A Prediction Model for Grafting Reactive Red 120 on Nanocellulose

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Nanocellulose, derived from bioresources, is a renewable material with broad application prospects. Due to its easily controllable viscosity, it has been studied by many researchers on its potential application on nano-ink for ink-jet printing by mixing dyes and nanocellulose. In this paper, a new method by grafting reactive dyes on nanocellulose is proposed. The well-known fabric dyeing was first applied for dyeing nanocellulose. The dyeing reaction was Reactive Red 120 (RR120) grafting on nanocellulose, which was influenced by the dosage of RR120, reaction time, and reaction temperature. The RR120 was successfully grafted on nanocellulose, and a model for RR120 grafting on nanocellulose was proposed as "$y = 0.2 * (0.0039T^2 - 0.5T + 20) * (e^{0.72R}) * (3 - 0.99^t)$", to predict the RR120 grafting amount at different reaction conditions.

Keywords: Nanocellulose; Dyed nanocellulose; Reactive dye; Reactive Red 120; Grafting model

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INTRODUCTION

Nanocellulose is a novel nanomaterial that has extensive applications in many domains, such as composite reinforcement materials (Liu *et al.* 2016; Lefatshe *et al.* 2017), biomedical materials (Lin and Dufresne 2014; Mertaniemi *et al.* 2016), and many others. Researchers develop different kinds of nanocellulose and their derivatives every year, but the research on dyeing nanocellulose, especially reactive dye grafting on nanocellulose, is seldom recognized or studied by researchers.

Reactive dye is commonly used to dye fiber fabric in the textile industry; the first commercial reactive dye for cotton fabric was developed by Imperial Chemical Industries (ICI) company in 1956 (Vickerstaff 1957). Since then, the reactive dye has become a representative of the modern dyestuff industry for its brief dyeing process, high bonding strength, and bright and complete color spectrums (Surhone *et al.* 2011). To efficiently achieve the advantages of reactive dyes, the digital ink-jet printing machine was developed (Wang 2005; Liu 2009). The production process of the digital ink-jet printing machine is accurate, easy to operate, and low energy-consuming when printing reactive dyes onto cotton fabric (Daplyn and Lin 2003). Inspired by the printing process of reactive dyes *via* the digital ink-jet printing machine and the dyeing process of fiber fabric with reactive dyes, it was proposed that reactive dyes could be grafted onto nanocellulose and the grafted nanocellulose could be used as Nano-Ink of ink-jet printers.

Normal fiber fabric and nanocellulose have many characteristics in common. For example, both fiber fabric and nanocellulose contain a large number of hydroxyl groups (Gardner *et al.* 2008). It may even be feasible to dye nanocellulose using reactive dyes by

referring to the dyeing mechanisms of reactive dyes grafted on normal fiber fabric (Fig. 1 (Surhone *et al*. 2011)). Furthermore, dyed nanocellulose is promising in its potential use in printing and the papermaking process as a new anti-counterfeiting technology.

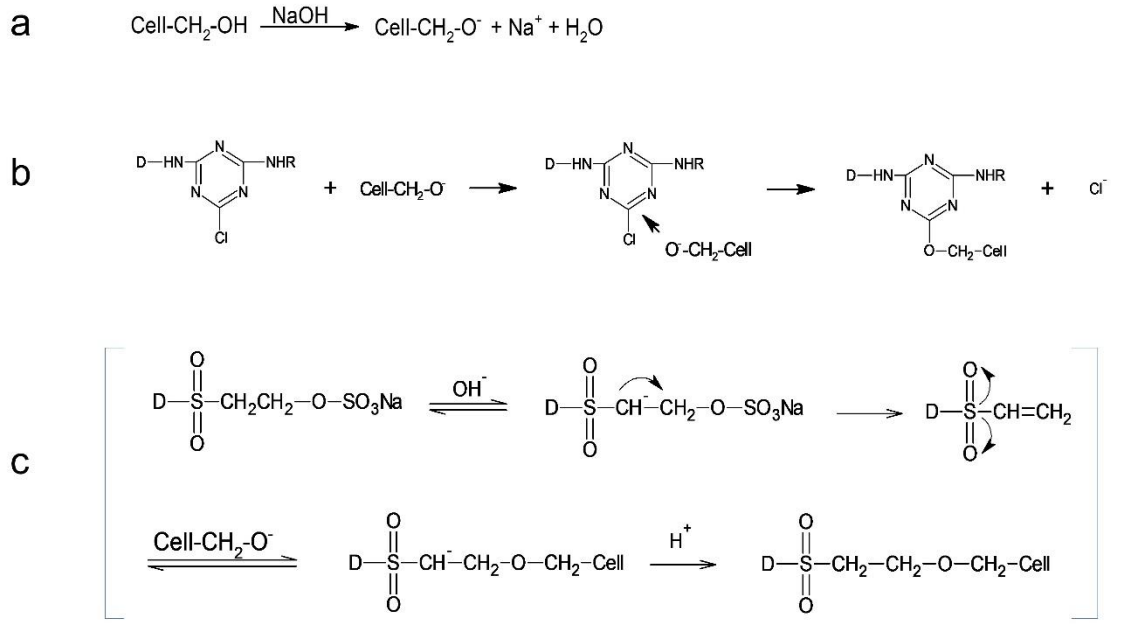

Fig. 1. The mechanisms of reactive dye grafting onto fiber fabric: (a) Hydroxyl groups in cellulose change into hydroxyl radicals in alkaline environment; (b) Hydroxyl groups nucleophilic substitution reaction of three azine ring; and (c) hydroxyl radical for electrophilic addition of dyes in alkaline environment.

In this paper, the feasibility of reactive dye grafting on nanocellulose was confirmed. Reactive red 120 (RR120) was used to react with nanocellulose at different RR120 dosages, temperatures, and reaction times. The optimal RR120 grafting amount on nanocellulose was calculated, and a prediction model of the grafting process is proposed.

EXPERIMENTAL

Materials

Nanocellulose was prepared by TEMPO-mediated oxidation and high-pressure homogenization. Reactive Red 120 (RR120) and TEMPO (2,2,6,6-Tetramethylpiperidine 1-oxyl) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). Sodium bromide and sodium hypochlorite were purchased from Guangzhou Chemical Reagent Factory, China.

A TENSOR 27 Fourier transform infrared (FTIR) spectrometer (Bruker, Billerica, USA) was used to verify if the RR120 grafted onto nanofibrillated cellulose (NFC) successfully. A Transmission electron microscope (TEM 1400, type: JEM-1400 Plus) (JEOL Ltd., Tokyo, Japan) was used to identify the nanomorphology of the original NFC and dyed NFC.

Nanocellulose preparation

Nanocellulose was prepared through TEMPO-mediated oxidation and high-pressure homogenization. Hardwood dissolving pulp solution (3000ml) at a concentration of 1% and a constant temperature of 25 °C was prepared. According to the conventional preparation methods, 0.45g TEMPO, 3g NaBr, and NaClO (effective chlorine was 6 mmol/g compared to oven-dried pulp) were added to the solution. The pH of the reaction solution was adjusted to between 9.8 and 10.0 using 0.5 mol/L NaOH during the reaction process. The reaction was stopped when the pH remained unchanged for 3 min at the absence of NaOH.

The obtained solution was centrifuged using a Sigma 3K15 high-speed refrigerated centrifuge (Sigma Centrifuges, Osterode, Germany) several times to purify the cellulose solution. This purified solution was handled at 800 bar for 3 times with a homogenizer (UH-60). The obtained nanocellulose was nanofabricated cellulose (NFC) at a concentration of 0.87%.

The grafting experiment was conducted in a 1000-mL three-necked flask in a water bath. 500 mL NFC solution was added into the three-necked flask. After 5 min, solid NaCl was added to the flask to form a 20 g/L solution. The water bath was then raised to a certain temperature (60 °C, 70 °C, or 80 °C). Solid Na_2CO_3 was added to the flask to form a 10 g/L solution. After 5 min, a certain weight of RR120 (22.5 mg to 100 mg) was added to the flask. This time was recorded as the starting point of the grafting reaction. After every 10 min, 1.5 mL reaction solution was picked up and cooled down *via* an ice water mixture. The cooled sample was centrifuged at a speed of 9000 rpm for 5 min to precipitate NFC. After centrifugation, 0.5 mL supernatant, which was mainly a solution of the unreacted dissolved RR120 was picked up and poured into a separate tube with 3 mL deionized water added beforehand. Next, the solution was shaken well and measured using an ultraviolet (UV)-visible spectrophotometer (INESA Intelligent Tech Inc., Shanghai, China) at 513 nm (513 nm was the maximum absorption peak wavelength of RR120). The influence of reaction time (5 min to 260 min) on RR120 grafting weight was investigated in the reaction process. The subsequent experiments also proved RR120 dosage and reaction temperature had big influence on the grafting weight. Additionally, a prediction model of grafting weight was calculated through these data.

Methods

Absorbance standard curve of RR120

A standard curve of the measured absorbance value *versus* RR120 concentration was performed. The result is listed in Eq. 1,

$$a = 23804 * c \ (n = 5, R^2 = 0.9999) \quad (1)$$

where a is the light absorbance at 513 nm, and c is the RR120 concentration (g/mL).

Calculation of RR120 grafting weight

The RR120 grafting weight per g of NFC was calculated *via* Eq. 2,

$$y = \frac{m_{\mathrm{dye}} - \frac{a*7}{23804} * V}{m_{\mathrm{NFC}}} * 1000 \quad (2)$$

where y is the RR120 grafting weight per g of NFC (mg), m_{dye} is the dosage of RR120 used in the experiment (g), a is the light absorbance at 513 nm, V is the total volume of the reaction liquid (mL), and m_{NFC} is the total dried weight of NFC used in the experiment (g).

RESULTS AND DISCUSSION

Characterizations of Original NFC and Dyed NFC

The characterizations of original NFC and dyed NFC (NFC reacted with RR120) were compared *via* normal visual observation, FTIR, and transmission electron microscope (TEM). The normal visual observation (Fig. 2) showed a clear difference between the original NFC and dyed NFC before and after being centrifuged. In Fig. 2, the samples in the first column were original NFC. The samples in the second and third columns were dyed NFC. It was clearly shown that the original NFC was colorless, but the dyed NFC was red in color. This difference indicated that the RR120 was grafted onto the NFC successfully.

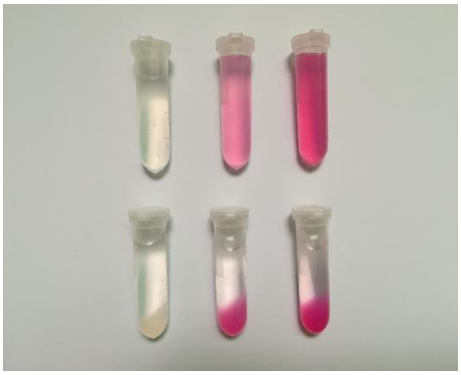

Fig. 2. The comparison of original NFC and dyed NFC; the samples of the first row are samples before centrifugation, and the samples of the second row are the samples after centrifugation; samples in the first column are original NFC, and samples in the second and third columns are dyed NFC at different concentrations.

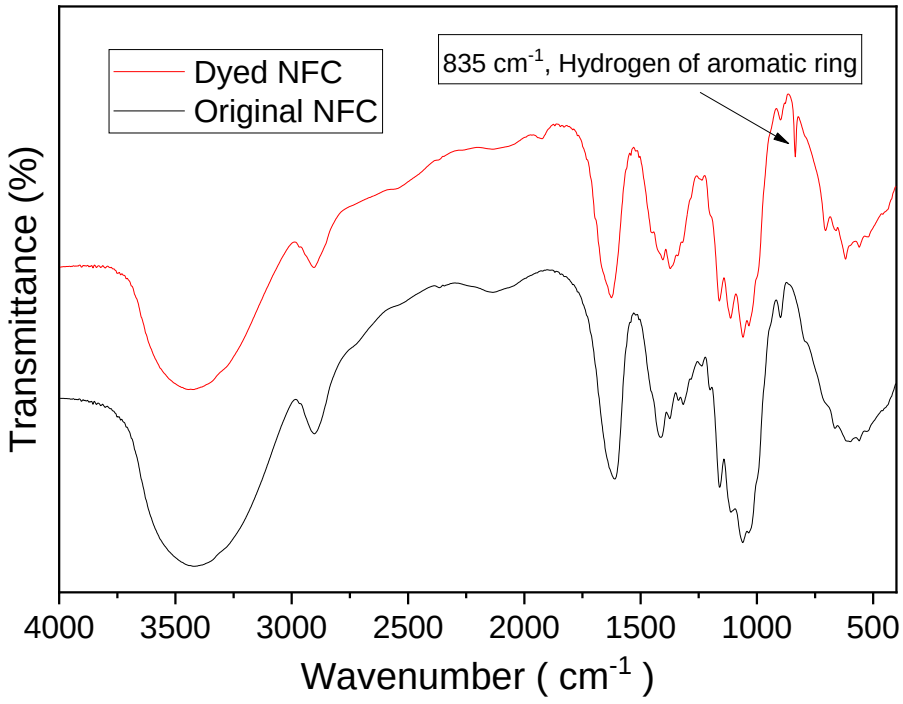

Fig. 3. FTIR spectra of original NFC and dyed NFC in the range from 400 cm^{-1} to 4000 cm^{-1}

The FTIR results (Fig. 3) also confirmed this inference. There was an obvious additional peak at 835 cm^{-1} observed at the spectrum of dyed NFC compared to the spectrum of original NFC. Compared with a standard spectrum library, the additional peak can be confirmed as the stretching vibration of hydrogen of an aromatic ring. The normal visual observation and FTIR characterization clearly demonstrated that the RR120 successfully grafted onto NFC in this experiment. The TEM results (Fig. 4) showed the successful preparation of NFC and illustrated that the grafting process had no influence on NFC morphology.

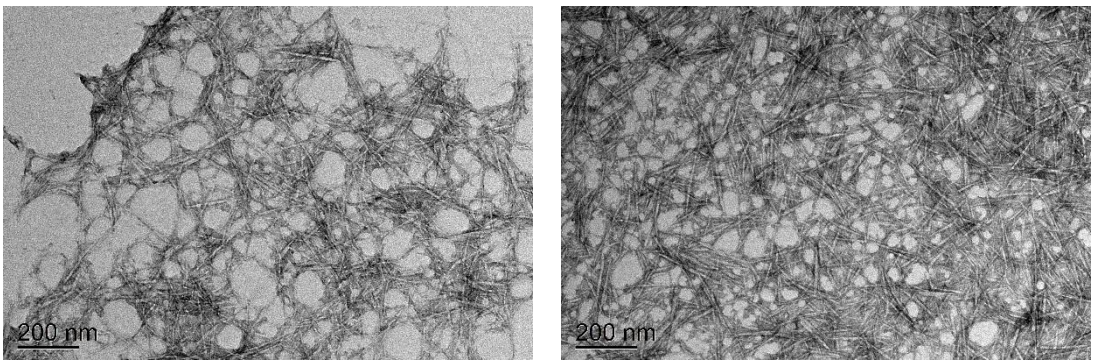

Fig. 4. TEM pictures of original NFC and dyed NFC

Influence of Reaction Time on Grafting Amount

The NFC was grafted with RR120 under different reaction times, temperatures, and dosages of RR120. In this section, the influence of reaction time on the quantity of RR120 grafted onto NFC is discussed.

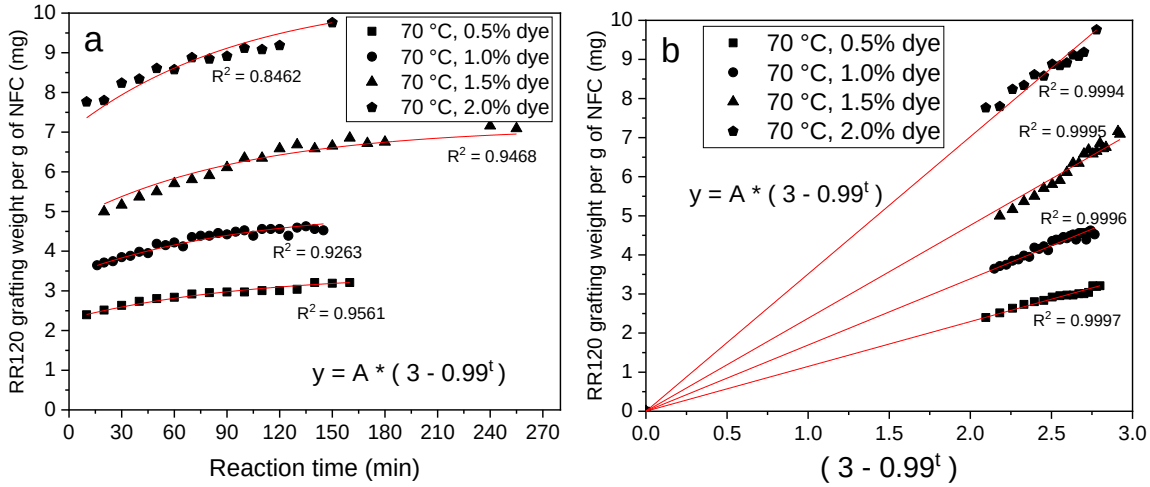

Fig. 5. (a) Evolution of the quantity of RR120 grafted onto NFC with increasing reaction time; (b) evolution of the quantity of RR120 grafted onto NFC with increasing (3 - 0.99^t) ("*t*" represents reaction time) time; the reaction temperature was 70 °C; the dosage of RR120 was 0.5%, 1.0%, 1.5%, and 2.0% (compared to oven-dried NFC)

Figure 5a shows the development of RR120 grafting weight per g of NFC with different reaction times at different dosages of RR120 at 70 °C. With an increase in reaction time, the RR120 grafting weight per g of NFC increased. The quantity of RR120 grafted

onto NFC rapidly increased with increasing dosages of RR120. Through a mathematical fitting, it was found that there was a functional relationship between the quantity of grafted RR120 per g of NFC and reaction time. The grafting weight per g of NFC and 0.99^t (*t* represents the reaction time) had a linear relationship, no matter how much RR120 (dosages from 0.5% to 2.0%) was used in the experiments.

Figure 5(b) shows the linear relationship intuitively. As a result, the relationship between grafting weight and reaction time can be presented in a function: $y = A * (3 - 0.99^t)$ ($R^2 \geq 0.8462$). Among the function, *y* represents the RR120 grafting weight per g of NFC, *t* represents the reaction time, and *A* is a factor related to the reaction temperature and dosage of RR120.

Influence of RR120 Dosage on Grafting Amount

The influence of reaction time on grafting amount was discussed above. Both the reaction time and dosage of RR120 had a large influence on the RR120 grafting amount (Fig. 5). In this section, the influence of the dosage of RR120 on the quantity of grafting weight per g of NFC is discussed.

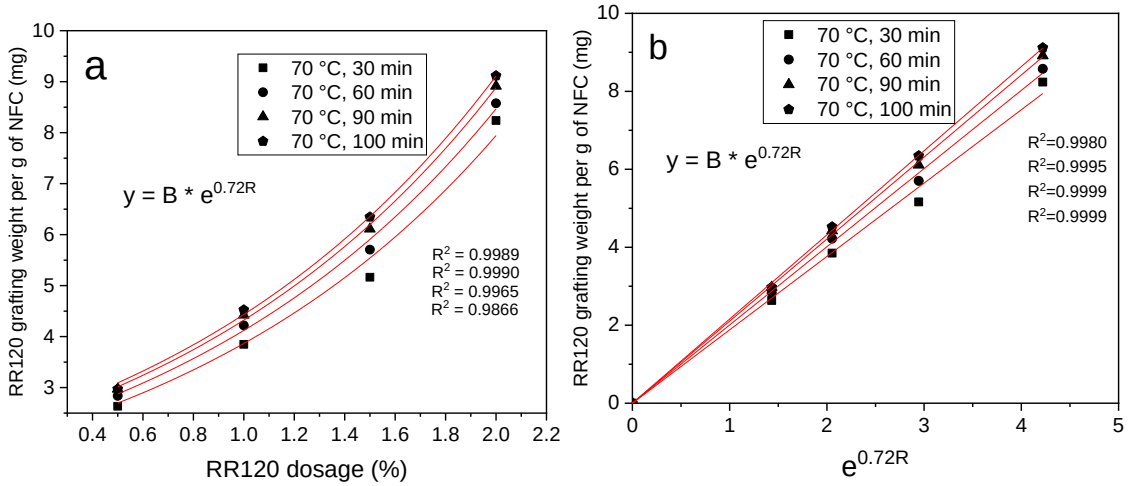

Fig. 6. (a) Evolution of the quantity of RR120 grafted onto NFC with increasing RR120 dosages; (b) Evolution of the quantity of RR120 grafted on NFC with increasing "$e^{0.72R}$" ("*R*" represents the dosage of RR120 and "*e*" is the natural constant). The reaction temperature was 70 °C; the reaction times were 30 min, 60 min, 90 min, and 100 min.

Figure 6 shows the evolution of the quantity of RR120 grafted per g of NFC with increasing RR120 dosage. From what is clearly seen in Fig. 6(a), the RR120 grafting weight increased with increasing dosage of RR120 at different reaction times. Through a mathematical fitting, it was found that the grafting weight was proportional to $e^{0.72R}$ ("*R*" represents the dosage of RR120 and "*e*" is the natural constant). Figure 6(b) shows the linear relationship between RR120 grafting weight per g of NFC and $e^{0.72R}$ clearly. Consequently, the grafting formula could be concluded as "$y = B*e^{0.72R}$". Among the function, "*y*" represents the RR120 grafting weight (mg) on per g of NFC, "*R*" represents the dosage of RR120 compared to dried NFC, and "*B*" is the coefficient related to reaction temperature (°C) and time (min).

Influence of the Reaction Temperature on Grafting Amount

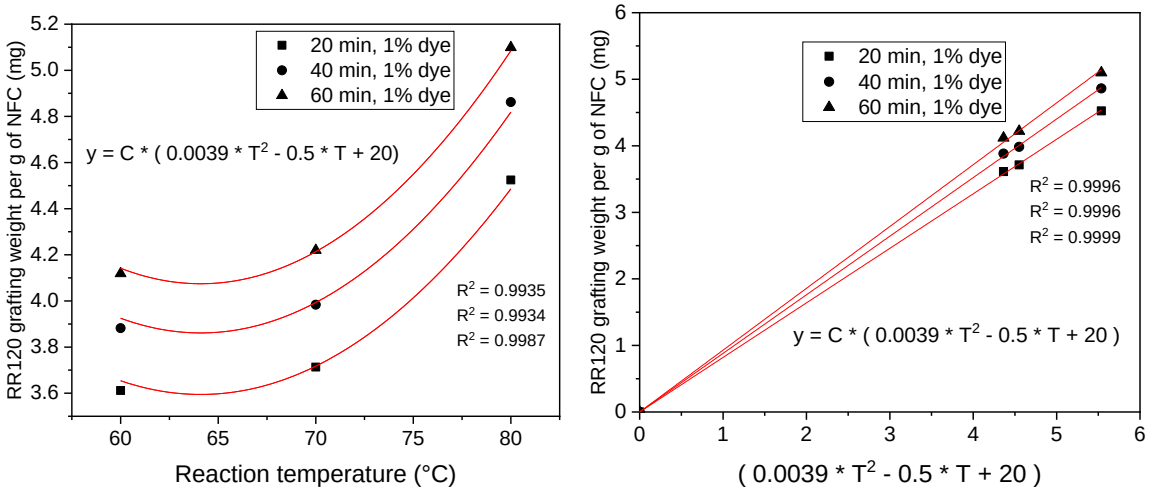

Fig. 7. (a) Evolution of the quantity of RR120 grafted onto NFC with increasing reaction temperature; (b) evolution of the quantity of RR120 grafted onto NFC with increases in ($0.0039T^2$ - 0.5T + 20) ("*T*" represents reaction temperature); the dosage of RR120 used in this part was 1% and the reaction times were 20 min, 40 min, and 60 min.

Figure 7 shows the development of RR120 grafting weight per g of NFC with increasing reaction temperature. From 60 °C to 80 °C, the RR120 grafting weight increased with increased reaction temperature when the RR120 dosage was 1% (compared to dried NFC) at different reaction times. Through a mathematical fitting, a quadratic function relationship was discovered between the reaction temperature and RR120 grafting weight. Figure 7(b) clearly shows the linear relationship between RR120 grafting weight and "$0.0039T^2$ - $0.5T$ + 20" ("*T*" represents the reaction temperature). Accordingly, the relationship between RR120 grafting weight and reaction temperature could be calculated as "$y = C * (0.0039T^2 - 0.5T + 20)$". In this formula, "*y*" represents the RR120 grafting weight (mg) per g of NFC, and "*C*" is a factor related to dye dosage and reaction time.

The Establishment and Verification of RR120 Grafting Model

As a summary of the discussion above, the RR120 grafting weight and reaction time had a functional relationship (($y = A * (3 - 0.99^t)$), where "*A*" is a factor related to RR120 dosage and reaction temperature), the RR120 grafting weight and RR120 dosage had an index relationship ($y = B * e^{0.72R}$, where "*B*" is a factor related to reaction time and reaction temperature), and the RR120 grafting weight and reaction temperature had a quadratic function relationship ($y = C * (0.0039T^2 - 0.5T + 20)$, where "*C*" is a factor related to RR120 dosage and reaction time). Consequently, the RR120 grafting weight per g of NFC can be concluded as "$y = D * (0.0039T^2 - 0.5T + 20) * (e^{0.72R}) * (3 - 0.99^t)$", where "*D*" is an unknown constant number, "*y*" represents the RR120 grafting weight (mg) per g of NFC, "*T*" represents the reaction temperature (°C), "*R*" represents the dosage of RR120 (mg), and "*t*" represents the reaction temperature (°C).

When the reaction temperature was 70 °C, according to Fig. 5 through mathematical fitting, the formula can be rectified as $y = A * (3 - 0.99^t) = D * (0.0039 * T^2 - 0.5T + 20) * (e^{0.72R}) * (3 - 0.99^t)$. After calculating, all the mathematical fitting values of

"*D*" were approximately equal to 0.2, no matter how much RR120 was used (Table 1, The Mean Square of Residual was 0.0034).

Table 1. Mathematical Fitting Values of Factor *D*

RR120 Dosages	0.5	1	1.5	2
Fitting Value of *D*	0.1947	0.2007	0.1965	0.2024

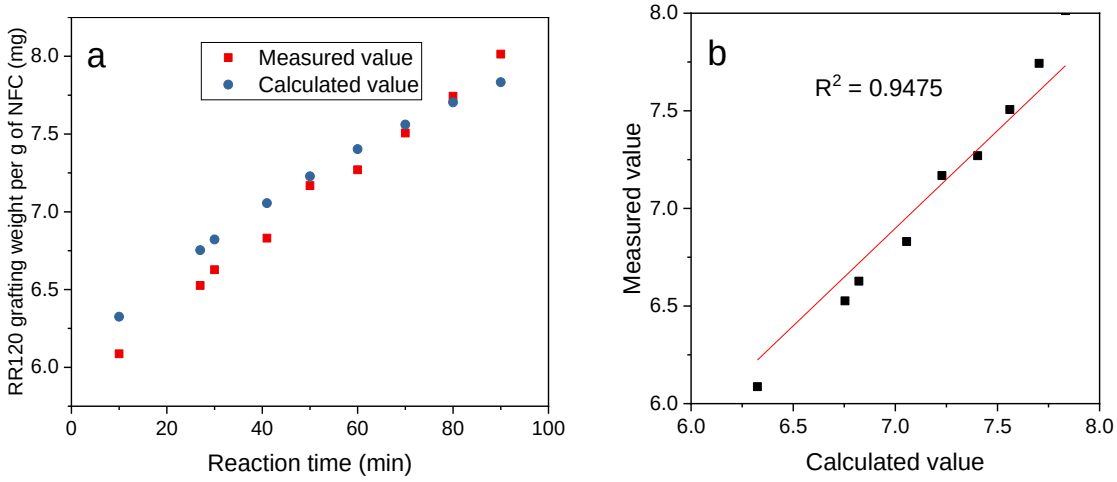

Fig. 8. The comparison of measured values by verification experiment and calculated values by grafting model (the verification experiment was conducted at 75 °C, RR120 dosage was 1.7%, and the reaction time was from 10 min to 90 min)

In summary, the RR120 grafting weight per g of NFC in this NFC dyed experiment could be calculated by the formula "$y = 0.2 * (0.0039T^2 - 0.5T + 20) * (e^{0.72R}) * (3 - 0.99^t)$". The function "*y*" represents RR120 grafting weight (mg) per g of NFC, "*T*" represents reaction temperature (°C), "*R*" represents RR120 dosage (%), and "*t*" represents reaction time (min). The verification experiment was also conducted to check the reliability of the predicting model. The results showed that when the temperature was 75 °C and the RR120 dosage was 1.7%, the calculated values matched well with the measured values at different reaction times (Fig. 8). Thus, the formula of this grafting model was reliable for predicting the grafting weight of RR120 onto NFC.

CONCLUSIONS

1. A method for nanocellulose dying is reported in this paper. The experimental results showed that RR120 could successfully graft onto nanofibrillated cellulose (NFC).
2. A grafting model of this dyeing process of RR120 grafted onto NFC was discovered and verified. The results showed that RR120 grafting weight per g of NFC could be calculated by a formula "$y = 0.2 * (0.0039T^2 - 0.5T + 20) * (e^{0.72R}) * (3 - 0.99^t)$". When the range of reaction temperature (*T*) was between 60 °C to 90 °C, the range of RR120 dosage (*R*) was 0.5% to 2.0%, and the range of reaction time (*t*) was from 10 min to

180 min. The grafting model could be a foundation for reactive dye grafting onto nanocellulose.

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