Changes of Dark Couverture Chocolate Hardness During Storage Tempered Using Automatic Tempering Machine with Tank and Tempering Temperature as Variables

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Abstract. Couverture chocolate is highly demanded by consumers. Dark couverture chocolate is known as chocolate with high proportion of cocoa. There are several parameters that need to be considered to ensure the quality of this chocolate. One of the important chocolate qualities is hardness. In chocolate making, which is affected by the tempering process. Generally, the tempering process is carried out manually or automatically. Manual tempering is done by hand and is difficult to control the process temperature. Therefore, an automatic tempering machine was chosen in this study by controlling the tank and tempering temperatures. The purpose of the research was to optimize the combined effect between tank temperatures and tempering temperatures of the automatic tempering machine on the chocolate hardness parameter. Different ranges of the tank and tempering temperatures were applied to the chocolate mass processed in the machine. Chocolate hardness during storage was in the range 12.27 to 20.19 N/mm^2 in 45^{o}C tank and 32.5^{o}C tempering temperature. The optimum of the tank and tempering temperatures were 45^{o}C-32.5^{o}C (A), 48^{o}C-32.5^{o}C (B), and 50^{o}C-31.5^{o}C (C) which resulted in different k values and glossy appearances. The *k* values for A, B, and C were -0.00195; -0.0024; and -0.0031, respectively. While the determination coefficients for A, B, and C were 0.8970; 0.8887; and 0.9013, respectively.

Keywords: Dark chocolate couverture, tempering, hardness, Newton's law of cooling.

1 Introduction

Chocolate is a range of foods derived from cocoa (*Theobroma cacao*) seeds and it is becoming one of the most popular sweet products worldwide [1–3]. Chocolate is a complex mixture of cocoa and finely powdered sugar in a continuous fat phase, mainly cocoa butter, to produce a solid confectionery [4–6]. Its consumption rate continues to grow by year [7]. The consumer importance of chocolate is very high due to its taste and health benefits, especially as a source of antioxidants [8–10]. Bean-to-bar process sequences consist of mixing, refining, conching, tempering, moulding, and demoulding are widely known to produce high-quality chocolate products [6, 11].

Chocolate undergoes a tempering process to obtain a good texture and appearance [12]. The fat ingredient, named cocoa butter is one of the main ingredients of chocolate which has a unique composition and character [13]. Cocoa butter crystallizes in six polymorphic forms known as γ, α, β2', β1', β2, and β1. Form β2 also known βV is the most desirable polymorphic form of the well-tempered chocolate products. Thus, the products have a good contraction, shiny, even-coloured, snap, smooth taste [4, 11, 14–16]. While bad-tempered chocolate gives a chewy, chalky, grainy, or whitish colour, known as the fat or water-bloom phenomenon during storage [17–19].

Conventionally, tempering was introduced manually on a marble table. It requires skilled and experienced manufacturers. Manual tempering constraint is insufficient crystal formation because of the homogeneity of the temperature not reached in the sample. This could affect hardness. Hardness is the key attribute of the final quality of chocolate, it is also an indicator of proper temperature control and a stable fat crystal network [11, 20]. The tempering machine is more often used in industrial activities and has some temperature controls to maintain the process. The untempering and under-tempering regimes exhibit different crystallization behaviours, resulting unstable fat crystal nucleation, therefore the tempering process is necessary [4, 13, 21].

Several studies have reported the importance of tempering, temperature control, and storage to chocolate hardness parameter. The increase in bar hardness has been evaluated during storage and positively accepted by the panelists through sensory evaluation [22]. In addition, the storage or maturation process improves the chocolate crystal formation to be more stable [23].

The objective of the study is to investigate the effect of temperature combinations between the tank and tempering temperature using the automatic tempering machine on the hardness of the chocolate. Temperature control is important as it affects the successful tempering process [24]. Further analysis examined in this research is obtaining constant (k) value as the rate of hardness changes during storage and determination coefficient (R^2) using kinetics order following Newton's law of cooling (NLC) model during chocolate storage.

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2 Materials and Methods

2.1 Research Location

Research was conducted at the Laboratory of Postharvest and Food Engineering, Faculty of Agricultural Technology, Universitas Gadjah Mada, Indonesia.

2.2 Materials

The untempered dark chocolate was used for the materials for the research. It was purchased from a local market in Yogyakarta, *nDalem Cokelat*. The samples contained 72% cocoa according to the following formulation: 41% of cocoa butter, 31% of cacao solid, and 28% of sugar content. The tempering process was carried out using the automatic tempering machine, Pomati T8 (Pomati Group S.r.l, Fidenza, Italy).

2.3 Tempering Procedures

The solid chocolate was melted in the melting cabinet at a temperature of 55^{0}C. After the melting process, the molten chocolate was placed in the tempering machine tank, letting it flow through the pipe. Some temperatures were set for the tank and the tempering in the machine. The chocolate mass was then moulded, vibrated on the vibrating table to eliminate bubbles, and put in the chiller cabinet at 10^{o}C to form the chocolate bar. Then,demould.and stored at a controlled temperature of 18-20^{o}C.

2.4 Research Design

The observation was designed in some temperature settings. The factorial research design, namely 6 x 4 x 7 (tank temperatures, tempering temperatures, storage time) was used. In this research, six different temperatures for the tank temperature (T), namely 45^{o}C, 46^{o}C, 47^{o}C, 48^{o}C, 49^{o}C, and 50^{o}C were used. Meanwhile, the tempering temperature (P) was set at 31^{o}C, 31.5^{o}C, 32^{o}C, and 32.5^{o}C. In continuous tempering, molten chocolate is held at 45^{o}C while in a common tempering process, temperature of 50^{o}C is needed by chocolate to completely melt [11, 25]. Variation of tempering temperature were used between 31-32.5^{o}C considering that those temperature are in the range of 29-34^{o}C which could generate βV crystals [26,27]. Temperature variation from 0.5 to 1^{o}C affects chocolate properties during tempering [27]. The chocolate sample in the experiments can flow through the processing pipe when the tempering temperature is set from 31^{o}C and another consideration is the engine overheats at 33^{o}C. Chocolate hardness observations were made on the first day and every 5 days until the 30th day of storage (1st, 5th, 10th, 15th, 20th, 25th, and 30th day of the maturation process).

2.5 Analytical Method

2.5.1 Hardness Measurement

Texture analyzer Brookfield Engineering Labs, Inc. was used to measure the hardness of chocolate bars and was carried out at a room temperature of 20^{o}C. A needle probe was applied (TA39, diameter 2 mm) to the instrument and samples were penetrated to a depth of 3 mm with a constant speed of 0.5 mm/s [28]. All measurements were done in triplicate. The chocolate samples were stored for 30 days. Hardness value was calculated using Equation (1),

$$\sigma = \frac{load \times \alpha}{\pi \times r^2} \quad (1)$$

Where σ defines the hardness (N/mm^2), load is the maximum load (kg), α is gravitational acceleration (m/s^2), r is needle probe radius (mm).

2.5.2 Data Analysis

Data Analysis was performed by IBM SPSS version 26.0 for Analysis of Variance (ANOVA). Posthoc Tukey test and Levene's test were performed, then followed by one way ANOVA test. Prior to the two-factor analysis of variance using Repeated Measures, the normality of the data was tested. The principal component analysis (PCA) was used to visualize the chocolate samples and hardness parameters. The applicability of NLC was proposed as a method to model the order kinetics of hardness during storage. The value of constant (k) and prediction model were obtained from the equation (2) and (3),

$$\ln\frac{\sigma_e - \sigma_t}{\sigma_e - \sigma_0} = k.t \quad (2)$$

$$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{kt} \quad (3)$$

Where $\boldsymbol{\sigma_e}$ defines the final hardness, σ_t defines the hardness at certain time, $\boldsymbol{\sigma_o}$ defines hardness before storing (N/mm^2), $\boldsymbol{k}$ is constant, and $\boldsymbol{t}$ is the storage time (hours).

3 Results and Discussions

3.1 The relationship between the temperature combination to the hardness

Two factor repeated measures on tank and tempering temperatures give a significant difference ($p<0.05$). Hardness was affected by storage time, tank temperature, temperature treatments, as well as their interaction, as described in Table 1. Storage time influenced the hardness as Saputro [12, 27] mentioned that chocolate storage or maturation would create more stable βV crystals. Tank temperature was associated with the initial temperature of the molten chocolate and the tempering temperature was the final temperature of tempering process of the chocolate when moulding. The combination of tank and tempering temperatures showed a significant difference to the hardness parameter.

Table 1. Relationship among research variables to the hardness of chocolate

Treatments Variables	Hardness
Storage Time (A)	*
Tank Temperature (B)	*
Tempering Temperature (C)	*
Interaction between A x B	*
Interaction between A x C	*
Interaction between B x C	*
Interaction between A x B x C	*

Significant difference at $p<0.05$

Kurniasari et.al. [20] mentioned that storage time affected the hardness. The research also showed a tempering method by using the oven and stirred manually. The manual tempering did not show a clear trend of hardness because the expected heating and cooling temperature could not be reached by molten chocolate and resulted in the unsuccessful formation of βV crystal. Therefore, the use of an automatic tempering machine was expected to make the temperature distributed evenly in the molten chocolate and could stimulate the growth of βV crystal.

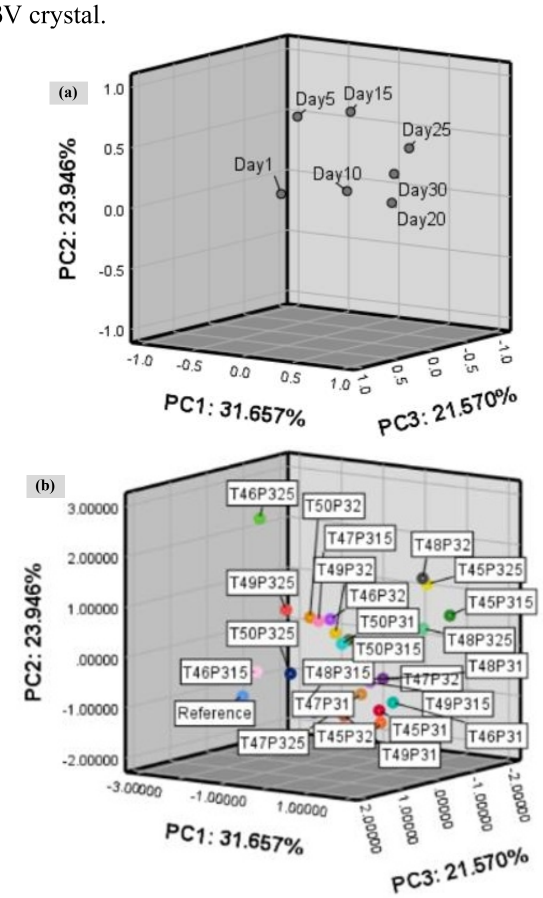

Fig. 1. Principal Component Analysis (PCA) and its associated (a) loading plot also (b) score plot. PCA shows the distribution of different combinations between tank and temperature treatments.

Degree of tempering (tempering temperatures) affects the hardness of the chocolate. A well-tempered chocolate tends to have higher hardness than poor tempered or untempered chocolate [12, 21, 24-25]. The tempering process is used to obtain a desirable crystalline state of the cocoa butter resulting a glossy appearance, good snap, contraction, and long shelf life [31-32]. Over-tempered caused increasing hardness, stickiness, and reduced gloss or darkened surface. Meanwhile, under-tempered led to lower hardness, fat bloom, and surface defects [28-29].

Tempering has four important steps on the temperature control which consists of complete melting at 50ºC, cooling to the point of crystallization at 32ºC, crystallization at 27ºC, and melting out any unstable crystal at 29-31ºC. Temperature is important for continuous tempering process design. Optimum tempering temperature is in the range of 29-34ºC for successfully generating βV crystals [25, 30, 35].

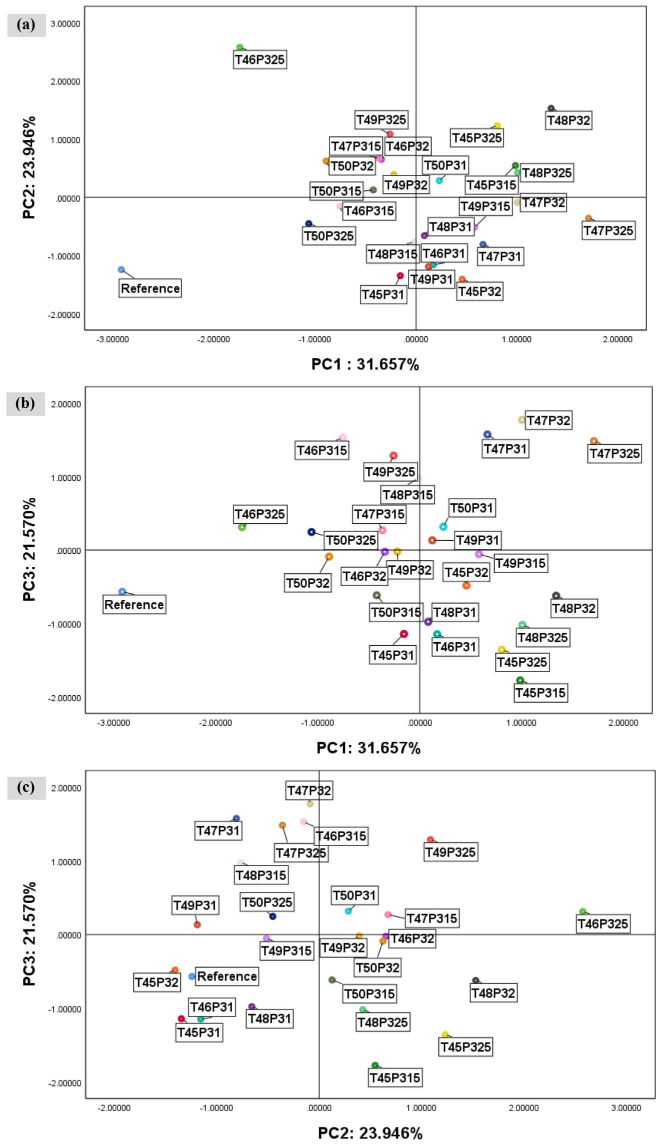

Fig. 2. PCA score plot in the two-dimensional view from the different tank and tempering temperature distribution (a) PC1 vs PC2, (b) PC1 vs PC3, (c) PC2 vs PC3.

PCA of the tank temperature treatment on each different day of measurement was done in a three-dimensional view. The PCA data represented 77.174% of the total variance in the first three factors (Figure 1), namely PC1: 31.657%, PC2: 21.570%; and PC3: 23.946%. The PCA loading plot (Figure 1a) shows that generally the storage time or days of measurements were located at the same cluster along PC1 and PC2. This shows that hardness increase over storage time [22]. While storage time namely day 1 was in different clusters along PC2 and PC3. This shows that there were differences in chocolate hardness amongst clusters on the first day of measurements.

The PCA score plot of the first three principal components shows a clear distinction between samples (Figure 1b). The reference or the untempered sample was located along negative PC2 and PC3 values. This was associated with the untempered chocolate character which had a lower hardness. Figure 2 shows a two-dimensional view of each treatment to the sample hardness. The reference sample was located at the very end of the negative PC1 and PC2, negative PC1 and PC3, also negative PC2 and PC3. It showed the reference sample had the lowest hardness value.

Some samples named T45P31, T45P32, T46P31, T46P315, T46P32, T48P31, T48P315, T49P315, T49P32, T50P315, T50P32, and T50P325 were in the same quadrant as the reference sample having lower hardness value. Different hardness characteristics showed by another sample by tank and tempering treatments. Larger hardness shown along positive PC1, PC2, and PC3 by T45P315, T45P325, T46P325, T47P31, T47P315, T47P32, T47P325, T48P32, T48P325, T49P31, T49P325, T50P31. Some tank and tempering combinations give a greater hardness supported with glossy appearance.

3.2 Hardness

It can be observed in Figure 3 that the hardness of chocolate varied but tended to increase during storage. The line showed that the chocolate was affected by the combination of tank and tempering temperature. Figure 3 consists of 6 groups (six different tank temperatures) describing hardness changes in different tempering treatments over storage.

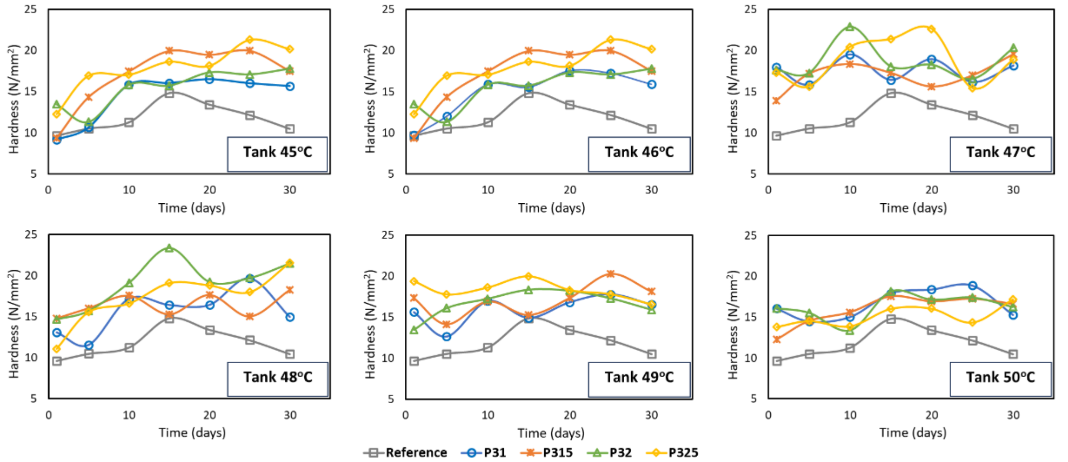

Fig. 3. The hardness value of chocolate was measured in the different tank and tempering temperatures during 30 days of storage.

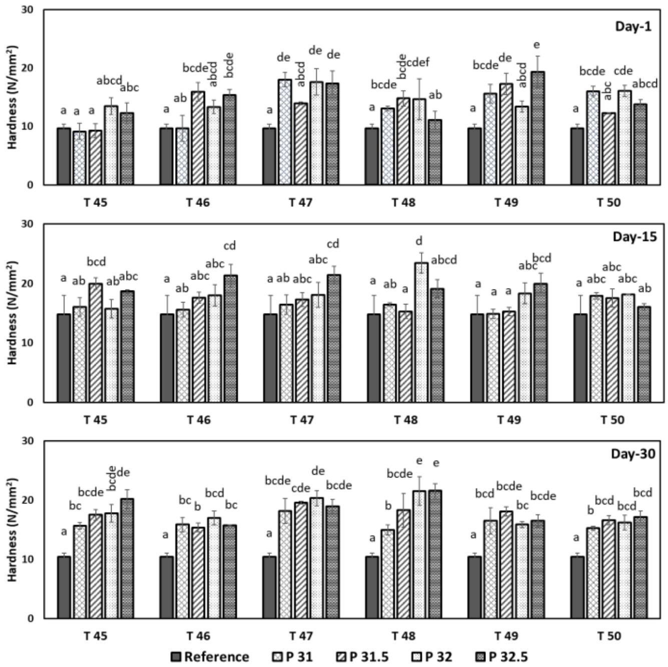

Fig. 4. Hardness profile of dark chocolate. Different lowercase denotes a significant difference ($p<0.05$)

The grey line (Figure 3) describes the reference sample. It positioned at the lowest compared to other treatments, the hardness ranged between 9.65-14.82 N/mm^2 for the reference sample. These findings were in agreement with previous results reported by Afoakwa [24] who found that the hardness of the untempered chocolate sample is low (soft) and difficult to demould (bad contraction). The decrease of hardness in some temperature combinations in this research also associate with the experiment on bar chocolate, hardness decrease in the first four weeks of storage [36]. This is also in line with the study that some treatments experienced a decrease in hardness during 30 days of storage.

Chocolate was stored between 18-20°C inside the chiller to maintain its quality attributes. According to Machálková [37], the higher temperature for example 30°C, was not suitable for short-term storage. A storage temperature of 20°C generated a good colour and texture, but not in terms of sensory evaluation. Tempered chocolates are resistant to fat bloom. Therefore, to preserve its original attributes, it should be kept at 12°C.

In this study, storage time and tank-tempering temperature treatment affected the chocolate hardness. Figure 4 explained the hardness profile based on storage time. Significant difference calculated at $p<0.05$ using one-way ANOVA. The reference sample showed a different superscript on each day of measurement which associated to there is a difference between the hardness of the reference and tempered sample.

3.3 Chocolate Appearance

The appearance of the chocolate is also important to determine the best combination of tank and tempering temperature during 30 days of chocolate storage. Chocolate with fat bloom reduced the quality attributes and appeared as a loss of initial glossiness. In dark chocolate, phase separation, and polymorphic crystal transformation along with storage time is the most common explanation to describe fat bloom [14, 19, 25].

It was also noticeable, as seen in Table 2, that the reference sample on day-1 gives a smooth and fine appearance (1a). Then, it showed a bloomed formation after 30 days of storage, which means that the quality decreased. The same blooming effects also appeared on T48P31 and T48P32 sample treatments.

Table 2. Chocolate image during storage at 48ºC tank temperature

Time (day)	Reference (a)	T48P31 (b)	T48P31.5 (c)	T48P32 (d)	T48P32.5 (e)
1					
5					
10					
15					
20					
25					
30					

Some combinations of tank and tempering temperatures were also defined as a good surface quality of the chocolate. Sample T48P315 and T48P325 were examples of glossy appearance. In this present study, the hardness value combined with the visual appearance could determine a good combination of tank and tempering temperature.

3.4 Hardness Change Kinetics

The adaptation of Newton's law of cooling (NLC) along storage time could be proposed as a real-time hardness prediction model. Figure 5 showed that the hardness changes over time could be predicted smoothly using this adaptation. The constant value (k) of hardness change is obtained from the exponential graph. The highest k value was -0.0031 supported by the glossy appearance of the combination 50ºC tank and 31.5ºC tempering temperature. The coefficient of determination (R^2) is 0.9013 using that temperature combination. Negative signs showed a declining hardness rate during storage (Table 3).

Table 3. Constant (k) value and R^2 of the tank and tempering temperature treatment

Treatment	***k*** value	R^2	Prediction Equation	Appearance
T45P31	-0.0035	0.8297	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{-0.0035t}$	Blooming
T45P315	-0.0038	0.8800	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{-0.0038t}$	Blooming
T45P32	-0.0017	0.6974	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{-0.0017t}$	Glossy
T45P325	-0.00195	0.8970	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{-0.00195t}$	Glossy
T46P31	-0.0029	0.8596	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{-0.0029t}$	Blooming
T46P315	-0.00008	0.1358	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{-0.00008t}$	Blooming
T46P32	-0.0016	0.2738	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{-0.0016t}$	Glossy
T46P325	-0.0004	0.0054	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{-0.0004t}$	Blooming
T47P31	0.00026	0.0005	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{0.00026t}$	Blooming
T47P315	-0.00173	0.3731	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{-0.00173t}$	Glossy
T47P32	-0.00033	0.0013	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{-0.00033t}$	Blooming
T47P325	-0.00057	0.0364	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{-0.00057t}$	Blooming
T48P31	-0.00093	0.4206	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{-0.00093t}$	Blooming
T48P315	-0.00156	0.1936	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{-0.00156t}$	Glossy
T48P32	-0.00154	0.6188	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{-0.00154t}$	Blooming
T48P325	-0.0024	0.8887	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{-0.0024t}$	Glossy
T49P31	-0.00043	0.3134	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{-0.00043t}$	Glossy
T49P315	0.0001	0.3421	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{0.0001t}$	Glossy
T49P32	-0.00268	0.5161	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{-0.00268t}$	Glossy
T49P325	0.00211	0.4286	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{0.00211t}$	Blooming
T50P31	-0.00126	0.2304	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{-0.00126t}$	Glossy
T50P315	-0.00311	0.9013	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{-0.00311t}$	Glossy
T50P32	-0.00056	0.1811	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{-0.00056t}$	Blooming
T50P325	-0.00122	0.4773	$\sigma_t = \sigma_e - (\sigma_e - \sigma_0)e^{-0.00122t}$	Blooming

Therefore, the three highest R^2, and appearance by investigating the blooming effect were selected. Table 3 described treatment T45P32, T48P325, and T50P315

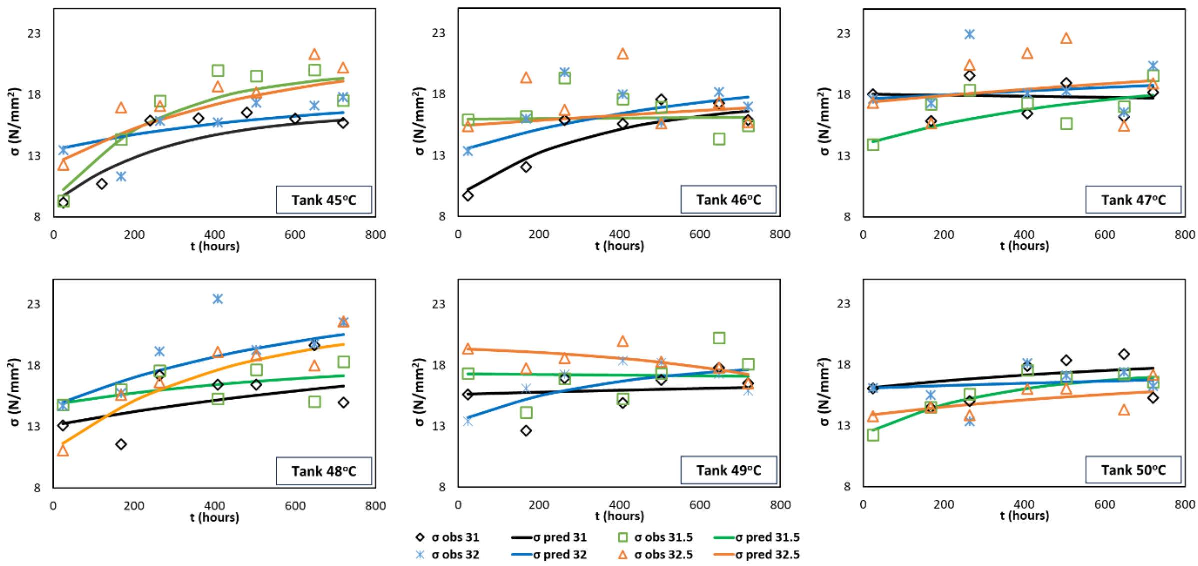

Fig. 5. Hardness changes kinetics at a corresponding storage time using an adaptation of NLC method.

were considered as three temperature combinations resulting in high k values and higher R^2 with anti-blooming effect at appearance. The use of NLC is often introduced to temperature prediction in such conditions for example, cooling or heating. Konovalenko [38] used a method for the adaptation of NLC to the prediction of an object's (cargo's) temperature prediction in a cold supply chain under the condition of ambient temperature instability and the method generally creates better performance.

This NLC approach can be used to predict the hardness change during storage. Based on the NLC kinetics, some tank and tempering temperature combination provided a good fitting of the prediction line over the observation dots. However, those fittings sometimes were not in line with the appearance. T45P31, T45P315, T46P31 had high k values of -0.0035; -0.0038; -0.00291 respectively and R^2 of 0.8297; 0.8800; 0.8596 respectively. Those values were not considered since the appearance of chocolate showed a defect or blooming surface. This could be associated with over-tempering and under-tempering. Afoakwa [30] mentioned that optimal tempering of dark chocolate was important to desired texture and appearance.

4 Conclusion

Storage time, tank temperature, tempering temperature, and their interactions have influenced the hardness of dark chocolate. The hardness increased over storage time in some combination of tank and temperature treatments. The combination of tank and tempering temperature delivered a glossy appearance along with a high value of coefficient of determination (R^2). The treatment T45P325, T48P325, and T50P315 were chosen since it resulted in high R^2 values for the model use, namely 0.8970, 0.8887, 0.9013 respectively, and showed the glossiest appearance.

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