SPECIALTY RUBBER LATEX FOR DIPPED PRODUCTS APPLICATION

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ABSTRACT

Epoxidized natural rubber (ENR) is a chemically modified form of natural rubber (NR) through epoxidation reaction by reacting with hydrogen peroxide and formic acid. Among the essential characteristics of ENR are excellent oil and chemical resistance with low air permeability due to the presence of the polar epoxy groups. The applications of ENR in dry rubber products sector, i.e. tyre tread, engine mounting and shoe sole have extensively explored which resulted in the positive product characteristic enhancement. The ENR advantages are further investigated for latex based product particularly in dipped product application as currently, the work on the matter is limited owing to ENR latex could not form film by coagulant dipping process. This is due to the presence of non-ionic surfactant that restrict the formation of ENR latex film onto the former. In attempts to develop ENR latex that could be easily dipped, ENR latex is concentrated via ultrafiltration system for removal of surfactant and increase the total solid content (TSC). ENR latex with higher TSC (60%) was compounded with conventional sulphur acceleration system at various pre-vulcanization time (1, 2 or 3 days). The pre-cure measurement of ENR latex was observed via chloroform number and linear swelling index. Apart from that, the physical characteristics of the ENR films were determined for its tensile strength (TS). The study shows that the ENR latex using SPVL system able to be dipped and form a satisfactory continuous film. The tensile strength of ENR film shows dependency with the pre-vulcanization time; i.e tensile strength increase at 2 days of prevulcanization time.

Keywords: Epoxidized natural rubber (ENR), dipped product, sulphur vulcanizing (SPVL) system

BACKGROUND

Epoxidized natural rubber (ENR) is a modified natural rubber (NR) produced through reacting natural rubber with organic peracid such as performic acid in either solution or latex system [1]. The presence of polar epoxy groups in the ENR exhibit low air permeability, good oil and chemical resistance characteristic [2, 3]. Exploitation of these characteristic in latex dipped goods able to widen the ENR applications for rubber goods applications. However, published work shown that uncompounded ENR latex is not suitable to be processed via coagulant dipping. This is due to its inability to gel on the former, which resulted in a very thin latex film [4]. The main reason for this occurrence is due to the ENR latex being highly stabilised with non-ionic surfactant. Whilst the non-ionic surfactant is necessary to keep the latex stable during epoxidation reaction, it cause the latex to be chemically stable against the calcium salt coagulant such as calcium nitrate.

In attempts to develop ENR latex for dipped applications, the latex was concentrated via ceramic ultrafiltration membrane process as the conventional centrifugation method based on density separation is not suitable. Alternatively, concentration via membrane technology was used with the concept of selective separation according to particles size and molecular weights with pressure as the driving forces during separation (Devaraj Veersamy et al. 2003). This membrane concentration increase its total solid content (TSC) and reduce the surfactant level in the ENR latex. Prior to the production of the ENR latex concentrated, the latex was than compounded with other active ingredients to be applied for coagulant dipping process. Hence, this project is aim to optimize ENR dipping system and subsequently to ensure the consistency of ENR latex dipped based on the optimized formulations. The observation of the resultant ENR dipped film was evaluated by physical properties. Furthermore, the oil resistance of ENR dipped film was also measured.

METHODOLOGY

Materials

Epoxidized natural rubber latex containing 25% epoxy level (ENR-25) was reacted at RRIM Malaysian Rubber Board according to the process and procedure from Gelling,I.R. (1982). The reaction was conducted using conventional batch reactor with working volume capacity of 400L with LA-TZ as the starting raw material. The reacted ENR latex was further treated with ammonia and ammonia laurate prior to ultrafiltration concentration using ceramic membrane system as disclosed in PCT/MY2013/000163[5]. Potassium laurate (K.Laurate), Potassium hydroxide (KOH), Sulfur (S), Zinc oxide (ZnO), Zinc diethyldithiocarbomate (ZDEC), Zinc mercaptobenzothaizole (ZMBT), Wingstay-L, Titanium dioxide (TiO_2) were supplied from Excelcos Sdn Bhd. Calcium nitrate ($Ca(NO_3)_2 4H_2O$) and industrial methylated spirit (IMS) were purchased from Systerm.

Compounding latex

The ENR latex was prepared by compounding of ENR latex according to the formulations shown on Table 1. The K.Laurate and KOH were added first, followed by the addition of vulcanising ingredients. The mixtures were allowed to mature at room temperature for 48 h.

Table 1: Formulation of prevulcanized latex

Compounding Ingredients	TSC (%)	Dry weight (phr)
ENR Latex	60	100
K. Laurate	20	0.1
KOH	10	0.1
Sulphur	50	0.4
ZDEC	50	0.4
ZDBC	50	0.2
ZnO	50	0.3
WL	50	1.0
TiO_2	50	5.0

Preparation of dipped films

Coagulant-dipped films were prepared using flat ceramic formers. The former was first heated to 80ºC before dipping into a 20% calcium nitrate solution (coagulants dipping). The flat ceramic formers were then oven dried in an air oven at 80ºC before dipping into the ENR latex compound for 10 seconds. The resulting wet films were air dried under room conditions for 10 min before being subjected to leaching in distilled water for 2 minutes. The leached films were then dried in the oven at 80 ± 5ºC for 10 min before heating up for vulcanisation at 100 ± 5ºC for 30 min. The films were then removed from the oven and cooled to room temperature, before being powdered with grade corn starch and stripped off the formers.

Chloroform number

A sample of ENR latex is coagulated by mixing with an equal volume of chloroform and the degree of vulcanization is evaluated from the appearance of the coagulum. The coagulum is graded as listed in Table 2 below.

Table 2: The chloroform number grade

Nature of coagulum	Chloroform number	Degree of prevulcanization
Tacky lump	1	Unvulcanised
Tender lumps, break short	2	Lightly vulcanized
Non-tacky crumbs	3	Moderately vulcanized
Fine dry crumb	4	Fully vulcanized

The equilibrium swelling test

In this method, the degree of vulcanization is measured from the extent of equilibrium swelling of films dried down from the latex using toluene. Firstly, the latex film was cut into a disc shape with a 23 mm diameter then soaked in the toluene for 30 minutes. . The ratio of swollen diameter/original diameter of disc gives the level of pre-cure (swelling index) (Table 3).

Table 3: Degree of vulcanization

Swelling index	Degree of cure
> 2.6	Unvulcanized
2.0 – 2.6	Lightly vulcanized
1.8 – 2.0	Moderately vulcanized
< 1.7	Fully vulcanized

Physical properties measurement

Tensile testing of the samples were done according to ISO 37 [6] test method using dumb bell shaped test specimens in a Universal Testing Machine INSTRON at a cross head speed of 500 mm min^{-1}. At least five samples were tested in each case and the average values are reported.

Oil resistance

Circular shaped samples with a diameter of 23 mm was cut from the ENR dipped latex film and the thickness of the sample was measured with an accuracy of ± 0.01 mm[7]. The initial weight of the cut sample was recorded before and after immersing in cooking oil. The oil swollen sample was blotted with lens tissue and acetone to remove the excess oil on the surface and edges of the sample. Then the sample was re-weighed and re-immersed into cooking oil for three days.

RESULTS AND DISCUSSION

ENR Latex concentrate properties

The typical latex properties of ENR and HA latex are listed in Table 4 below. The ENR latex properties for total solid content (TSC) [8], dry rubber content (DRC) [9], alkalinity content [10] and particle size shows comparable value to the HA latex. However, the viscosity of ENR is slightly higher which might due to the presence of zinc oxide (ZnO) in the LATZ as the starting material of ENR latex. With this similar properties, ENR latex has a good potential to be used for dipping purposes.

Table 4: Typical properties of ENR latex

Latex	Epoxidized natural rubber (ENR)	HA
Total solid content, TSC (wt%)	59.0	60.0
Dry rubber content, DRC (wt%)	57.0	62.0
Alkalinity content (wt%)	0.2-0.5	0.2-0.8
Particle size (µm)	0.6-1.0	0.6-1.0
Brookfield viscosity (cps)	20-300	20-150
pH	9.18	10.7

The concentration process via the ceramic ultrafiltration membrane system for ENR-25 latex shown an increment of TSC from 36.4% to 62.9% (Table 5). In respect to the alkalinity value, ENR latex concentrate was preserved at lower level of ammonia which reflected to alkalinity level of 0.14%. This is comparable to the standard alkalinity value for the low Ammonia (LA-TZ) latex concentrate (ISO 2027:1990(EN)).

Table 5: Comparison of latex properties between commercial available latex concentrate and ENR latex (before and after concentration)

Latex Properties	Commercial available latex concentrate (LA-TZ)	ENR Latex (after concentration)	ENR Latex (before concentration)
DRC, wt%	56.5	60.4	35.7
TSC, wt%	58.0	62.9	36.4
Alkalinity, wt%	0.19	0.14	0.11

On the aspect of surfactant level, concentration process via membrane system reduced the surfactant level in the ENR latex concentrate. This is shown in the NMR spectra illustrated in Figure 1.

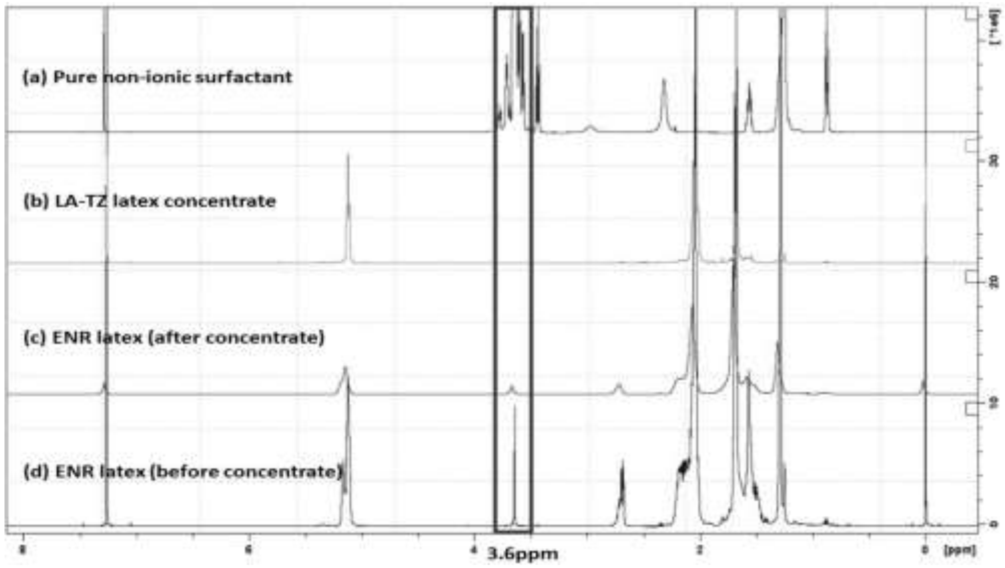

Figure 1: NMR spectrum of (a) pure non-ionic surfactant, (b) LATZ latex concentrate, (c) ENR latex after concentrate and (d) ENR latex before concentrate

The presence of surfactant was detected at integration peak of δ = 3.6 ppm and the intensity of the peak reduces from the pure surfactant (a), ENR latex (before concentrate, d) to ENR latex (after concentrate, c). With the removal and reduction of the surfactant level in the ENR latex, it has the potential to be explored for dipped product application in order to obtain continuous dipped film.

Effect of maturation time on latex properties

Table 6 shows the effect of chloroform number, swelling index, pH and viscosity at different maturation/prevulcanization time. These experiments were carried out to measure the pre-cure state of ENR latex compounding before proceed for dipping process. The chloroform number and swelling index at day 1 and 2, show the latex is in a moderately vulcanized condition. This indicate that the ENR latex compounding need further time for maturation in order to reach a suitable degree (<1.7). The ENR latex was fully vulcanized after 3 to 6 days of compounding time. This phenomena occurred due to the higher amount of active ingredient that tends to slow the rate of pre-vulcanization and consequently affected to chloroform number and linear swelling index.

Table 6: Effect on latex properties with time

Days	Chloroform number	Swelling index, Q	pH	Viscosity
1	2	2.01	10.4	150
2	3	1.92	10.3	140
3	3	1.78	10.2	180
4	4	1.70	10.4	140
5	4	1.70	10.1	120
6	4	1.70	10.1	130

Final thickness of dipped ENR latex films

Thickness of the dipped good product is one of the important characteristics that need to be consider in dipped latex films. The thickness of deposited layer can be manipulated through increasing (i) dwell time in the compounded latex, (ii) the concentration or total solids content of compounded latex, (iii) the concentration of coagulant solution and (iv) the dwell time during dipping[11]. The thicknesses of dipped ENR latex film as a function of latex TSC and coagulant concentration are shown in Figure 2 and Figure 3 respectively. Generally, the thickness of the ENR dipped films increases as the concentration of latex TSC and coagulant increased. This is reflected to the variation of film thickness from 0.12 – 0.32 mm. The variability of the thickness can be achieved by choosing an appropriate concentration of latex TSC and coagulant.

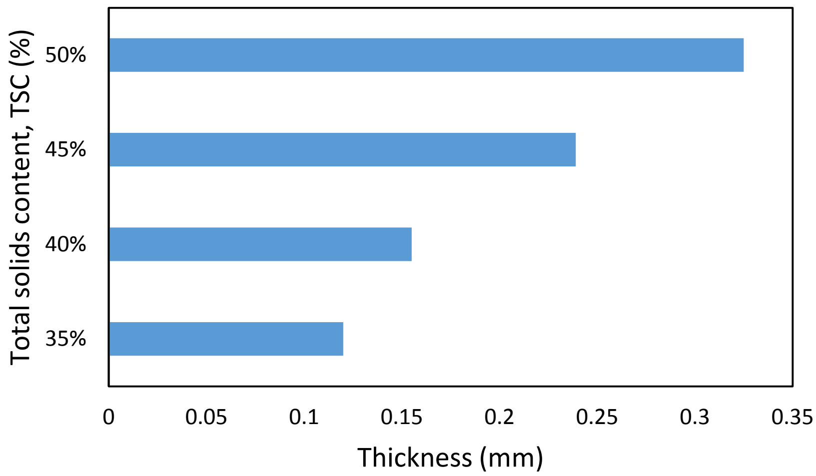

Figure 2: Thickness of dipped ENR latex films at different total solids content (TSC)

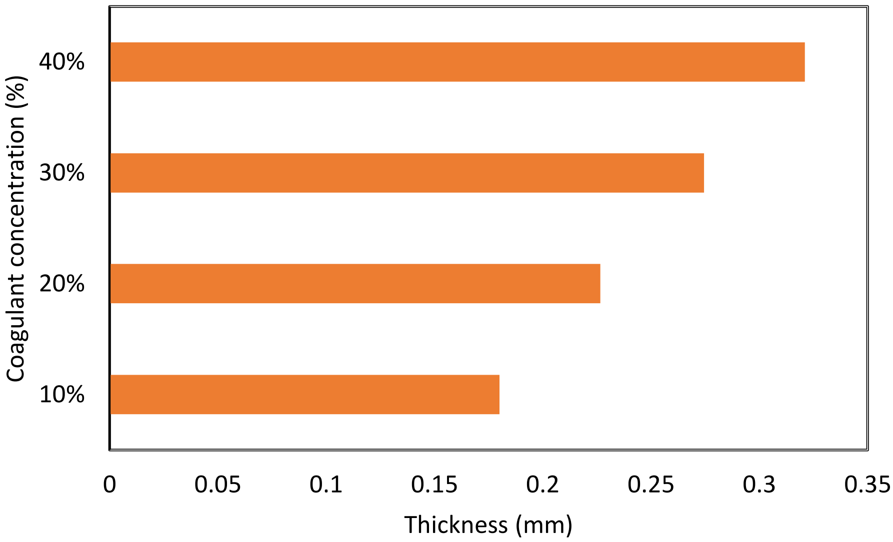

Figure 3: Thickness of dipped ENR latex films at different coagulant concentration

Tensile properties

The tensile strength of ENR dipped films at different pre-vulcanization time are shown in Figure 4. Based on the results, ENR dipped films prepared at third days of compounding gives higher tensile properties (17 MPa) than compounding at first (15 MPa) and second days (16 MPa). Pre-vulcanization time at third days shown optimum crosslinking is obtain in the ENR dipped film. This results also attributed due to denser network chain and restriction in chain mobility.

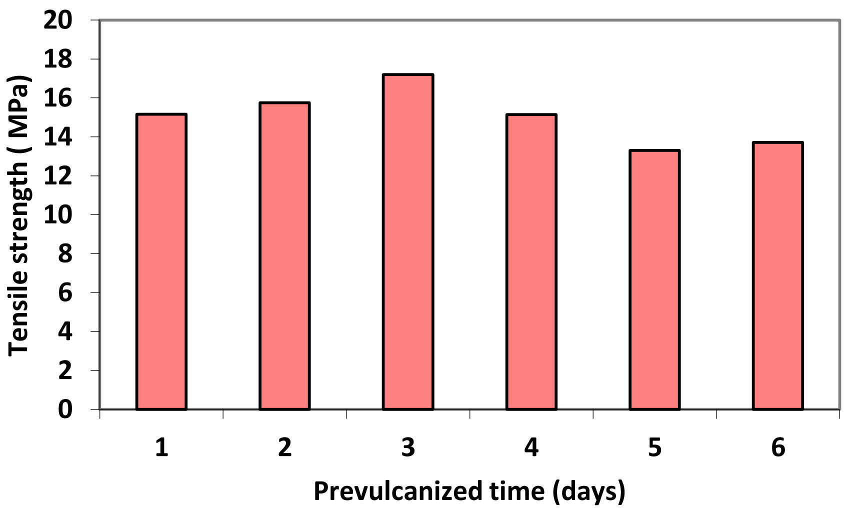

Figure 4: Tensile properties of ENR film

Oil resistance

Gloves with good swelling resistance to oils and fats is one of the requirement for food industry application. ENR in dry rubber form has a good oil resistance and it is governed by its epoxidation level. The oil resistance properties for ENR latex film tabulated in Table 7 shows the mass uptake (amount) of cooking oil absorbed into ENR latex film, nitrile film and HA latex film. As expected, nitrile film absorb less oil than HA film and ENR dipped films. This suggested that the nitrile resist to the oil much better than natural rubber. However, the mass uptake of oil ENR dipped film showed better than natural latex glove. This might be due to the polarity of the ENR than the HA latex film.

Table 7: The oil swollen for different sample of gloves and dipped films

Samples	**Thickness, mm**	**diameter before, mm**	**diameter after, mm**	**oil swollen, g**	**oil swollen, %**
HA film	0.100	23	27	0.0403	4.03%
Nitrile film	0.086	23	23	0.015	1.50%
ENR film	0.100	23	24	0.03	3.00%

CONCLUSION

ENR latex is an alternative latex that can be used in coagulant dipping application to prepare thin walled product such as gloves. The latex properties of ENR latex are similar with NR. This was also reflected to the properties of dipped film as the ENR film gives comparable results to the NR film. However minor changes in the formulations need to be done in order to obtain the higher strength properties of latex films.

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