

EFFECT ON THERMAL STABILITY OF NITRILE BUTADIENE RUBBER WITH ADDITION OF NANOCELLULOSE

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ABSTRACT

Acrylonitrile-butadiene rubber (NBR) exhibit poor thermal stability without the reinforcing fillers and this limits its application as heavy duty gloves. Nanocellulose crystalline (NCC) was chosen as it possesses high surface area, surface functionality and high crystallinity properties. Indeed, the hydrophilicity properties of NNC promote better dispersion within NBR matrix. . NBR nanocomposites with NCC were prepared using dipping method at different filler loading. It was confirmed that the NCC nanoparticles with average size of 10 to 18 nm were well distributed within the NBR matrix. Good interfacial bonds of NCC and NBR have been established by formation of inter hydrogen bonds. The reinforcement of NBR was contributed by the crystallinity of NCC. This factor brought to the increment of NBR thermal stability up to 75 % with only addition of 2 phr NCC. Meanwhile the thermal stability of the NBR/NCC nanocomposite increased by ~75% compared to the NBR matrix at 2phr NBR/NCC and similar trend is observed for activation energy. Good interfacial bonds of electrostatic interaction of NBR/NCC composites, ccrySTALLINITY and nanosized of NCC are the main factors that influenced the thermal stability of the NCC/NBR composites.

BACKGROUND

NBR provides excellent compression set, tear and abrasion resistance but limiting in heat resistance. Many literatures studied of thermal stability and kinetics properties of NBR reinforcement fillers such as clay. Ge et. al., 2015 have incorporated inorganic filler with long alkyl chain such as bentonite with expectation to increase the total decomposition temperature of NBR polymeric system [1]. Indeed, the combination of NBR with clay/carbon nanotubes show the same patent like previous study which thermal degradation of the nanocomposites increased as clay-CNTs filler present in NBR reduce the diffusion speed of the degradation and cause the activation energy increased accordingly. It has demonstrated the effect on hindered phenol within NBR polymeric chains and confirmed that the glass transition of NBR shifted from -16°C to 2.5°C with addition of 20 phr of phenol [2]. The main limitations of rubber

nanocomposites materials are greatly influenced by the degree of mixing between the matrix and fillers and the compatibility in terms of physical and chemical interaction between two phases. Poor physical and chemistry attraction between the matrix and filler resulted in weaker materials such as low thermal stability and etc.

METHODOLOGY

NBR latex was mixed with zinc oxide, titanium oxide, accelerator and the other additives for 1 hour at 50rpm. After that, pH of latex was adjusted to pH9 using ammonia as reduction agent to maintain the pH. NCC was added to latex compound and mix vigorously for overnight at room temperature. The amounts of NCC added were 1 to 5phr of rubber. Marble plates were dried in the oven at 100 oC for 5 minutes. After that, the dried marble plates were dipped followed by drying for another 5 minutes at the same temperature. Once the marble plates was taken out form oven, it was cooled down at room temperature for 30 seconds before dipped into latex compound. The marble plates were cured at 125 oC for 20 mins, followed by leaching with DI water. Next, the former were dried at 125 oC for 10 minutes. Finally, the marble was cooled down at room temperature and latex film was stripped out from the marbles. The produced samples was thermally analyzed by the thermogravimetry analysis (TGA).

RESULTS AND DISCUSSION

The degradation of the NCC nanoparticles was determined using the percentage of weight loss vis-à-vis temperature. The TGA thermogram is shown in Fig 1. It is clear that NCC nanoparticles undergo degradation in two steps, which is similar to the degradation profile of NCC produced via sulfuric acid hydrolysis [1-3]. The main NCC degradation occurs between 150 - 250°C due to depolymerization, dehydration, and the decomposition of amorphous regions as they likelihood contained higher sulfate groups. The presence of sulfate groups decreases the thermal stability from dehydration due to them being attached to the outer layer of the NCC, which is easily broken when the temperature was increased up to 200°C. Furthermore, the sulfate group act as catalyst in degrading NCC and causes the prolonged degradation of NCC occurring multiple steps as mentioned before. The small shoulder above 300°C in the DTG plot is indicative of oxidation and breakdown of the char to lower molecular weight gaseous products also the crystalline regions degraded at this temperature as well.

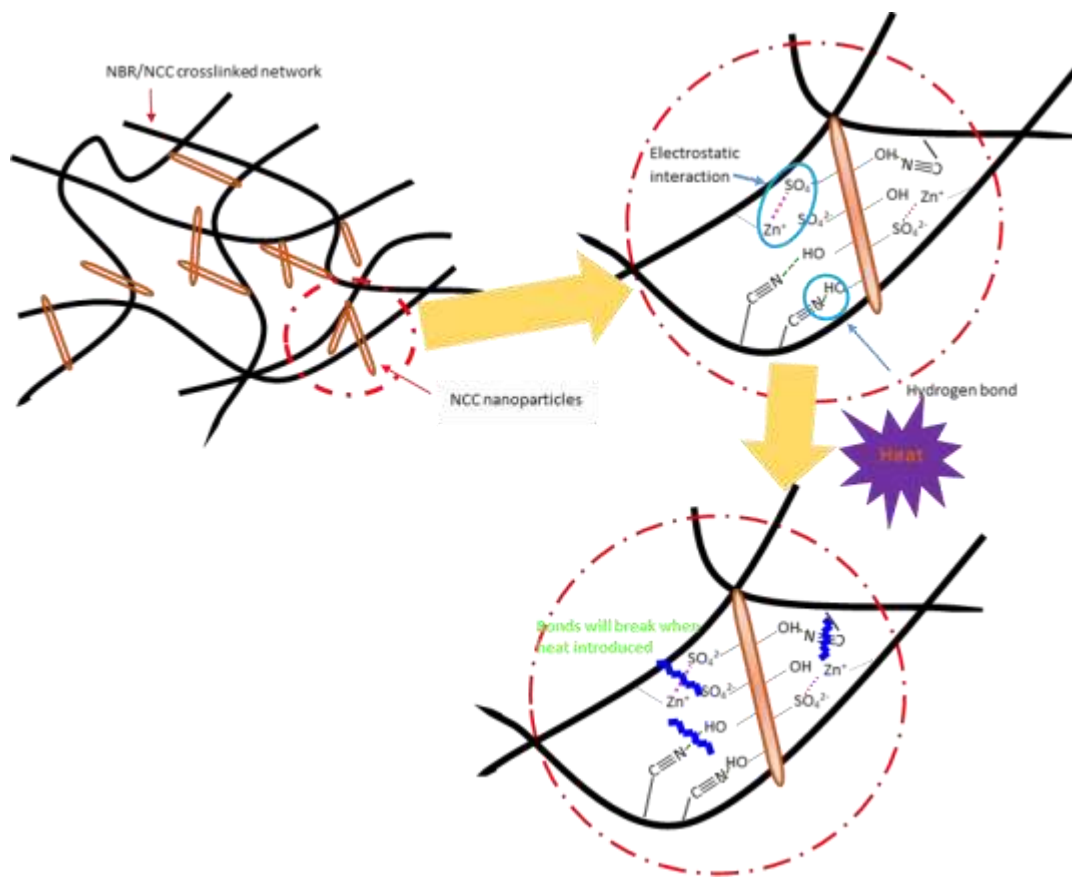


Figure 1: The possible scheme of the crosslinked network in NBR/NCC nanocomposites and the possible reaction when heat was introduced in thermogravimetry analysis.

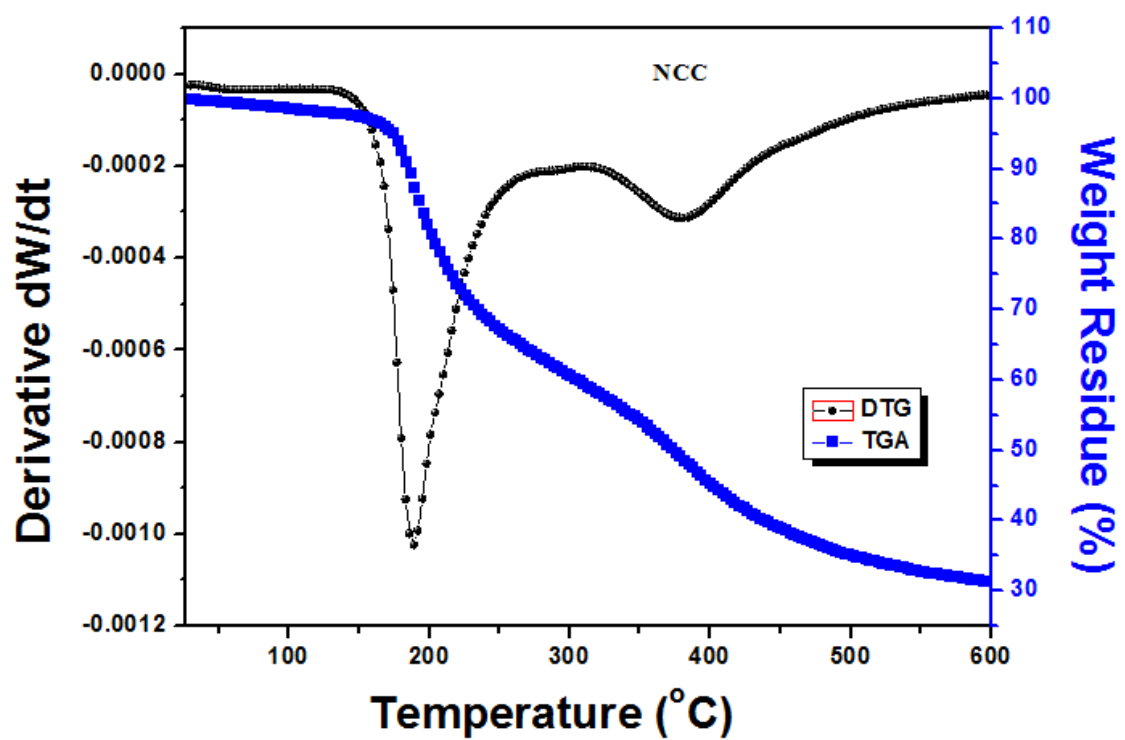


Figure 2: DTG and TGA curves of the NCC

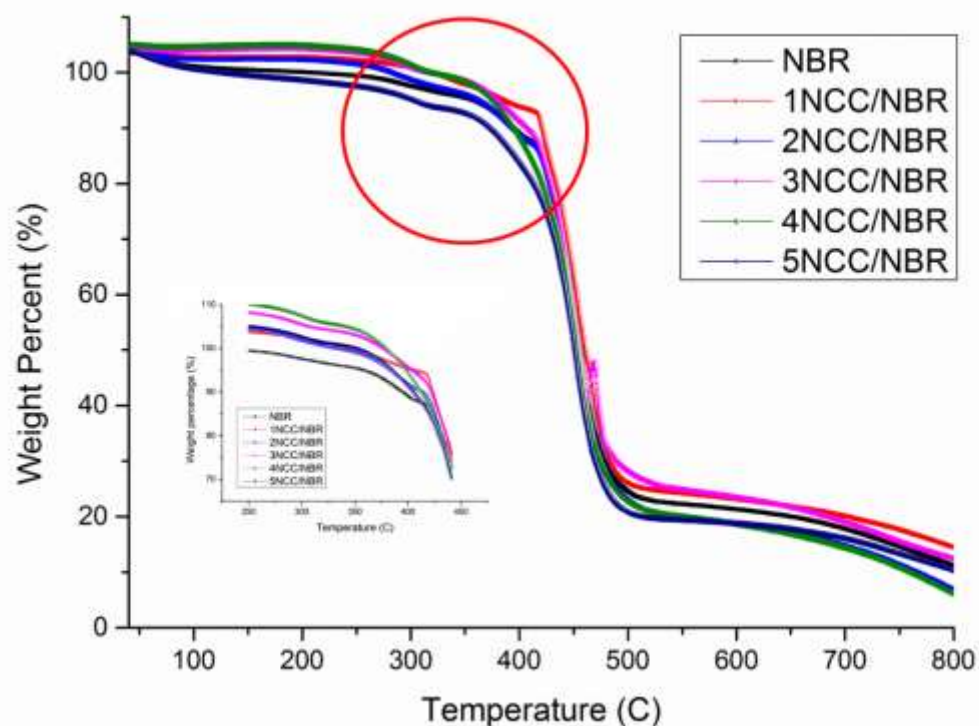


Figure 3: TGA curves of the NBR/NCC nanocomposites

Polymers can be degraded due to the formation of cross-links and breakage. The TGA thermogram of NCC/NBR nanocomposites is shown in Figure 2. The first region at 350 - 420°C is a small shoulder observed on the left side of the thermogram curve, representing the degradation of the NCC. This is supported by the percentage of weight loss based on the NCC content within the NBR matrix [4]. The second region at 400 - 470°C shows a major weight loss of >80%, which was attributed to the degradation of the NBR. The third region was a minor peak at the end of the temperature range at a total loss of >90%. The nanocomposites began degrading and exhibit maximum degradation almost the same temperature as pure NBR and no significant trend exhibit with the increasing of NCC content. These results suggest that the incorporation of NCC in NBR doesn't have significant enhancement in the thermal stability.

Weight residue in percentage (%) is presented in Table 1 and indicate that with increase in filler loading, the percentage of weight residue also increase accordingly. Reason, in this work nitrogen atmosphere was applied and only polymer and lower molecular weight ingredients like sulfur and

zinc oxide undergoes the thermal degradation whereas carbon element are remain unaffected and become residue [5-6]. Also, weight residue is depending on the decomposition process of the elastomer as well as filler contents where the fact can be attributed to the heterogeneity of the composites. It has been stated that the synthetic rubber itself such as NBR observed the weight residue less than 10% produced by random chain scission with intramolecular hydrogen transfer. Similar result was observed in this study where NBR residue is 6%. It is apparent from Table 1 that filled nanocomposites, the weight residues are increased marginally as it was attributed by the crosslinking during vulcanization process and remaining mass of the additives that are used during compounding [7].

The maximum degradation temperature of the nanocomposite is summarized in Table 2 as well. Another major region of degradation is between 400 - 470°C, which is related to the polymer chain scission and cross-link linkage. Based on Figure 2, during vulcanization of NBR/NCC there are 2 possible interactions that might be occurred inside the composites which is 1) the hydrogen bonding interaction between NCC and NBR chain. NCC possess abundance of hydroxyl groups in the surfaces while NBR chains consists $-C\equiv N$ groups. In $-C\equiv N$ groups, the nitrogen had lone pair of electron will reacted with NCC forming hydrogen bonding of $-O-H-N\equiv C-$. [3] 2) The electrostatic interaction between sulphate group (negative charge) from NCC surfaces with hydrogen from NBR chains. Thus the NCC might absorb the NBR chains onto its surfaces. Since NCC also possess bulky chains, it is restricted the mobility of the polymer chain and served as multifunctional cross-linker [5]. When the heat are applied into the NBR/NCC polymer network, the electrostatic interaction will be breakage and was reflect in first step of degradation as discuss above.

The thermal stability of the NCC/NBR nanocomposite showed a slight increment due to the addition of the NCC up till 2NCC (465°C). It is believed that at lower concentrations of NCC, the Zn/NCC complex and percolation network are crucial towards increasing the thermal stability of the nanocomposite. Furthermore, it has been stipulated that NCC is covered by the NBR matrix, which translates to strong interactions between the NCC and NBR molecules. Also, in low filler loading of filler, NCC network are form and responsible for the conduction of the heat through the network and thereby leads to degradation [6]. At 5phr of NCC, the maximum degradation temperature decreased about 10% with increased loading of NCC. NCC possesses hydroxyl

groups and tends to agglomerate, since it believe to forms inter hydrogen bonding with other NCC chains. The NCC reinforced natural rubber, and found that the high surface polarity of NCC due to the hydroxyl groups lead to the agglomeration of the filler particles at higher loadings of NCC. Moreover, NCC have a number of oxygen in its backbone that could in theory decrease thermal stability.

Table 1: Summarize of the decomposition temperatures of NCC, plain NBR and NBR/NCC nanocomposites

Composition NCC (phr)	Tmax Decomposition 1st step	Onset temperature 2nd step	Tmax Decomposition 2nd step	Weight residue at 800°C (%)	Activation Energy (kJ/mol)
NCC	180	NA	280	NA	NA
NBR	346	411	451	6	88.13
1NCC/NBR	361	406	460	14	53.14
2NCC/NBR	345	416	465	12	56.17
3NCC/NBR	336	411	455	12	54.83
4NCC/NBR	350	395	450	10	49.65
5NCC/NBR	331	386	410	10	49.25

The activation energy (E) of the composites was calculated from TGA thermograms using Arrhenius equation to study the decomposition kinetic of the polymer. Based on literature, there are various factors that are effected in rubber composites during degradation process occurred inside the samples such as mass and heat transfer, which vary with the types of matrix, fillers, and also strongly influenced by the type of degradation suffered by the material [7]. The argument made was proved with NCC had low thermal stability due to possess more hydroxyl groups inside the cellulose chain in this study.

The activation energy of NBR is recorded as 88.13 kJ/mol constant heating rate which was recorded at 10°C/min. Generally, we observed as NCC content increases the activation energy of the composite shows gradual decrease, resulted in the thermal stability of the composites reduce accordingly and the value are less than 100kJ/mol. It stated that activation energy less than 100kJ/mol happened when there are heterogeneous catalyst, biological reactions and reactions where the limiting step is the diffusion of small molecules through or their evaporation from a condensed phase. The highest activation energy for composites recorded at 2NCC/NBR and the value slightly decreased afterwards until 5NCC/NBR. The highest value in activation energy is believed related to dispersion of NCC inside the matrix because the activation energy is the energy barrier that is preventing polymer chain movement when the heat is introduced. In addition, the interfacial adhesion was improved as well [4] . The decreasing in activation energy with the addition of NCC due to the agglomeration between NCC chains itself as NCC consisting of more hydroxyl groups in cellulose chain and weak interfacial adhesion between NCC and NBR. In order to improve the interaction between matrix and filler, the surface modification for NCC will be introduced.

CONCLUSION

The dispersion of the NCC inside the NBR matrix was analyzed using AFM, which proved that the NCC nanoparticles are well dispersed at 5 phr. This supposition was supported by the data reported by the TGA. The thermal degradation temperature is much higher than the thermal degradation temperature of the NCC nanoparticles. The highest temperature was 465°C at 2phr NCC. It was concluded that the incorporation of NCC into the NBR matrix enhanced the thermal stability of the resulting nanocomposite. The increasing in thermal stability of the NBR/NCC nanocomposite renders it suitable for various applications such as heavy duty gloves and metalworking industry

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