

THE EFFECT OF DRYING TEMPERATURE ON MECHANICAL PROPERTIES OF NATURAL RUBBER LATEX PRODUCTS WITH CASSAVA PEEL WASTE POWDER MODIFIED ALKANOLAMIDE

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Abstract

Natural rubber latex (NRL) products filled with cassava peel waste powder was produced by coagulant dipping method. Cassava peel waste powder was modified by alkanolamide. Alkanolamide is a compound derived from Refined Bleached Deodorized Palm Stearin (RBDPS) and diethanolamine. The fillers were prepared 10 pphr into formulated latex system, followed by pre-vulcanization at 70 °C. The products were dipped by plate formers and dried at 100 °C and 120 °C for 20 minutes. From this study, it shows that higher drying temperature will improve the mechanical properties and crosslink density of natural rubber latex products.

Keywords: Natural rubber latex, Cassava peel waste, Alkanolamide, Pre-vulcanization, Drying temperature.

1. Introduction

Natural rubber latex (NRL) is a stable colloidal dispersion system consists of cis-1,4-polyisoprene as a main constituent with a high molecular mass in liquid [1]. NRL is used as a raw material for production of elastomeric products such as gloves, rubber thread, balloons, catheters, bandage, condoms, and inflatable stethoscope [2]. In recent years, NRL products were manufactured by incorporating organic fillers such as cassava starch, corn starch and potato starch [3-5] and inorganic fillers such as calcium carbonate [6]. The addition of fillers in NRL matrix was done in order to improve the properties of NRL products as it was

Nomenclatures	
$(2M_c^{-1})$	Crosslink density
V_r	Rubber volume fraction
V_0	Solvent molar volume, mol.m ⁻³
W_d	Dry rubber weight, kg
W_{sol}	Solvent weight, kg
Greek Symbols	
ρ_{NRL}	Rubber network density
ρ_D	Dry rubber density
ρ_{sol}	Solvent density
χ	Solvent interaction parameter
Abbreviations	
ALK	Alkanolamide
CPW	Cassava Peel Waste
CPWP	Cassava Peel Waste Powder
NRL	Natural Rubber Latex

shown in several studies mentioned before. Generally, the manufacturing of NRL products in industry used conventional fillers such as calcium carbonate and carbon black because they are cheap, resistant of heat, and have excellent surface area [7]. The alternative fillers for NRL products that commonly used were mineral fillers such as montmorillonite and kaolin [8, 9].

Cassava peel waste (CPW) is a byproduct of tapioca flour processing, fermented cassava, and foods made from cassava. The potential of cassava in Indonesia is very abundant since this country is one of the world's largest cassava producer and its production continues to increase each year [10]. It should be considered that these wastes contained crude fiber and cellulose. It indicates that these wastes have a possibility to become an alternative filler in NRL matrix because the peel's constituent could enhance the properties of rubber products as well as thermoplastic composites [11]. In addition, the utilization of CPW will be beneficial in terms of both ecological and economic standpoint.

The major problem in preparing NRL products filled with organic filler is the chemical incompatibility between the hydrophilic filler and hydrophobic matrix. In order to overcome this problem, some modifications are needed by performing ion exchange cation on the filler surface by using an organic surfactant. This process was achieved by attaching hydrocarbon chain in surfactant to the surface layer of hydrophilic filler excipients which allowed the fillers to mixed with hydrophobic matrix [12]. The organic surfactants which have been used in several previous studies are octadecylamine and octadecyltrimethyl ammonium bromide (ODTMA) [12] and polyethylene glycol (PEG) [13]. Keawkumay et al. [12] observed that the addition of surfactant octadecylamine and octadecyltrimethyl ammonium bromide (ODTMA) in NRL products filled with montmorillonite (MMT) increases the interfacial strength between matrix and filler [12]. González et al. [13] studied the addition of PEG surfactant in natural rubber latex products filled with montmorillonite (MMT) increases the tensile and interfacial strength between matrix and filler [13].

Alkanolamide as non-ionic surfactant could be used as organic modifier of filler surface. Alkanolamide is widely used as an ingredient in a mixture of foam booster and other useful surfactant materials such as dishwashing liquid. Alkanolamide is also used in the manufacture of shampoos [14]. It could be obtained by synthesizing the Refined Bleached Deodorized Palm Stearin (RBDPS), a byproduct of palm oil processing with diethanolamine. The long hydrocarbon chain of alkanolamide acts as non-polar group whereas amide group acts as polar group [15]. Therefore, it explains that alkanolamide could modify the fillers in rubber matrix as it was revealed in previous study in which alkanolamide modified silica and kaolin [15, 16].

In this study, the fillers were modified by alkanolamide in order to increase the dispersion of CPW fillers in latex system. In preparing the NRL products by dipping method, the drying temperature is an important factor that determines the properties of products formed. Thus, the effect of drying temperature on the properties of NRL products such as crosslink density, tensile strength, tensile modulus and elongation at break will be studied. The products formed were characterized further by Fourier Transform Infra-Red and Scanning Electron Microscope (SEM) study to learn the IR spectra and films morphology.

2. Experimental Procedure

2.1. Materials

High Ammonia Latex with 60% of dry rubber content was obtained from local market. Cassava peel waste (CPW) was obtained from cassava crackers factory in Medan, Indonesia and dried at 100 °C for 24 hours. The dried cassava peel was milled and sieved until the size of 100 mesh obtained. Potassium hydroxide (KOH), sodium hydroxide (NaOH), acetic acid (CH₃COOH), calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O), toluene (C₆H₅CH₃), chloroform (CHCl₃), diethanolamine ((C₂H₄OH)₂NH), sodium chloride (NaCl), diethyl eter ((C₂H₅)₂O), methanol (CH₃OH), sodium methoxide (CH₃ONa), sodium sulphate (Na₂SO₄) were used as supporting chemical substances in this study. The materials were laboratory grade (MERCK) and purchased from CV. Multi Kreasi Bersama, Medan, Indonesia. The curatives for prevulcanization system of NRL consist of sulphur as crosslinking agent, zinc oxide (ZnO) as activator, zinc diethyldithiocarbamate (ZDEC) as accelerator, and antioxidant (AO). The curatives were obtained from Farten Technique (M) Sdn Bhd, Pulau Penang, Malaysia.

2.2. Methods

2.1.1. Preparation of alkanolamide

The reaction was carried out at atmospheric pressure in a 1000 ml reaction vessel fitted with a heater and a stirrer. Typically, 1.0 mol of RBDPS and 3.0 mol of diethanolamine, sodium methoxide and methanol (as catalysts) were placed in the reaction vessel. The mixture was stirred and heated; the reaction temperature was kept constant at 70 °C for about five hours. The resultant mixture was extracted with diethyl ether, and washed with saturated sodium chloride solution. The crude alkanolamide was purified with anhydrous sodium sulphate, and then concentrated by a vacuum rotary evaporator.

2.1.2. Pre-vulcanization and vulcanization

The fillers of 10 pphr (part per hundred rubber) were prepared by dispersing it inside ball mill which consists of water and alkanolamide (ALK). The alkanolamide used was 0; 0.5; 1.0; 1.5; 2.0; 2.5 wt% (weight percent). Table 1 provides the formulation of pre-vulcanized latex with the fillers and designated by the codes.

Table 1. Pre-vulcanized latex system with fillers and designated codes.

Samples	CPWP	Alkanolamide	Water	Codes
NRL	0	0	0	A
NRL + CPWP	10	0	90	B
NRL + CPWP + ALK 0.5%	10	0.5	89.5	C
NRL + CPWP + ALK 1.0%	10	1.0	89	D
NRL + CPWP + ALK 1.5%	10	1.5	88.5	E
NRL + CPWP + ALK 2.0%	10	2.0	88	F
NRL + CPWP + ALK 2.5%	10	2.5	87.5	G

The formulation for NRL compounding was shown in Table 2. It is shown that pre-vulcanized latex was mixed with 10 pphr filler dispersion system. The pre-vulcanized system was done at 70 °C in order to achieve the curing of the system. During this period, with interval time of 3 minutes, 3 drops of mixing system were taken as sample and tested by 5 drops of chloroform to observe whether the system has cured or overcured. The pre-vulcanization was stopped after the chloroform number has reached number 3.

Table 2. Formulation for NRL compounds ingredients.

Compounds	Weight (gram)
100% High Ammonia Latex	166.7
50% Sulphur	3
50% ZDEC	3
30% ZnO	0.83
50% Antioxidant	2
10% Potassium Hydroxide	3

After it had been pre-vulcanized, the mixture was left for 24 hours in order to release the bubbles into the surface. After all the bubbles are released, the latex compound was formed into films by coagulant dipping using thin stainless steel plate formers. The plates were washed by 10% potassium hydroxide solution and 10% acetic acid solution then continued by water to release the impurities on the plates. Then it were coagulated by dipping it in 10% calcium nitrate solution. The plates then were dried in the oven by hanging it. After it had dried, the plates were dipped in the latex system and the dwell time was set at 5 seconds. Finally, the film formers were hanged inside Memmert oven at 100 °C and 120 °C for 20 minutes.

2.1.3. Mechanical testing and morphology study

The films were tested in accordance to ASTM D412 using GOTECH AL-7000M with cross-head speed of 500 mm/min. The tensile strength, elongation at break, tensile modulus such as modulus at 100% elongation (M_{100}), and modulus at 300% elongation (M_{300}) were evaluated. Later, the morphological study in the fracture of the film is analyzed via Scanning Electron Microscope (SEM) JEOL-JSM 6360-LA. Then the film is characterized by Fourier Transform Infra-Red (FTIR) via Shimadzu IR-Prestige 21.

2.1.4. Determination of cross-linking density

The NRL products were made into small piece of about 0.2 grams. The data to calculate the crosslink density is obtained from swelling data which is performed in accordance to ASTM D471. Then, the calculation for crosslink density is done using the calculation given by Flory-Rehner according to following equation [17]:

$$(2M_C^{-1}) = \frac{[-\ln(1-V_r) - V_r - \chi V_r^2]}{2 \cdot \rho_{NRL} \cdot V_0 (V_r^{1/3})} \quad (1)$$

where ($2M_C^{-1}$) is the physical crosslink density, V_0 and χ is the molar volume and interaction parameter of the solvent (for toluene, $V_0 = 108.5 \text{ mol.cm}^{-3}$ and $\chi = 0.39$), ρ_{NRL} is density for rubber network = 0.932 [18]. V_r is the volume fraction of rubber in the swollen gel which can be obtained using this following equation [17]:

$$V_r = \frac{W_d / \rho_d}{W_d / \rho_d + W_{sol} / \rho_{sol}} \quad (2)$$

where W_d and ρ_d are the weight of dry rubber (for vulcanised rubber, $\rho_d = 0.9203 \text{ g.cm}^{-3}$) [18], and W_{sol} and ρ_{sol} are the weight and density of the solvent (for toluene, $\rho_{sol} = 0.87 \text{ g.cm}^{-3}$).

3. Results and Discussion

3.1. Crosslink density

Figure 1 shows the effect of drying temperature on NRL films filled with alkanolamide-modified CPWP. It could be observed that films with higher value of crosslink density occurs at drying temperature of 120 °C. At higher temperature, the particles in the films such as curatives and filler dispersion will be diffused more and this will strengthen the crosslink formation. It should be noticed that modifier content has influence in enhancing the crosslink formation. Sample D (1.0 wt% of alkanolamide) shows a maximum value of crosslink density while further loading of modifier will decrease the value of crosslink density. Further loading of modifier will hampered the intercalation and exfoliation between the curatives and fillers with the NRL matrix.

3.2. Tensile strength

Crosslink density value in Fig. 1 is important value in determining the properties of NRL films. From Fig. 2, the value of tensile strength is more likely in line with

Fig. 1 which the higher value of tensile strength is found at higher drying temperature. Sample D (1.0 wt% of alkanolamide) gives the highest value of tensile strength in the films. This shows alkanolamide reaches its maximum capacity in modifying CPWP surface area thus creating a strong interaction between NRL and CPWP. Then as the NRL products were stretched, the crosslink inside NRL products have responsibility to hold on the stress distribution hence it required more force to break it. However at sample E (1.5 wt% of alkanolamide), the tensile strength drops dramatically. This occurrence might be due to agglomeration of fillers in the films hence deteriorating the rubber.

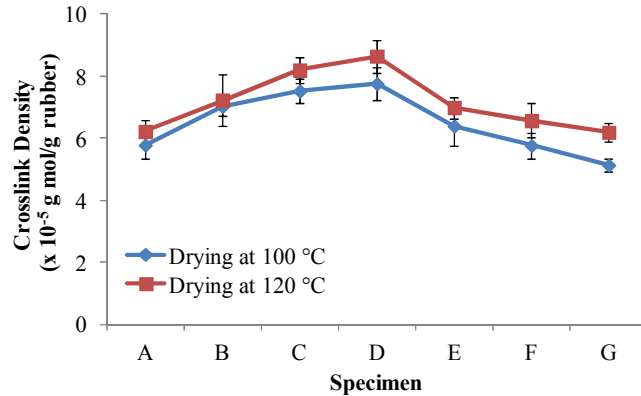


Fig. 1. The effect of drying temperature on crosslink density of NRL filled with alkanolamide-modified CPWP.

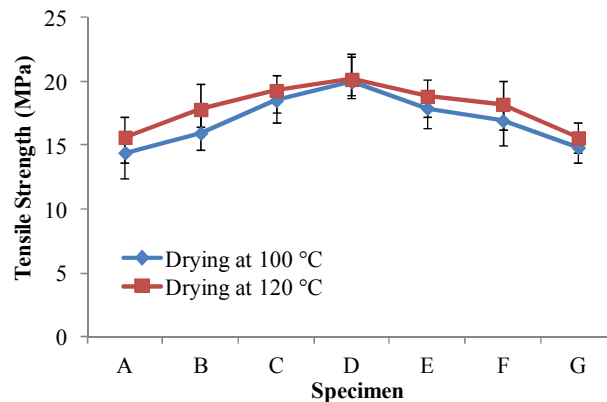


Fig. 2. The effect of drying temperature on tensile strength of NRL filled with alkanolamide-modified CPWP

3.3. Elongation at break

Figure 3 shows that NRL products dried at 120 °C give a higher results of elongation at break than products dried at 100 °C. Addition of fillers will give stiffness to the NRL products. Thus, the elongation at break will be decreased. It was shown that the lowest elongation at break with addition of 1.5% wt of

alkanolamide for both drying temperature. But the further addition of alkanolamide until 2.5% wt make the NRL products more elastic than unmodified NRL products. This may be attributed to the function of alkanolamide as a plasticizer in CPWP filled NRL products.

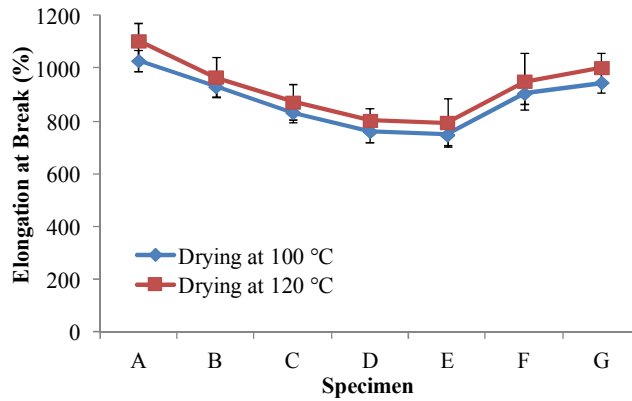


Fig. 3. The effect of drying temperature on elongation at break of NRL filled with alkanolamide-modified CPWP.

3.4. M100 and M300

Figures 4 and 5 show effect of drying temperature on M_{100} and M_{300} for the NRL products. In M_{100} and M_{300} , drying temperature at 120 °C gives a higher tensile modulus than drying temperature at 100 °C. It was shown an incisive increase in NRL filled CPWP modified by alkanolamide until 1.5% wt addition of alkanolamide. This shows that addition of alkanolamide until 1.5% wt able to give stiffness in NRL products by increasing interaction between NRL and fillers.

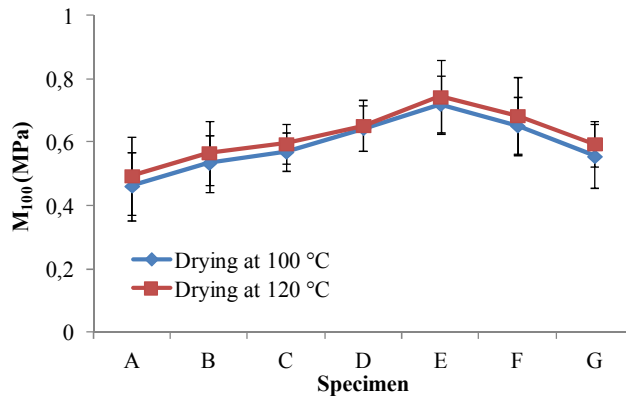


Fig. 4. The effect of drying temperature on M_{100} of NRL filled with alkanolamide-modified CPWP.

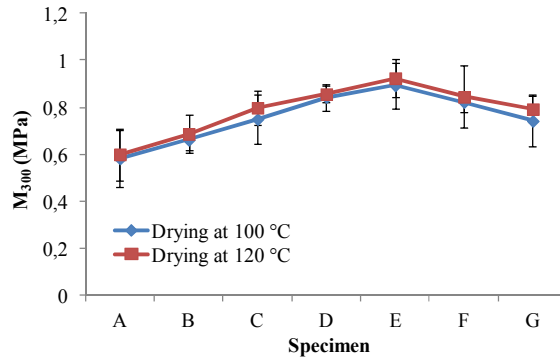


Fig. 5. The effect of drying temperature on M_{300} of NRL filled with alkanolamide-modified CPWP.

3.5. Characterization of fourier transform infra-red (FTIR)

The NRL products such as NRL filled with CPWP and NRL filled with CPWP-alkanolamide were characterized by FTIR which is given in Fig. 6. It can clearly be seen that alkanolamide has modified the functional group of CPWP and NRL. It has been shown at IR band of 2353.16 cm^{-1} which is free -OH groups from carboxylic acids on the surface of CPWP and IR band of 3240.41 cm^{-1} which is free -OH groups from alcohols on the surface of NRL were depleted as the result of alkanolamide addition. Alkanolamide has modified the -OH groups from the surface of CPWP and -OH groups from the surface of NRL. This occurrence is due to the long hydrocarbon chain acts as non-polar group which it modifies the -OH groups from the surface of NRL whereas amide group acts as polar group which it modifies the -OH groups from the surface of CPWP.

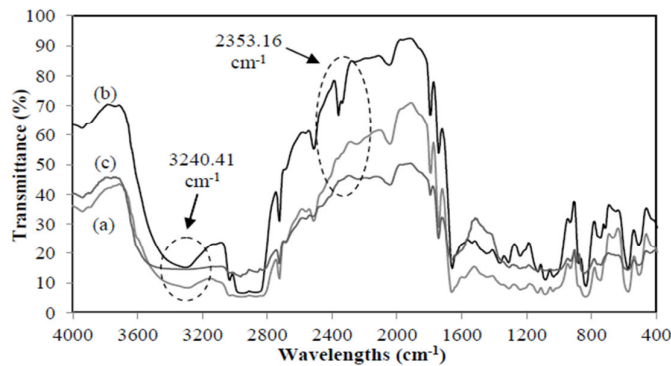


Fig. 6. FTIR Analysis of: (a) NRL (b) NRL filled CPWP; (c) NRL filled CPWP-alkanolamide.

3.6. Scanning electron microscope (SEM) study

The morphology of NRL films were examined by SEM which is shown in Fig. 7. Figure 7 shows the SEM micrographs of CPWP, NRL filled CPWP and NRL filled CPWP-alkanolamide (0.5% wt and 2.5% wt) respectively. It can clearly seen that alkanolamide affect the morphology of the NRL products. The addition

of alkanolamide up to 2.5% wt made fillers were more distributed in matrix than without the addition of alkanolamide. Higher drying temperatures also produce a better surface morphology. It was proved that higher drying temperatures improved the mechanical properties of the NRL products.

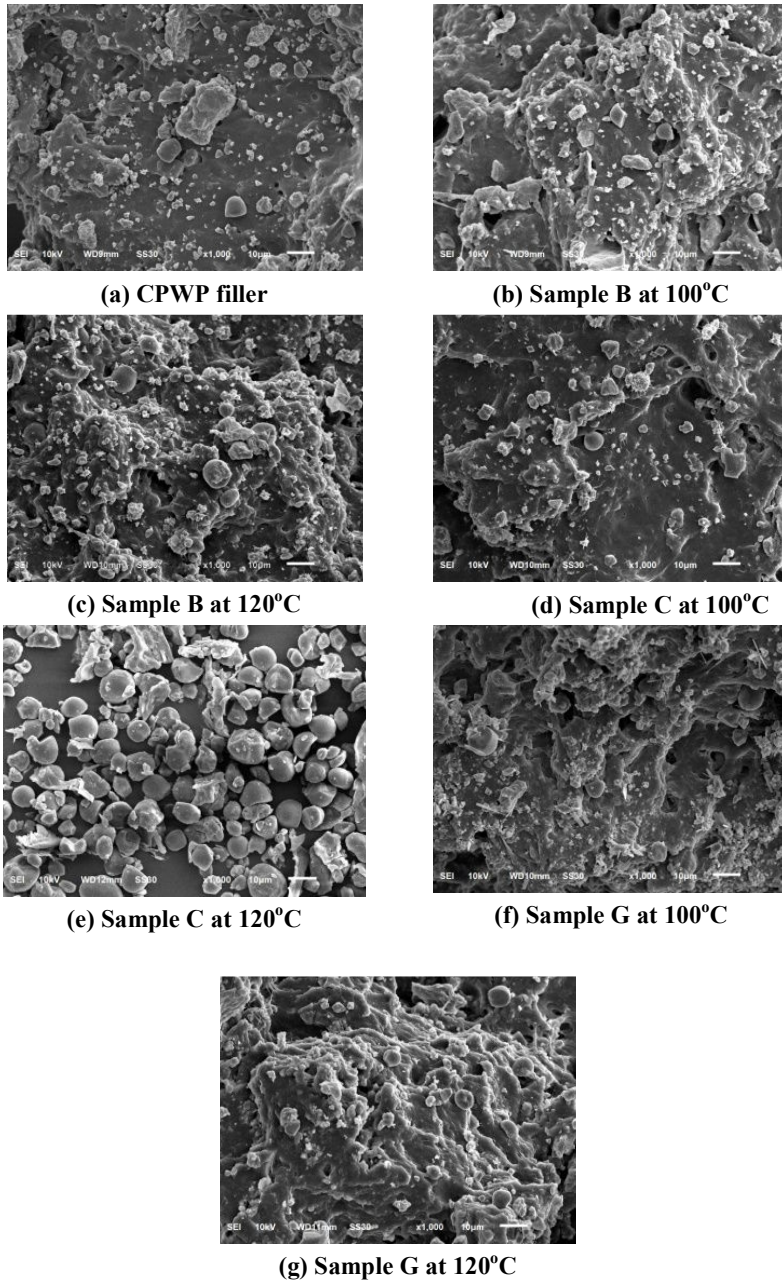


Fig. 7. SEM images of various samples.

4. Conclusions

It is observed that utilization of alkanolamide as modifying agent can modify CPWP properties. It also shows that alkanolamide provides better mechanical properties on NRL products such as tensile strength until the addition of 1% wt of alkanolamide. The highest crosslink density was obtained at the addition of 1% wt of alkanolamide. Thus, higher drying temperature will improve the properties of NRL products such as crosslink density, tensile strength, tensile modulus, and elongation at break. The addition of alkanolamide also improve the interfacial strength between matrix and filler as shown in FTIR analysis and SEM micrographs.

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