RADIATION RESPONSE OF PHILIPPINE NATURAL RUBBER LATEX

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Abstract

Our earlier work has shown that the natural rubber latex (NRL) produced and processed in the Philippines is suited for radiation vulcanization. The cast films from NRL with 50% TSC exhibited maximum tensile strengths of 25 - 32 MPa at 15 kGy, which is the vulcanization dose or Dv. In the manufacture of dipped NRL products, certain specifications such as %TSC, protein content, and tensile properties must be met to ensure an acceptable product. For radiation vulcanization of natural rubber latex (RVNRL) to be accepted as an alternative process, it must also meet the requirements. Thus, this paper presents additional data on the radiation response of local NRL at different total solids content (TSC), leachable proteins from NRL films as a function of dose, and the thermal activities of irradiated natural rubber latex (INRL). Different formulations of NRL showed varying tolerances to nBA. Data showed that as %TSC increases, the maximum concentration of nBA that can be added without affecting the stability of the latex decreases. The Dv increases as the %TSC increases and the nBA content decreases. This difference in response may be attributed primarily to a lower concentration of nBA in formulations with higher %TSC. These data indicate that the parameters in the radiation treatment will be dictated by the intended applications of INRL. The thermogravimetric data showed greater stability of INRL to thermal oxidation relative to the unirradiated NRL, which correlate directly with the tensile properties of the INRL. A radiation dose of 10 kGy increased the amount of proteins leached from cast latex films. The amount of extractable proteins did not increase significantly at higher doses. The SDS PAGE analysis of the extractable proteins from unirradiated latex film showed distinct bands. An additional band at 60 Kda appeared at 10 kGy. All these bands became diffuse at higher doses indicating the radiolysis of the proteins.

INTRODUCTION

Radiation vulcanization of natural rubber latex (RVNRL) offers a potential alternative to the conventional process of sulfur vulcanization. RVNRL involves the radiation-induced crosslinking of rubber molecules. Developments to improve the radiation process and the properties of the radiation vulcanized natural rubber latex (NRL) have been reported (1-5).

Our earlier work has shown that Philippine produced-latices are suited for radiation vulcanization (6). The cast films from NRL with 50% TSC and mixed with 5 phr of the sensitizer, n-butyl acrylate (nBA) exhibited maximum tensile strengths of 25-32 MPa at 15 kGy.

The irradiated NRL was stable during the experimental period of 12 months having physico-mechanical properties within values acceptable to the latex industry.

This paper presents additional studies to further characterize the radiation response of Philippine NRL as affected by factors of importance to the dipped products industry. These parameters are total solids content, viscosity, thermal stability and extractable proteins.

MATERIALS AND METHODS

Philippine high ammonia concentrated latex obtained from a local rubber processor (JCA) with the following properties was used for the study: TSC = 63.2%, DRC = 62.42%, MST = 1,102 sec., pH = 10.14 and Green strength = 5.014 MPa.

A. Irradiation of NRL Samples

NRL was diluted to varying TSC (52%-60%) with NH_4OH and mixed with 0.2 phr KOH and n-BA (1, 2, 3, 4, 5, 6 phr) as sensitizer. Irradiation of the NRL was carried out at the PNRI ^{60}Co Irradiation Facility for different radiation doses (0, 10, 15, 20, 25, 30, 35, 40, 45 kGy) at a dose rate of 2.57 kGy/hr.

B. Preparation of cast NRL Films

Twenty five (25) ml of NRL was cast unto a glass plate (19cm x 13cm) to make a film of 0.4 - 0.6 mm thickness. The film was removed from the glass plate, air-dried and leached in 1% NH_4OH overnight. It was then washed with tap water, air-dried for 24 hours and cured at 70 °C for two hours.

C. Physico-mechanical Properties of NRL

Viscosity measurements were done on NRL using a Brookfield viscometer (Model DV-II, spindle # 14) at 60 rpm and at room temperature. NRL films were cut into dumbbell pieces and their tensile strengths measured using the Instron testing machine (Model 1011). Thermal analysis of the NRL films were performed using the Shimadzu TGA-50 thermogravimetric analyzer.

D. Protein Analysis of Extractable Proteins from NRL films

Around 8 grams of NRL films were cut into small pieces and leached in 100 ml of 1 % NH_4OH overnight. The protein content from leachates was determined using bicinchioninic acid (BCA) assay method with an incubation time of 1 hour at room temperature (7).

The proteins from 1 ml of the leachate was precipitated with saturated $(NH_4)_2SO_4$ centrifuged, re-dissolved in a 0.2 ml of water and added with 0.5 ml of absolute ethanol to precipitate out any excess $(NH_4)_2SO_4$. The solution was evaporated to dryness using a water bath. The sample was then analyzed by sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) using the standard Laemmli method for gel electrophoresis. The separating gel used was at 11 % with 4% of stacking gel. The proteins were initially electrophoresed at 25 mA up to the end of the run. Staining was done using the silverstein method (8).

RESULTS AND DISCUSSION

A. Radiation Response of Different NRL Formulations

The dipped products industry requires different formulations of the NRL depending on the applications. In radiation vulcanization, different formulations for NRL are achieved by varying the total solids content (% TSC) and the concentration of the sensitizer. The vulcanization dose, Dv, which is the absorbed radiation dose required for maximum tensile strength, was studied for each formulation of Philippine latex.

Since nBA affects the stability of the latex, the maximum concentration of the sensitizer that can be added to each formulation without causing coagulation of the latex was first established. As shown in Table I, NRL with higher % TSC is stable with lower concentration of nBA. Thus, NRL with 60% TSC can only be mixed with $\leq$ 1 phr of nBA to remain stable while NRL with 52% TSC can tolerate 5 phr nBA.

The radiation response of NRL at different formulations is shown in Table I and Figure 1. The Dv increases as the % TSC increases and the nBA concentration decreases. Generally, the vulcanization rate increases with increasing rubber content (9). This effect is overshadowed by the sensitizing effect of nBA. NRL with 52% TSC and 5 phr nBA requires a lower radiation dose for maximum tensile strength than one with 60% TSC and 1 phr nBA.

B. Effect of n-BA Concentration on Viscosity of NRL at Different Radiation Dose

An increase in nBA concentration somehow increases the viscosity of NRL (1). The present study confirms this earlier observation as shown in Figure 2. The viscosity of the unirradiated NRL (52% TSC) increases slightly upon addition of 1 to 4 phr nBA. A marked

Table I. Radiation Response of Different NRL Formulations

% TSC	Maximum nBA Concentration ,phr	Dv, kGy	Maximum Tb, MPA
52%	5	15	33
54%	4	25	33
56%	3	35	35
58%	2	45	30
60%	1	>50	25 (at 50kGy)

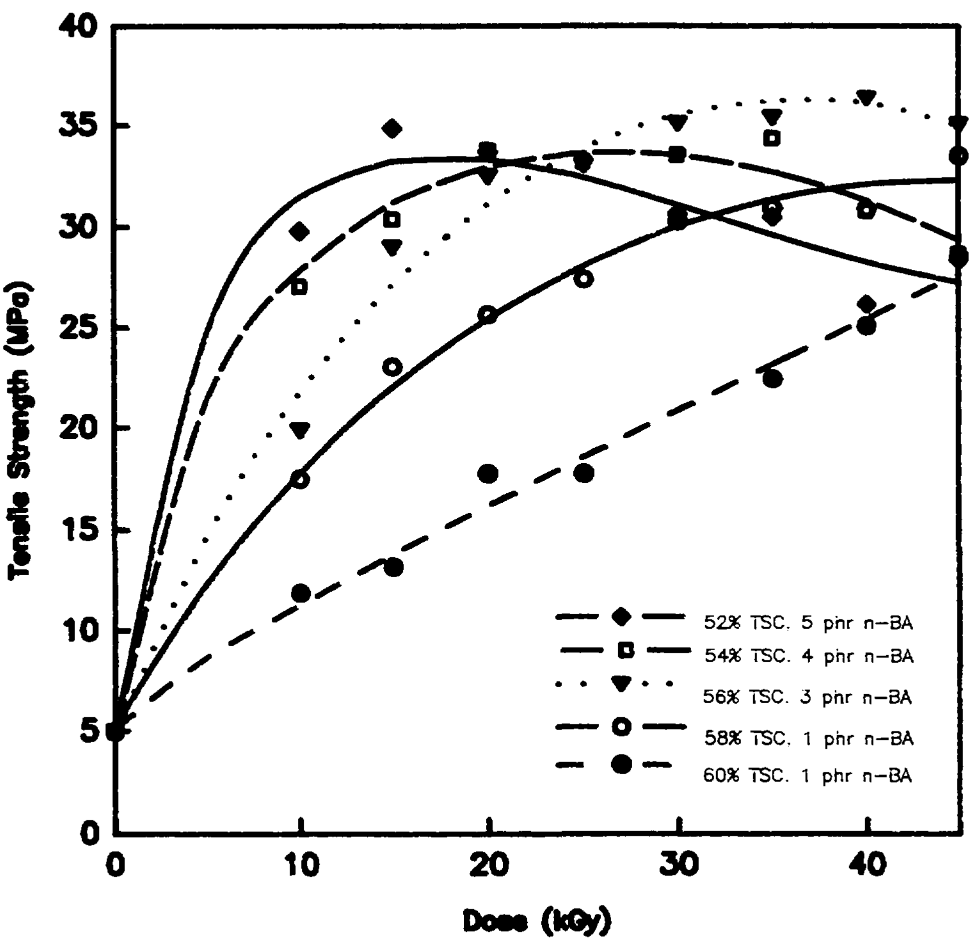

Fig.1. Dose Response Curve of RVNRL at Different TSC and n-BA Concentrations

increase in viscosity was observed upon addition of 5 to 6 phr nBA. The viscosity of NRL with 3 to 6 phr nBA increased tremendously upon storage for 14 days. Under the basic conditions of present latex formulations, nBA hydrolyzes to acrylic acid and butanol which exert destabilizing effect on the latex (10). For maximum stability of the latex, it should therefore be irradiated within hours upon addition of nBA.

Irradiated NRL contains residual nBA which decreases exponentially with dose. About 90% and 40% of original nBA has been found to remain in the latex after a radiation dose of 5 and 20 kGy respectively (10). The decrease in residual nBA was correlated with a a corresponding increase in tensile strength. The data in the present study indicate the effect of the residual nBA on the viscosity of the NRL. Figure 3 shows the effect of nBA concentration on the viscosity of NRL (52% TSC) at different radiation doses. With 1 phr nBA, the viscostiy remains the same. At all radiation doses, with 2 phr nBA, the viscosity slightly increases at 5 and 10 kGy, then decreases and remains constant at 15 kGy and higher doses. With 3 to 6 phr nBA, the

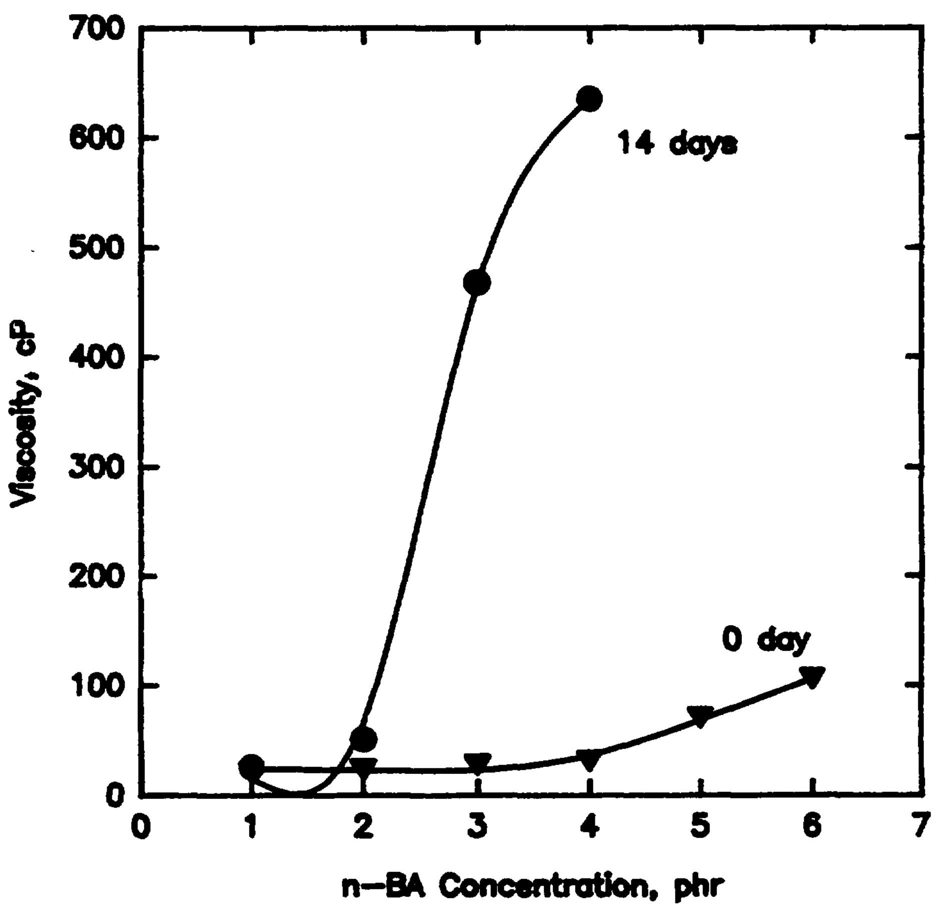

Figure 2. Effect of Storage on the Viscosity of Unirradiated NRL with Different n—BA Concentrations

viscosity increased significantly at 5 - 15 kGy, then decreases to a constant value at higher doses. The constant viscosity values obtained at higher doses increased as the original nBA concentration increased. The data indicate that the residual nBA in the latex emulsion after irradiation causes an increase in viscosity, and this increase is dependent on the concentration of the residual nBA using the data of Chunlei and co-workers (10). The concentration of residual nBA could be approximated. A concentration of 1 -1.5 phr of residual nBA would not affect the viscosity of the latex. As shown in Table II, the maximum tensile strengths were not affected by increases in viscosities and residual nBA (Fig. 3).

Table III presents the thermal activities of INRL at different doses. The thermogravimetric data indicate greater stability of INRL to thermal oxidation relative to the unirradiated NRL. The TGA curves of the INRL was shifted to higher temperatures. The onset of degradation, the temperature at 10% mass loss and at constant mass loss all occur at higher temperatures for INRL relative to the control samples. The thermogravimetric data indicate greater stability of INRL.

Table II. Dose Response of NRL with Different nBA Concentration

nBA Concentration (phr)	Tensile Strength, MPa						
	Radiation Dose, kGy						
	5	10	15	20	30	40	50
1	15.08	16.50	21.06	23.16	26.25	25.06	29.51
2	14.76	21.61	24.90	25.39	29.45	31.51	31.99
3	19.37	22.52	30.19	31.84	33.22	32.35	32.35
4	20.82	26.67	29.72	32.57	30.37	32.27	29.28
5	22.87	28.19	33.07	33.44	30.33	27.99	24.61
6	25.25	31.26	30.13	29.21	26.72	25.38	23.11

Table III. Thermal Activities of NRL at Different Radiation Doses

Parameters	Radiation Dose, kGy					
	0	5	10	15	20	30
Temperature (°C) at Initial Mass Loss	276.74	309.18	285.71	311.224	275.510	292.86
Temperature (°C) at 10% Mass Loss	337.96	346.939	354.082	356.122	353.061	356.122
Temperature (°C) at Constant Mass Loss	368.89	373.84	371.66	369.78	377.11	377.83
% Mass Left at 500 °C	6.89	1.02	8.51	6.16	6.31	6.26

C. Extractable Proteins from NRL Films

The total protein content of latex is approximately 1% of which 20% is adsorbed in the rubber phase, 20% is associated with the bottom fraction and the rest are dissolved in the serum which are the water soluble fraction (11). These water soluble (extractable) proteins are considered to be the primary source of latex allergy, a kind of Type I allergy. Irradiation of NRL increases the water soluble proteins as shown in Figure 4. At dose 10 kGy, the amount of proteins leached from the latex films increased significantly from 2 to 9 mg/g latex film. As observed by other workers, radiation increased the leachability of latex films (12). There is no significant change in the leachability of proteins with increasing radiation dose. The increased leachability of proteins in RVNRL is of great importance as it would result in lower protein content of the dipped rubber products, thus less allergic reactions to sensitive users.

SDS PAGE analysis of these leachable proteins are shown in Figure 5. At 0 kGy, 2 distinct bands with molecular weights of 68 and 45 Kda were observed. Other bands were also

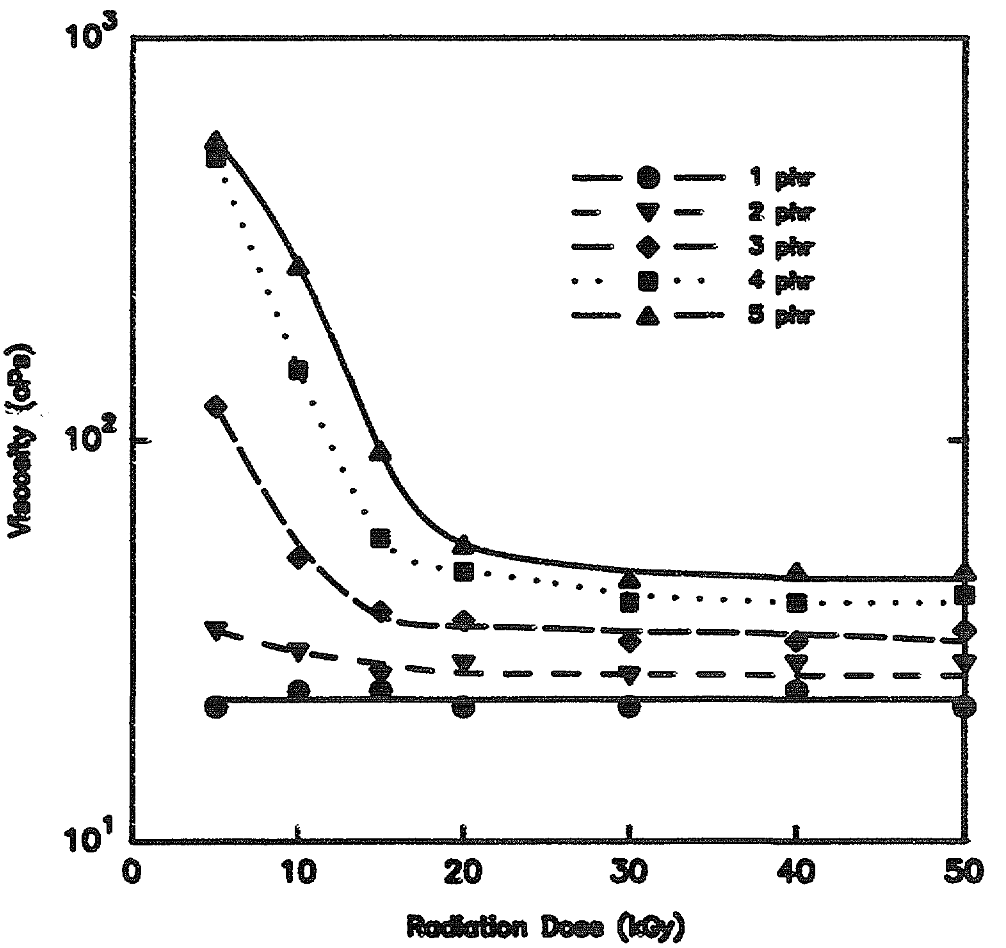

Fig. 3 The Effect of n–BA Concentration on the Viscosity of NRL at Diffrent Radiation Doses

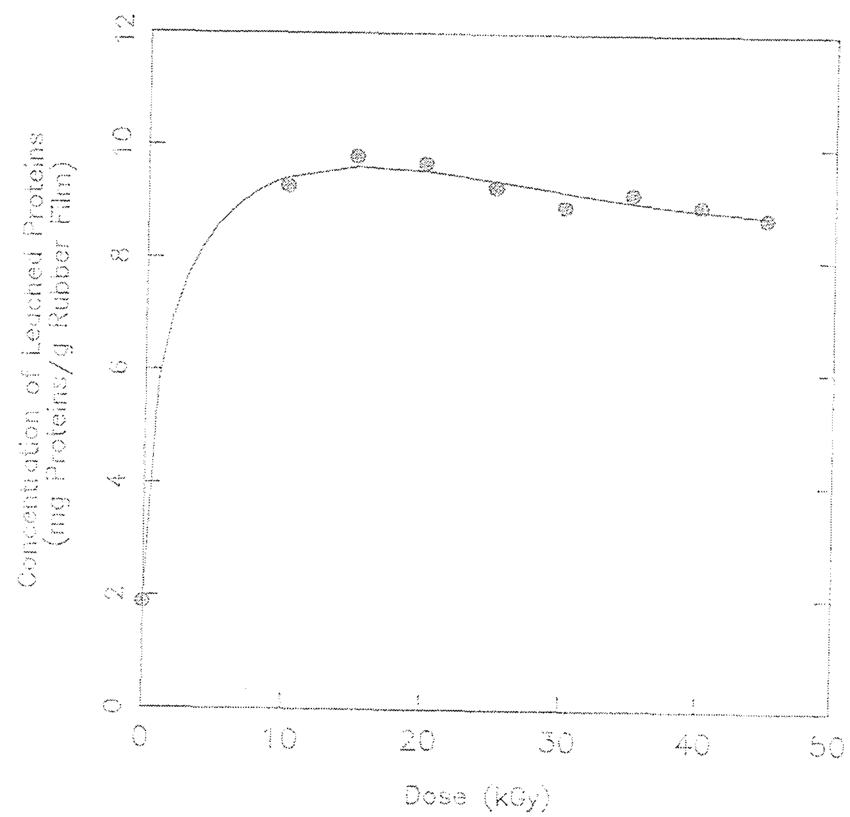

Fig. 4. The Effect of Dose on the Leachable Proteins of RVNRL

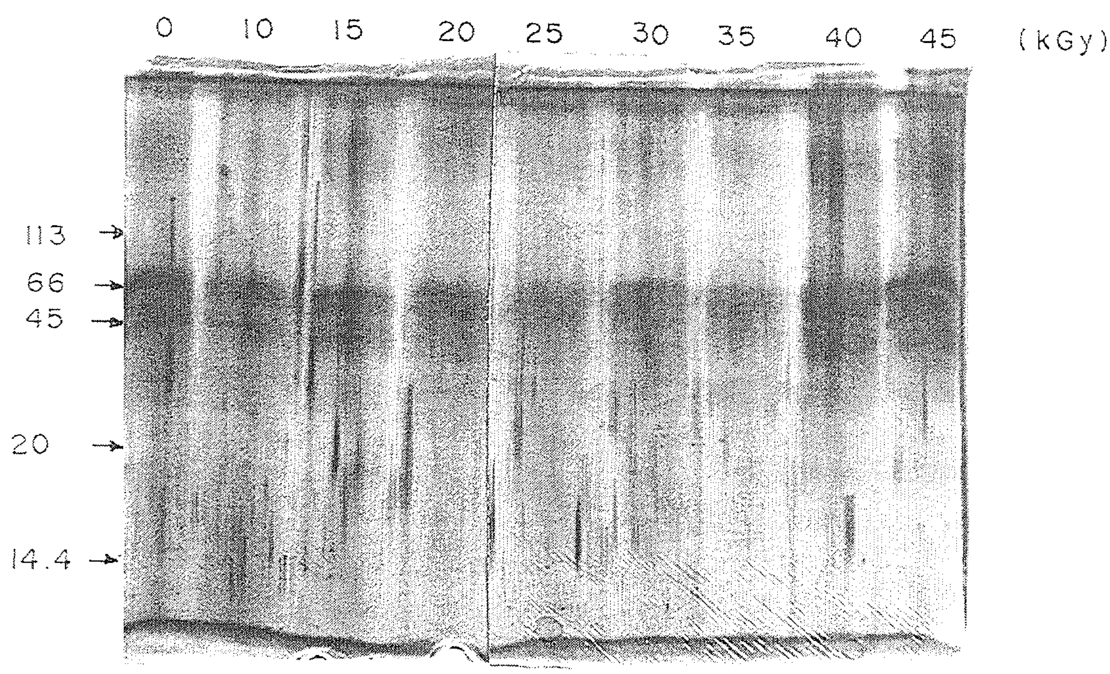

Fig. 5 SDS–PAGE Electrophoresis of Leachable Proteins

present but unclear. An additional band of 60 Kda appeared at 10 kGy which became more prominent at 15 kGy. The appearance of this band only indicates that gamma radiation facilitates the degradation of proteins in NRL resulting in the formation of new water soluble proteins. Higher doses of 20 kGy and above indicated tailing effects of the bands. Molecular weights of the proteins were no longer decipherable. This effect became more pronounced at higher doses of 40 and 45 kGy. This again would indicate effects of protein radiolysis especially at higher doses.

CONCLUSION

Philippine NRL like any other latex is greatly affected by the concentration of n-BA. NRL with different %TSC require varying concentrations of n-BA to maintain its stability while achieving the required tensile strength after irradiation. Residual n-BA can be directly correlated with the increase in viscosity. Thermal gravimetric data indicate greater resistance of INRL to thermal oxidation as compared to non-irradiated NRL. Irradiation increases the leachability of the water soluble proteins both in quantity and the type of proteins.

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