

Studies on the Dipping Characteristics of RVNRL and NR Latex Compounds

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Received 5 June 2000; accepted 8 November 2000

ABSTRACT: The dipping characteristics of radiation-vulcanized natural rubber latex and natural rubber latex compounds were investigated with a lab-model semiautomatic dipping machine. The effect of the variation of the speed of immersion and withdrawal, dwell time, compound viscosity, and concentration of coagulant on the thickness of the latex deposit was investigated. The results of the study show that the deposit thickness depends on the withdrawal speed of the former, the concentration of the coagulant, dwell times, and the viscosity of the latex compounds. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3141–3148, 2001

Key words: radiation-vulcanized natural rubber latex; prevulcanized natural rubber latex compound; dry coagulant; viscosity modifier; immersion speed; withdrawal speed; dwell time

INTRODUCTION

Radiation-vulcanized natural rubber latex (RVNRL) is a modified form of latex in which the dispersed rubber particles are crosslinked. The production process for RVNRL consists of mixing natural rubber (NR) latex with sensitizer, irradiating it with γ rays, and adding antioxidants. Latex vulcanized by this technique contains no sulfur, zinc oxide, or accelerators. It is free from the decomposition products of the accelerators, particularly the carcinogenic nitrosoamine.^{1,2} One important application stipulated for RVNRL is for the manufacture of dipped products like surgical gloves, examination gloves, condoms, catheters, and so on.³

The principal latex dipping processes are simple or straight dipping, coagulant dipping, heat-sensitized dipping, and electrodeposition. In

straight dipping, the clean and dry former is immersed into the latex, slowly withdrawn, inverted, rotated, and dried. In coagulant dipping, the former is dipped into a coagulant solution (e.g., calcium nitrate, calcium chloride), withdrawn, and allowed to dry partially. It is then lowered into the latex compound and, after a suitable dwell time, slowly withdrawn, inverted, rotated, and dried.

Straight dipping gives a very thin deposit of latex film, whereas coagulant dipping gives a higher thickness of latex film deposited on the former.⁴ The thickness of the latex film deposited on the former depends on several factors, namely, the properties of the latex compound, the type and temperature of former, the concentration and nature of the coagulant, the rate of withdrawal, and the dwell time of the former.

In this study, the dipping characteristics of RVNRL and NR latex compounds were compared with a laboratory-model semiautomatic dipping

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Journal of Applied Polymer Science, Vol. 81, 3141–3148 (2001)
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Table I Properties of 60% Centrifuged NR Latex for Production of RVNRL

Property	Value	Requirements (BIS 5430-1981)
Dry rubber content (%)	60.00	60 ^a
Nonrubber solids by mass (%)	1.5	2 ^b
Sludge content by mass (%)	0.05	0.10 ^b
Ammonia content by mass (%)	0.7	0.6 ^a
Potassium hydroxide number	0.5	1 ^b
Mechanical stability time (s)	1000	475 ^a
Volatile fatty acid number	0.02	0.15 ^b
Coagulum content by mass (%)	0.03	0.05 ^b
Copper content (ppm)	1.00	8.00 ^b
Manganese content (ppm)	Trace	8.00 ^b

^a Minimum.^b Maximum.

machine supplied by Diptech (Stroud, UK). The following factors were studied:

- The effect of the variation of the rate of immersion of the former and the dwell time on the thickness of the latex deposit.
- The effect of increasing the viscosity and dwell time on the thickness of the latex deposit.
- The effect of the variation of the concentration of coagulant on the total deposit thickness at different dwell times.
- The effect of the variation of the rate of withdrawal of the former on the thickness of the latex deposit.
- The effect of the variation of the speed of withdrawal and immersion (keeping them equal) on the thickness of the deposit.

EXPERIMENTAL

Materials

RVNRL

The RVNRL used in this work was procured from the RVNRL Pilot Plant situated at Rubber Research Institute of India (RRII), Kottayam.

Table II Typical Formulation for the Preparation of RVNRL (1000-L Batch Capacity)

Ingredient	Batch Weight (kg)
60% HA centrifuged NR latex	788.0
10% KOH (solution)	14.2
50% <i>n</i> -BA (emulsion)	47.2
0.5% Ammonia water	96.6
Total	946.0

The 60% centrifuged NR latex [high-ammonia (HA) type], given in Table I, conformed to BIS specification 5430; it was collected from rubber board and was mixed with 0.3 phr potassium hydroxide and 5-phr *n*-butyl acrylate (*n*-BA) and diluted to 50% total solids content by adding ammonia water. A typical formulation of one batch is given in Table II.

The NR latex was then irradiated with γ rays for a period of 9 h 40 min to get a radiation dose of 15 kGy. The radiation dose rate of the source was 1.55090 kGy/h. After irradiation, the RVNRL was mixed with 2 phr of antioxidant tris(nonyl phenyl)phosphite added as a 50% emulsion. The properties of RVNRL are given in Table III.

NR Latex Compounds

The formulation of the NR latex compounds used in this study are given in Table IV. Centrifuged NR latex HA type with 60% dry rubber content conforming to BIS 5430 was used to prepare the compounds. Sulfur, zinc diethyl dithio carbamate, and zinc oxide were added as fine dispersions prepared by ball milling.

The prevulcanized NR latex compound was prepared by the reaction of latex with ingredients as per the formulation given in Table V and heating in a water-jacketed vessel at 60°C for 4 h.

Table III Properties of RVNRL

Properties	Value
Dry rubber content (%)	51.6
Total solids content (%)	53.0
Alkalinity (%)	0.6
Volatile fatty acid number	0.03
Potassium hydroxide number	0.08
Mechanical stability time (s)	1200
Manganese content (ppm)	Trace

Table IV Formulation for NR Latex Compound (HA Type)

Ingredient	Wet Weight
60% Concentrated latex	167.0
10% KOH (solution)	0.5
50% Sulfur (dispersion)	2.4
50% Zinc diethyl dithio carbamate (dispersion)	2.0
50% ZnO (dispersion)	0.5
Vulcanization 1 h at 100°C	

Equipment

Laboratory dipping equipment supplied by M/s Diptech was used in this study. The machine was the rising-tank type with variable speed and was suitable for products up to 430 mm in dipped length. The machine was composed of an MKI electrohydraulic rising tank dipping unit and an integral control cabinet. The dipping unit was suitable for two tanks, one for latex and one for the coagulant. The control of dipping action was manual or automatic and initiated by push-button control. Other equipment included a digital micrometer manufactured by M/s Cadar Electronic (Sheffield, UK), a Brookfield viscometer (LVT model, Stoughton, UK), and a tensile tester (Instron 4411 model, Buckinghamshire, UK).

Experimental Procedure

Viscosity determinations were carried out at 25°C with the Brookfield viscometer LVT model and a number 2 spindle (ASTM D2526-229). All viscosity measurements were done just prior to dipping and were expressed in mPa · s (Brookfield). The characteristics (Table I) determinations were carried out with test methods IS 3708 (part 1): 1985 for dry rubber content, IS 9316 (part 3): 1987 for coagulum content, IS 3708 (part 2): 1985 for sludge content, IS 3708 (part 4): 1985 for alkalinity as ammonia, IS 3708 (part 5): 1985 for potassium hydroxide number, IS 3708 (part 6): 1985 for mechanical stability time, IS 3708 (part 7): 1986 for volatile fatty acid number, IS 9316 (part 8): 1987 for copper content, and IS 9316 (part 9): 1987 for manganese content. A test for nonrubber solids was also conducted, which examined the difference between total solids content and dry rubber content; total solids content was determined as per IS 9316 (part 4): 1988.

Tensile properties of RVNRL, NR, and prevulcanized NR latex vulcanizate were measured

from the casted films. Five test pieces were taken from each sample and were tested for tensile properties, according to ASTM D3188. The results are given in Table VI.

Swelling ratio (Q) and crosslink density (V_0) of RVNRL, NR, and prevulcanized NR latex vulcanizates was determined by keeping 1g of the sample sheet immersed in toluene for 48 h at 25°C. The sample was taken out and blotted quickly with filter paper and weighed. Q was calculated with the following formula: $Q = 1 + (d_1/d_2)(W_2/W_1) - (d_1/d_2)$, where W_1 is the weight of film before immersion, W_2 is the weight of the film after immersion, and d_1 and d_2 are densities of rubber and toluene, respectively.

V_0 was computed with Flory and Rehner equation:⁵ $V_0 = K \times Q^{-5/3}$, where $K = 4.71 \times 10^{20}$. The results are given in Table VII.

Effect of the Variation of the Rate of Immersion of the Former in RVNRL

The clean glass former was first fixed on the former holding bar and kept over the coagulant tank. A 10% solution of calcium nitrate was taken in the coagulant tank. The former was then immersed in the coagulant through the hydraulically lifting of the tank at a speed of 100 cm/min and withdrawn at the same speed. The former was then moved over the RVNRL tank and dipped in it at a speed of 109 cm/min, allowed to dwell for 60 s at room temperature (27°C), and slowly withdrawn at a speed of 35 cm/min. The former was inverted and rotated to obtain a uniform latex deposit. The former was then dried in an air-circulating hot-air oven at 70°C. The former was cooled, and the deposit was removed from the former with talc. The thickness of the deposit was measured with a digital micrometer to 0.001-mm accuracy. The arithmetic mean of five measurements was taken for each thickness.

Table V Formulation of Prevulcanized NR Latex Compound

Ingredient	Wet Weight
60% Concentrated latex (HA)	167
10% KOH (solution)	0.5
50% Sulfur (dispersion)	2.4
50% Zinc diethyl dithio carbamate (dispersion)	2.0
50% ZnO (dispersion)	0.4
Prevulcanization 4 h at 60°C	

Table VI Tensile Properties of RVNRL, NR, and Prevulcanized Latex Vulcanizates

Properties	RVNRL Vulcanizate	NR Vulcanizate	Prevulcanized NR Vulcanizate
Tensile strength (mPa)	23.6	29.5	25.7
Modulus 300% (mPa)	1.727	1.952	1.821
Modulus 500% (mPa)	4.656	5.500	4.700
Elongation at break (%)	950	801	925

The speed of immersion in to the latex was increased to 120, 124, 129, 133, 138, and 144 cm/min with all other parameters constant. The thickness of the deposit was measured in all cases. The experiment was repeated with prevulcanized and unvulcanized latex compounds.

To study the effect of the variation of the dwell time on the thickness of latex deposit, the dwell time was varied as 10, 20, 30, 40, 50, 60, 120, 210, and 270 s at a speed of 100 cm/min with a RVNRL latex of viscosity of 25 mPa · s (Brookfield) and a total solids content of 53%. The same experiment was repeated with a NR latex compound with a viscosity of 27.5 mPa · s and a total solids content of 52% and with a prevulcanized NR latex compound with a viscosity of 25 mPa · s and a total solids content of 55%.

To study the effect of viscosity and dwell times, latex compounds were mixed with 0.125 phr sodium carboxy methyl cellulose (5% solution) and 0.25 phr ammonium caseinate (10% solution.) The viscosity of the RVNRL, unvulcanized latex compound, and prevulcanized latex compound increased to 60 mPa. Dipping was carried out at various dwell times, namely, 10, 20, 30, 40, 50, 60, 120, 150, 210, and 270 s.

The experiment was repeated with 10% calcium chloride as a coagulant in the case of compounds mixed with ammonium caseinate.

To study the effect of various dwell times and concentrations of coagulant on the thickness of the latex deposit, dry coagulant dipping was car-

ried out at 100 cm/min at various dwell times, namely, 10, 20, 30, 60, 90, 150, 210, and 270 s, and at various concentrations of the coagulant calcium nitrate, namely, 10, 15, 20, 25, and 30%, with all other factors constant. The same experiment was repeated with NR latex and prevulcanized latex. Prevlcanized latex create the problem of slippage during withdrawal.

Effect of the Variation of the Rate of Withdrawal of the Former in RVNRL, NR, and Prevlcanized NR Compounds on the Thickness of the Latex Deposit

To study the effect of the variation of the rate of withdrawal of the former from the latex on the thickness of the deposit, the experiment was conducted at different speeds of withdrawal, namely, 35, 44, 65, 95, 115, and 140 cm/min, at a constant immersion speed (100 cm/min). The coagulant used was 10% calcium nitrate. Single, dry coagulant dipping was done at a dwell time of 60 s.

Effect of the Variation of Withdrawal and Immersion Speed (Keeping Them Equal) on the Deposit Thickness

In the automatic dipping unit, the withdrawal and immersion were done at the same speed. Hence, an experiment was carried out in which the withdrawal and immersion into the coagulant and latex were all done at the same speed. The

Table VII Q and Vo for RVNRL, NR Latex, and Prevlcanized NR Latex Vulcanizates

Property	RVNRL Vulcanizate	NR Vulcanizate	Prevlcanized NR Vulcanizate
Q	4.962	4.4874	4.5580
Vo (crosslink/mL × 10 ¹⁹)	2.2336	2.7629	2.6918

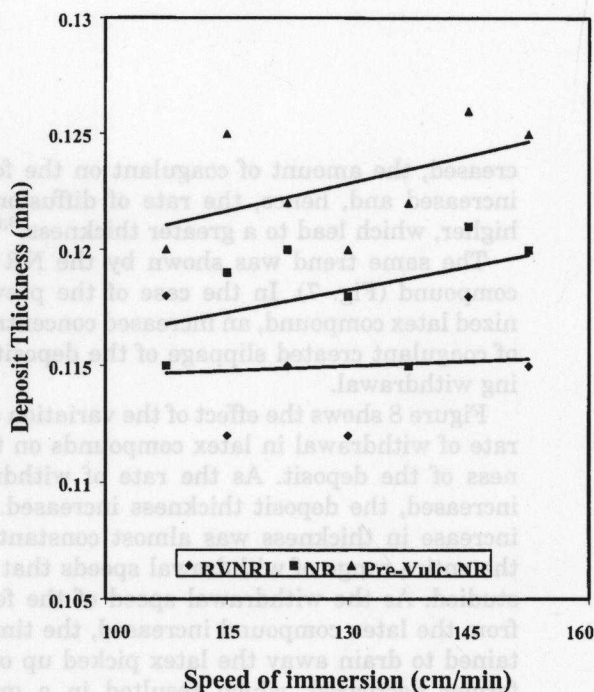


Figure 1 Variation of the thickness of the deposit with immersion speed.

speeds were 60, 75, 100, 110, 115, 120, and 144 cm/min.

The experiment was done for RVNRL, NR latex compound, and pre-vulcanized NR latex compound. Single, dry coagulant dipping was carried out with 10% calcium nitrate as the coagulant and a 60-s dwell time.

RESULTS AND DISCUSSION

Figure 1 shows the variation of thickness with the speed of immersion. As the speed of immersion was increased from 109 to 144 cm/min, the thickness of the deposit increased slightly. The figure shows that an increase in the speed of immersion did not have much effect on the thickness of the deposit formed. Similar results were obtained for pre-vulcanized and unvulcanized latex compounds. Figure 2 shows the variation on thickness of deposit with dwell time. There was a sharp increase initially up to a 50-s dwell time, and then, there was only a marginal increase. As the former with coagulant was immersed in latex, a layer of rubber coagulum was formed immediately, and then, the coagulant ions had to diffuse into the latex to form more coagulum.⁶ The same

trend was seen for the NR latex compound and pre-vulcanized latex compound. The deposit thickness was found to be slightly higher for that of the pre-vulcanized latex compound. This may have been caused by the higher total solids content of the pre-vulcanized compound used.

Figure 3 shows the effect of dwell time on the thickness of the deposit for the viscosity-modified compound. The deposit thickness obtained with viscosity-modified latex was higher than with the unmodified latex compound. This was because a higher volume of wet latex was retained up on the former, and hence, the thickness of the dried deposit was greater.^{4,7}

Figure 4 shows the variation of thickness with dwell time for the ammonium-caseinate-modified latex compound. The deposit thickness decreased from 0.240 to 0.155 mm for RVNRL of 60 mPa viscosity and from 0.250 to 0.150 mm for the NR latex compound with same viscosity. This behavior was different from that of sodium-carboxymethyl-cellulose-modified compounds. It was proposed by Blackley, Burgar, and Shukri that the deposit that forms in a coagulant dip consists of two distinctive regions, an inner region that comprises a strong coherent gel and an outer regions that comprises a nongelled but rather viscous la-

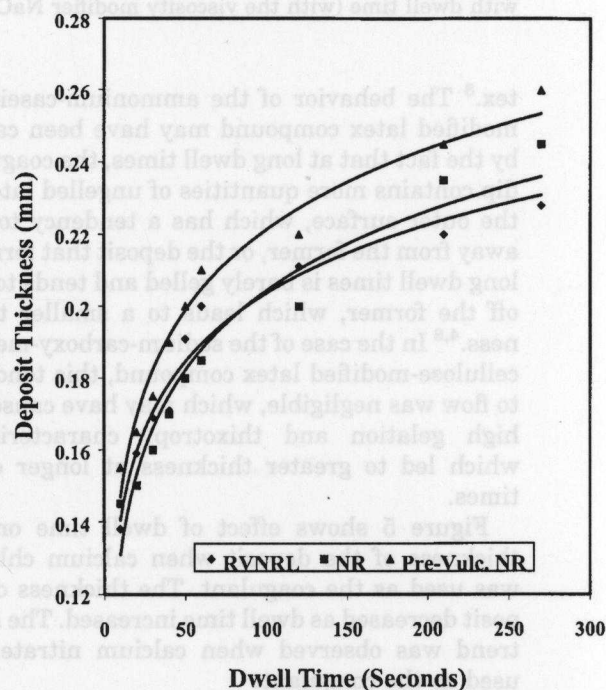


Figure 2 Variation of the thickness of the deposit with dwell time.

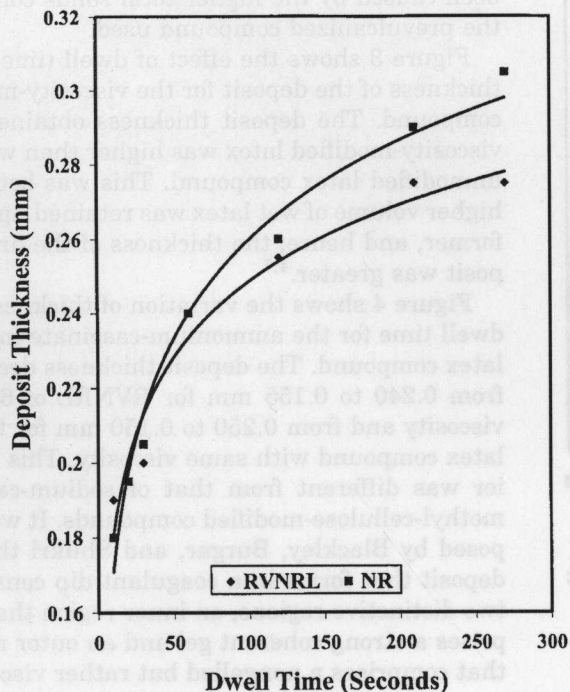


Figure 3 Variation of the thickness of the deposit with dwell time (with the viscosity modifier NaCMC).

tex.⁸ The behavior of the ammonium-caseinate-modified latex compound may have been caused by the fact that at long dwell times, the coagulant dip contains more quantities of ungelled latex on the outer surface, which has a tendency to flow away from the former, or the deposit that forms at long dwell times is barely gelled and tends to flow off the former, which leads to a smaller thickness.^{4,8} In the case of the sodium-carboxy-methyl-cellulose-modified latex compound, this tendency to flow was negligible, which may have caused by high gelation and thixotropy characteristics, which led to greater thickness at longer dwell times.

Figure 5 shows effect of dwell time on the thickness of the deposit when calcium chloride was used as the coagulant. The thickness of deposit decreased as dwell time increased. The same trend was observed when calcium nitrate was used as the coagulant.

Figure 6 shows the effect of the variation of dwell time and coagulant concentration. As the dwell time increased, there was an increase in the deposit thickness, and as the concentration of the coagulant increased, the deposit thickness increased. This may have been caused by the fact that as the concentration of the coagulant in-

creased, the amount of coagulant on the former increased and, hence, the rate of diffusion was higher, which lead to a greater thickness.^{6,9}

The same trend was shown by the NR latex compound (Fig. 7). In the case of the prevulcanized latex compound, an increased concentration of coagulant created slippage of the deposit during withdrawal.

Figure 8 shows the effect of the variation of the rate of withdrawal in latex compounds on thickness of the deposit. As the rate of withdrawal increased, the deposit thickness increased. This increase in thickness was almost constant over the entire range of withdrawal speeds that were studied. As the withdrawal speed of the former from the latex compound increased, the time obtained to drain away the latex picked up on the former decreased, which resulted in a greater thickness for the deposit. This was consistent with the report given by T. D. Pendle.⁷

Figure 9 shows the effect of the variation of the immersion and withdrawal speeds on thickness of the deposit formed for latex compounds. As the withdrawal and immersion speeds increased, the deposit thickness increased. This may have been caused by the lesser drainage of the latex compound from the former.

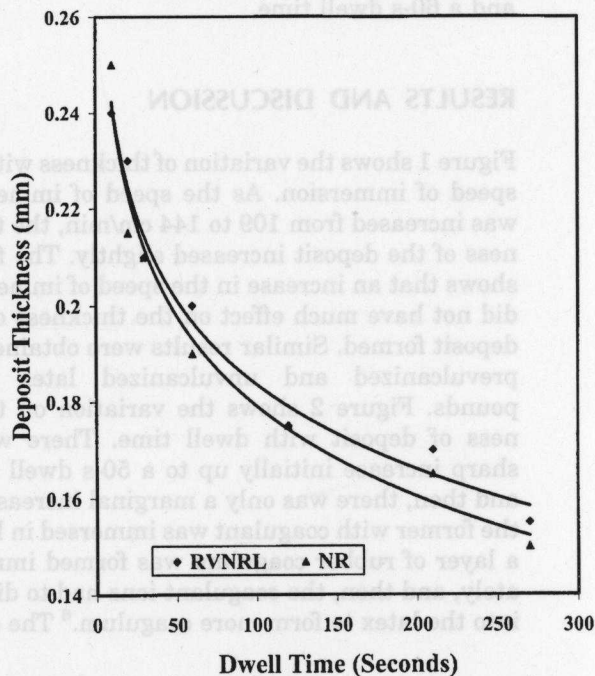


Figure 4 Variation of the thickness of the deposit with dwell time (with the viscosity modifier ammonium caseinate).

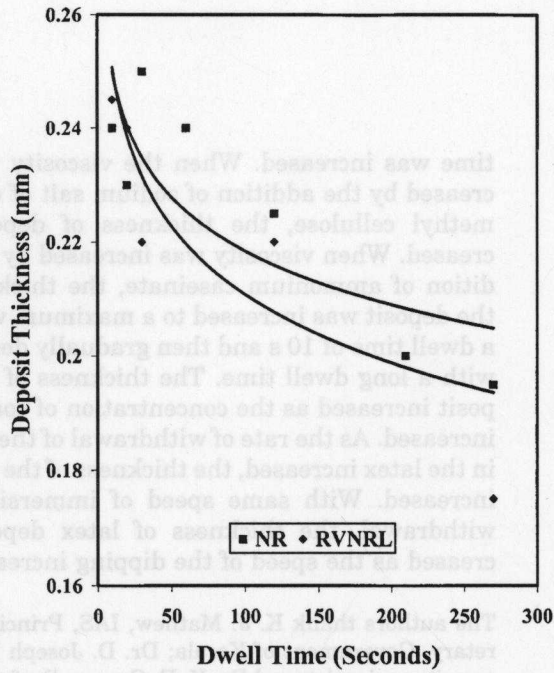


Figure 5 Variation of the thickness of the deposit with dwell time (with the viscosity modifier ammonium caseinate and the coagulant calcium chloride).

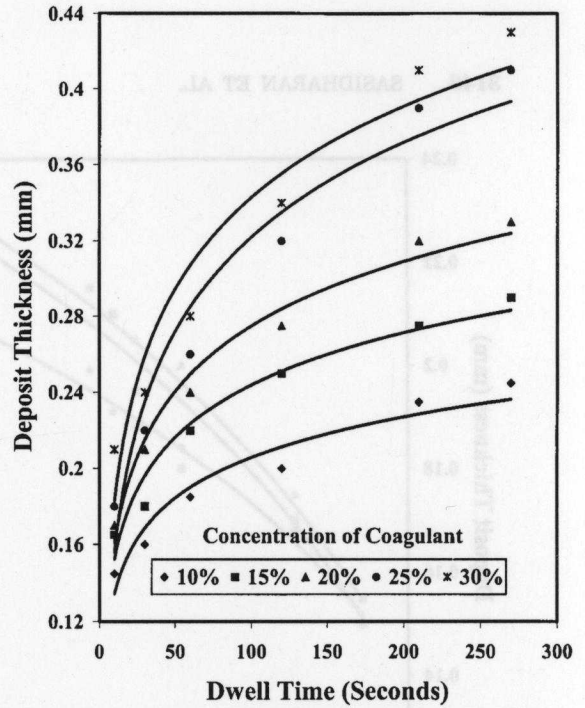


Figure 7 Variation of the thickness of the deposit with the concentration of coagulant and dwell time in NR latex compounds.

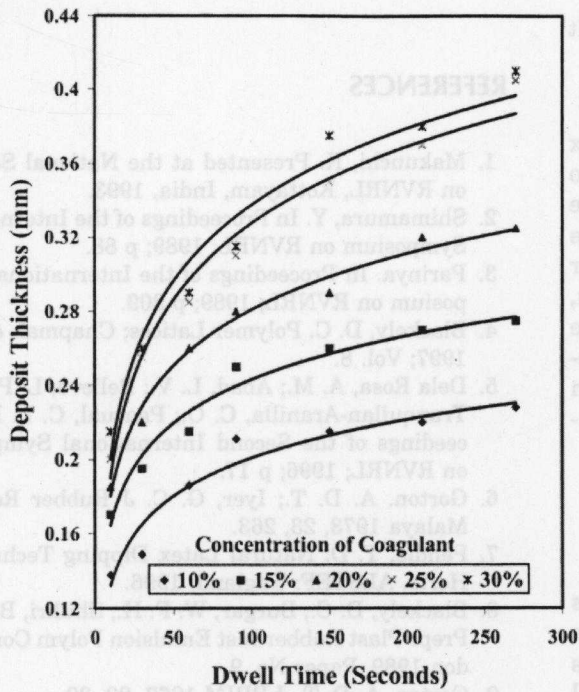


Figure 6 Variation of the thickness of the deposit with concentration of coagulant and dwell time in RVNRL.

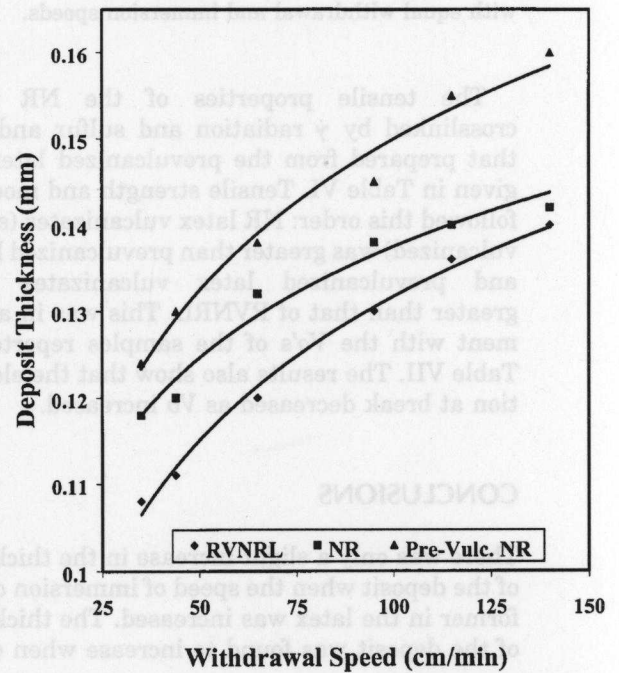


Figure 8 Variation of the thickness of the deposit with withdrawal speed.

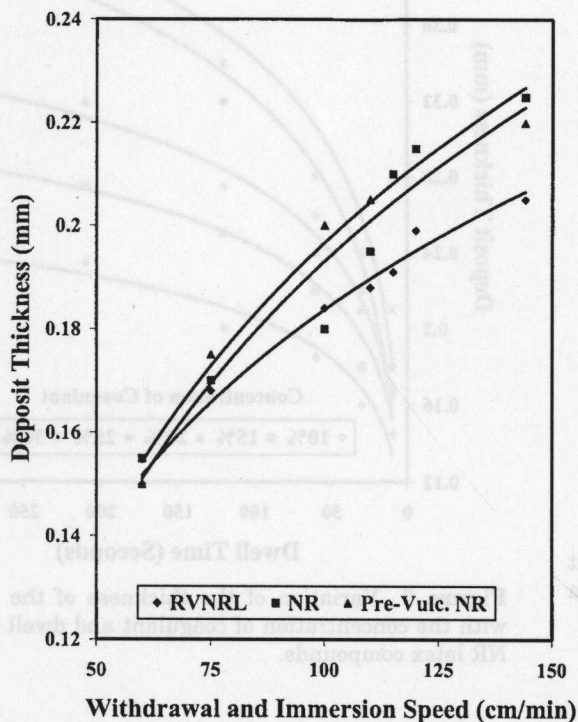


Figure 9 Variation of the thickness of the deposit with equal withdrawal and immersion speeds.

The tensile properties of the NR latex crosslinked by γ radiation and sulfur and also that prepared from the prevulcanized latex are given in Table VI. Tensile strength and modulus followed this order: NR latex vulcanizates (sulfur vulcanized) was greater than prevulcanized latex, and prevulcanized latex vulcanizates were greater than that of RVNRL. This was in agreement with the V_o 's of the samples reported in Table VII. The results also show that the elongation at break decreased as V_o increased.

CONCLUSIONS

There was only a slight increase in the thickness of the deposit when the speed of immersion of the former in the latex was increased. The thickness of the deposit was found to increase when dwell

time was increased. When the viscosity was increased by the addition of sodium salt of carboxy methyl cellulose, the thickness of deposit increased. When viscosity was increased by the addition of ammonium caseinate, the thickness of the deposit was increased to a maximum value at a dwell time of 10 s and then gradually decreased with a long dwell time. The thickness of the deposit increased as the concentration of coagulant increased. As the rate of withdrawal of the former in the latex increased, the thickness of the deposit increased. With same speed of immersion and withdrawal, the thickness of latex deposit increased as the speed of the dipping increased.

The authors thank K. J. Mathew, IAS, Principal Secretary, Government of Kerala; Dr. D. Joseph Francis, emeritus scientist; and Dr. K. E. George, Professor and Head, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi, for their invaluable help. The authors also thank Georgie Mathew, Kottayam; Anil Kumar; and S. K. Devidhathan, RRII, for their invaluable help with our work.

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