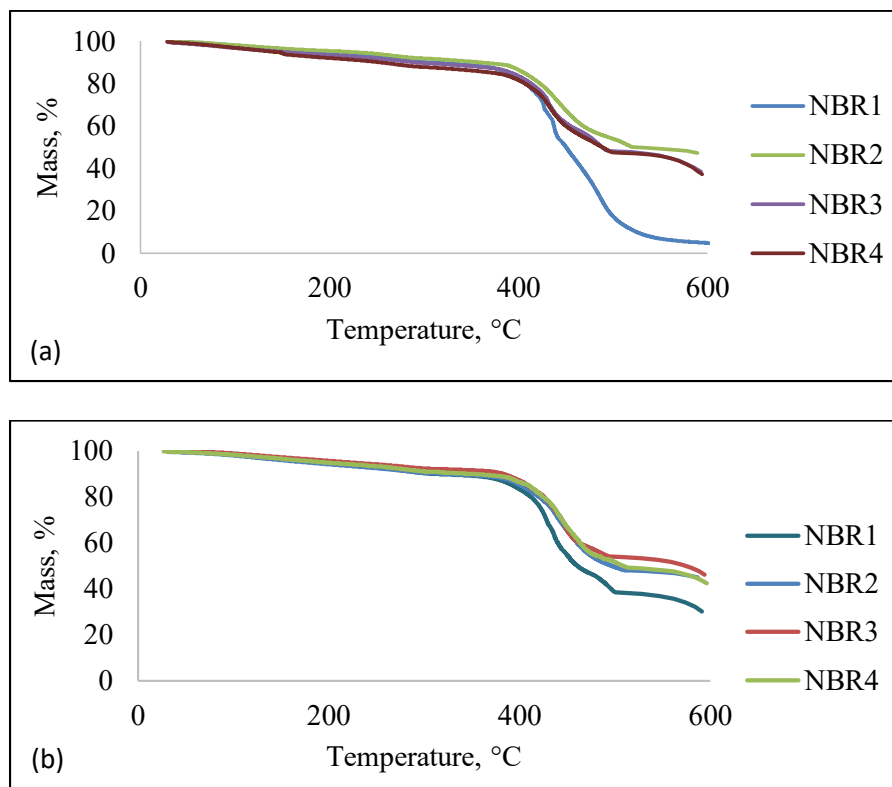
$$Swelling\ percentage\ (\%) = \frac{(w_1 - w_0)}{w_0} x\ 100 \tag{7}$$

Where w_1 is the mass of test piece after immersion and w_0 is the mass of test piece before immersion.

3. Results and discussion

3.1. Thermogravimetry
Thermogravimetry analysis (TGA) is one of the common methods for thermal analysis that show a function of decreasing mass to temperature. TGA measures the rate of mass changed as a function of time or temperature. The thermogravimetric curve with different heating rate can be shown in Figure 1.
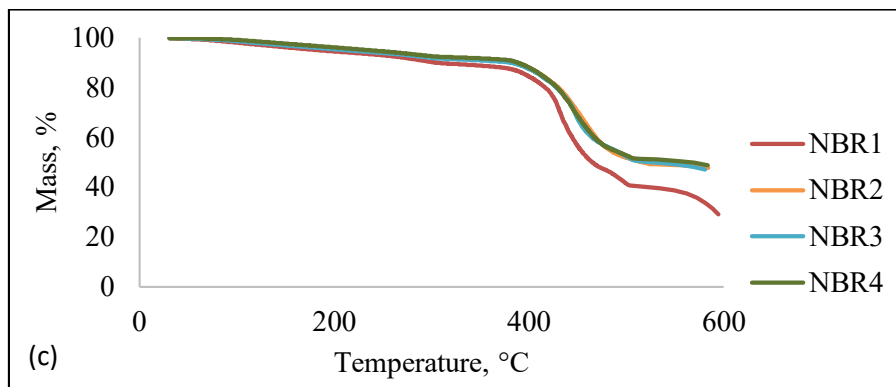

(a)

(b)

Figure 1. Thermogravimetric curves of NBR composites with the heating rate of (a) 10 °C (b) 15 °C (c) 20 °C.

Figure 1 shows that NBR1 give the lowest mass at 600 °C for all heating rate. At that temperature, the NBR composites haven't been perfectly degraded, The mass graph continues to decrease that means the burning temperature (BT) was not reached. BT is the temperature at which the mass is constant at the end of the combustion stage. At burning temperature, there has been a perfect decomposition, no more mass degradation occurs.

The degradation of NBR composites in this study occurs in two stages. The initial stage of NBR is dehydration of water content and releasing the volatile substance such as DCP, MAH (boiling point 110, 200 °C) at up to 100°C. The first stage occurs at 362 – 384 °C until 458 – 501 °C. This stage is the releasing step of non-rubber substances such as process oils, stearic acid, TMQ, TMTD, and MBTS (boiling point 302, 361, 320, 307, and 305 °C).

Table 2. Degradation of NBR composites.

Composite	Heating rate, °C/min	Stage I		Stage II	Mass decomposed at 600 °C, %
		Temp., °C	Peak temperature, °C	Peak temperature, °C	
NBR1	10	362 – 458	425	483	94.86
	15	367 – 475	432	580	69.87
	20	375 – 488	433	581	70.94
NBR2	10	376 – 489	430	563	52.75
	15	376 – 493	434	564	54.97
	20	378 – 512	456	571	52.31
NBR3	10	379 – 474	429	578	61.46
	15	380 – 486	444	579	53.85
	20	384 – 498	444	554	52.85
NBR4	10	367 – 462	428	583	62.86
	15	383 – 487	424	580	57.44
	20	383 – 501	440	569	51.19

The second stage is the process of NBR degradation. The second stage occurs at temperatures from 459 – 512 °C to more than 600 °C. At this stage, the chemical bonds of NBR start to break and the thermal resistance decrease. The degradation of NBR composites happens until more than 600 °C. At the 600 °C, the mass decomposed of filled NBR composites reach 51.19 – 63.47 %. Unfilled NBR gives higher mass decomposed as 69.87 – 94.86 %. It indicates that the filler provides good thermal resistance

to NBR composites. The stages that occur in thermal degradation of NBR composites can be seen in Table 2.

Table 2 shows that for overall composites, the higher heating rate, the higher starting degradation temperature, and also the higher peak in each stage. Increasing the heating rate makes the range of temperatures increases, which may have been because of the limitations of the heat transfer. It is accordance with studied by the previous researcher [7, 8]. The increase in heating rate does not affect the degraded mass, this is in accordance with the research by Abed *et al.* [7].

The degradation temperature at first stage has no significant difference in overall composites except unfilled NBR. Unfilled NBR provides the lowest initial degradation temperature (362 °C). This is in accordance with research by Alneamah *et al.* [12] that NBR without filler is degraded at lower temperatures. The increasing of thermal resistance strongly depends on the interfacial adhesion between the filler-rubber as a result of the compatibilization [11].

Unfilled NBR provides the greatest decomposing mass (78.56%), followed by NBR4 (57.16%), NBR3 (56.05%), and NBR2 (53.34%). CB as a reinforcing filler provide high crosslink density and improve the thermal resistance. CB also provide more compatible composite than unfilled composite. This shows that CB plays an important role improving the thermal stability. HAF-composite gives the lowest mass decomposed at 600 °C. HAF has the lower particle size than SRF, this makes the HAF more easily dispersed on NBR thus providing better thermal resistance than SRF. Salehi *et al.* also get the result that CB with the lower structure has better thermal stability than CB with higher structure [3]. The higher structure shows the higher number of particle per aggregate.

CB can be a good reinforcement if the particle of CB is well dispersed in the rubber matrix. But in a certain amount of CB, it can decrease some of its mechanical properties because of the agglomeration and the poor dispersion. This agglomeration and poor dispersion may happen in HAF/SRF-composite so that the mass decomposed higher than HAF- and SRF-composite.

3.1.1. Kinetic parameter. TG data can be used to calculate the activation energy and pre-exponential factor to get the optimum design to make the best product. The kinetic parameters in stage 1 can be plotted from equation (6) and the activation energy (Ea) and pre-exponential factor can be calculated. The kinetic parameters of NBR composites in stage 1 are shown in Table 3.

Table 3. Kinetic parameters of NBR composites in stage I.

Composite	Heating rate, °C/min	Ea, kJ/mol	Average Ea, kJ/mol	A, min^{-1}	Average A, min^{-1}	R^2
NBR1	10	68.31	80.81	0.195	2.351	0.9599
	15	86.66		3.379		0.9780
	20	87.45		3.480		0.9695
NBR2	10	76.55	80.60	0.599	1.452	0.9879
	15	79.21		0.995		0.9797
	20	86.04		2.761		0.9843
NBR3	10	72.76	80.01	0.317	1.513	0.9772
	15	80.93		1.237		0.9747
	20	86.34		2.985		0.9804
NBR4	10	62.09	72.98	0.055	1.775	0.9663
	15	67.40		0.115		0.9332
	20	89.43		5.157		0.9876

From the Table 3, it is known that the correlation coefficient (R^2) at all heating rate for all composites entirely close to 1, this proves that the activation energy can be approached exactly by first-order reaction. Table 3 shows that the value of activation energy is positive. It shows that there is no transition phase at the selected temperature. Activation energy indicates the amount of energy required to start the degradation and break the chemical bond. Table 3 shows that the Ea value in stage I is NBR1> NBR2> NBR3> NBR4. In this study, the activation energy and pre-exponential factors that can be calculated just in stage I. It can't represent the function of CB as reinforcing filler in NBR, because at the first stage just step of releasing the non-rubber materials. While the NBR degradation is happening in the second stage, but in this study, the kinetic parameters of the second stage can't be calculated because the degradation is not yet done at 600 °C.

Activation energy may change depends on the composite's composition and the heating rate. Differences in the determination of the heating rate also affect the calculation of Ea. From Table 3, the higher the heating rate, the higher the Ea. This result suitable with previous research by Apay-dinvarol *et al.* [19]. Therefore, it is preferred to use low-speed heating. But, it also depends on the speed of the reaction and the type of material [13].

3.2. Swelling
Swelling occurs because there are the free volume to facilitate the mass transfer of solvent. The swelling percentage was investigated at room temperature by IRM uptake until equilibrium swelling was reached. Swelling percentage of NBR composites from equation (7) are shown in Table 4.

Table 4. Swelling percentage of NBR composites.

Composite	Swelling percentage, %
NBR 1	27.1
NBR 2	6.3
NBR 3	6.9
NBR 4	2.1

The lower swelling percentage indicated a high crosslink density [17]. Table 4 shows that unfilled NBR has the highest swelling percentage. The filled composites have higher crosslink in the composite's matrix than unfilled composite. The presence of CB proves the better interfacial interaction in NBR composites. The enhancement of interaction between NBR and filler increasing the formation of crosslink density. CB makes higher rubber network, the polymer chain is trapped or entangled in the microstructure and the porosity of CB. So, the rubber chains become highly immobilized. In addition, the high crosslink density is due to the chemical bonds from the presence of electron acceptor on the surface where macroradical rubber is formed because of the degradation during the vulcanization process [18].

HAF give better swelling resistance than SRF because HAF has a smaller particle size, that means the larger surface area so that the physical crosslink climbs up. Fillers with higher surface area provide a higher reinforcing effect on rubber [3, 6, 20]. Combination HAF/SRF give the best swelling density.

4. Conclusion
From the result, unfilled NBR gives the lowest initial degradation temperature (362 °C) and the highest decompose mass (78.56%) at 600 °C. NBR unfilled also give the highest swelling percentage (27.1%). CB makes interaction with rubber thus reinforcing the composites. HAF with lower particle size than SRF has better filler interaction with NBR. The CB filler improves the thermal stability and swelling resistance. The low-speed heating rate is proper for TG analysis. HAF give better thermal stability and swelling resistance because of the better particle interaction due to its smaller particle than SRF. HAF is proper filler for NBR to reach the best thermal stability and good swelling resistance, especially in automotive application. The TG analysis should be done at a temperature above 600 °C. Because at this

temperature, the burning temperature of NBR composites hasn't been reached yet. This information is valuable to get the efficient production process and also knowing the suitable storage and application conditions.

Acknowledgment

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