

COMPARISONS BETWEEN POLYVINYL ALCOHOL (PVOH) AND SODIUM DODECYL SULPHATE (SDS) AS SURFACTANTS IN NATURAL RUBBER (NR)/POLYVINYL ACETATE (PVAc) LATEX BLENDS

Abstract

Solutions of sodium dodecyl sulphate (SDS) and polyvinyl alcohol (PVOH) were used respectively as surfactants in comparative viscosity measurements of pure polyvinyl acetate (PVAc) emulsion, natural rubber (NR) latex and their blends using Ostwald glass capillary viscometer. Results show the efficacy of each surfactant in bringing about thickening of the latexes which is an important step in latex stabilization after formulation. Higher thickening phenomenon was observed when SDS rather than PVOH was used in pure PVAc and the blends. Overall findings agree with earlier literature on similar studies.

Keywords: Latex thickening, latex blends, PVAc emulsion, capillary viscometer

Introduction

Originally, the term “Latex” refers to the milky-white liquid substance obtained from the bark of rubber trees, in particular, the species known as *Hevea brasiliensis*. Today, the definition of latex has expanded so as to encompass both the traditional latex derived from *Hevea brasiliensis* as well as the aqueous dispersion of water insoluble polymers made by emulsion polymerization using free radical initiators (Brown and Garrett, 1959; Hellgren *et al.*, 1999; Satheesh Kumar and Siddaramaiah, 2007). Latexes as well as products based on them, for example, all water-borne coatings/adhesives systems require surfactants for stability in aqueous medium (Amalvy and Soria, 1996). The surfactants reduce the free energy of the various interfaces of the system, thus providing kinetic stability to the formulation. Surfactants are used as emulsifier for binder, as pigment dispersant, and needed to improve wetting on low energy substrates, to control foaming during application and processing, and to prevent film defects caused by surface tension gradients. In addition, surface active polymers, often referred to as “associative thickeners” are widely used to optimize the rheological

properties of the formulation. Some examples include anionic polyelectrolytes such as polyphosphates which are commonly used as pigment dispersing agents (Brown and Garrett, 1959; Hellgren *et al.*, 1999; Peethambaran *et al.*, 1990) and non-ionic types such as polyvinyl alcohol, sodium carboxymethyl cellulose, hydroxymethyl cellulose, gum acacia, poly (vinyl pyrrolidone), as thickeners (Qiao *et al.*, 2002).

Polyvinyl alcohol (PVOH), along with other surface-active substances **has** been studied for their effect in NR latex by measurement of the viscosity of the resulting mixture (Peethambaran *et al.*, 1990). In a similar vein, SDS's role on PVAc has been studied (Hellgren *et al.*, 1999). Research has been going on in our laboratory aimed at using NR/PVAc latex blends in a single product formulation, such as films (Ochigbo *et al.*, 2009) for packaging, waterborne paints (Ochigbo, 2006) etc. Consequently, it becomes expedient to carry out further research in order to find out which one out of these two surfactants (PVOH or SDS) that will be more suitable for stabilizing these blends. To the best of the researcher's knowledge, no similar study has been reported in the literature.

When surfactant is incorporated into latex system, the influence of the former is usually evaluated from the nature of flow behaviour or viscosity that results because surfactants addition leads inevitably to latex thickening ("increased viscosity"). As a matter of fact, traditionally, the number one objective for adding surfactant is the modification of the flow behaviour of latex to suit the manufacturing process adopted. Secondly, with emulsions of small particles which are not observable with a conventional microscope, where the structure to be examined would be destroyed by drying specimens for inspection under an electron microscope, we must depend upon indirect evidence (usually flow properties) to elucidate the mechanism of latex thickening (Peethambaran *et al.*, 1990; Brown and Garrett, 1959). Therefore, measurement of the blends' viscosity is utilized in this paper as a means for comparing the two surfactants and judging the preferred one. To date, the choice of an appropriate surfactant or mixture of surfactants, for particular latex is still a rather empirical procedure, and optimal amounts have to be found by trial and error.

63

64 **Experimental**

65 **Materials**

66 The PVAc homopolymer emulsion used was obtained from Makeean Polymers, South
67 Africa with the trade name ML50 (solids contents = 52.5%, pH = 6.5). Field NR latex
68 was provided by the Rubber Research Institute of Nigeria (RRIN), Iyanomo. It has a
69 solids content of 45%. Both the SDS and PVOH used were analytical grade quality
70 manufactured by Merck Chemicals.

71 **Preparation of the NR/PVAc aqueous-based latex blends**

72 Ten percent (10wt. %) of each of NR latex and PVAc emulsion **were** made, calculated
73 based on dry solids contents. Both dispersions were then blended into the compositions
74 as hereby stated: NR/PVAc (0/100; 25/75; 50/50; 75/25 and 100/0, respectively).

75

76

77 **Preparation of **surfactants** solutions**

78 Three different concentrations (0.5, 1.0, and 2.0 % w/w) for each of SDS and PVOH
79 were separately prepared. The range of concentration was chosen so as to
80 accommodate dilute (0.5%), limiting level for diluted (1.0%) and concentrated (2.0%)
81 solutions for these surfactants, respectively.

82 **Measurement of blends' viscosity**

83 The viscosity was measured using Ostwald type glass capillary viscometer. The flow
84 rate (efflux time) of the different samples **was** first determined as the time, t needed for
85 the liquid to pass through two marked points on the capillary as described in Billmeyer
86 (1984). The measurements of the flow rate of each of the latex blends were made in the
87 absence and presence of the varied concentration of each of SDS and PVOH at about

the same ambient conditions (22°C ±1). From the efflux times, the relative viscosities were calculated using Equation 1.

$$\eta_{rel} = t/t_0 \quad (1)$$

Where, η_{rel} = relative viscosity, t = efflux time of dispersion, t_0 = efflux time of pure water.

Results and discussion

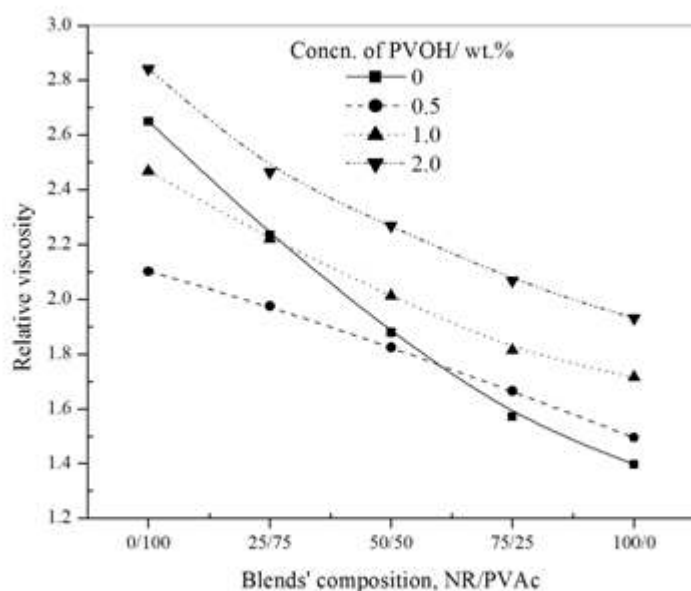


Fig.1. Relative viscosity vs. blends' composition in different concentration of PVOH

The change of blends' viscosity with composition both in the absence (0 wt. %) and presence of PVOH in varied concentration is shown in Figure 1 above. It is

generally observed that the relative viscosity decreases with increasing ratio of the NR component in the blends' composition. It has been reported that NR latex is intrinsically a pseudoplastic fluid, which implies that its particles are constantly involved in random motion (Peethambaran, 1990). Therefore, with an increase in NR component in the blends' composition, a corresponding increase in the random motion ensue, and hence a reduction in the systems' viscosity. The viscosity of a fluid is its resistance to motion, and it is usually inversely proportional to fluid mobility. It is also seen in Figure 1 above that the viscosity increases proportionally with the concentration of the PVOH solution. This increase is attributed to the interactions between the particles of the latexes and the added surfactant (PVOH) molecules. Such interactions reduce the freedom of mobility of the latex particles, which show up as increase in viscosity. Although the scope of the work is insufficient to provide details regarding the type of interactions occurring, it is assumed to involve adsorption, or absorption or both simultaneously. Whichever is the case, there is a possibility for the mobility of the latex particles to be slowed down through the interaction taking place.

It must be noted that this increase of viscosity with concentration of PVOH is most accentuated with blends having a preponderance (>50%) of NR latex component in the blends' composition. The order of viscosity increase within this region of blends' composition can simply be described as follows: $0 < 0.5 < 1.0 < 2.0$ wt. % PVOH, respectively. Within the region of a blends' composition having NR component less than 50%, the viscosity of blends without PVOH (i.e., 0 wt. %) slightly surpasses those containing 0.5 or 1.0 wt. % PVOH. This is attributed to a number of competing factors for and against viscosity increase in this region that go beyond the scope of this work for satisfactory explanation unless further investigation is pursued at molecular level.

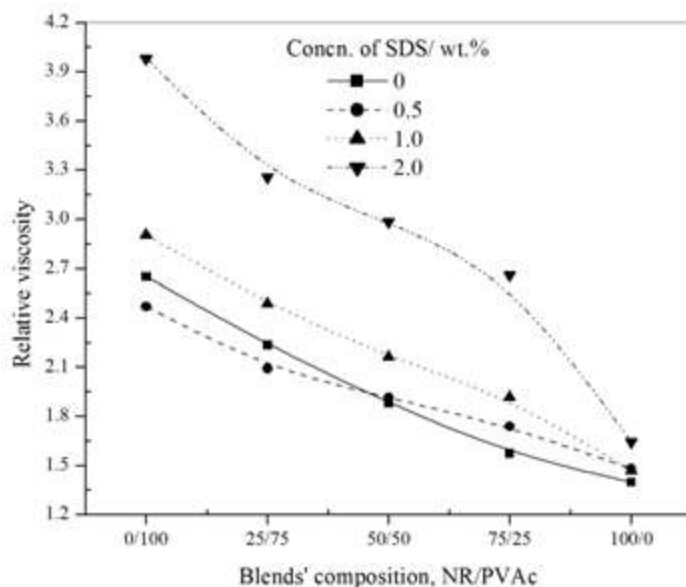


Fig.2. Relative viscosity vs. blends' composition in different concentration of SDS

The change of blends' viscosity with composition both in the absence (0 wt. %) and presence of SDS in varied concentration is shown in Figure 2 above. As similar to the trend observed in Figure 1, it is also generally observed that the relative viscosity decreases with increasing ratio of the NR component in the blends' composition due to pseudoplasticity of the NR component. Furthermore, the viscosity of the blends increases with concentration of the added surfactant as a result of the adsorption/absorption of the surfactant molecules on the latex particles. This is consistent with the findings by Peethambaran *et al.* (1990) and Hidi *et al.* (1995). All the viscosity curves for the blends containing the surfactant are each at a higher level than for the blend without (0 wt. %) SDS except again, as similar to the case in Figure 1, in the region where the composition of NR component is less than (<) 50%. Similar explanation as stated in the case of Figure 1 will suffice to this. Noteworthy in this present result is an unusual increase in the viscosity observed with the blends containing 2% SDS within the region for blends containing 25-75% NR component. It is suggested that this unusual increase in viscosity in the stated region is due to

absorption of SDS in the PVAc component of the blend. Such absorption was reported by Hidi *et al.* (1995). Using light scattering and ultracentrifugation techniques, Hidi *et al.* (1995) reported that, in aqueous solutions of some anionic surfactants at a critical concentration, in particular sodium dodecyl sulphate (SDS), PVAc latex particles swell up to 60 times their original volume and the phenomenon was associated with the unusual viscosity increase.

Side-by-side comparisons of the effect of both surfactants (SDS and PVOH) on the blends' composition are shown in Figures 3-5 below.

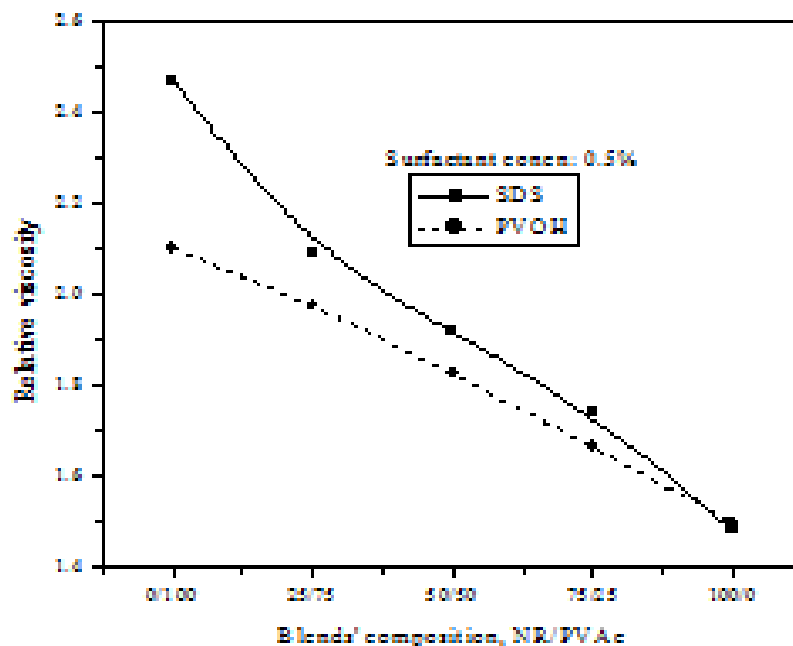
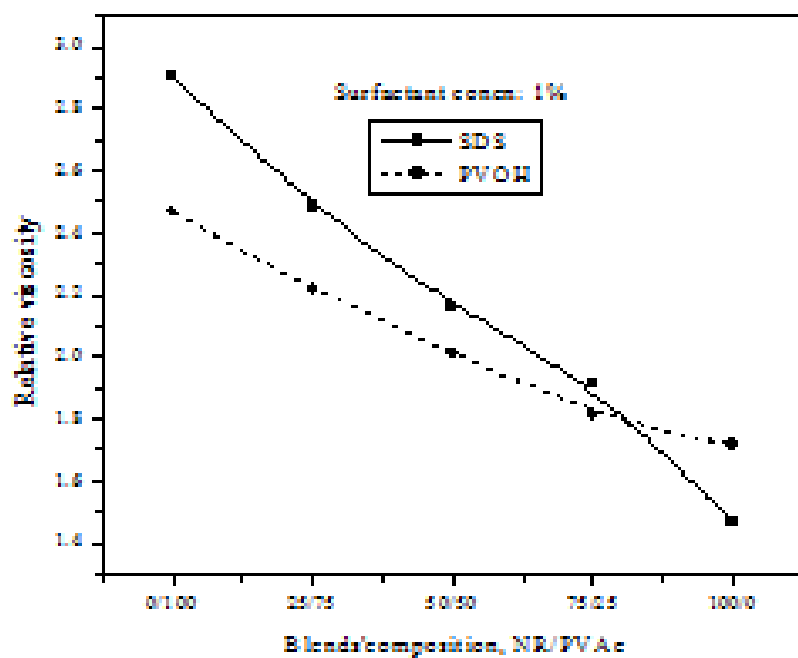


Figure 3. Relative viscosity vs. blends' composition modified with 0.5% surfactant solutions

164
165
166
167
168



169
170 Figure 4. Relative viscosity vs. blends' composition modified with 1.0% surfactant
171 solutions

172
173
174
175
176
177

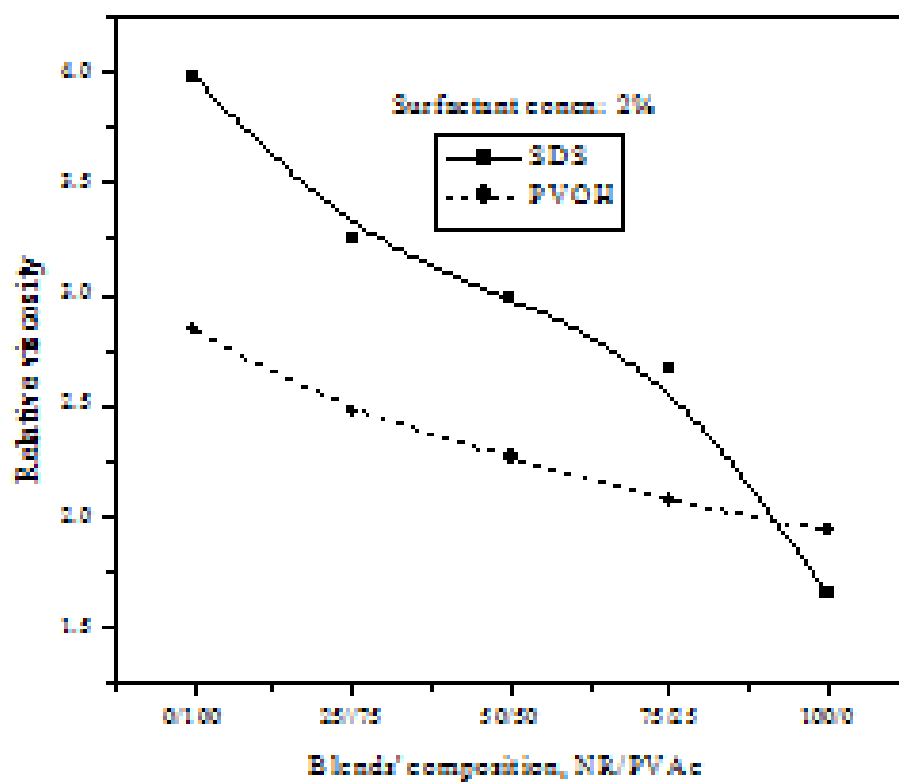


Figure 5. Relative viscosity vs. blends' composition modified with 2.0% surfactant solutions

As seen, in all the cases, viscosity decreases with increasing ratio of NR component in the blends' composition. This observation and the reason accountable for it is the same as had earlier been stated. The pattern of decrease of the viscosity, however, varies with the concentration of the surfactants (SDS and PVOH). At a concentration of 0.5%, the gap between the two viscosity curves due to SDS and PVOH respectively, gets narrower with increasing NR content in the blends' composition, as similar to the others (Figs. 4 & 5), but without a crossover. The two viscosity curves more or less synchronize at blends' composition equivalent to NR/PVAc, 100/0. For the rest of the concentrations (1 % & 2 %), crossovers were observed giving a situation in which the viscosity of pure natural rubber latex (NR/PVAc, 100/0) is higher in PVOH than in SDS. It is significant to note that the gap between the two curves in the case for 0.5% concentration of surfactant is narrowest. This implies that at this level of concentration, the viscosities of the systems in both surfactants are comparably close. This is attributed to the plasticizing of PVAc component by the excess water of the much diluted surfactant solution resulting in lowering of its viscosity. This ability of water to plasticize PVAc emulsion has earlier been reported by Chuu and Meyers (1987). On the other hand, it is known that the viscosity of natural rubber latex is unaffected by dilution. From the results, it can be seen that the viscosity of pure polyvinyl acetate emulsion (NR/PVAc, 0/100), and that of the blends too, are always higher in SDS than in PVOH. The latter is seen to yield higher viscosity only in the presence of pure natural rubber latex (NR/PVAc, 100/0). The increase in viscosity observed in these results is synonymous with thickening of the systems earlier reported by Brown & Garrett (1959) and this phenomenon leads to latex stabilization after formulation.

Conclusions

The solutions of SDS and PVOH have been compared as surfactants for the latex blends of polyvinyl acetate emulsion and natural rubber latex, with the following conclusions based on the obtained results:

1. Each of the solutions has shown to have specific interactions, which may either be physical or physico-chemical in nature, with each component of the blends.
2. The interactions result in increase in viscosity, otherwise called 'Latex thickening', which is concentration dependent in respect of the surfactant solution.
3. Each solution behaves uniquely to a particular component of the blends, such that SDS yields higher viscosity in pure PVAc emulsion and the blends, whereas PVOH offers higher viscosity only in pure NR latex.
4. From (3) above, the implication from the point of view of latex stabilization is that SDS is to be preferred for pure PVAc and NR/PVAc emulsion blends, while PVOH for pure NR latex.
5. Water has a plasticizing effect on PVAc emulsion, and hence lowers its viscosity which is in keeping with much earlier findings of Chuu and Meyers (1987). On the other hand, the presence of water has insignificant effect in lowering the viscosity of NR latex.

References:

1. Amalvy JI, Soria DB, Vibrational spectroscopic study of distribution of sodium dodecyl sulphate in latex films, *Prog Org Coat*, **28**, 279-283, 1996.
2. Brown GL, Garrett BS, Latex thickening: Interactions between aqueous polymeric dispersions and solutions, *J Appl Polym Sci*, **1**, 283-295, 1959.
3. Hellgren A-C, Weissenborn P, Holmberg K, Surfactants in water-borne paints. *Prog Org Coat*, **35**, 79-87, 1999.
4. N.R. Peethambaran, Baby Kuriakose, ManjariRajan, A.P. Kuriakose, Rheological Behaviour of Natural Rubber Latex in the Presence of Surface-active Agents, *J Appl Polym Sci*, **41**, 975-983, 1990.
5. Qiao L, Coveny PK, Easteleal AJ, Modifications of poly (vinyl alcohol) for use in poly (vinyl acetate) emulsion wood adhesives, *Pigment & Resin Technology*, **31**, 88-95, 2002.
6. Satheesh Kumar MN, Siddaramaiah, Studies on melamine formaldehyde (MF) loaded polyvinyl acetate-polyester nonwoven fabric composites. *J Thermopl Compos Mater*, **20**, 305-318, 2007.
7. Billmeyer FW, Jr. Textbook of Polymer Science, 3rd ed.; Wiley: New York; p. 149, 1984.
8. Ochigbo S.S., Luyt A.S., Focke W.W. Latex derived blends of poly (vinyl acetate) and natural rubber: thermal and mechanical properties. *Journal of Materials Science*, **44**, 3248-3254, 2009.
9. Ochigbo, S.S. Latex Blending of Polyvinyl Acetate (PVAc) with Natural Rubber (NR) for Development of Water-based Paint, PhD Thesis, Federal University of Technology, Minna, Nigeria, 2006.
10. Hidi, P., Napper, D.H., Sangster, D.F. Reversible swelling of poly (vinyl acetate) latex particles in sodium dodecyl sulphate solution, *Macromolecules*, **28**, 6042-6054, 1995.

283 11. Chuu MS, Meyers RR. The effect of moisture on the dielectric behaviour of poly
284 (vinyl acetate)-natural rubber blend. Journal of Applied Polymer Science 34:
285 1447-1457, 1987.
286