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## Effect of Nano-fibril Cellulose (NFC) Filler towards the Swelling and Diffusion Behavior of Superabsorbent Polymer Composite

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# Effect of Nano-fibril Cellulose (NFC) Filler towards the Swelling and Diffusion Behavior of Superabsorbent Polymer Composite

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**Abstract.** Superabsorbent polymers (SAP) exist as a three-dimensional network consisting of branched or linear chains that are chemically or physically crosslinked and possess the ability to retain large amounts of fluids. To be in coherence with the global demand for more biodegradable materials, nano-fibril cellulose (NFC) is introduced as fillers during the synthesis of SAP. The objective of this study is to investigate the effects of different amounts of NFC addition to swelling and diffusion behavior of the final product (SAP/NFC). Inverse suspension polymerization was employed to produce the NFC/SAP, in which acrylic acid (AA) was used as a monomer, acrylamide (AM) as co-monomer and N,N'-Methylenebis(acrylamide) (NNMBA) as the crosslinker. The reaction was conducted at temperature, 55°C for 3 hours. In water absorbency analysis, SAP with 0.006 wt% of NFC shows the highest water absorbency, up to 135%. Swelling kinetic study shows that all SAP exhibit second order of swelling kinetic, and obeys Fickian diffusion behavior. FTIR analysis confirmed the characteristic of SAP and the presence of NFC by identifying C=O, N-H, O=C-H, C-N, O-H, C-H, C=C, C-H, and C-OH bonds. The morphological study shows that the presence of NFC inhibits the formation of SAP in regular bead shape. In thermal stability analysis, SAP with 0.006 wt% of NFC shows the highest thermal stability compared to the other SAPs. It is concluded that the addition of 0.006 wt% NFC is the most optimum condition for cellulose-based SAP synthesis due to the highest water absorbency and thermal stability.

## 1. Introduction

Superabsorbent polymer (SAP) was firstly synthesized in 1938 by thermal polymerization of acrylic acid (AA) and divinylbenzene in an aqueous medium. The advancement of the material field in the latter part of the 1950s, the first generation of superabsorbent polymers comprises a wide range of crosslinking procedures involving the chemical modifications of a monomer or polymer with an initiator [1]. Later of the 1960s, the first cross-linked network material was developed from a polyhydroxyethylmethacrylate (pHEMA) superabsorbent polymer for medical application. The compositions of these SAPs were mainly based on hydroxyalkyl methacrylate and other related monomers, with their swelling capacity, could achieve up to 40 to 50%. Nowadays, SAPs supersedes and replaces conventional absorbents in personal health care products and provides notable improvements in the effectiveness of feminine hygiene products and adult incontinence products [2].

Superabsorbent polymer, by definition, is a water-swollen and crosslinked polymeric network produced by the polymerization of one or more different monomers. It is a polymeric material that exhibits the ability to swell and retain a significant fraction of water within its structure without dissolving in water



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[3]. SAP is highly hydrophilic due to its chemical structure, which consists of carboxylic acid, carboxamide, hydroxyl, amine, imide groups that are insoluble in water [4]. The physical and thermal properties of superabsorbent polymers depend on the properties and amount of the monomers used in the synthesis as different monomers used will obtain different amounts of swelling capacity. The common superabsorbent hydrogel frequently produced from acrylic acid (AA), its salts, and acrylamide (AM) via grafting, solution, or inverse-suspension polymerization techniques [5]. The mechanism of SAPs' water diffusion can be considered as a physical process, which initially; water retention occurs by capillary force within macroporous materials, and then the formation of hydrogen bonds between water and hydrophilic functional groups occurred [1].

The current upsurge in global demand for nanomaterials that are more environmentally friendly and possess high biodegradability contributes to increasing researches and developments [6-8] of nanocomposite such as a combination of nanocellulose with a polymer matrix. It is expected that the polymer matrix to perform outstanding applications [7], if suitable filler selection, due to the efficient interaction between filler and matrix [8]. In this work, nano-fibril cellulose (NFC) was isolated from the oil palm empty fruit bunches, which classified under natural or organic material. However, limited researches were done using nano-fibril cellulose (NFC) as the filler in inverse suspension polymerization for the SAP formation.

In this research, the effect of different amounts of NFC as the filler for the SAP/NFCs composite using inverse suspension polymerization was investigated. The swelling and diffusion behavior of the SAP/NFCs composite was analyzed using kinetic and power-law equations and the characteristics of the SAP/NFCs composite were also studied. It is expected that the addition of NFC as the filler will improve the swelling and diffusion behavior will be improved.

## 2. Experimental

### 2.1. Materials

Acrylic acid (AA) with 99% purity as monomer and acrylamide (AM) as co-monomer, N,N'-Methylenebis(acrylamide) (NNMBA) with 99% purity as crosslinker, NFC isolated oil palm fruit bunch as the filler and ammonium persulfate (APS) with 98% purity is used as the initiator. Sorbite anhydride monostearic acid ester (Span 80) and cyclohexane (reagent grade with 99.5% purity) acts as a continuous solution for polymerization. All the chemicals were supplied by Merck.

### 2.2. Methods

**2.2.1. Synthesis of SAP/NFC via Inverse Suspension Polymerization.** For continuous phase, 1:10 v/v of Span 80 and cyclohexane was mixed in a two-neck round bottom flask equipped with a magnetic stirrer and reflux condenser. Then, the mixture was purged with nitrogen gas, and NFC, as filler with amount varies from 0 – 0.01 wt% and 0.009 wt% NNMBA was added to the continuous phase. The mixture was then stirred with 300 rpm agitation speed until it was well-mixed. For the dispersed phase, 1:1.6 w/v ratio of AM and AA was mixed with 0.25 wt% of APS in a beaker. After that, the dispersed phase was added gradually into the continuous phase. This mixture was stirred at 300 rpm for 3 hours at a polymerization temperature of 55 °C. After the reaction, the products, SAP/NFC at different filler amounts were filtered and washed with methanol. The SAP/NFCs were then dried at 60 °C in an oven until constant weight [9]. The samples were noted as control for SAP with 0% NFC, while SAP/  $X$  NFC for different amounts of filler (wt%);  $X$  is from 0.002 to 0.01.

**2.2.2 Swelling Measurement.** Around 0.1 – 0.15 g of SAP was placed inside a tea bag and weighed. Then, the tea bag was immersed in 1 L of distilled water at room temperature. The teabag was removed from the beaker and weighed for every 15 minutes interval until equilibrium. Before the weighing process, the tea bag was allowed to drain for 10 minutes until excess water was removed. Water swelling ability,  $S$  (g water/g dry sample), is calculated using equation (1).

$$S = \frac{m_t - m_i}{m_i} \quad (1)$$

where  $m_t$  is the weight of the sample after time,  $t$  and  $m_i$  is the initial weight of the sample. The general equation for the swelling rate at any time can be expressed as Equation (2).

$$\frac{dm}{dt} = K(m_\infty - m_t)^n \quad (2)$$

where,  $K$  represents the swelling rate constant,  $m_\infty$  is the mass of sample at equilibrium,  $m_t$  is the mass of sample at a time,  $t$ , and  $n$  is the order of the reaction, first-order reaction;  $n = 1$ , second-order reaction;  $n = 2$ .

Upon integration, the following expression is obtained as first-order swelling kinetic (Equation (3)) and second-order swelling kinetic equations (Equation (4)).

$$\ln \frac{m_\infty}{(m_\infty - m_t)} = Kt \quad (3)$$

$$\frac{t}{w_t} = \frac{1}{(Km_\infty^2)} + \frac{t}{m_\infty} \quad (4)$$

The swelling data were analyzed and plotted as  $\ln m_\infty / (m_\infty - m_t)$  against  $t$  and  $t/m_t$  against  $t$  for the first order and second order of swelling kinetics, respectively.

The diffusion behavior can determine through the rearrangement of equation 1 using power law, as illustrated in equation (5).

$$\ln S = \ln K + n \ln t \quad (5)$$

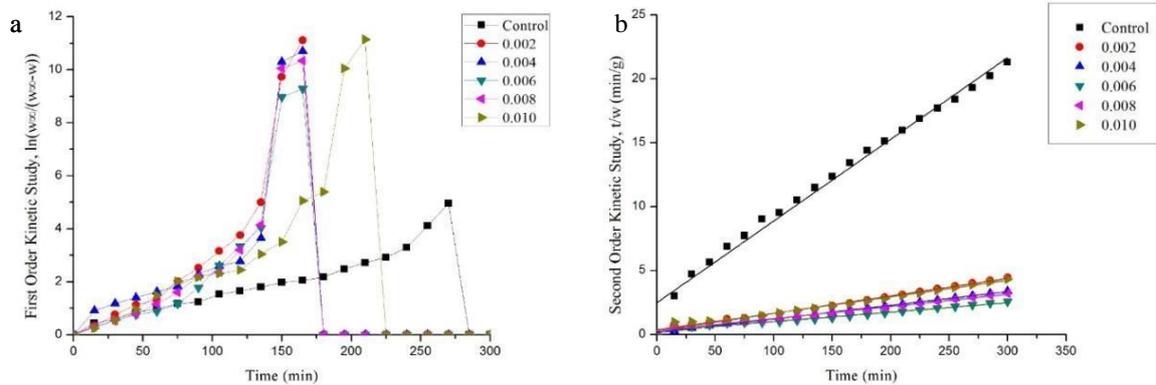
where  $S$  is the swelling capacity,  $K$  is the gel characteristics constant and  $n$  is the diffusional exponent.

*Characterization.* The SAP and SAP/NFCs composite were characterized by iS50 Thermo scientific Fourier Transformed Infrared Spectroscopy (FTIR) equipped with ATR. The bands were recorded within the region from 4000 to 500  $\text{cm}^{-1}$  with 32 scans to determine the surface functional groups. The surface morphology was analyzed using EVO 50 (ZEISS, USA), Field Emission Scanning Electron Microscopy (FESEM). While, the thermal properties will be characterized using TA instrument TGA Q500 between 25  $^\circ\text{C}$  to 900  $^\circ\text{C}$  at a heating rate of 10  $^\circ\text{C}/\text{min}$  under nitrogen gas flow.

### 3. Results and discussions

#### 3.1. Swelling Kinetic analysis

The swelling kinetics of the SAP/NFCs with different amounts of filler were further analyzed using the first (Equation 3) and second-order kinetic (Equation 4) equations to understand or determine the liquid diffusion environment towards the polymer. Figure 1 illustrated the trends of first and second-order kinetics at different amounts of filler (NFC). The swelling plots in Figure 1(a) were not exhibiting behavior with first-order kinetic because the trends disagreed with the linear fitting of the first order. While for the second-order kinetics (Figure 1(b)) shows that the swelling behavior fitted with the linear trend indicating the agreement of the swelling data with the second-order kinetic equation. This agreement indicates that the relaxation process exists in the SAP/NFCs polymeric chains [10]. The values of coefficient determination,  $R^2$  of the swelling data in the second-order kinetics are in Table 1.



**Figure 1.** (a) First-order and (b) second-order swelling kinetic trends of SAP (control), SAP/NFC composite at different amounts of NFC.

The values of swelling rate constant,  $K$ , and equilibrium weight of SAP/NFCs composite,  $m_{\infty}$  were determined from the second-order kinetic equation and summarized in Table 1. The  $K$  values for the sample fall within the range of 0.02 to 0.08 g/min, in which the fastest constant rate was reported for SAP/0.004 NFC with a rate of 0.081 g/min. Theoretically, the swelling rate will increase with the reduction of polymer network density [11]. However, NFC (filler) is hydrophilic in nature which attracts the water molecule to the polymer network. As a result, the swelling rate increase with the NFC addition up to the optimum amount, and the rate reduces again with the continuous NFC addition. The constant rate for control and SAP/ 0.006NFC were the lowest rate, 0.0026 g/min, however, both samples (control and SAP/ 0.006NFC) recorded deviation in terms of equilibrium weight,  $m_{\infty}$ . The weight at equilibrium stands for the maximum amount of water that the SAP/NFCs composite can absorb over time. The lowest  $m_{\infty}$  is recorded by the control sample with 15.62g while the maximum  $m_{\infty}$  is at 135.14g recorded by the SAP/0.006NFC composite. The addition of NFC in the SAP matrix will increase the water absorption ability, however, once the SAP matrix filled with a high amount of NFC, a dense polymer composite was produced. As a result, it will reduce the water absorption capacity, as recorded in the SAP/0.008NFC and SAP/0.01NFC. Based on data in Table 1, the optimum filler for the SAP matrix using the inverse suspension polymerization is at 0.006 wt% of NFC with the highest water absorption ability.

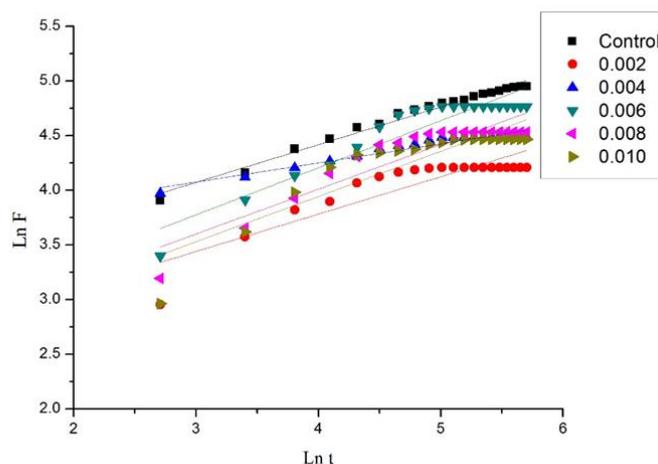
**Table 1.** Prediction of swelling rate constant and theoretical weight at equilibrium for SAP/NFCs

Weight Percentage of NFC, %	Swelling Rate Constant, $K$ (g /min)	Weight at Equilibrium, $m_{\infty}$ (g water/g sample)	Coefficient of Determination, $R^2$
0 (Control)	0.026	15.625	0.98
0.002	0.050	73.529	0.99
0.004	0.081	93.458	0.99
0.006	0.028	135.135	0.97
0.008	0.033	105.263	0.98
0.010	0.035	78.125	0.98

### 3.2 Diffusion behavior analysis

The diffusion behavior is able to determine the mechanism of liquid diffusion in the polymer network by using the swelling data and Equation 5. The diffusional exponent,  $n$  indicates the liquid diffusion

process whether obeying the fickian or non-fickian diffusion's law. Figure 2 shows that the swelling characteristics of the SAP can be fitted into a linear best-fit line. This indicates that the swelling capacity,  $K$ , and diffusional exponent,  $n$  calculated, is reliable due to the  $R^2$  values being near to 1. The values of swelling capacity,  $K$ , and diffusional exponent,  $n$  was calculated from slopes and intercepts of the linear plots as summarized in Table 2. The diffusional exponent obtained shows that the NFC/SAPs composite obeys the Fickian diffusion behavior as the values are less than 0.5. Fickian diffusion is a condition where the rate of water diffused into the polymer networks is less than the polymer chain relaxation [12].



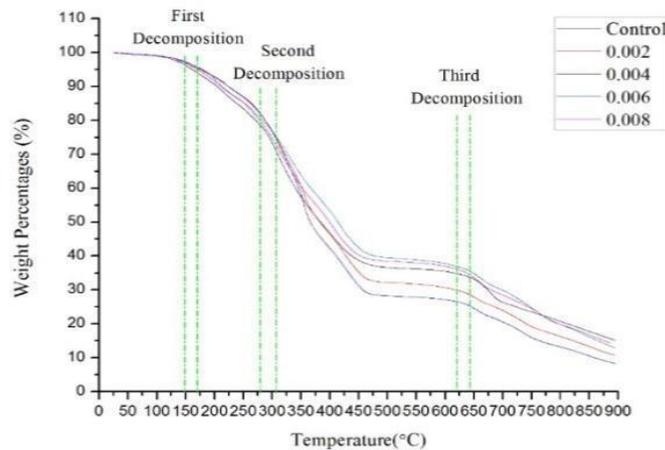
**Figure 2.** Diffusion behavior SAP/NFC at different NFC content.

**Table 2.** Data of the diffusion behavior.

Weight Percentages of Nanocellulose, %	Gel Characteristics Constant, $K$	Diffusional Exponent, $n$	Coefficient of Determination, $R^2$
Control	20.84	0.345	0.98
0.002	11.18	0.342	0.80
0.004	34.81	0.175	0.93
0.006	11.96	0.431	0.88
0.008	10.69	0.410	0.85
0.010	9.87	0.413	0.80

### 3.3 Thermal behavior analysis

Thermal gravimetric analysis (TGA) is used to evaluate the thermal stability of the SAP/NFC composite from the mass degradation from 25 to 900°C. The degradation curve at a constant rate for the SAP/NFC composite is shown in Figure 3. In general, the samples are showing a consistent degradation trend for the first stage and second stage of decomposition. The temperature range for the first stage is within 150 - 200°C due to the removal of moisture and volatiles matters. While for the second stage, the decomposition temperature is within 275 - 550°C due to the NFC filler degradation. The third stage of decomposition occurred in a range of 600 - 640°C, which might be due to the polymer matrix degradation.

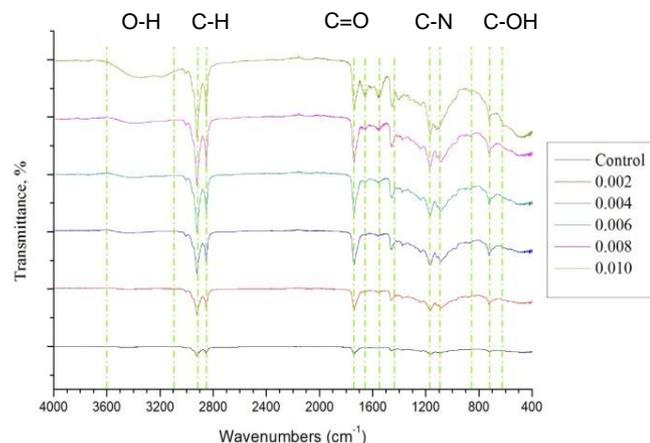


**Figure 3.** Thermal decomposition curves for SAP (Control) and SAP/NFC at different NFC amounts.

The first stage of decomposition averaged until a temperature of 200 °C and resulted in 12.16 to 15.29 % of weight loss. While, the second decomposition stage is leading to the highest weight loss of 46.88 to 59.79 %, of the SAP/NFC composite. Finally, the weight loss of the third stage of decomposition recorded 19.79% to 26.68 % reduction before remained as ash. It can be observed that SAP with NFC was generally more thermally stable than the pure SAP at the beginning of the decomposition. As the decomposition continued, it can be observed that SAP with 0.006 wt% of NFC portrayed the highest thermal stability.

### 3.3 Functional Groups Analysis

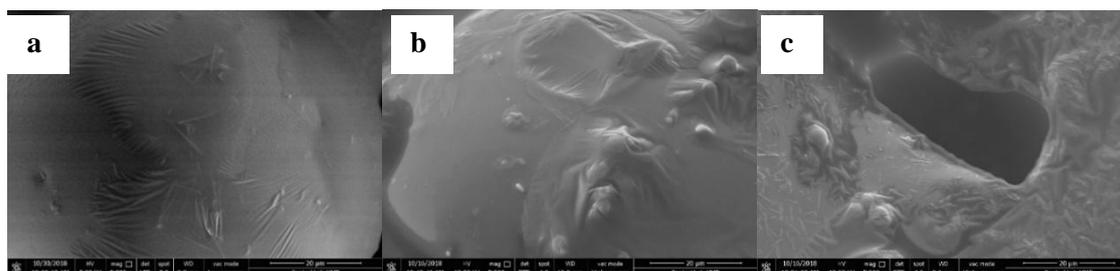
Fourier-transform infrared spectroscopy (FTIR) was performed to identify functional groups contained in the SAP with different content of NFC ranging from 400  $\text{cm}^{-1}$  to 4000  $\text{cm}^{-1}$ . Figure 4 shows the functional groups detected from the SAP/NFC composites at different filler content. Based on the peaks, the SAP and NFC possessed similar functional groups including O-H bond, C-H bond, C=C bond, and C-O-H bond. Functional groups such as C-O bond, C=O bond, N-H bond, O=C-H bond, and C-N bond were found to be parts of superabsorbent polymer chemical structure.



**Figure 4.** FTIR curves for SAP (Control) and SAP/NFC at different NFC amounts.

### 3.4. Surface morphology

The surface morphology of the SAP/NFC composites was performed using FESEM to investigate the presence of nano-fibril cellulose (NFC) on the surface. Physically, the produced SAP can be clearly seen in the form of regular bead within the size of 135  $\mu\text{m}$  [13]. However, as the NFC content increases, the composites become more irregular and disrupt the bead shape. Figure 5 illustrated the morphology of control (SAP), SAP/0.04 NFC, and SAP/0.1 NFC at 5000 times of magnification. The surface of control SAP (Figure 5(a)) is smoother compared to the SAP/ 0.04NFC and SAP/ 0.1 NFC. It is clearer in the morphology of SAP/0.1 NFC (Figure 5(c)) in the presence of long fibers (needle shape) due to the high presence of NFC. It is predicted that excessive NFC content prevents the formation of SAP in regular bead shape.



**Figure 5.** Surface morphology of (a) SAP as control, (b) SAP/0.004NFC and (c) SAP/0.01NFC at 5000 X magnification.

## 4. Conclusions

The superabsorbent polymer (SAP) with a weight percentage of NFC ranging from 0 - 0.01% were successfully synthesized using inverse suspension polymerization. The SAP/0.006NFC composite recorded the highest ability, which is 135.14 g water/g sample of swelling capacity. The SAP/NFCs composite obeys the second-order of swelling kinetic while the water diffusion obeys the Fickian's behavior as the  $n$  values less than 0.5. The thermochemical properties through TGA and FTIR show consistent characteristics for the SAP/NFCs composite at different amounts of filler. In conclusion, the addition of 0.006 wt% of NFC in the SAP matrix can improve the water swelling capacity as well as the thermal stability of the composites.

## Acknowledgments

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