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Effect of Compounding Characteristics on Heat Sensitization of PVME Blended Natural Rubber Latex Compound

Shera Mathew

Scientist (RT), Technical Consultancy Division, Kottayam, Kerala, India

Dr. Siby Varghese

Joint Director, Technical Consultancy Division, Kottayam, Kerala, India

Abstract:

This paper reports the results of a systematic investigation of the compounding characteristics which affect the heat-sensitization of natural rubber (NR) latex compound by polyvinyl methyl ether (PVME). Possible mechanisms for the heat-sensitization of aqueous latices by water soluble polymers such as PVME are outlined, and observations concerning the behavior of PVME in high ammonia natural rubber latex compound and the effects of pH, level of non-ionic stabilizer, zinc oxide and PVME upon heat-sensitization are reported and discussed. Results for the effects of the variables listed above upon the heat-sensitization being a consequence of PVME adsorbed at the surface of the rubber particles at the cloud point temperature of PVME.

Keywords: heat-sensitization, polyvinyl methyl ether, cloud point temperature, non-ionic stabilizer, adsorption

1. Introduction

Natural rubber latex obtained from latex vessels of rubber tree (*Hevea brasiliensis*) is called field latex, which is a colloidal dispersion of rubber particles in an aqueous medium. The concentrated latices prepared from preserved field latex by various concentration methods like centrifuging and creaming are used for different product manufacturing techniques such as dipping, casting, extrusion etc. The properties of rubber latex make it an extremely versatile raw material for dipping and moulding processes. The ability of the rubber particles to coalesce and produce a coherent polymer film that is impermeable to water and air makes latex suitable for an extremely wide variety of products.

Most of the latex products available are prepared by the dipping process. There are different methods of dipping such as straight dipping; coagulant dipping and heat sensitized dipping. Heat sensitized dipping involves immersing a hot former in to a suitably heat sensitized latex compound (Blackley, 1997, vol. 3). Heat sensitization of NR latex can be imparted by zinc amine ions and hydrophilic polymers. Poly vinyl methyl ether (PVME) is a hydrophilic polymer with a cloud point in the range of 32-34^oC (Blackley, vol. 3, 1997 and Vladimir et al., 2006).

Blackley, vol. 3, 1997 and Ben, 2003 have been reported that heat sensitized NR latex by PVME can be used for the manufacture of a variety of latex products such as dipped products like teats, baby soothers, meteorological balloons, foamed carpet backing, extruded latex tubing etc. The advantage of heat sensitized dipping compared to usual dipping technique is higher thickness in a single dip. This reduces the problems related to delamination and labour. In heat sensitized dipping the latex compound is formulated so as to be heat sensitive and a deposit is allowed to form around the former by dipping a hot former into the latex compound. The degree of heat sensitization can be estimated by measuring the gelling time or the thickness of the deposit in heat sensitized dipping (Blackley, 1997, vol. 3). The thickness of the dry deposit formed will depend on a number of compound characteristics such as pH of the latex compound, concentration of ZnO, concentration of PVME, nature and level of surfactants etc., (Calvet, 1982). The thickness of the dry deposit also depends upon the number of processing parameters such as rate of immersion, dwell time, temperature of the former, heat capacity of the former etc. (Shera Mathew and Siby Varghese, 2015).

The literature survey on heat-sensitization of NR latex by PVME reveals that publications giving detailed investigation about the effect of different compounding parameters on heat sensitization are very limited. This work has been undertaken to standardise the effect of few compound parameters such as dosage of non-ionic stabilizer, ZnO, PVME, pH of the latex compound on the heat sensitization of a typical natural rubber latex compound containing PVME.

2. Materials And Methods

2.1. Raw materials

The raw materials used were 60% centrifuged latex conforming to BIS 5430-1981, Vulcastab VL a non-ionic stabilizer manufactured by M/s Alkali & Chemical corporation of India Ltd., Calcutta, the molecular formula is given below in (Figure 1).

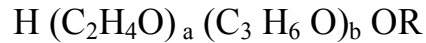


Figure 1: Vulcastab VL- Ethylene oxide and/or propylene oxide condensation product

Wherein R is selected from the group consisting of hydrogen and hydrocarbon chains having from 2 to 20 carbon atoms, 'a and b' are each from 0 to 35 and a+b is from 5 to 35.

Zinc dibutyl dithiocarbamate (ZDBC) an ultra-accelerator manufactured by M/s R.T. Vanderbilt Company Inc, USA, laboratory grade sulphur, ZnO and formaldehyde manufactured by EMERK Ltd, Mumbai and dispersing agent Dispersol F manufactured by M/s ICI Ltd., Calcutta. The base ingredient of this study poly vinyl methyl ether (PVME) was procured from M/s. BASF Ltd. Cheadle, UK. It was a water soluble synthetic polymer of the composition and its structure is given below

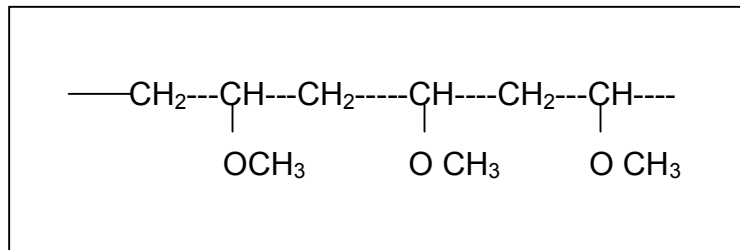


Figure 2: Chemical structure of PVME

2.2. Preparation of Latex Compounds

For preparing latex compound fifty per cent dispersion of sulphur, ZnO and ZDBC were prepared separately by grinding in a ball mill using Dispersol F as the dispersing agent. For the study a base latex compound was prepared. The prepared latex compound was kept for 24h maturation. Formulation of this compound is given in Table 1.

Sl.no	Ingredients	Parts by weight
		Dry, phr
1.	60% Centrifuged latex (HA)	100
2.	20% Vulcastab VL solution	0.25
3.	50% Sulphur dispersion	1
4.	50% ZnO dispersion	0.5
5.	50% ZDBC dispersion	1
6.	5% Formaldehyde solution	To pH 9.75
7.	10% PVME solution	0.5

Table 1: Formulation of the base latex compound used in the study

2.3. Experiment

For studying the effect of compound characteristics on the heat sensitization of natural rubber latex using PVME as sensitizer the following parameters were varied in matured latex compound prepared as discussed above. The different compounding ingredients were varied as given below and keeping others constant.

- Level of Vulcastab VL (0.25phr to 1.5 phr)
- Level of ZnO (0.5-1.5 phr)
- Level of PVME (0.5-2.5 phr)
- pH of the compound (8.5-9.75)

The processing parameters used for studying the compounding parameters were former temperature 100°C, dwell time 30sec and total solid content of the latex compound 50%. Heat sensitized dipping was carried out using steel formers. Thicknesses of the films were measured using digital micrometre. The effects of compounding parameters on heat sensitization were represented as graphs in (Figs 3 to 9).

3. Results and Discussion

Effect of compound characteristics on heat sensitization

The effect of varying the levels of vulcastab VL, ZnO, PVME on heat sensitization in terms of film thickness were given in (Figure3).

3.1. Level of Vulcastab VL

The effect of varying the level of vulcastab VL (Polyethylene oxide condensate) on heat sensitization (as measured by the thickness of dipped films) using latex compound was given in (Figure3).

It was seen that for the latex compounds the concentration of VL has got remarkable effect on heat sensitization. As the dosage of VL increased, thickness increased initially, reached a maximum and thereafter, decreased. Maximum thickness was obtained at a level of 0.75 phr.

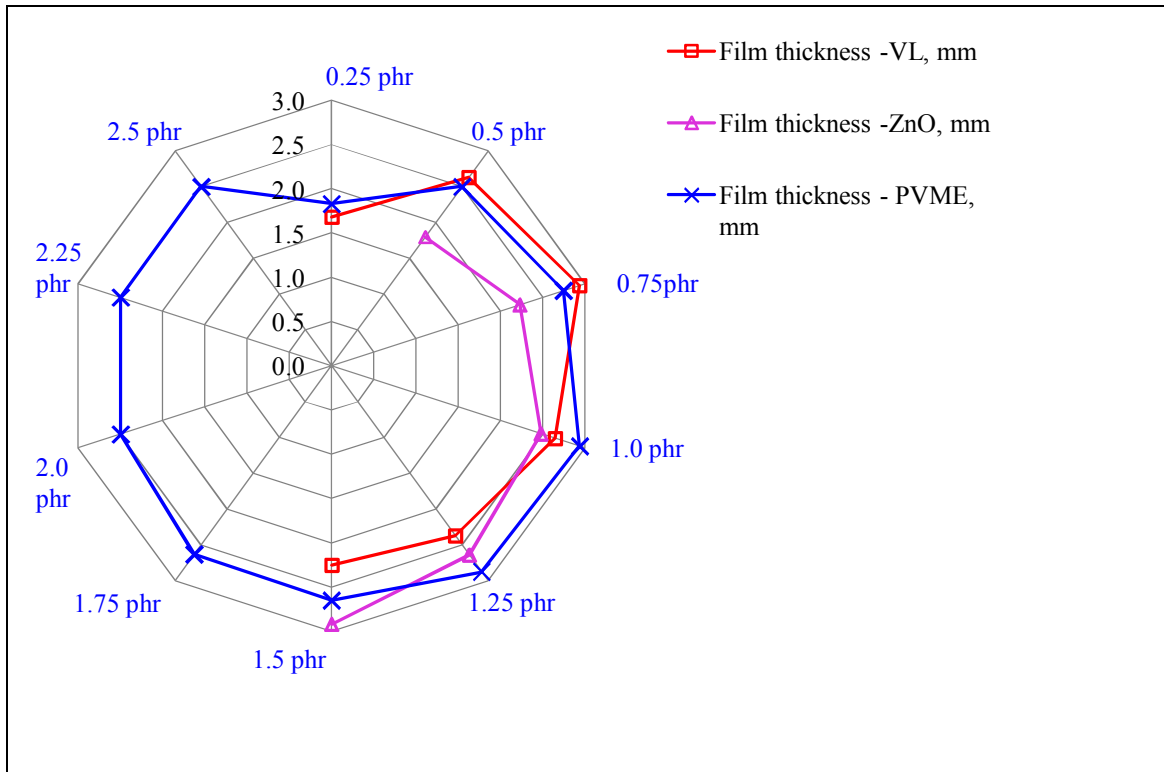


Figure 3: Effect of varying dosages of vulcastab VL, ZnO, PVME on thickness of latex film

Vulcastab VL is a non-ionogenic stabilizer and is less soluble in hot water than in cold water. Vulcastab VL complement to the heat sensitizing property because its solution gets turbid at higher temperature, its surface activity and the ability to confer fugitive colloid stability as the temperature is getting high. In natural rubber latex, any added surface active agent has to compete for the available surface with the naturally occurring surface active agent such as soaps and proteins (Blackley, 1997 vol 1; Gorton, 1972; Archer and Sekhar, 1955; Tata, 1980; Dennis and Light, 1989; Dennis *et.al*, 1989; Light and Dennis, 1989; Arreguin *et. al*, 1988). Only when sufficient quantity of VL was adsorbed on to the surface of the rubber particle, the heat sensitivity imparted by it becomes significant. The initial increase in heat sensitization as the level of VL increased may be due to this.

Hasma, 1992 and Portal *et.al*, 1992 reported one mechanism for heat sensitization in which it was suggested due to the adsorption of PVME in the latex particle surface. Very few adsorption sites may be required to anchor the PVME macromolecules to the surface of the rubber particles in sufficient numbers and to a sufficient extent to impart heat sensitivity (Blackley *et.al.*, 1990). Thus when sufficient VL was present to block these sites the heat sensitivity was reduced and reaches a minimum.

The viscosities of the latex compound containing different amounts of VL at different periods of storage at 25⁰C were given in ((Figure4).

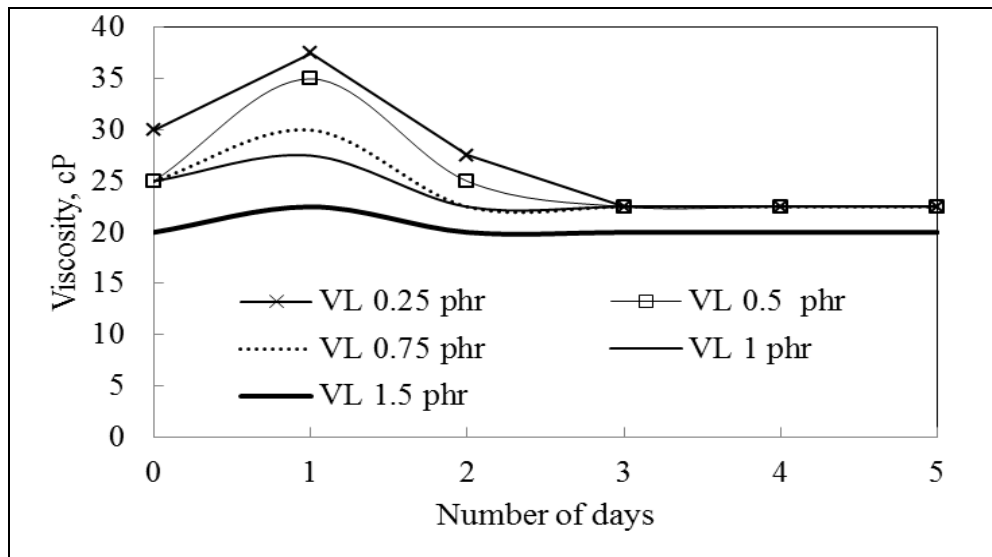


Figure 4: Viscosities of the latex compound containing different amounts of VL at different periods of storage at 25°C

It was seen that latex compounds with lower dosages of VL show marked changes in viscosity compared to latex compounds with higher amounts of VL. The stability of latex compound with 0.75 phr VL remained comparatively constant. The slight increase in viscosity during the initial stages may be due to the time required for displacing the stabilizers already present in the latex by VL. Once it was sufficiently adsorbed on rubber particle the stability of the latex does not change much with storage.

3.2. Level of ZnO

The effect of varying the level of ZnO on thickness of heat sensitized dipped films using latex compound was also given in (Figure3). It was seen that as the dosage of ZnO increases thickness also increases.

The result shows that the heat sensitivity of NR latex by PVME was very sensitive to the addition of ZnO present in a compound (Hasma, 1992). Zinc oxide reacts with ammonia to form zinc amine ions and the effect of zinc oxide may be due to the fact that these zinc ammine ion interact with surface bound carboxylate ions, thereby creating additional sites for the adsorption of PVME at the particle surface. In the latex compound the viscosity increases in the first two days (Figure5) then decreases and remain almost stable for a period of up to one week.

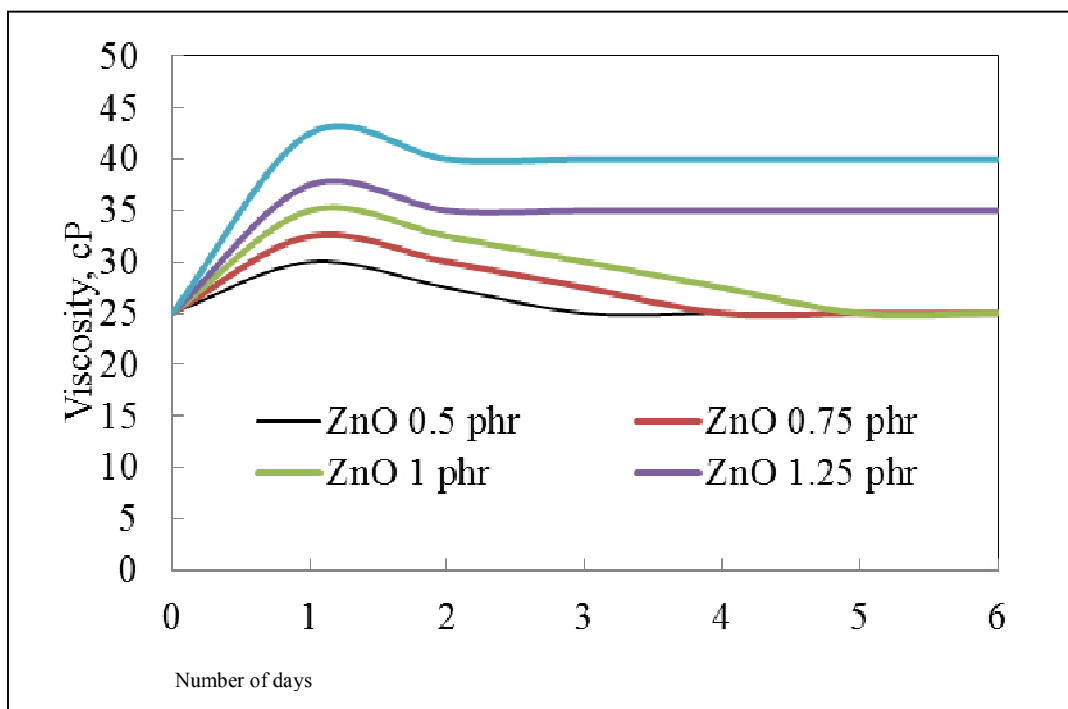


Figure 5: Viscosities of the latex compound containing different amounts of ZnO at different periods of storage at 25°C

3.3. Level of Poly Vinyl Methyl Ether (PVME)

From the (Fig.3), it can be seen that as the dosage of PVME increases thickness increases reaches a maximum and thereafter decreases. The maximum thickness of 2.94mm obtained at 1 phr PVME.

The result shows that only small amount of PVME (1-2phr) required to impart significant heat sensitivity to ammonia preserved natural rubber latex (Cockbain, 1956). The initial increase in thickness may be due to the fact that as the level of PVME increases, more PVME was adsorbed on the surface of the rubber particle but when sufficient amount capable of producing heat sensitivity has been adsorbed, further increase in PVME has no effect.

The effect of PVME on natural rubber in a latex compound are schematically represented in the ((Figure6) given below

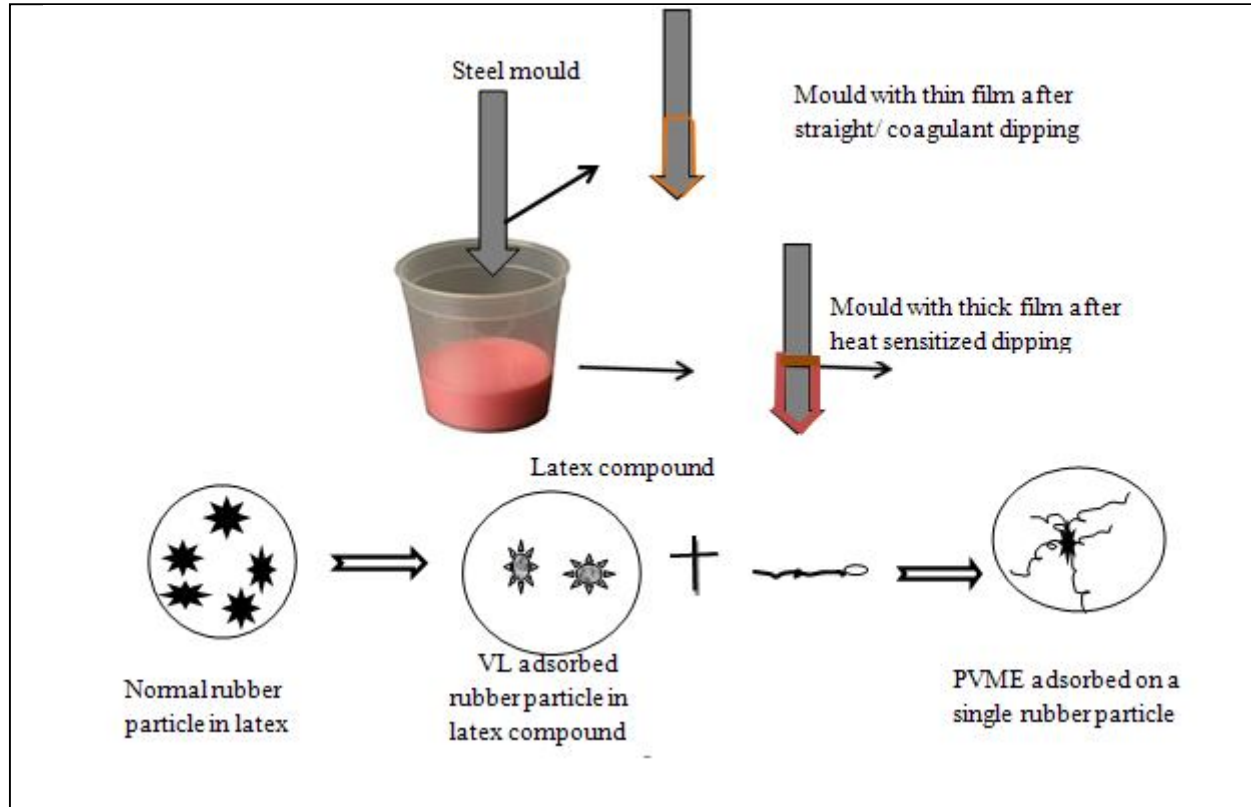


Figure 6: Schematic representation of the effect of PVME on a natural rubber particle in the latex compound

Viscosities of latex compound containing different amounts of PVME are plotted in (Fig.7). It was seen that as the level of PVME increases viscosity increases (Kuan and Sommer, 1981).

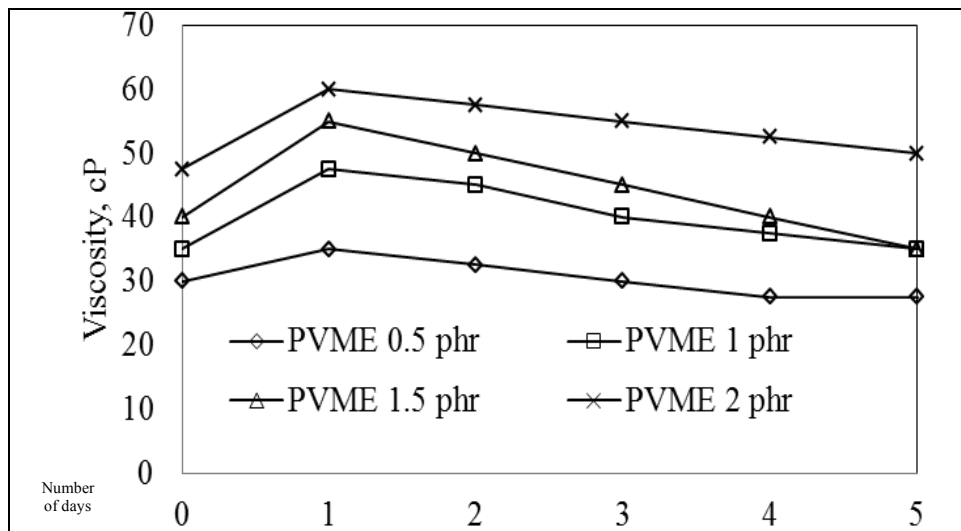


Figure 7: Viscosities of the latex compound containing different amounts of PVME at different periods of storage at 25°C

As the period of storage increases viscosity increases initially and after a period of one or two days get reduced slowly and becomes stabilized. The heat sensitized latex compound remains stable for a period of 20 days.

The increase in viscosity as the dosage of PVME was raised may be due to the fact that PVME interacts with the colloid stabilizers already present in the latex. Due to this interaction the initial viscosity increases on storage. But PVME being a hydrophilic polymer can act as a stabilizer due to the steric/ hydration effect. The decrease in viscosity on prolonged storage may be due to this effect.

3.4. pH of Latex Compound

Effect of varying the pH on heat sensitization of latex compound containing 1 phr of ZnO was given in (Figure8). As the pH was decreased, thickness of the deposit increased for both the compounds. The result shows that the pH has got profound effect for heat sensitization of latex compound. But when the pH was reduced below 8.5 the colloidal stability was lost. Therefore a pH of 9 was selected for the standard compound while studying the processing parameters and technological properties.

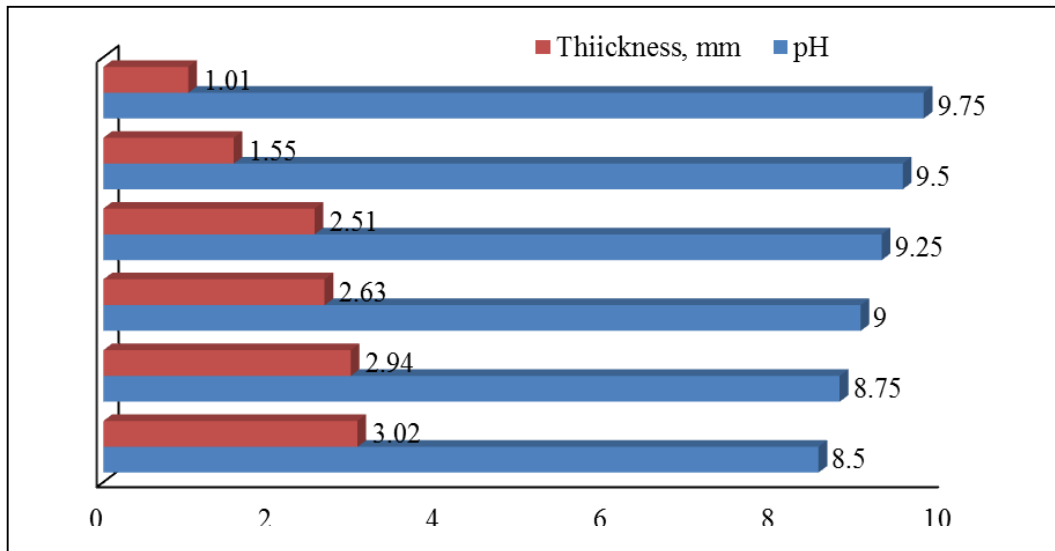


Figure 8: Effect of varying the pH on heat sensitization of latex compound

The above results showed that the heat sensitization by PVME depends on pH. This can be due to the ionization of adsorbed carboxylates groups present at the particle surface as the pH was reduced. This probably facilitates adsorption of PVME on the particle leading to more heat-sensitization (Blackley et.al., 1990).

The stability of latex compounds at different pH was measured by viscosity, which was plotted against storage period. In (Figure9) it was clear that the viscosity was highly sensitive to pH below a value of 8.5. A moderate stable viscosity was obtained at a pH of 9. From the above study of compound characteristics formulations of the standardized compound was given in Table 2. The effect of processing variables on heat sensitization and their results are discussed below.

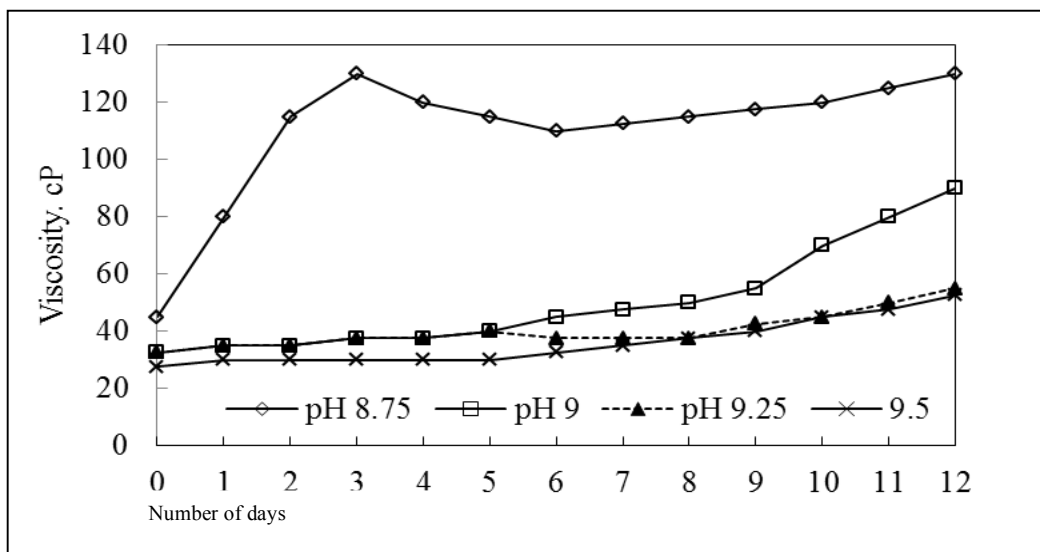


Figure 9: viscosities of the latex compounds at different pH at different periods of storage at 25°C

3.4.1. Storage Stability of the Standardised Compounds

From the Table 3 it was observed that on storage at all temperatures namely 15^oC, 25^oC and room temperature (32^oC), the viscosity first increased and after one or two days decreased and reached a stable value.

Brookfield viscosity, Cp in different days						
Viscosity	RPM	I st	II nd	III rd	IV th	VII th
At 15 ^o C	6	200	175	125	125	125
	60	32.5	32.5	35	30	35
At 25 ^o C	6	175	160	125	125	150
	60	25	27.5	27.5	30	30
At room temperature, (32 ^o C)	6	200	175	150	150	150
	60	35	60	177.5	200	200

Table 3: Compound stability study

The viscosities at 60 rpm were less than the viscosities at 6 rpm for all the samples at temperatures 15^o and, 25^oC. This showed that the compound behaves like a pseudo plastic fluid at those temperatures. After storage time of four or five days at room temperature viscosity increased at higher shear rates. This may be due to the fact that colloidal stability of the latex might had reduced at 32^oC, which was near the cloud point temperature of PVME.

3.4.2. Technological Properties

The tensile properties of latex films prepared from the heat sensitized latex compound are given in Table 4. It was seen that the films have good tensile properties and ageing resistance.

Property	Before ageing	After ageing (70 ^o C for 7 days)
Tensile strength, MPa	18.95	16.4
Elongation at break, %	1200	831
Modulus at 100% elongation, MPa	0.63	0.73
Modulus at 300% elongation, MPa	0.97	1.38

Table 4: Technological properties

4. Conclusion

In this paper heat sensitization of natural rubber latex by polyvinyl methyl ether was investigated. The effects of varying compound parameters were evaluated in the base latex compound. Optimum compound formulation for the system had been standardized and their stability also was noted. From the study following conclusions were drawn.

Sl.no	Ingredients	Parts by weight
		Dry
1.	60% Centrifuged latex (HA)	100
2.	20% Vulcastab VL solution	0.75
3.	50% Sulphur dispersion	1
4.	50% ZnO dispersion	1
5.	50% ZDBC dispersion	1
6.	5% Formaldehyde solution	To pH 9
7.	10% PVME solution	1

Table 5

These compounds were having good storage stability at 15^oC and 25^oC. The vulcanized film from the above latex compound had good technological properties and ageing resistance.

5. Acknowledgement

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6. References

- i. Aguilar, M.R., Elvira, C., Gallardo, A., Vázquez, B. and Roman, J.S. (2007). Topics in Tissue Engineering, Chapter 6, Vol. 3, Eds. N Ashammakhi, R Reis & E Chiellini, 1-27.
- ii. Archer, B. L. and Sekhar, B. C. (1955). The proteins of Hevea brasiliensis latex. I. Protein constituents of fresh latex serum. *Biochemical Journal* 61(3), 503-508.
- iii. Arreguin, B. Lara, P. and Rodriguez, R. (1988). Comparative study of electrophoretic patterns of latex proteins from clones of Hevea brasiliensis, *Electrophoresis*. 9(7), 323-326.
- iv. Ben van Baarle LPRI, (2003). Latex technology: review & processing, *Natuurrubber* 31 - 3rd quarter, pp 1-9.
- v. Blackley, D.C. (1997). Polymer latices, 2nd ed., Science and technology Volume 1: Fundamental principles Chapman & Hall, 306-345.
- vi. Blackley, D. C. (1997). Latex-dipping processes Science and Technology: Applications of latices Polymer latices, Chapman & Hall. vol.3, ch17, 155-156.
- vii. Blackley, D. C., Gorton, A. D. T. and Sivagurunathan, L.(1990). Heat- sensitization of ammonia-preserved centrifuged natural rubber latex concentrate by polyvinyl methyl ether. I. Effects of maturation, former temperature, dwell time, latex pH, level of zinc oxide, dilution and concentration and molecular weight of polyvinylmethyl ether *Journal of Dispersion Science and Technology*, **11**(3) 215-248.
- viii. Calvet, K.O. (1982). Polymer latices and their Applications: Applied Science Publishers, London, UK.
- ix. Cockbain. E.G., (1956). Transactions of the Institution of the Rubber Industry. 32, 97-110.
- x. Dennis, M. S. and Light, D. R. (1989). Amino acid sequence of rubber elongation factor protein associated with rubber particles in Hevea latex. *Journal of Biological Chemistry* 264:18608-18617.
- xi. Dennis, M.S., Hengel, W. J., Bell, J., Kohr, W. and Light, D.R. (1989). A 14 kilodalton protein, rubber elongation factor (REF), was associated with the rubber particle in a ratio of one REF to one rubber molecule., *Journal of Biological Chemistry*, 264: 18618-18628.
- xiii. Gorton, A. D. T. (1972). Natural Rubber Latex Concentrate Properties and Processibility. *Rubber Chemistry and Technology*., Vol. 45, No. 5, pp. 1202-1223.
- xiv. Hasma. H.(1992). Proteins of natural rubber latex concentrate, *Journal of natural Rubber Research*, 7(2), 102-112.
- xv. Kuan, T. H. and Sommer, J. G.(1981). Water-Resistant Release Coating for Uncured Rubber. *Rubber Chemistry and Technology*: 54, (5) 1124-1131.
- xvi. Light, D.R., and Dennis, M.S., (1989). Rubber elongation by farnesyl pyrophosphate synthases involves a novel switch in enzyme stereospecificity. *Journal of Biological Chemistry*, 264: 18589-18607.
- xvii. Pendle, T. D. (1995). Dipping with Natural Rubber Latex. NR Technical Bulletin. The Malaysian Rubber Producers Research Association Brickenbury, U.K.
- xviii. Porter, M., Rosemaze bt. Rawi, Sapi ai bin Abdul Rahim, (1992). Chemistry of the latex prevulcanisation process. Part 1. Migration of reactants from the solid phase into rubber particles. *Journal of Natural Rubber Research*, 7(2), 85 – 101.
- xix. Tata, S.J. (1980). Distribution of proteins between the fractions of Hevea latex separated by ultracentrifugation. *Journal of the Rubber Research Institute of Malaysia*, 28(2), 77–85.
- xx. Vladimir O. Aseyev, Heikki Tenhu, Françoise M. Winnik,(2006). Temperature Dependence of the Colloidal Stability of Neutral Amphiphilic Polymers in Water, Conformation-Dependent Design of Sequences in Copolymers II, *Advances in Polymer Science*, Volume 196, pp 1-85.