

Full Length Research Paper

Adhesive formulations with ternary blends using simplex lattice design

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Three different polymer latices (latexes) derived from natural rubber (NR), Acrylic (Ac) and Vinyl Acetate/Veova (VA/Ve) copolymer emulsions were blended to yield ten compositions using the principle of simplex lattice design, after adjusting their TSCs solids to 30% (v/v) by dilution with distilled water. The blends were characterized for the determinations of pH, conductivity and refractive indexes, after which they were used in formulating corresponding number of water-based adhesives. Adhesive joints were prepared in pairs for every formulation by bonding two wood pieces with the adhesive. One set was for curing in sun and the second in oven temperature conditions, respectively. Bond strengths of the cured joints were evaluated using a locally improvised tool due to lack of standard testing device. It was observed that the highest value of bond strength was obtained after sun curing for the adhesive based on the blend which contained NR, Ac and VA/Ve in the ratio of 1/6:2/3:1/6, respectively. This blend was thus regarded as “optimum blend”. It was generally observed that the bond strengths obtained after sun-curing process were always higher than similar values obtained for oven dried conditions. This suggested that sun-curing conditions are more suitable for curing the prepared adhesives than oven-curing conditions. Bond strength measured from adhesive joint similarly prepared using a popular commercial wood based adhesive (Top Bond) in Nigeria was also compared to bond strength of the adhesive based on the optimum blend as mentioned above. Interestingly, it was observed that the value of bond strength from the latter was more promising.

Key words: Ternary blends, latexes, simplex lattice design, substrates, adhesive joints, adhesive formulations.

INTRODUCTION

Polymer blends (PBs), polyblends or simply blends are interchangeable terms referring to any physical mixture of two or more different polymers or copolymers that are not covalently bonded. Sometimes, blend is used for a mixture of polymers/copolymers of the same chemical composition but different in grades, for example, different molecular masses (Olabisi et al., 1979; Alger and Dyson, 1990). PBs continues to be a subject of investigations in both academia and industries because of their simplicity and effectiveness of mixing two or more different polymers to obtain new materials (Krupa and Luyt, 2001; Zeng et al., 2004). Since blends involve the use of pre-existing materials, without recourse to synthesis, they

offer pecuniary advantage and time-saving economy. The rubber industry as well as commodity plastics producers have used blending so as to continuously improve on the properties of their products and to meet customers' specifications (McDonel et al., 1978). PBs also has great potentials for development of adhesives. Adhesives are substances that are capable of joining two different surfaces so as to resist separation and they are usually obtained from polymeric materials. Latexes, also known as polymer colloids (Sperling, 1992), provide opportunities for making water-based adhesives which are environmentally friendly. Due to stringent legislation against solvent based systems by Environmental Protection Agencies (EPA), water based adhesives are increasingly gaining prominence in contemporary times. Dangers such as fire hazards, environmental pollution and ozone depletion common with solvent systems are

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completely avoided with water-based systems.

Latexes are obtained either naturally, as for example natural rubber latex from *Hevea brasiliensis*, or by synthesis with several examples now available. The synthetic ones are prepared from raw materials based on petroleum and/or coal which are non-renewable and, therefore, must be used with economy. NR is an agricultural product which is abundantly cultivated in Nigeria and other parts of the world. It is, therefore, cheap and being biodegradable does not constitute hazards to environment. It has excellent resilience and abrasion resistance. However, NR, due to presence of unsaturation in its stem, is thermally unstable and susceptible to oxygen degradation in presence of light which are factors that tend to limit its applications. VA/Ve emulsions are both synthetic latexes and costly. Acrylics are known for their good film hardness and good adhesions on a number of substrates but, unfortunately give rise to flat finishes which, apart from being brittle at low temperature, also have weak solvent resistance. VA/Ve has excellent gloss, high water resistance, UV resistance and alkali resistance which lead to superior durability. However, they are more expensive than acrylics and need to be stabilized by surfactants to be able to exhibit the required hardness/flexibility for formulation of a range of high performance water-based products.

In this paper, a systematic method for optimizing properties from three or more component mixtures, known as "Simplex lattice design" (SLD) was employed in the blending procedure. The use of this technique has been reported by Morphy et al. (1989) in making adhesives from three polymer emulsions, based on acrylic, epoxy and urethane the three different latexes. In this paper, NR, Ac and VA/Ve were blended systematically and used in formulation of water-based adhesives. The decision to blend these three polymers is predicated on the possibility for obtaining a composite product that can be much better than any single component alone. After the blends were compounded as water-based adhesives, the latter were then used to bond wood specimens. Curing of the specimens followed immediately under sun and oven conditions separately, in order to ascertain the effect of the different climatic conditions on bond strength.

EXPERIMENTAL

Materials

Natural rubber latex (LA-TZ grade) was supplied by Rubber Research Institute of Nigeria (RRIN), Iyanomo, Benin City; VA-Veova emulsion by NYCIL Ltd, Sango Otta, Nigeria and Acrylic was donated by Chemstar Paint Nigeria Ltd., Lagos, Nigeria. All these materials were used as received without need for further purification.

Determination of total solid contents (TSCs) of the lattices.

The three polymer lattices, as received, were thoroughly stirred and portions from each weighed into three different petridishes using a Metler weighing balance (Model: 13300D-12951). These were then heated in an oven at fixed temperature of 50°C. After regular intervals the samples were taken out, cooled in a dessicator and then re-weighed. The process was heating, cooling and re-weighing was repeated until constant weights were obtained. The percentage TSCs of each sample was therefore evaluated using the equation below:

$$\% \text{ TSCs} = W_f/W_i \times 100 = (W_3 - W_1)/(W_2 - W_1) \times 100 \quad (1)$$

Where, W_1 = weight of empty dish, W_2 = weight of dish + sample content before drying, W_3 = weight of dish + sample content after drying, W_i = Actual weight of the wet sample, W_f = Actual weight of the dried sample.

A set of three measurements were taken for each sample and the values reported as average total solid contents.

Preparation and Characterization of Diluted Aqueous Dispersions Latices

Determination of water of dilution

Using the values obtained for TSCs, the individual samples were subsequently diluted to 30% (v/v) aqueous dispersions using distilled water. The quantity of water required for the desired dilution was determined based on the following expression:

$$V_{H_2O} = V_i(C_i - C_f)/C_f \quad (2)$$

Where, V_i = Initial volume of original emulsion taken for dilution, C_i = Initial TSCs of the emulsion before dilution, C_f = Final TSCs in the diluted emulsion, V_{H_2O} = Volume of water required for dilution so as to yield the final (expected) TSCs.

Characterization of the physical properties of the diluted dispersions

The pH of the diluted aqueous dispersion was determined using a pH meter (Model: Kent E/L 704/46), conductivity, using conductometer (Model: Kent E/L 5007) and refractive index, using refractometer (Bellingham + Stanley Limited, England).

Measurement of drying rates of dispersions' films

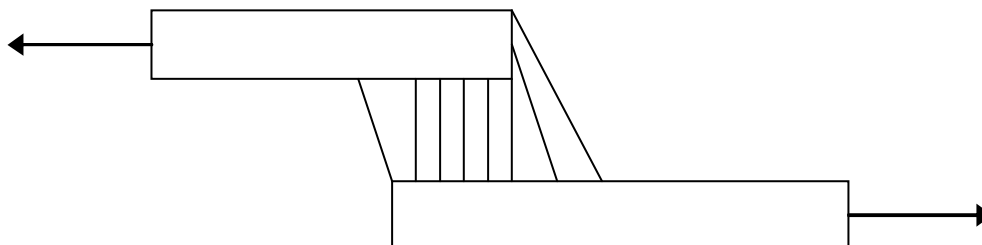
Casting surfaces were first prepared by fastening, using adhesive tapes, transparent polyester (PE) sheets on rectangular glass sheets (Dimension: 21 × 20 cm). An appropriate quantity of each of the dispersions that can cover the respective casting area was then poured on the casting surfaces, after which a spreader ("Doctor Blade") was glided smoothly over the dispersion thereby spreading it as a thin film on the casting surface in defined direction. The spreader is a polished metal mold designed with different dimensions of gauge gaps so as to provide choice of different thicknesses of the cast films, viz: 0.25, 0.50, 0.75 and 1.00 mm, respectively. In this paper, the gauge gap of 0.5 mm was adopted throughout for casting of all the films. Immediately after the casting, the wet films were left on the substrates for air-drying at ambient conditions while their drying rates were being monitored at set time

Table 1. Schematic representation of the simplex lattice design for blends' formulation.

Formulation no.	Natural rubber	Acrylic	VA/Veova
1	1	0	0
2	0	1	0
3	0	0	1
4	$\frac{1}{2}$	$\frac{1}{2}$	0
5	$\frac{1}{2}$	0	$\frac{1}{2}$
6	0	$\frac{1}{2}$	$\frac{1}{2}$
7	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
8	$\frac{2}{3}$	$\frac{1}{6}$	$\frac{1}{6}$
9	$\frac{1}{6}$	$\frac{2}{3}$	$\frac{1}{6}$
10	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{2}{3}$

Table 2. Recipe for the adhesive formulations.

Ingredient	Function
Natrosol	Thickener
Texapin N70	Surfactant
Paraffin oil	Plasticizer
Glycerol	Coalescing agent
Sulphur (powder)	Curing agent
CaCO ₃	Filler
Phenol	Antioxidant
Sodium benzoate	Preservative

**Figure 1.** Single lap joint design for bonding with the adhesives.

intervals until they were set-to-touch, which means when the cast films could no longer stain the hand when touched with a finger.

Adhesive formulations

Ten different blends were first prepared from the diluted aqueous dispersions of the latex samples based on simplex lattice design (SLD) (Table 1). This experimental design requires that the sum of mixing ratios of all the components that is used for blending at each instance is a constant value equal to unity (in this case, based on 60 cm³ total volume of the dispersions). For blends which involve a component that is acidic, as for example, acrylic with NR, the NR was initially pre-mixed with ammonia solution to adjust its pH to about 9 in order to prevent coagulation of NR before homogenization. All the blends obtained from the dilute aqueous dispersions were formulated into adhesives using the recipes shown in Table 2.

Characterization of the adhesives' properties

Following the formulations, the adhesives were characterized for determination of such parameters as pH, conductivity and total solids contents, respectively as similarly previously determined with the aqueous dispersions of the latexes and in addition, for the adhesive bond strengths. In order to examine the bond strengths, the adhesives were applied to bond two adherends based on single lap joint design as shown in Figure 1. After air drying, the resulting adhesive joints were tested for bond strengths using an improvised device based on wooden substrate, as illustrated schematically in Figure 2.

Prior to application of the adhesives, the surfaces of the substrates/adherends were, however, firstly specially pretreated by planning, smoothening with sand paper followed by air-blasting to remove accompanying dust. After the surface treatment, the adherend/substrate pair was joined following application of thin film of the adhesive on pre-measured area of coverage. Two sets of test

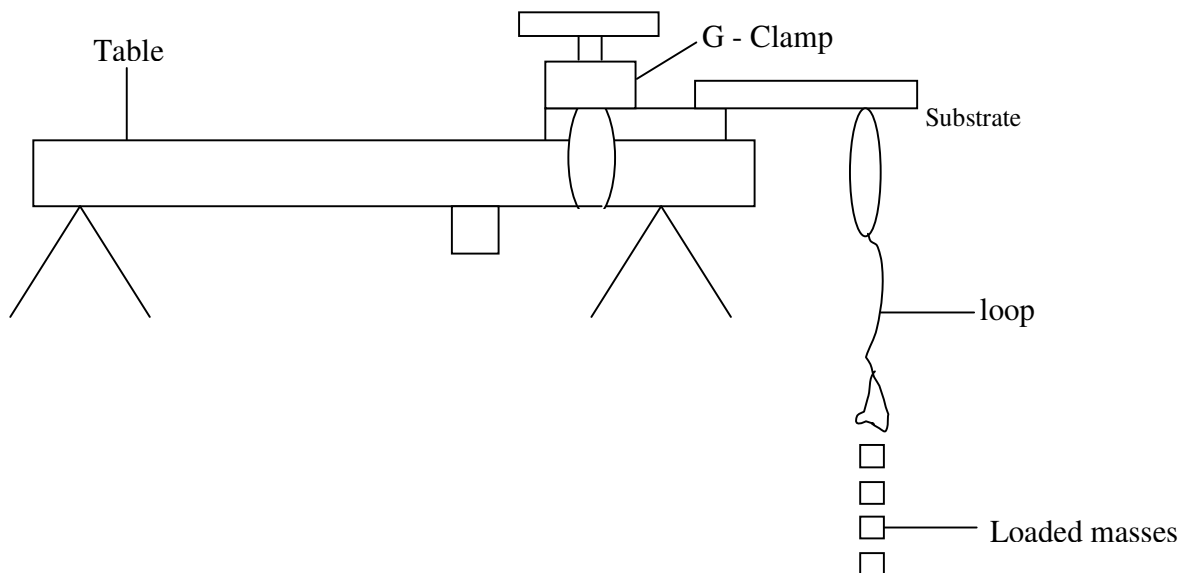


Figure 2. The device used for measurement of bond strength.

samples were made for every particular adherend/substrate combination, one for drying in the air and the second for drying in oven condition at a constant temperature (50°C) for comparative purposes. After the curing process, the procedure used to measure the bond strength involved the clamping of the bonded specimens as schematically shown in Figure 2. One end of the bonded specimen was firmly attached to the flat surface of a table by means of the clamp. On the other end of it, standard weights were gradually applied via a loop until the point of failure of the specimen, which could either be at the bond joint or any other point on the substrate. The formula used for evaluating the bond strength was determined from the minimum amount of load that would result in failure at the adhesive joint and was evaluated using the expression below.

$$\text{Bond strength} = \frac{\text{Force at specimen failure}}{\text{Surface area of contact}}$$

Similarly, same test procedure was used in assessing and comparing bond strength of a commercial adhesive with those of the ones prepared in our laboratory.

RESULTS AND DISCUSSION

Characteristics of the dispersions

The results of the determination of TSCs of the undiluted samples as received were 41.21, 50.20 and 53.00 wt% for NR, VA/Ve and Ac latexes, respectively. These were mean values obtained from three different determinations for each sample. From the results, it is observed that NR has the lowest value of TSCs followed by VA/Ve with the Ac polymer having the highest value. These results were in good agreement with the physical condition of the

samples. For example, in terms of physical appearance, the acrylic polymer, which has the highest value of TSCs, was the most viscous of the three. Being synthetic, both acrylic and VA/Ve latexes can be formulated to varied TSCs by the controlled addition of additives in order to increase bulk and hence lower the costs of production as well as impart other properties as desired. The characteristic value of TSCs of NR latex that is freshly obtained from the trees is reported (Onwueme, 1979) to fall usually around 35 wt%. Usually, through a process of concentration, which may involve evaporation, centrifuging or creaming, the TSCs of the freshly obtained latex can appreciate to a value of about 60 – 65 wt%. In the present study, the observed measured TSCs of NR was determined to be 41.21wt%, which was a little above the literature value of 35 wt%. This difference could also be due to partial concentration of the latex through some evaporation of water from the latex during transportation and/or storage.

The properties of the diluted aqueous latexes (conc., 30% (v/v)) are shown in Table 3. Of these, the most important technically, from adhesive point of view is the rate of drying. From the results obtained, NR took the longest period (123 min) to dry after casting as a thin film, followed by Acrylic (93 min) and finally the VA/Ve copolymer. It is suggested that NR took such a long period to dry because its drying process involve both a chemical process, known as “oxidative polymerization” as well as a physical process which is essentially evaporation of water and other volatiles. The chemical process is characteristically a much slower process and leads to crosslinked network structure that is responsible for the water-proofing property of NR however, the first stage of the drying process of NR is the evaporation of its

Table 3. Properties of the diluted aqueous dispersions as determined.

Sample	pH	Conductivity	Refractive index(μ /cm)	Dry time (min)
NR	10.98	640	1.490	123
Acrylic	7.95	480	1.510	93
VA/Veova	4.64	240	1.500	67

Table 4. TSCs of sample-based and commercial adhesives.

Adhesive type	TSCs (wt %)
NRL	50.81
VA/Veova	63.23
Acrylics	73.00
Top bond (Commercial)	55.00

water and other volatiles contents which is relatively a much faster process than the subsequent second step involving the chemical process. On the other hand the drying process of the other two remaining latexes, namely Acrylic and VA/Veova, usually occur more or less exclusively by evaporation of its water content which takes comparatively shorter time. The probable reason that acrylic took longer time than VA/Veova to dry was attributed to its higher solid contents than that of VA/Veova. The higher the solid contents of a system, the slower the mobility of molecules of its liquid contents and consequently, the longer correspondingly the time it takes for the system to dry than with a system with lower solid contents. Also from Table 3, it is seen that the conductivity values of the aqueous dispersions differ markedly between themselves and these values seem to bear a direct proportional relationship with the systems' pH. For example, as seen, NR with the highest pH value has the highest conductivity value, while VA/Veova with the lowest value of pH is correspondingly least in the value of conductivity. The high pH value of NR is undoubtedly due to the presence of ammonium hydroxide which was added as a preservative to prevent coagulation of the latex shortly after tapping. The acrylic latex with a pH value of 7.95 is seen as slightly alkaline while VA/Veova with a pH value of 4.64 is purely acidic. Traditionally, basic medium is favoured for formulation of water based adhesive systems, as they tend to lower surface tension thus enhancing wetting of the substrate surface. In similar vein, high conductivity for this kind of system tends to aid adhesion to surfaces via electrostatic interaction between the substrate and the adhesive. The measurement of refractive indices was undertaken in order to characterize the optical properties of the dispersions. Such determinations help in decision for use of materials in special applications. As seen from the results, there seems to be no systematic pattern in the variation of values of refractive indices obtained for all the dispersions. The significance of the refractive index

measurement is that it gives indication of the turbidity of a system. The refractive indices shown in Table 3 are higher than the refractive index of water, thus indicating that the systems are far less transparent. In some instances, certain liquid adhesives are formulated in form of clear solutions/dispersions, depending on intended application (s) and/or choice of end user (s).

The results of TSCs determined for the formulated adhesives compared with similar value obtained for that of a commercial adhesive are presented in Table 4. The differences observed between the solids contents of the formulated adhesives were inherited from the original dispersions from which they have been prepared since the same recipes applied to all. On the other hand, the differences in solids contents between that of the commercial adhesive (Top Bond) and of formulated adhesives could reasonably only be attributed to disparity in method/ingredients of formulations.

Determination of bond strengths of adhesive

Bond strengths were measured based on adhesive joints formed under two separate drying conditions, viz sun and oven drying. The results obtained are shown in Table 5.

As seen from Table 5, among the adhesives based on individual dispersions, the highest bond strength recorded is represented by the component, 0:1:0 (Ac.) under sun-dried process while in the case of the blends, the highest recordable bond strength was represented by components with ratio, 1/6: 2/3:1/6 under oven-dried process. It can be observed that bond strengths obtained under sun-cured conditions were always of greater magnitude than that recorded based on oven-cured conditions. The generally lower values of bond strength attained against oven conditions might be due possibility that the oven conditions impacts degradative effect on the polymer of the adhesive which leads to partial destruction of its mechanical integrity and consequently,

Table 5. Bond strengths of adhesive formulated from each blend.

NR:Ac:VA/Veova	Bond strength (N/m ²)	
	Sun-dried	Oven-dried
1: 0: 0	20	16
0: 1: 0	48	40
0: 0: 1	40	36
1/2: 1/2: 0	36	28
1/2: 0: 1/2	32	24
0: 1/2: 1/2	C.N.D.	36
2/3: 1/6: 1/6	32	20
1/6: 2/3: 1/6	C.N.D	48
1/6: 1/6: 2/3	C.N.D	40
Top bond	52	48

C.N.D. = could not be determined.

reduced bond strength as observed. The spaces with C.N.Ds against them are those for which the bond strengths were too strong that the test method used could not cause bond failure at the adhesive joints. Thus, it was assumed that the bond strengths, though undetermined, were correspondingly higher than that of the comparable pair measured against oven-dried conditions.

From the results, it seems that solid contents of adhesives play a crucial role in their bonding ability. Looking at the TSCs of these adhesives (Table 4) vis-à-vis their recorded bond strengths obviously leads to the generalization that, the higher the solid's contents, the higher the values of bond strength. For example, NR which has the lowest TSCs was found to have the least bond strength whereas acrylic latex which has highest value of solids contents showed the highest bond strength. It is, therefore, to be advised that, in formulating adhesives, it is important to note the significant role of solids contents with a view to optimize the influence of this key factor in order to achieve the desired adhesive bond strength.

The characteristics of the commercial adhesive ("Top Bond") are shown in Table 5. Given its TSCs value of 55.0 and following from the above discussion on the relationship between bond strengths and TSCs, it would have been expected that the bond strength of this commercial adhesive is between that of NR and VA/Veova. However, its bond strength of 52 obtained under sun-dried condition is higher than the value recorded for any of the individual component based adhesives, prepared and cured under same condition. This implies that, though TSCs is a key factor, it might not be the only determinant factor of adhesive's bond strength. The ingredients used in formulation could be the greatest influence.

Conclusion

Using the SLD, adhesives have successfully been prepared from three components namely NR, VA/Veova

and acrylic dispersions, respectively. The resulting adhesives along with its precursors, that is, the dispersions have also been characterized. The properties of the adhesives were found to be affected by the nature of polymer dispersion used in preparing them. It has also been observed that the conditions under which curing took place influenced the value of bond strength obtained for the adhesives. Typically it was seen that the adhesive joints formed as a result of curing under sun drying condition showed bond strengths that were of higher value than for those cured in oven drying condition. This has been attributed to ageing effect that could have been more pronounced by oven condition than in the case with sun drying condition. Finally, it was found that the characteristics of the adhesives formulated showed better adhesive potentials than what were found for a popular commercial adhesive (Top bond) used comparatively in this study.

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