GLOBAL JOURNAL OF PURE AND APPLIED SCIENCES VOL. 10, NO. 2, MARCH 2004: 307 - 314

EFFECTS OF ADOPOL EVS-9279X ON THE EMULSION AND FILM PROPERTIES OF POLY (VINYL ACETATE) AND ACRYLIC RESIN

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(Received 15 August 2003; Revision accepted 17 September 2003)

ABSTRACT

The effects of Adopol EVS-9279X on the emulsion and film properties of poly (vinyl acetate) and acrylic resin were investigated using 5% - 10% w/w sample formulations. Results indicate that Adopol EVS-9279X increased the surface tension of poly (vinyl acetate) from 2.060 x $10^{-3}Nm^{-1}$ to a maximum of 8.966 x 10^{-2} Nm^{-1} at 9% w/w formulation and reduced same for acrylic resin from 3.988 x $10^{-2}Nm^{-1}$ to 2.702 x $10^{-2}Nm^{-1}$ at 6% - 7% w/w formulations. It lowered the solid content of poly (vinyl acetate) and acrylic resin from 38.2% to 33.3% and 45.8% to 41.8% respectively at 10% w/w formulation. Water resistance was improved by a reduction in water absorption from 45.8% to 38.5% minimum for poly (vinyl acetate) and 37.2% to 34.0% minimum for acrylic resin at 5% w/w formulation.

Drying time was reduced from 74 minutes to 51 minutes at 5% w/w formulation for poly (vinyl acetate) and 68 minutes to 58 minutes at 7% w/w formulation for acrylic resin. Specific gravity was lowered from 1.05 to 0.91 at 6% w/w formulation for acrylic resin, while pH was lowered at low concentration from 4.70 to 4.49 at 6% w/w formulation for poly (vinyl acetate) and 8.86 to 8.50 at 9% w/w formulation for acrylic resin. Apparent viscosities and flexibility were unaltered within the concentration range of 5% - 10% w/w formulation studied for both polymers.

KEY WORDS: Emulsion, Adopol EVS-9279X, Polymer.

INTRODUCTION

Poly (vinyl acetate) and acrylic resin are used in the formulation of emulsion paints, they act as film forming materials (Challa, 1993). However, the properties and performances of these paints differ slightly (Mc Graw-Hill, 1997).

The effect of compositional heterogeneity on the physical and mechanical behaviour of poly (vinyl acetate-co-butyl acrylate) has been widely studied (Chujo et al, 1969; Vijayendran et al, 1980; Makawinata et al, 1981). Poly (vinyl acetate) and poly (methyl methacrylate) are emulsion polymers. Surfactants play major roles in their emulsion polymerization processes, and are also essential for the stabilization of the lattice during post polymerization processes, such as, stripping to remove residual monomers, formulation, storage, shipping and application (Candau and Ottewill, 1990).

A systematic approach to the selection of surfactant for a given application is the hydrophile – lipophile balance (HLB) system (Griffin, 1949; Griffin, 1956). Attempts have been made to use the HLB system to select surfactants for the emulsion polymerization of vinyl monomers (Greth and Wilson, 1961; Jagodic et al, 1976; Jagodic and Fajt, 1977; Merkel, 1982). Optimum stability of poly (vinyl acetate) lattices were prepared using surfactants of HLB 14.5 – 17.5 in its emulsion polymerization processes, 12.1 – 13.7 for poly (methyl methacrylate), 11.8 – 12.4 for poly (ethyl acrylate), 11.95 – 13.05 for 50:50 (by weight) methyl methacrylate – ethyl acrylate copolymer.

A number of conventional emulsifiers/surfactants have been used to stabilize poly (vinyl acetate) and acrylic resin lattices (Vanderhoff, 1985). Adopol EVS-9279X is an emulsion viscosity stabilizer formulated and commercially produced by Gamor Chemical and Allied Limited, PortHarcourt for use in the stabilization of emulsion paint, cosmetic products and agro-industrial suspensions (Airuehia, 1992), with sodium salt of ethyl methyl cellulose and sodium benzoate as active components.

Ebosie studied the "differential film formation in Adopol Standard Defoamer, Adopol EVS-9279X and Poly (vinyl acetate) – their characterization and application" (Ebosie, 1996). No investigation on the effects of Adopol EVS-9279X on the emulsion and film properties of poly (vinyl acetate) and acrylic resin which are film forming materials in most emulsion paints has been reported.

This paper describes the effects of this emulsion viscosity stabilizer on the emulsion and film properties of poly (vinyl acetate) and the acrylic resin- poly(methyl methacrylate), shown in Fig.1 and 2 respectively, which are necessary to determine its suitability for various applications.

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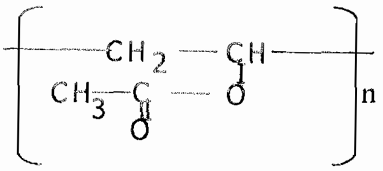

Fig.1: Poly (vinyl acetate)

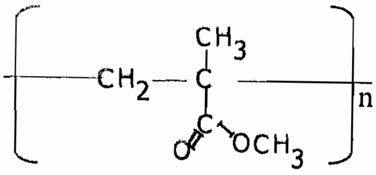

Fig. 2: Poly (methyl methacrylate)

EXPERIMENTAL

MATERIALS

Poly (methyl methacrylate), average molecular weight 30,000 – 40,000, which is the acrylic resin used as well as poly (vinyl acetate), average molecular weight 100,000 – 120,000 were obtained from Chemlap Industries Limited, Aba. These polymers were amorphous and provided as emulsion. Adopol EVS-9279X was obtained from Gamor Chemical and Allied Limited, PortHarcourt. These materials were used as received.

SAMPLE PREPARATION

200 g of poly (vinyl acetate) and acrylic resin were measured into different plastic plates. Varying quantities of Adopol EVS-9279X (ranging from 10 g – 20 g) were measured and added to each of the 200 g poly (vinyl acetate) and acrylic resin respectively as shown in Table 1.

Table 1:Sample Formulation

Sample	Poly (vinyl acetate) samples A (g)	Acrylic Resin samples B (g)	Quantity of Adopol EVS-9279X (g)	% w/w formulation
1	200	200	0	0
2	200	200	10	5
3	200	200	12	6
4	200	200	14	7
5	200	200	16	8
6	200	200	18	9
7	200	200	20	10

The mixtures were properly homogenized by stirring with the aid of a glass rod to obtain 5% - 10% w/w sample formulations. The plates were covered with their lids and allow to stand for 24 hours before measuring the emulsion and film properties of the samples.

MEASUREMENT OF EMULSION PROPERTIES

The emulsion properties investigated include:- viscosity, surface tension, specific gravity, pH and solid content.

Surface Tension

Surface tension of the samples was measured by the traveling microscope method as reported by Raymond (Raymond, 1977). 0.2 cm diameter glass capillary tubes and 250 ml beakers were first cleaned with detergent solution, nitric acid, thoroughly rinsed with distilled water and then allowed to dry in air. A known volume of each prepared sample was put into the beakers, the capillary tube immersed into the sample in the beaker and clamped in a vertical position. The rise of the sample in the capillary tubes was then measured with Graffin travelling microscope. The surface tension of the samples was calculated using the following equation:

$$\tau = \frac{1}{2} r \rho g h \qquad (1)$$

where g = acceleration due to gravity (m/s^2), ρ = density of the sample (kg/m^3), r = radius of the capillary tube (cm) and h = rise of the sample in the capillary tube (cm).

Specific Gravity

Standard specific gravity bottle method was used (Airuehia, 1992). A 50 ml specific gravity bottle was thoroughly washed with detergent solution, rinsed with nitric acid, then distilled water and allowed to dry. The dry bottle was weighed and a known volume of distilled water introduced into the bottle and re-weighed. The bottle was emptied and allowed to dry and a known volume of the sample was introduced into the bottle and weighed using a Mettler analytical balance.

The following equation was used to calculate the specific gravity of the samples:

$$S.G. = \frac{W_3 - W_1}{W_2 - W_1} \qquad (2)$$

where, W_1 = mass of empty specific gravity bottle (g), W_2 = mass of bottle filled with water (g), W_3 = mass of bottle filled with sample (g).

Viscosity

100 g of each of the samples were dissolved in 350 ml distilled water and their viscosities measured using a Fann V-G viscometer. The apparent viscosities were calculated using the following equation:

$$Apparent\ Viscosity\ (cp) = \frac{Reading\ at\ 600\ rpm}{2} \qquad (3)$$

pH

0.01 % w/v dilution of the samples was obtained by dissolving 1.0 g of each of the samples in 100 ml distilled water contained in conical flasks. Mettler Delta 340 pH meter, calibrated using a buffer solution was used in measuring the pH of the diluted samples.

Solid Content

The ASTM D-1489 method was used (ASTM, 1960). A porcelain crucible was weighed and the mass of the crucible recorded. Some quantities of each sample were slowly introduced into the crucible until the mass of the crucible increased by 1.0 g (i.e. a measurement of 1.0 g of the sample).

The crucible with the sample was heated on a hot plate until the content became solid dry. It was then removed from the hot plate, cooled and re-weighed. This process was repeated until a constant mass was obtained. The solid content (%) for each sample was calculated using the following equation:

$$Solid\ Content\ (\%) = \frac{M_{CD} - M_C}{M_{CS} - M_C} x \frac{100}{1} \qquad (4)$$

where, M_C = mass of crucible (g), M_{CS} = mass of crucible and sample (g) and M_{CD} = mass of crucible and dry sample (g).

MEASUREMENT OF FILM PROPERTIES

Film properties investigated include: water resistance, flexibility and drying time.

Water Resistance

Water absorption was used as an index for the measurement of water resistance. 2 cm x 4 cm glass sheets were cleaned with detergent solution, nitric acid and rinsed with distilled water. They were allowed to dry in air for atleast 72 hours. The sample sheets were weighed again before dipping them into 100 ml beakers, containing distilled water, enough to cover the coated portion of the glass sheets. The set up was allowed to stand for one hour before being brought out, cleaned of the dripping water on the surface and re-weighed.

The surfaces of the films were carefully examined and the percent increase in weight of the sample due to water absorption, which is inversely proportional to the samples' water resistance was calculated using the following equation:

$$Water\ Absorption\ (\%) = \frac{Z-Y}{Z-X} x \frac{100}{1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where, X = mass of glass sheet (g), Y = mass of glass sheet + dry sample (g) and Z = mass of glass sheet + dry sample + water absorbed (g).

Flexibility

The method reported by Raju and Yaseen was used (Raju and Yaseen, 1983). Neatly prepared glossy paper strips measuring 4 cm x 10 cm were cut to size. A conical bent test apparatus with different metal pipe diameters of 1″ ¾″ ¼″ and 1/6″ mandrels respectively were secured in positions. The samples were uniformly applied to the glossy paper strips and allowed to dry for 72 hours.

The paper strips containing the samples were clamped in position and formed round the mandrels of 1″, ¾″, ¼″ and 1/6″.diameters respectively.

The test papers were examined after each test to determine the minimum diameter at which failure by stretching and cracking occurred.

Drying Time

ASTM D-1640 standard test method was used in the determination of Dry to-Touch Time (DTT) of the samples(ASTM, 1960). Each sample was uniformly applied to 3 cm x 3 cm glossy paper and time taken for the sample to no longer adhere and rub up when a finger was slightly rubbed across the surface was measured using a stopwatch.

RESULTS AND DISCUSSION

Tables 2 and 4 show the results of the effects of Adopol EVS-9279X on some emulsion and film properties of poly (vinyl acetate) acrylic resin respectively. Tables 3 and 5 show the results of the flexibility measurements of poly (vinyl acetate) and acrylic resin respectively.

Results shown in Tables 2 and 4 respectively indicate that Adopol EVS-9279X increased the surface tension of poly (vinyl acetate) with increase in the quantity added. The surface tension was found to have increased from 2.060 x 10^{-2} Nm^{-1} for the control to a maximum of 8.966 x 10^{-2} Nm^{-2} at 9 % w/w formulation (sample A6), while the surface tension of acrylic resin was reduced, particularly at low formulation concentration. A minimum value of 2.702 x 10^{-2} Nm^{-1} at 6 % - 7 % w/w (sample B3 & B4) formulation was achieved as against a value of 3.988 x 10^{-2} Nm^{-1} (sample B1 – control). Fig.3 shows the

Table 2: Results of Emulsion and Film Properties of Poly (vinyl acetate).

Sample	Surface Tension (N/m)	Specific gravity	Apparent Viscosity (cp)	pH	Solid Content (%)	Water Absorption (%)	Drying Time (min)
A1	2.060 x 10^{-3}	1.05	3.5	4.70	38.2	45.8	74
A2	3.502 x 10^{-2}	1.02	3.5	4.52	36.7	38.4	61
A3	3.579 x 10^{-2}	0.91	3.5	4.49	36.2	38.6	57
A4	5.627 x 10^{-2}	0.94	3.5	4.57	35.3	49.5	53
A5	7.562 x 10^{-2}	0.96	3.5	4.85	34.6	52.6	51
A6	8.996 x 10^{-2}	0.96	3.5	5.47	34.0	53.6	60
A7	8.951 x 10^{-2}	0.97	3.5	4.70	33.3	68.4	66

Table 3: Results of the Flexibility Measurements of Poly (vinyl acetate)

Sample	Size of Mandrels (Inches).				Remark
	1	¾	¼	1/6	
A1	1	¾	¼	1/6	Passed
A2	1	¾	¼	1/6	Passed
A3	1	¾	¼	1/6	Passed
A4	1	¾	¼	1/6	Passed
A5	1	¾	¼	1/6	Passed
A6	1	¾	¼	1/6	Passed
A7	1	¾	¼	1/6	Passed

Table 4: Results of Emulsion and Film Properties of Acrylic Resin.

Sample	Surface Tension (N/m)	Specific gravity	Apparent Viscosity (cp)	pH	Solid Content (%)	Water Absorption (%)	Drying Time (min)
B1	3.988×10^{-2}	1.09	2.0	8.86	45.8	37.2	**68.0**
B2	2.866×10^{-2}	1.08	2.0	8.76	43.9	34.0	**66.5**
B3	2.702×10^{-2}	1.08	2.0	8.83	43.8	36.1	**59.0**
B4	2.702×10^{-2}	1.08	2.0	8.75	43.4	41.6	**58.0**
B5	2.711×10^{-2}	1.08	2.0	8.71	42.5	44.5	**60.0**
B6	3.167×10^{-2}	1.08	2.0	8.50	42.0	51.1	**63.0**
B7	3.173×10^{-2}	1.08	2.0	8.86	41.8	51.7	**65.0**

Table 5: Results of the Flexibility Measurements of Acrylic Resin

Sample	Size of Mandrels (Inches).				Remark
	1	¾	¼	1/6	
B1	1	¾	¼	1/6	Passed
B2	1	¾	¼	1/6	Passed
B3	1	¾	¼	1/6	Passed
B4	1	¾	¼	1/6	Passed
B5	1	¾	¼	1/6	Passed
B6	1	¾	¼	1/6	Passed
B7	1	¾	¼	1/6	Passed

plot of the trend of the variation of surface tension with quantity of Adopol EVS-9279X added. This shows that Adopol EVS-9279X exhibits some surfactant characteristics in the case of acrylic resin. This property improves wetability and reduces cissing in the films formed.

Fig.4 shows the variation of solid content, water absorption and drying time with the quantity of Adopol EVS-9279X (see Tables 2 and 4). It was observed that the solid content was lowered by Adopol EVS-9279X in both poly (vinyl acetate) and acrylic resin. For poly (vinyl acetate), a reduction from 38.2 % to 33.3 % (i.e. 0 % - 10 % by weight – samples A1 – A7) was achieved while a reduction from 45.8 % to 41.8 % was achieved for acrylic resin. This reduction in solid content, is believed to be caused by the very low solid content of Adopol EVS-9279X (Airuehia, 1992). This slight reduction in the solid content will result in slight reduction in their film forming capacities.

At low formulation concentration of 5 % by weight, water absorption was found to be reduced to a minimum value of 38.4 % from 45.8 % for poly (vinyl acetate) and 34.0 % from 37.2 % for acrylic resin. This invariably shows that the samples' water resistance was improved at this concentration.

The implication of this observation is that the particles of Adopol EVS-9279X adsorb on these polymer particles and tend to overlap one another, thereby reducing the possibility of water penetration into the film. Reversal of this trend was observed at formulation concentration of 7% and above.

The drying time investigated was found to be reduced within the concentration range studied with the optimum reduction achieved at 5 % w/w sample formulation for poly (vinyl acetate), where the drying

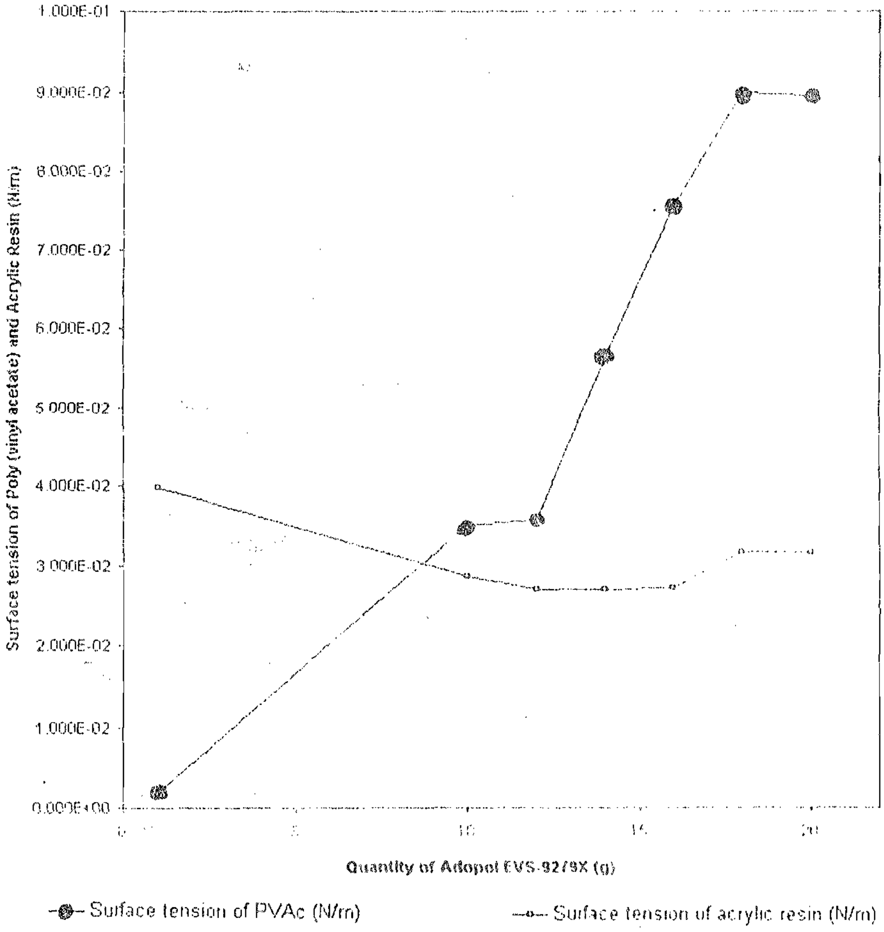

Fig. 3: Variation of Surface tension of Poly (vinyl acetate) and Acrylic Resin with Quantity of Adopol EVS-9279X

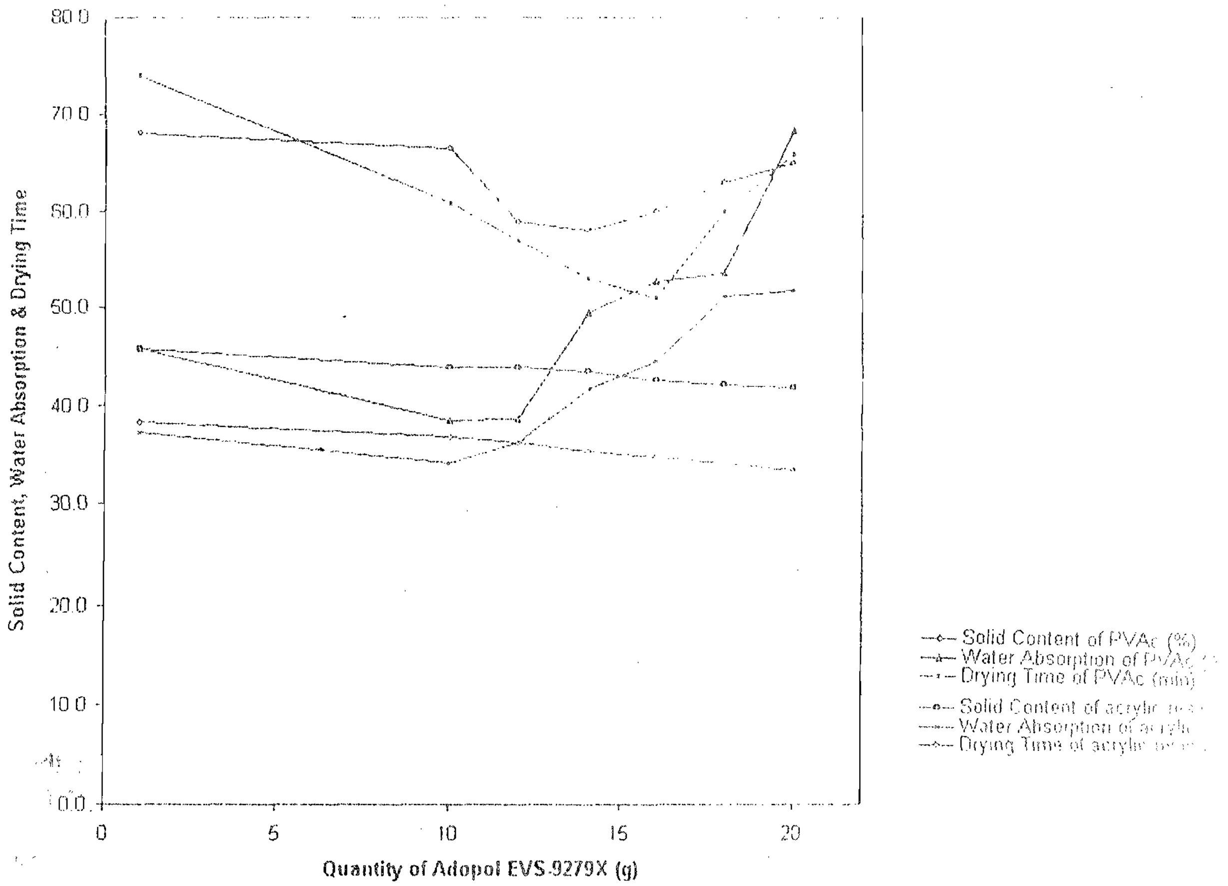

Fig. 4: Variation of Solid Content, Water Absorption & Drying Time of Poly (vinyl acetate) and Acrylic Resin with Quantity of Adopol EVS-9279X

time was reduced from 74 minutes to 51 minutes and 7 % for acrylic resin, where the time was reduced from 68 minutes to 58 minutes. This shows that Adopol EVS-9279X acting like a plasticizer, lowers the glass transition temperature (Tg) of these polymers below room temperature, thus enhancing their coalescing to form film at room temperature.

The variation of specific gravity, pH and apparent viscosities of the samples with quantity of Adopol EVS-9279X is shown in Fig. 5. The specific gravity was found to decrease with increasing quantity of Adopol EVS-9279X for both polymers. This indicates that the emulsion viscosity stabilizer has the ability of increasing volume more than the associated increase in mass, thus resulting in a decrease in density and therefore a decrease in specific gravity. This is advantageous in film formation where more area is covered.

The pH of poly (vinyl acetate) and acrylic resin was found to decrease slightly at lower concentration, but increased at high concentration as shown in Fig.5. This is attributable to the increase in the activity of hydroxonium ion in poly (vinyl acetate) and acrylic resin at low concentration, which is suppressed at high concentration. This is probably due to the effect of sodium benzoate, a component of Adopol EVS-9279X, which is polar and promotes acid dissociation thus increasing the activity of hydroxonium ion in aqueous solution at low concentration. As the concentration of Adopol EVS-9279X increases, the contrasting effect of non-polar ethyl methyl cellulose component predominates, thereby lowering the activity of hydroxonium ion, resulting to pH increase.

Apparent viscosities were found to be unaffected by Adopol EVS-9279X irrespective of concentration for both polymers. The apparent viscosity of poly (vinyl acetate) remained at 3.5 cp while that of acrylic resin remained constant at 2.0 cp. This shows that Adopol EVS-9279X alter the shear stress and the shear rate of the samples in a proportional manner for the apparent viscosities to remain constant. The apparent viscosities were unaltered by Adopol EVS-9279X because of its low solid content ≈ 2.2% and compatibility with water, since it is made of sodium salt of ethyl methyl cellulose and sodium benzoate.

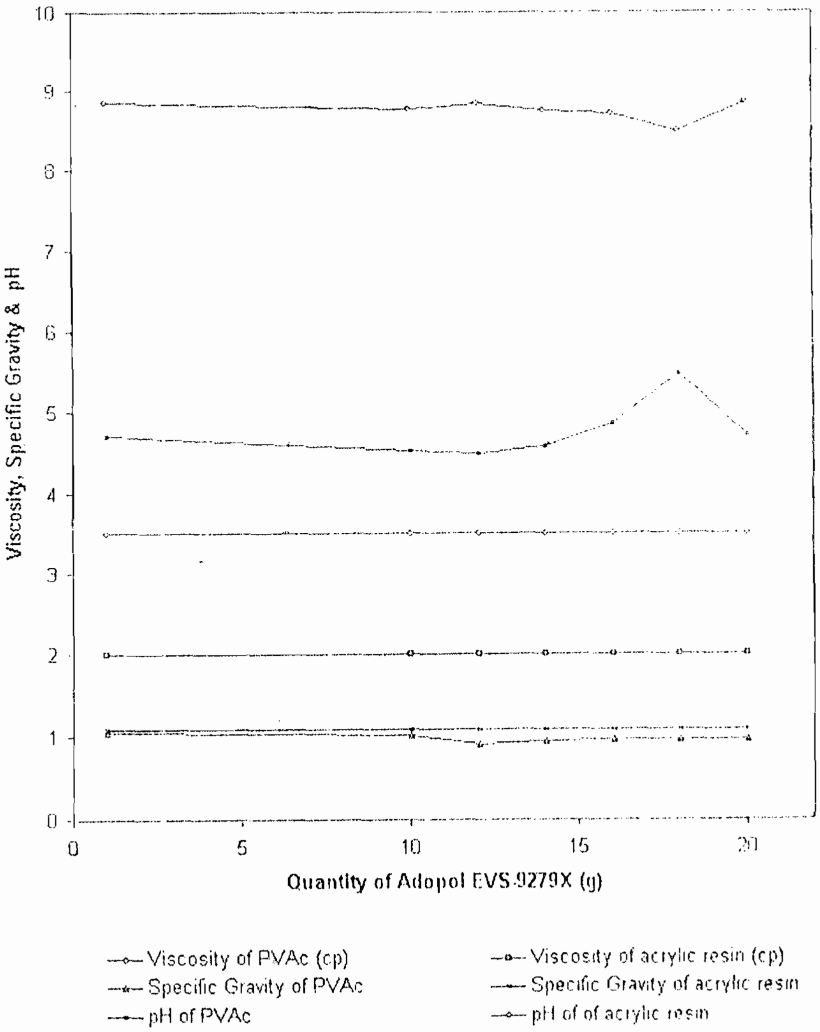

Fig. 5: Variation of Viscosity, Specific Gravity & pH of Poly (vinyl acetate) and Acrylic Resin with Quantity of Adopol EVS-9279X

High solid content of an additive is necessary to change solution apparent viscosities of polymers. It does not react with the polymers and could therefore serve effectively as an emulsion viscosity stabilizer.

Poly (vinyl acetate) and acrylic resin films have been known to be flexible and Adopol EVS-9279X seem not to alter this flexibility characteristic. This shows that they are compatible within the concentration range investigated.

CONCLUSION

Adopol EVS-9279X has been shown to have various effects on the emulsion and film properties of poly (vinyl acetate) and acrylic resin investigated with the exception of flexibility and apparent viscosities, which visibly remained unaltered within the formulation concentration investigated.

Specific gravity, solid content and drying time were lowered for both polymers. Water absorption and pH that were reduced at low concentration, increased at higher concentration. Surface tension was increased in poly (vinyl acetate) but was decreased in acrylic resin. Adopol EVS-9279X could be of practical importance as an effective surfactant in formulation of acrylic resin.

The variation of the effects of this emulsion viscosity stabilizer on the emulsion and film properties of these polymers was found to be concentration dependent.

REFERENCES

Airuehia, G. I., 1992. Formulation, Characterization and Application of Newsprint Inks From Rubber Seed Oil and Cut-back Bitumen (Malthene), Fellowship Diploma Thesis, Nigeria Institute of Science Technology, Ibadan.

Airuehia, G. I., 1992. Products Data Manual, Gamor Chemical and Allied Limited, Port Harcourt, 5 – 6.

ASTM., 1960. Annual Book of ASTM D-1489 Standards, Part 25.

ASTM., 1960 Annual Book of ASTM D-1640 Standards, Part 15, 18, 26 and 41.

Candau, F. and Ottewill, R. H., 1990. Scientific Methods for the Study of Polymer Colloids and Their Applications, Kluwer Academic, London, 1 – 34.

Challa, G., 1993. Polymer Chemistry – An Introduction, Ellis Harwood, New York, 15 – 183.

Chujo, K.; Harada, Y.; Tokuhara, S. and Tonaka, F., 1969. J. Polym. Sci., Part C: Poly. Symp. 27, 321.

Ebosie, A. E., 1996. "Differential Film Formation in Adopol Standard Defoamer, Adopol EVS-9279X and Poly (vinyl acetate) – Their Characterization and Applications", M.Sc. Thesis, University of Port Harcourt.

Greth, G. G.and Wilson, J. E., 1961. J. Appl. Polym. Sci., 5, 135

Griffin, W. C., 1949. J. Soc. Cosmoet Chem., 1 (5): 311.

Griffin, W. C., 1956. Off Dig. Fed. Vanish Prod. Clubs, 28.

Jagodic, F.; Abe, M. and Ogrizek, N., 1976. Chem. Abstr., 85, 33460h, 63365y.

Jagodic, F. and Fajt, B., 1977 Chem. Abstr., 86, 44067g.

Makawinata, T.; El-Aasser, M. S.; Vanderhoff, J. W. and Pichot, C., 1981. "Preparation, Surface and Colloidal Properties of (vinyl acetate – butyl acrylate) Copolymer Lattices – Effect of Emulsion Polymerization Process and Copolymer Composition", Acta Polymerica 32, 583 – 592.

McGraw-Hill, 1997. Encyclopaedia of Science and Technology, McGraw-Hill Inc. New York, 8th ed., 13, 16 – 18 and 343.

Merkel, M. P., 1982. M. S. Thesis, Lehigh University, Bethlehem, Pennsylvania.

Raju, K. V. S. N. and Yaseen, M., 1983. The Effect of Part Replacement of Titanium Dioxide by Barytes on the Properties of Alkyd Paints, JOCCA, New York, 40 – 423.

Raymond, C. 1977. Physical Chemistry with Application to Biological Systems, Wiley, New York, 22 – 35.

Vanderhoff, J. W. 1985. Mechanism of Emulsion Polymerization, J. of Polymer Science: Polymer Symposium 72, 161 – 198.

Vijayendran, B. R., Bone, T. and Gajria, C., 1980. Organic Coating and Plastics, 43, 346.