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PREPARATION OF HIGHLY STABILISED NATURAL RUBBER LATEX FOR RADIATION VULCANISATION

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ABSTRACT

There is a bright future for radiation vulcanised natural rubber latex (RVNRL) but there are problems in manufacturing it as the centrifuged latex to be used for radiation has to be kept for at least a month or sometimes even three to six months before adding the sensitisers and even then the latex sometimes coagulates on adding the sensitisers.

This paper describes a process by which the latex can be stabilised by addition of an anionic soap before centrifuging so that it has a high mechanical stability and hence can be used even within one week of the manufacture of the centrifuged latex.

INTRODUCTION

At present it is not possible to use any centrifuged latex available in the market and produce RVNRL having consistent and acceptable physical properties in the films made from it. Hence it appears very necessary to change the process of manufacture of centrifuged latex so that consistent and acceptable physical properties such modulus at 300%, tensile strength and elongation at break are obtained from it.

Normal centrifuged latex has to be matured for at least 3 to 4 weeks before using it to make latex based products using conventional sulphur vulcanisation. For radiation vulcanisation, it has been reported that stabilised natural rubber (NR) latex between 3 to 6 months after production should be used for radiation vulcanisation. This very long storage of latex is a serious disadvantage for the commercial implementation of radiation vulcanisation of natural rubber latex.

This paper describes the preparation of special types of centrifuged natural rubber latex which can be used even a few days after manufacture, has a very much higher stability than the normal centrifuged latex available in the market, is stable after adding 1,6-hexanediol diacrylate(A-HD) and/or n-butyl acrylate (n-BA) or carbon tetrachloride (CCl_4) addition, is stable after radiation vulcanisation.

EXPERIMENTAL

Material

Field latex was received from Rubber Research Institute of Sri Lanka. Technical grade n-BA, A-HD, CCl_4, and ammonia were used. Industrial grade lauric acid, zinc oxide (ZnO), sodium di ethyl carbonate (SDEC) and DAHP were used. All chemical were supplied by the established companies in the country and used without further purification.

The gamma cell installed at University of Colombo was used. The activity of Co-60 was 2900ci and dose rate was 0.6 Mrad/h.

Preparation of centrifuged latices:

a. Preparation of highly stable LA-TZ: (HS-LATZ)

The field latex was treated with 0.35% ammonia, with the required amount of DAHP, with 0.025% tetramethyl thiuram disulphide (TMTD)/ZnO (1:1) and with ammonium laurate at 0.2% on latex. The latex was allowed to stand for 48 hr and 0.025% TMTD/ZnO (1:1) added.

b. Preparation of highly stable LA-SZ: (HS-LASZ)

The field latex was treated with 0.35% ammonia, with the required amount of DAHP, with Zno at 0.01% and with sodium diethyl dithiocarbanate (SDEC) at 0.05% on latex and with ammonium laurate at 0.2% on latex. The latex was allowed to stand for 48 hr and centrifuged, the ammonia content brought up to 0.2% and ZnO at 0.01% on latex and SDEC at 0.05% on latex added.

c. Preparation of highly stable HASZ: (HS-HASZ)

This latex is the same as No.(b) but having an ammonia content of 0.7% instead of 0.2%.

d. Preparation of LA-TZ:

Commercially available low ammonia centrifuged latices were used.(LATZ(1) & LATZ(2))

The latices were used after diluting with distilled water to rubber content of 50%. The sensitisers were added neat.

Irradiation

Measured weights of the sensitiser were added to weighed amounts of NR latex and mixed with a magnetic stirrer for 20 minutes. The mixture then kept standing for over night at room temperature. About 50-100 ml of the mixture was irradiated in a glass bottle with a screw cap in an environment of air.

The irradiated latices were dried on glass plates at room temperature for about 3 days till the films were clear. The films were leached in distilled water for 24 h. Then the films were dried in air till the films were clear and were then dried further at 80 C for 1 h. The tensile properties of the films were measured. The crosslinking density was measured after the specimens were immersed in toluene at room temperature for 24 h.

Stability of the various latices after adding sensitisers

A combination of 2.5 phr n-BA and 2.5 phr A-HD were added to the various latices (50% drc) given in Table 1 in neat form. Observations on the stability of the latices after adding the sensitisers, after radiation and details of film are given in Table 2.

Table 1: Properties of centrifuged latices used.

Type of latex	Total solids %	Dry rubber content %	MST in sec.	Ammonia content %	Viscosity	pH
HS-LASZ	63.2	62.0	>1200	0.17	40.0	9.6
HS-HASZ	62.5	62.1	>1800	1.0	37.5	10.2
HS-LATZ	60.6	61.7	>1700	0.22	42.5	9.6
LATZ(1)	61.6	59.7	920	0.20	32.5	9.70
LATZ(2)	59.3	60.2	150	0.20	10.5	9.8

Table 2: Effect of adding sensitisers in latex (2.5 phr n-BA + 2.5 phr A-HD added neat)

Type of Latex	Stability of latex after 18 h of sensitiser addition	Stability of latex after irradiation	Film appearance		
			Drying	Clarity	Transparency
LATZ(1)	gives clumps on stirrer	-	-	-	-
*LATZ(1)	stable	stable for 21 days	bad	bad	bad
LATZ(2)	gives clumps on stirrer	-	-	-	-
*LATZ(2)	stable	stable for 21 days	slow	good	good
HS-LATZ	stable	stable for 40 days	fast	good	good
**HS-HASZ	stable	stable for 21 days	fast	good	good
HS-LASZ	stable	stable for 40 days	fast	good	excellent

*After adding 0.35% potasium laurate

**Latex diluted and irradiated

RESULTS & DISCUSSION

The properties of the centrifuged latices used by us are given in Table 01. It can be noted that LATZ (2) has a very low MST, whilst all the highly stabilised latices have a very high stability.

Table 02 shows the effect of adding sensitisers in latex. Of the five latices tested, four were low ammonia and one was high ammonia and it is HASZ. Only the high ammonia latex gives thickening. An explanation of this may be as follows.

It is known that the higher pH of high ammonia latex will cause more hydrolysis of the lipids and proteins than the lower pH of low ammonia latex. The KOH no is a measure of breakdown of lipids and proteins during storage. Thus if high NH_3 latex is stored for 3 months, it has been reported that KOH no. rises by 11 units. ie. from 0.47 to 0.58 whilst if LATZ latex is stored for three months, the KOH number rose by only 3 units. ie. from 0.49 to 0.56 (John et al 1976). When sensitiser is added to centrifuged latex it diffuses into the latex particle and swells it and it is the protein layer surrounding the latex particle which prevents the latex particles from coalescing and this protein layer must be kept intact to have a stable compound latex. Eventhough the MST of this latex is over 1800 (ie. it has enough soap in it) it was unstable on adding the sensitisers. In the case of LATZ latices though there was some instability by clumps forming on the stirrer on adding the sensitisers, this was corrected by adding potassium laurate.

The important observation of Table 3 is that HS-LASZ and HS-LATZ latices were more stable latices compared to others after irradiation and the drying was fast, the film clarity was good and transparency was good. Tensile strength of the films made from HS-LASZ & HS-LATZ latices were 27.4 Mpa and 30.6 Mpa at 1.4 Mrad with 2.5 phr A-HD & 2.5 phr n-BA as sensitisers respectively. Hence these latices we would recommend for use in RVNRL.

Table 3: Relationship between MST of latex and Tensile Strength of film at radiation dose 1.4 Mrad, Sensitiser dosage 2.5 phr A-HD & 2.5 phr n-BA.

Type of latex	MST in sec.	Crosslink density (no. of crosslinking moles per unit volume x 10^{-4})	Modulus 300% in MPa	TS in MPa
LATZ(1)	920	0.95	0.80	23.2
LATZ(2)	150	0.77	0.74	16.4
HS-LATZ	>1700	1.16	1.11	30.6
HS-LASZ	>1200	1.48	1.31	27.4
HS-HASZ	>1800	1.41	1.25	27.7

Table 3 shows the relationship between MST of latex and Tensile Strength of films at 1.4 Mrad, with 2.5 phr & 2.5 phr n-BA sensitiser system. The higher the MST of the latex the higher the stability of the compound latex and higher the tensile strength. It will be noted that LATZ(1) and LATZ(2) gave tensile strength below 25 Mpa whilst all the other highly stabilised latices gave a tensile strength of above 25 Mpa.

Table 4: MST of latices with sensitisers after 24 hr.

Type of latex	MST in Secs. 2.5 phr A-HD + 2.5 phr n-BA	MST in Secs. 1.5 phr A-HD + 2.5 phr n-BA + 0.5 phr CCl_4
HS-LA-TZ	501	782
HS-LA-SZ	695	592
HS-HA-SZ	coagulated	coagulated

The different latices with 2.5 phr n-BA and 2.5 phr A-HD and also with 2.5 phr n-BA, 1.5 phr A-HD and 0.5 phr CCl_4 were tested for MST after 24 hr after adding sensitisers. The results are given in Table 4. It confirms that HA latex even if highly stabilised is not suitable to add sensitisers in a neat form but LA latex if highly stabilised is suitable. Further the MST was done at 55% drc. Hence the modified LA latices can be irradiated at 55% drc instead of 50%drc.

A combination of 2.5 phr n-BA and 1.5 phr A-HD and 0.5 phr CCl_4 was added to highly stabilised LATZ latex: (HS-LATZ) and the results are given in table 05. It is seen that the addition of the 0.5 phr CCl_4 gives a better stability to the latex after addition and good drying properties even at very low radiation doses.

Table 5: Effect of adding sensitisers in HS-LATZ latex. (2.5 phr n-BA + 1.5 phr A-HD added neat)

Dose (Mrad)	Stability of latex after 18 h. of sensitiser addition	Stability of latex after irradiation	Drying	Clarity	Transparency
without CCl_4					
0.35	Stable	Stable for 21 days	good	good	excellent
0.7	Stable	Stable for 27 days	good	good	excellent
1.04	Stable	Stable for 30 days	good	good	excellent
1.4	Stable	Stable for more than 35 days	good	good	excellent
with 0.5 phr CCl_4					
0.35	Stable	Stable for more than 35 days	good	good	excellent
0.7	Stable	Stable for more than 35days	good	good	excellent
1.04	Stable	Stable for more than 35days	good	good	excellent
1.4	Stable	Stable for more than 35days	good	good	excellent

CONCLUSION

On improving the stability of the centrifuged latex so that it can be used to produced RVNRL even within a week of its manufacture.

Highly stabilised latices (HS-LATZ and HS-LASZ) are very stable after adding sensitisers in neat form to the latex and films made out of this HS latices have good physical properties specially tensile strength over 25 MPa.

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