UTILIZATION OF BINARY BLENDS OF LIQUID NATURAL RUBBER AND POLYVINYL ACETATE IN EMULSION PAINT

H.C. Ndibe^{1*}, J. U. Iyasele², E.O. Imanah², G. E. Okpara¹ and I. Eriamiatoe¹

¹Synthetic Chemistry Research Group, Department of Chemistry, University of Benin, Benin City, Edo State, Nigeria.

²Department of Chemistry, Faculty of Physical Sciences, University of Benin, Benin City, Edo State, Nigeria.

*Corresponding Author's email: henry_ndibe@yahoo.com Tel: +2347030987269

Received 10 December 2020; accepted 11 January 2020, published online 30 January 2021

ABSTRACT

Studies were conducted on blends of liquid natural rubber (LNR) and polyvinyl acetate (PVAc). The two polymers were characterized based on their physicochemical properties, and used in paint production. Results obtained showed that viscometric measurement and density of the polymers did not differ much. Five paints of different compositions labeled; Paint 1 (100% PVAc), Paint 2 (100% LNR), Paint 3 (75% LNR: 25% PVAc), Paint 4 (50% PVAc: 50% LNR), and Paint 5 (25% LNR: 75% PVAc) using standard emulsion paint formulation and method of production were employed. The paint samples were subjected to quality test. Most of the emulsion paint showed good quality test when compared by the Standard Organisation of Nigeria (SON). Paint 1 had an excellent viscosity and adhesion when compared with Paint 2 and other samples. Also, Paint 5 recorded 22.0 poise for viscosity and 0.68 kgf for adhesion when compared with other paint blends. This shows that, emulsion paint formulated blends of LNR/PVAc with percentage composition 25% LNR; 75% PVAc exhibited best performance characteristics in terms of test conducted. The results suggest that LNR and PVAc are compatible as binders in emulsion paint production. Therefore, LNR/PVAc blends could be used as binder in the coating industry as an alternative to PVAc binder based emulsion paint.

Keywords: High Cost, Blends, Liquid Natural Rubber, Polyvinyl Acetate, Emulsion Paint.

INTRODUCTION

Polymer blends are being increasingly used in many applications such as; coating, paint industry, automobile and aircraft industry, etc. Research in blends has become one of the biggest areas of polymer research, both in the industrial and academic world [2]. Blending two or more polymers may give rise to new polymeric system with new, interesting and “ad hoc” properties, different from those of the two components, thus eliminating the long and expensive route of synthesizing new polymers [3]. Hence, the aim of polymer blending is to develop products with unique properties that cannot be attained from individual constituents [1]. Polymers blends also consider the use of polymers from non-renewable sources. Polymers from non-renewable sources have attracted an increasing amount of attention over the last two decades, predominantly due to two major reasons: firstly, environmental concerns, and secondly, the realization that our petroleum resources are finite [4].

Polyvinyl acetate is a rubbery synthetic polymer with the formula ($C_4H_6O_2$) from a non-renewable source. It has a molar mass of

86.09 g/mol/unit. It belongs to the polyvinyl esters family with the general formula: $RCOOCHCH_2$ [5]. It is produced for use as binder in emulsion paints, adhesives and various textile-finishing operations [6].

Natural rubber (NR), on the other hand is an example of polymer from renewable source that consists of cis-1,4-polyisoprene as the main component, which exhibits excellent elasticity, resistance to tearing, and desirable dynamic properties. NR also contains non-rubber components such as phospholipids and proteins, which have a strong influence on the material properties [7]. However, the application of natural rubber is limited because it can be easily degraded by ozonolysis, exposure to light, and oxidation owing to the presence of double bonds in its chain. As a result of the limitations posed by NR, focus was given on the utilization of liquid natural rubber.

Liquid natural rubber (LNR) is a NR precursor or modified NR [8]. This differs from other liquid elastomers in the method of preparation. It is usually obtained by the partial

depolymerization of NR, and show some improvement previously found to be better than NR based on natural components that produce the color, appearance, and performance of NR [9]. For the preparation of LNR, two routes are normally adopted, one starting from dry rubber and the other from latex [10].

Today, the main advantages of the blended systems are simplicity of preparation and ease of control of physical properties by compositional changes [11]. The fact that the binders (LNR and PVAc) can be obtained in emulsion form and use directly in paints formulation especially water (emulsion) based paints promotes a better homogenous system [12].

Paints and coatings can be classified into the following major categories; architectural coatings, product coatings for original equipment manufacturers and special purpose coatings [13], of these three categories, emulsion paints as the paint of interest fall under the first category.

Emulsion paints are environmentally benign and show some qualities even comparable to oil based paints [14] as it evaporates water to the environment on application. The production quality of emulsion paints and performance depends largely on the properties of its constituents which include; pigments, solvents, extenders, binders and additives [15].

The binder (PVAc) usually takes between 17 – 33% total cost of production depending on paint type and this raw material is not available locally in Nigeria and therefore imported. Hence, there is high cost of this raw material (binder) and consequently high cost of production [16].

In this present work, we report on the utilization of binder blends of PVAc and LNR in emulsion paint formulation which to the best of our knowledge has not been previously studied.

EXPERIMENTAL SECTION

Raw Materials

Rubber latex was obtained from the Rubber Research Institute of Nigeria, Iyanomo, Benin City. Polyvinyl acetate (PVAc) was purchased

from Onitsha market, Anambra State, Nigeria. Chemicals and reagents used in this research work were of analytical grade and standard.

Liquid Natural Rubber Preparation

The LNR was prepared according to the method described by Okieimen and Akinlabi [17] with slight modification. Natural rubber latex was diluted to 22% dry rubber content (DRC) by adding distilled water and the latex was stabilized with 2% nonionic surfactant (Span 80). The latex was reacted with 50ml of 75% nitrobenzene. The reaction was allowed to proceed for various periods (up to 10 h) at 30°C under UV light with continuous stirring (60 rpm). The resultant product was coagulated with 2% formic acid. The yield was then washed with methanol and later with distilled water. The extent of depolymerization was determined by viscosity measurement using digital viscometer NDJ-SS.

Preparation of LNR/PVAc Blends

The blends of liquid natural rubber/polyvinyl acetate (LNR/PVAc) were prepared according to the ratio: 100:0, 75:25, 50:50, 25:75, 0:100.

Paint Production

The emulsion paints were formulated according to the Standard Organization of Nigeria (SON) [18] procedure with slight modification. First, distilled water was introduced into a 29.40grams empty container and stirred, calcium carbonate (CaCO_3) was then added, and the contents were stirred for some minutes. After some minutes, natrosol dissolved in distilled water was added into the previous contents. Subsequently, titanium oxide (TiO_2) and distilled water were added while stirring occurred for some minutes with the addition of formaldehyde, plasticizer, defoamer, anti-oxidant and binder. Finally, distilled water was added, the contents were stirred. The procedure was repeated for all formulations. Table1 presented the paint formulation recipes.

Table 1: Paint Formulation Recipes

Constituent	Raw material	Mass(g) Paint 1	Mass (g) Paint 2
Extender	Calcium Carbonate	150.0	150.0
Pigment	Titanium Oxide	2.0	2.0
Binder (Paint 1)	Poly(vinyl acetate)	100.0	0
Binder (Paint 2)	Liquid natural rubber	0	100.0
Thickener	Natrosol	5.0	5.0
Plasticizer	Ethylene glycol	5.0	5.0
Biocide	Formaldehyde	0.3	0.3
Antioxidants	Diphenylamine	-----	0.5
Defoamer	Kerosene	0.5	0.5
Solvent	Distilled water	90.0	90
	Total	352.8	353.3

Other Formulations of Binder Blends: Paint 3; 25% liquid natural rubber/ 75% polyvinyl acetate, **Paint 4;** 50% liquid natural rubber/ 50% polyvinyl acetate, and **Paint 5;** 25% liquid natural rubber/ 75% polyvinyl acetate.

Quality Parameter Tests of the Paint Produced

The performance characteristics of the paints were determined in terms of the followings; specific gravity (density bottle), pH (3020 digital pH meter), refractive index (refractometer), adhesion (testometric 200), viscosity (digital viscometer NDJ-SS). Procedure for other parameters is as follows:

Opacity (Hiding Power)

Alumni 1000 lecture theatre, University of Benin, Benin City, Nigeria, was used for the paint opacity. After two coats application on the substrate, the paint was allowed to dry and the coverage observed by visual assessment by three different observers.

Water Drop Test

Paint sample was applied on a glass panel and allow to dry. Then, 2ml of distilled water was placed on the film. The absence of cracking indicates good water resistance and vice versa.

Drying Time

Drying time of the paints on a vertical wall was observed with the aid of a stop watch and recorded.

Chemical Resistance Test

Coats of paint sample were applied on a slide and dipped in a beaker with 0.1M NaCl, 0.1M H₂SO₄ and 0.1M KOH respectively. The test piece was removed and air dried. The presence of surface defects such as peeling or change in colour indicates poor chemical resistance and vice versa.

RESULTS AND DISCUSSION

Table 2: Characteristics of Natural Rubber Latex Used

Parameters	Percent (by mass)
Dry rubber content (DRC) (%)	21.99
Total solid content (TSC) (%)	38.00
Sludge content (%)	7.37
Coagulum content (%)	32.37
pH	8.31
Mechanical stability time (sec)	90.00
Potassium hydroxide number (KOH No.)	0.74
Alkalinity (%)	0.03
Volatile fatty acid(VFA)	0.34

The dry rubber content (DRC) of the latex which indicates the exact amount of rubber present was found to be 21.99%. Thus, the DRC value could be as high as 60% [19].

Analysis of the latex sample also shows that the TSC is 38.00%; this implies the weight of the latex is non-volatile at a definite temperature [20]. Akinlabi *et al* [21] asserted that the total solid content is expected to be higher than the dry rubber content because dry rubber content is also embedded in the solids content of the rubber latex.

The KOH and VFA number is 0.74 and 0.34 respectively. These figures obtained indicate inadequate preservation of latex [22].

The sludge and coagulum content of the latex is 7.37% and 32.37% respectively. The sludge content is likely attributed to the non-

polymeric impurities ion present in the latex which sediment after centrifugation. On the other hand, the coagulum content indicates the percentage of latex that was coagulated with dilute acetic acid.

Table 3: Physico-Chemical properties of liquid natural rubber (LNR) and polyvinyl acetate (PVAc)

Parameters	LNR	PVAc
Appearance	Light brown	Cream
Viscosity (mPa.S)	138.59±0.84	2200.7±1.23
Density (g/cm ³)	1.791±0.06	1.057±0.01
Specific gravity	1.86±0.05	0.99±0.01
pH	7.94±0.46	6.58±0.01
Melting point	64.67± 2.52	80.67±3.06

Mean ± SD; n = 3

The PVAc binder has a high viscosity which accounted for 2200.7 (mPa.s) while the LNR accounted for 138.59 (mPa.s.). The difference in viscosity may arise as a result of variation in respective chain length. The use of high viscose binder is critical for obtaining quality emulsion paint [23].

The density of the synthesized LNR binder showed 1.791g/cm³, while that of the PVAc binder indicated 1.057g/cm³. The difference observed in the densities is likely attributed to the differences in the molecular features and morphology which influenced the packing nature of binder molecules.

The pH value of PVAc is 6.58 while LNR has a pH value of 7.94. This shows that LNR is more alkaline than PVAc. The pH values are within the acceptable range in the coating industry [24].

Physical Properties of Formulated Emulsion Paints

Some properties such as pH and specific gravity were compared with the specified range given by Standard Organization of Nigeria (SON) [18] for emulsion paint in Table 4.

Table 4: Comparison between Paint 1 and 2 Samples with SON Standard

Parameters	Paint 1	Paint 2	SON Standard
Specific gravity	1.26±0.01	1.81±0.01	1.30 – 1.40
pH	6.95±0.05	8.17±0.08	7.0 – 9.0
Opacity	P	P	Two coats
Viscosity (Poise)	20.87±0.03	15.93±0.003	6.0
Adhesion (kg-f)	0.82± 0.02	0.52±0.04	0.82-0.83
Refractive index	1.55±0.002	1.35±0.02	6.0
Surface drying time (min)	240	300	210
Water drop (resistance to cracking)	P	F	No cracking

Mean ± SD; n = 3

Key: P and F represent pass and fail respectively based on SON standard, Paint 1: 100% PVAc: 0% LNR, Paint 2: 100% LNR: 0% PVAc

pH of Paint

From Table 4 and 5, pH values of ‘Paint Samples’ produced fell within the specified range by the Standard Organisation of Nigeria (SON) [18]. The difference in pH values is influenced by the pH values of PVAc and LNR binder.

Opacity (Hiding Power)

Opacity is defined as the ability of a paint to cover a surface and mask it from view. Therefore, since paint binders are transparent, the job of hiding the surface falls primarily on the pigment [25]. Generally, Table 4 and 5 indicate that the ‘Paint Samples’ gave good hiding power after two coatings.

Viscosity and Adhesion of Paint

In Table 4, paint 1 displayed good adhesion and viscosity properties than paint 2. Therefore, it could be seen that PVAc binder has effects on the adhesion and viscosity of paint than the LNR binder used in Paint 2. The higher the proportion of the binder in the paint, the higher is the viscosity and binding strength [15].

From the result, it can be deduced that Paint 4 and 5 accounted for adhesion with values of 0.66 and 0.68 kg-f respectively which confirm that the binder blends have good binding strengths. Also, the painted area showed no chalking effects after two weeks of application while Paint 3 which had adhesion of 0.50 kg-f showed chalking effects and peeled on water exposure two weeks after application. The low adhesive tendency of the binder will be attributed to the effect.

Drying Time

From the result obtained, the delay in drying of the paint samples except for Paints 1 and Paint 4 to some extent may be due to non-volatile nature of LNR binder which account for many properties such as hardness, toughness and drying

Refractive Index

The result in Table 4 and 5 shows that Paint 2 also had a low refractive index. Hence, compared to other paint samples, it will most easily disintegrate on the surface on exposure to sunlight, releasing the pigments and allowing them to remain on the surface as powder or chalk. This observation is reinforced with cracking test failed by Paint 2 while others passed it.

Table 5: Comparison between Paint 3, 4 and 5 Samples with SON Standard

Parameters	Paint 3	Paint 4	Paint 5	SON Standard
Specific gravity	2.25±0.0	1.18±0.01	1.32±0.2	1.30 – 1.40
pH	7.52±0.29	7.51±0.03	7.21±0.9	7.0 – 9.0
Opacity	P	P	P	Two coats
Adhesion (kg-f)	0.50±0.07	0.66±0.06	0.68±0.7	0.82-0.83
Refractive index	1.52±0.002	1.37±0.004	1.52±0.2	6.0
Viscosity (Poise)	22.06±0.5	22.06±0.3	22.0±0.2	6.0
Surface drying time (min)	290	240	243	210
Water drop (resistance to cracking)	P	P	P	No cracking

Key: Mean ± SD; n = 3, P and F represent pass and fail respectively based on SON standard, Paint 3: 75% LNR: 25% PVAc, Paint 4: 50% LNR: 50% PVAc, Paint 5: 25% LNR: 75% PVAc.

Table 6: Chemical Resistance of Paint Samples.

Samples	Media		
	0.1M NaCl	0.1M H ₂ SO ₄	0.1M KOH
Paint 1	A	A	A
Paint 2	A	B	A
Paint 3	A	B	A
Paint 4	A	B	A
Paint 5	A	A	A

A= No effect, B = blistering

In Table 6, from the result obtained all the paint samples were unaffected by the salt medium and alkali solution. Paint 1 and 5 were unaffected by the acid solution while surface defects (blistering) was observed in the case of Paint 2, 3 and 4 respectively. The result also revealed that Paint 1 and 5 has a better chemical resistance than others. These differences are attributable to the difference in the binder used in the various media [26].

Conclusion

From the results obtained in this study, the following conclusions and recommendations were drawn; PVAc binder possessed better viscosity and adhesion (as properties that are of chief importance) than LNR binder. Since the cost of LNR is less than of PVAc, blending both binders will definitely lead to cost reduction for the production of emulsion paint. However, emulsion paint produced with 25%LNR: 75% PVAc binder blends showed best physical and chemical properties. Therefore, without compromising standard, efficient and cost effective emulsion paint can be produced using binder in PVAc to LNR ratios of 75:25%. In addition, the findings of this study can be applied in the scale-up emulsion paint production.

REFERENCES

- [1]. P. P. Kundu, D. K. Tripathy, and S. Banerjee. (1996). Studies on the miscibility of blends of polychloroprene and poly (ethylene-methyl acrylate) copolymer. *Polymer* 37, 2423–2431.
- [2]. M. T. Demeuse (1995). “High temperature polymer blends: An overview of the literature”. *Polymers for advanced technologies*, 6(2), 76 – 82 doi: 10.1002/part.1995.220060204
- [3]. P. Potschke and D. R. Paul (2003), Formation of Co-continuous Structure in Melt-mixed immiscible Polymer Blend. *J. Macromol. Sci. Part C. Polymer. Rev.* 43, 87-141. doi:10.1081/MC-120018022
- [4]. R. E. Drumright, P. R., Gruber and D. E. Henton (2000). Polylactic Acid Technology. *Advanced Materials*, 12(23), 1841–1846. doi:10.1002/1521-4095(200012)12:23<1841::aid-adma1841>3.0.co;2-e
- [5]. G. T. Murray (1997), *Handbook of Materials Selection for Engineering Applications*. CRC Press, pp 242.
- [6]. J. A. Brydon (1975), “Latex derived blends of poly (vinyl acetate) and natural rubber,” *Plastic materials*, 3rd ed., newness-butter worths, London, pp. 317-321
- [7]. Y. Tanaka (2001). Structural Characterization of Natural Polyisoprenes: Solve the Mystery of Natural Rubber Based on Structural Study. *Rubber Chemistry and Technology*, 74(3), 355–375. doi:10.5254/1.3547643
- [8]. Institut de Recherchessur le Caouthchouc (IRCA), (1985). Development of Liquid Rubber, Project no. UF/GLO/81/059, Final report, United Nations Industrial Development Organization (UNICO)
- [9]. Development of the Applications of Liquid Natural Rubber [Final Report]. UNIDO project, 1989
- [10]. N. R. Nair, N. M. Claramma, N.M. Mathew, S. Thomas, and S. S. Rao (1995). Flow properties of thermally depolymerized liquid natural rubber. *Journal of applied polymer science*, vol. 55, pp.723-731
- [11]. J.M. Yelwa, S. A. Osemeahon, I. I. Nkafamiya and S. Abdullahi (2017). Synthesis and Characterization of Hydroxylated Sunflower Seed Oil/Polyvinyl Acetate Copolymer As A Binder for Possible Application In the Coating Industry. *International Journal of Innovative Research and Advanced Studies*, vol. 4. Issue 7, pp.1-9.
- [12]. N. H. A. Azhar, H. M. Rasid and S. F. M. Yusoff (2016). Chemical Modifications of Liquid Natural Rubber. *American Institute of Physics*.doi:10.1063/1.4966762
- [13]. J.C. Dean (1981) “Coating: the U. S Coating Industry Strategy for Survival in the 80’s, the Chem Week, Vol.29
- [14]. V. Kumthekar and S. Kolekar (2011). Attributes of the latex emulsion processing and its role in morphology and performance in paints. *Progress in Organic Coatings*, 72(3): pp 380- 386.
- [15]. S. Abdulsalam and Y. U. Yahaya (2010). Effectiveness of Gum Arabic as a binder in Emulsion House Paint”, *Global Journal of Engineering research*, 10 (1 & 2). pp. 83 – 89.
- [16]. S. Abdulsalam and Z. D. Maiwada (2015). Production of emulsion house paint using polyvinyl acetate and gum Arabic as binder. *International Journal of Materials Science and Applications*. Vol. 4, No.5, pp. 350-353 doi: 10.11648/j.ijmsa.20150405.20
- [17]. F. E. Okieimen and A. K. Akinlabi (2002). Processing Characteristics and Physico-mechanical Properties of Natural Rubber and Liquid Natural Rubber Blends. *Journal of Applied Polymer Science*, vol. 85, 1070-1076.
- [18]. SON (1990). Standard for Emulsion paints (decorative purposes). Batch Test and methods of paint production. pp. 5-13.
- [19]. The International Organization for Standardization Natural Rubber Latex Concentrate, (2011) – Determination of alkalinity (ISO standard No. 126), 6th ed. Geneva, Switzerland: The International organization for standardization.
- [20]. D. C. Blackley (1997). *Polymer Lattices*, Science and Technology. (2nd

- Ed.) *Chapman and Hall*, London. Vol. 2. Chapter 3.
- [21]. A. K. Akinlabi, T. O. Akinola, R. K. Quadri, O. S. Babajide and I. A. S. Bankole (2016) Properties of Natural Rubber Compounded with Modified Banana Pseudostem Fibres and Calcium Carbonate. *Journal of the Chemical Society of Nigeria*. 41 (1) pp. 36-42.
- [22]. W. M. Philpott and D. R. Westgarth (1953). Stability and mineral composition of Hevea latex. *J. Rubb. Res. Inst. Malaya*, 14:133
- [23]. J. E. Bailey and D.F. Ollis (1977). Biochemical Engineering Fundamentals. *International Student Edition*, McGraw- Hill Kogakusha, Ltd, New Delhi.
- [24]. Nigeria Industrial Standard Specification for Emulsion Paints for Decoration Purposes (2008). Standard Organization of Nigeria. ICS: 87.040.
- [25]. T. Rodger (2007). Paint Technology Handbook, CRC Press, p. 82.
- [26]. S. A. Osemeahon and J.T. Barminas (2007). Study of a composite from reactive blending of methylol urea resin with natural rubber. *Afri. J. Biotechnol.*, 6(6): 810-817