Influence Of Renewable Polymer/Modifier Composition And Processing On The Properties Of Multifunctional Adhesive Leather Bonds From Pvac.

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***Abstract*—Environmentally friendly polymer was used to enhance the functionality of adhesive bondlines by esterification. In this experimental research starch-based adhesive was formulated from Ipomea batatas and copolymerized with PVAc. Starch extraction was carried out by conventional method and various formulations of the adhesive made by varying the quantity of fatty acid ester; quality assessment was then performed. The result showed that incorporation of 20 % polyvinyl acetate significantly improved the bond strength as well as mobility and storage stability of the adhesives system. The tensile lap-shear test and peeling rate were carried out on the modified and unmodified adhesives. The tensile lap-shear strength and shear modulus of the formulation was found to be 26.66 MPa and 0.53 GPa respectively, found to be higher than some other starch-based and gelatin-based adhesives and comparable to the commercial adhesive counterparts that was used as control. The result of mechanical strength analysis revealed that the adhesive is of good quality and will compete favorably with other starch-based adhesives. The bond strength analysis also confirmed that there was polymer compatibility between the polymer matrixes. Compared with gelatinized starch, FTIR showed the copolymer have new characteristic peaks of ester at 1070-1080.9 cm^{-1} in the infrared spectrogram. SEM/EDS also revealed that the grafting reaction between Starch/PVA and triethylamine greatly improved the component compatibility of the starch based adhesive as well as limited the phase separation between the starch and the polymer.**

Keywords—Biobased adhesive, bonding strength, renewable polymer and Polyvinyl Acetate.

1. INTRODUCTION

Virtually all synthetic adhesives and certain natural adhesives are composed of polymers, which are giant molecules, or macromolecules, formed by the linking of thousands of simpler molecules known as monomers. The formation of the polymer (a chemical reaction known as polymerization) can occur during a " cure" step, in which polymerization takes place simultaneously with adhesive-bond formation (as is the case with epoxy resins and cyanoacrylates), or the polymer may be formed before the material is applied as an adhesive, as with thermoplastic elastomers such as styrene-isoprene-styrene block copolymers. Polymers impart strength, flexibility, and the ability to spread and interact on adherend surface properties that are required for the formation of acceptable adhesion levels.

An example of a multi-billion-dollar global chemical industry featuring a wide variety of chemical products tuned for specific applications is the adhesives industry [1][2]. Generally, adhesives are materials used to join two or more other materials (often called adherends) through surface attachment to form a final assembly [2]. Adhesives have numerous applications, sometimes people exploit the adhesive properties of materials without even having any idea of what actually is behind it. The relevance of adhesives in these contemporary times cannot be over emphasized. As Buba *et al*., 2014, rightly stated People now routinely trust their fortunes and their lives to adhesively bonded structure and rarely think about it [3], but the subject of adhesives and adhesive bonding is of great importance to researchers. Adhesives are utilized on many scales throughout the world, with a large range of characteristics, by both nature and man. Global Industry Analysts Inc. mentions more specifically current widespread usage in the sectors of packaging, automotive, electronics, footwear, construction repair and remodeling, textiles, consumer goods and shipbuilding.

Recent applications of adhesives includes; (i) recovery of DNA from crime scene items (ii) assembly of load-carrying parts made of lightweight composites by the aerospace industry and (iii) wound closure, fracture fixation and micro scale vascular surgery [4].

Because of the widespread and numerous usage of adhesives, together with its diversity in the utilized chemistry, application methods and sources of the components, resulted to several methods of classification. Commonest among is classification based on the strength of the created joints [1][2]. This method makes a distinction between three main types: (i) pressure-sensitive adhesives, which possess a very limited adhesive strength; (ii) semi-structural adhesives (divided into hot-melt and solvent based groups), capable of supporting a small load (0.3 – 3 MPa) for a long time; (iii) structural adhesives, able to bear a significant load (> 7 MPa) for a long time. However, they are driven by strongly fluctuating prices and the products are derived from petroleum [1]. Because of the increased general concerns on the impact of industrialized societies on the environment and public health, adhesive producers are confronted with the challenge of becoming more sustainable [5]. The additional classification of natural product-based (or bio-based) adhesives, contrasted to fossil fuel-based (Synthetic), is therefore important to mention (since they have the corresponding general features of environmentally benign production, recyclability and biodegradability). Natural product-based adhesive includes; animal glues, casein glues, natural gums and resins, sodium silicates and vegetable glues.

Vegetable glues are starch-based and are made from starches and dextrins. Starch has several advantages as a raw material in the production of adhesives including; renewability, biodegradability, abundance, cheapness and stability in price. Starch-adhesives can be applied at ambient or moderately low temperature, are usually re-wet able, and have little or no odour or taste at all. Starch is a carbohydrate consisting of a large number of glucose units joined by glycosidic bonds. According to Ihenetu and Igbokwe, 2017, starch is the major component of flour, potatoes, rice, beans and corns [6]

2. MATERIALS AND METHODS

All materials used for this study were in good working condition, they includes;

2. 1 Apparatus

Beakers, Reagent bottles, storage containers, measuring cylinders, conical flasks, Analytical weighing Balance, glass rod, Petri dishes, spatula, pipette, oven, 100 µm Mesh, Muffle furnace, Volumetric flask, pH meter, crucible, visco meter or flow cup, Mosanto tensiometer and Muva peeling machine.

2.2 Reagents

De-ionized water (H_20), sodium hydroxide (Na0H), Borax ($Na_2B_40_7.10H_20$), Triethanolamine $N(CH_2CH_2OH)_3$, Polyvinyl alcohol ($CH_2CH(OH)$), Citric acid (CH_3COOH).

2.3 Sampling method

Ipomea *batata* roots (IBS) was obtained from a local farm settlement by the researcher in Zaria, Kaduna State, Nigeria and identified in the presence of the researcher at the Biological Science Department of Kaduna State University.

2.4 Isolation of starch dextrins.

Starch from Ipomea *batatas* was produced primarily by the wet milling of fresh Ipomea *batata' s* roots. Extraction of starch from fresh roots was performed based on the method of Akpa, 2012 [7].

2.5 Determination of tensile lap-shear strength

The adhesive was robbed on a parallel leather-leather surface and allowed to dry for about 20, 30, 40 and 50 minutes at a temperature of 30 ^{o}C. The specimens were positioned in the grips of the testing machine and the grips were tightened evenly and firmly to prevent any slippage and as tensile test started, the specimen elongated, the resistance increased and is detected by the load cell. The load cell was recorded until a fracture or rupture of the specimen occurred. The specimen was subjected to a pulling force and time taken for substrate to separate was noted. The shear strength was determined from the maximum load before adhesive failure [8].

2.6 Determination of peeling strength

Muva peeling machine (Model 5038) was used to monitor the polymer adhesion of leather-leather substrate (7.5 mm). 180 ^{o} peel test was employed to analyze the fracture behavior of the formulated adhesives. The current research examines the behavior of adhesively bonded joints under various loading rates (500 g to 2000g) by conducting peel test. In all tests, bonded thin sheets of leather substrates using the formulated adhesives were each subjected to different loadings to determine the peeling rate of the various specimens [9].

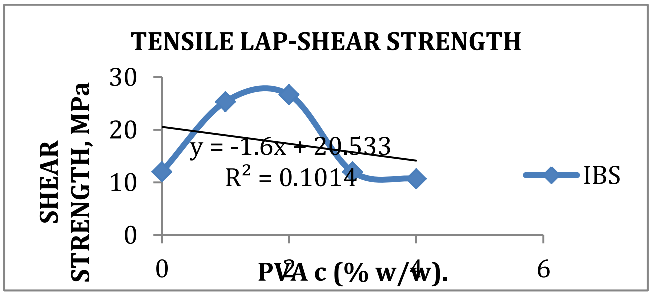

Fig. 3.1: Effect of modification on tensile-lap shear strength of IBS starch-based adhesives.

Fig. 3.2: Effect of modifier on IBS adhesives performance during storage.

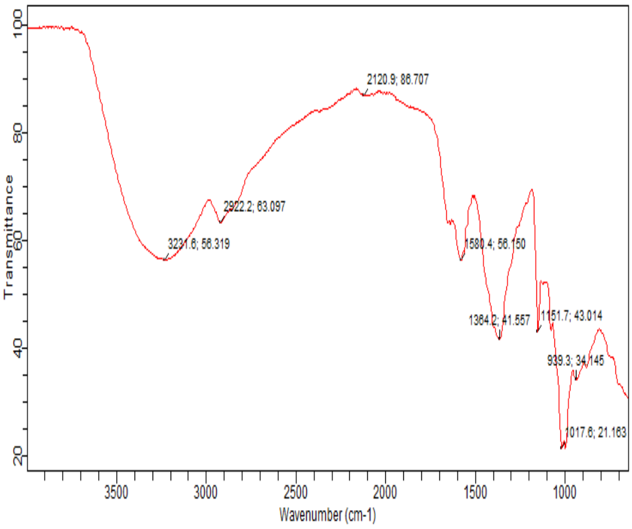

Figure 3.3(a): FTIR of Ipomea *batatas* Starch-based Adhesive Without PVAc.

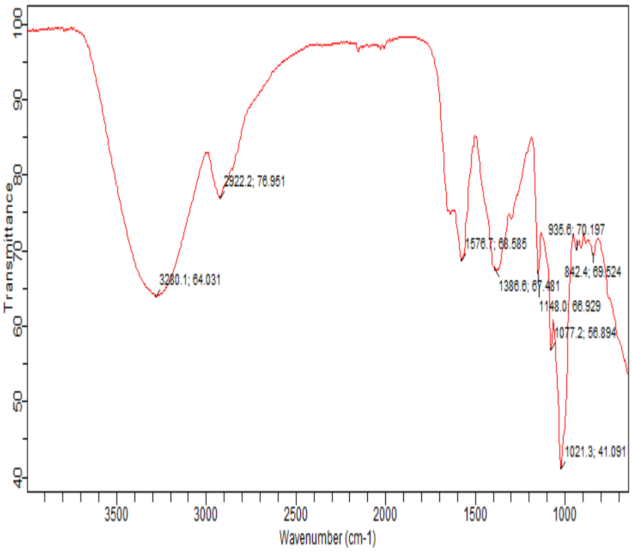

Figure 3.3(b): FTIR of Ipomea *batatas* Starch-based Adhesive With 20% PVAc.

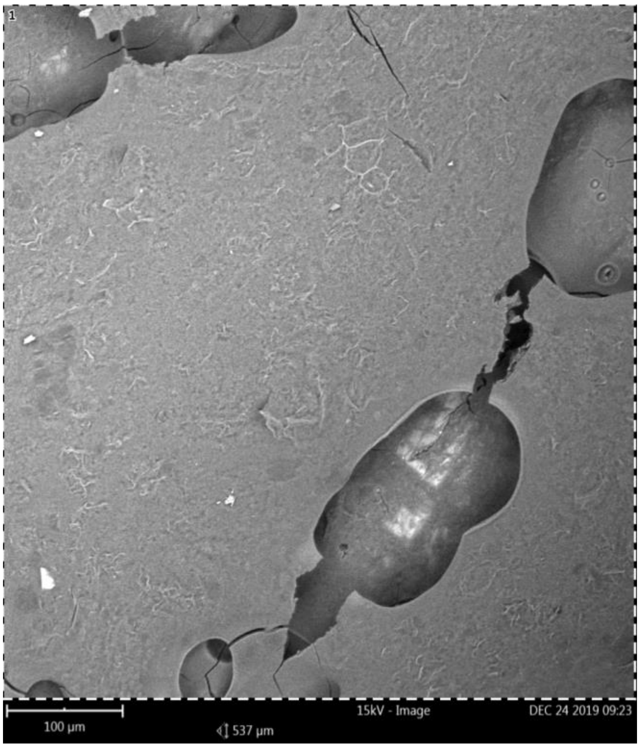

Figure 3.4(a): Scanning Electron Microscopy of Ipomea *batatas* adhesive in the abscence of PVAc.

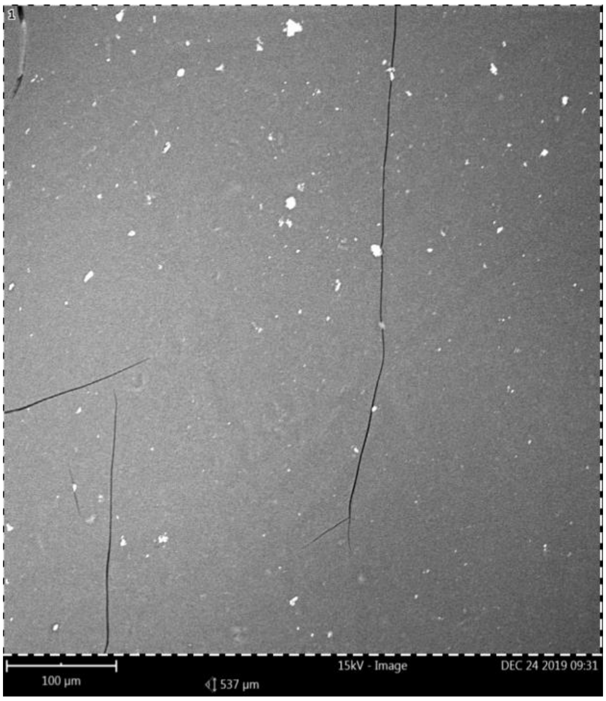

Figure 3.4(b): Scanning Electron Microscopy of Ipomea batatas adhesive in the presence of PVAc.

Table 3.1: Peeling strength of the formulated adhesive systems and the commercial counterpart.

ADHESIVES	% w/w MODIFIER	LOAD (g)	FORCE (N)	PEELING STRENGTH (MPa)	AVERAGE VELOCITY (cm/s)
IBS	0 % PVAc	750	7.5	1.00	0.15
	20 % PVAc	1250	12.5	1.66	0.18
COMM.		1500	15.0	2.00	0.16

Temperature: 60 ^{o}C.

3. RESULTS AND DISCUSSION

3.1 Effect of modifier on adhesives shear strength

The influence of 10-50% (w/w starch basis) PVAc addition on the shear strength of natural polymers is presented in Fig. 3.1. With addition of PVAc, the shear strength was increased in starch-based polymers which could be assigned to the grafting reaction promoted by PVAc along the growing polymer chain. The reaction efficiency was increased with increase in the number of active sites, thereby increasing the compatibility between starch molecules and PVAc which resulted in increased shear strength of 26.6666 MPa in Ipomea *batatas* adhesive system at 20% PVAc content and found to be comparable to that of the commercial counterparts (18-26.6666 Mpa) used as control. However, the strength in the samples generally began to decrease at PVAc content above 30 % due to the formation of micelles being formed by the addition of emulcifier. Similar kinds of results were found by Li *et al.,* 2017, who reported decrease in shear strength of the adhesives by addition of SDS and LSS/APEO [10]. The accumulation of micelles may have led to the formation of weak layers between adhesive and adherend which ultimately reduced the shear strength of the adhesive. Apparently, the bonding strength of the natural adhesives was improved by adding 20 % PVAc into the adhesive formulation. Additionally, this decrease in the strength of the adhesives as observed generally with increase in PVAc above 30 % could be due to the fact that there was little or no adhesive in the lumen of the leather substrate sample after the shear test. This finding can be attributed to the viscosity of the adhesive formulation which hindered the permeation of the adhesives emulsion on the substrate surface. In contrast, adhesive with a moderate viscosity infiltrated the lumen of the leather material. This finding could explain the stagnating tendency of the shear strength when the grafted monomer feeding ratio was more than 5:1. Therefore, the grafting modification treatment of natural polymers with PVAc can be a potential alternative for manufacturing adhesives in lieu of fewer environments friendly petroleum based adhesives.

Analysis of the results obtained in Table 3.0 indicates that the incorporation of PVAc into the natural polymers hindered the aggregation of latex particles and inhibited the retro-gradation of starch molecules. These findings are suggestive of the fact that high performance of starch-based adhesive may be tuneable with respect to the addition of PVAc. This is to say that PVAc can be used as a prominent source to improve the performance of natural based adhesive in order to compete with less environment friendly petroleum-based adhesives [11]. The increment in the shear strength of the adhesives system might be due to the formation of amide oligomers which formed hydrogen bonds with the surface of the material. The mesh structure formed by the covalent bonds between the ethylamine and polymer enhanced the cohesion and the stability of the adhesives.

Also the effect of curing time on the bond strength was determined. From the results, 30 minutes is recommended as a suitable curing time for the adhesive formulated. It is also pertinent to note that there was no significant difference in the curing time between the starch-based adhesives and the commercial counterparts.

As shown on the table 3.0, at least three parallel experiments were required to ensure precision of tests. According to Johannes *et al.,* 2007, the moduli of the studied polymers cover a wide range from 0.47 GPa for polyurethane and to 6.3 GPa for melamine-Urea-Formaldehyde (used on wood and natural fibre reinforced composites) by means of tensile test [12]. The results obtained for the current research in which modulus were found to be between 0.21 GPa-0.54 GPa is comparable to that of polyurethane and less than that of Melamine-Urea-Formaldehyde adhesive .

3.1 PEELING TEST

Peeling strength is an important property to characterize adhesion of materials. Cow Leather was used as the testing material, and an effective Muver peeling instrument (Model 5038) was set up to test peeling force. This peeling test is a debonding process, hence it is an energy driven process. In the peeling test, calibrated weights were hung at one edge of the leather-leather test piece. With the gravity of the calibrated weights, the adhesive test piece slowly peeled off from the substrate. The peeling off procedure was observed, so the peeling strength and peeling rate as well as the peeling force were calculated as presented in Table 3.2. The strength of the starch-based adhesive from (Ipomea *batatas*) with 20 % PVAc was found to have a higher peeling strength value (1.66 MPa) compare to the adhesive in the absence of modifier (1.0 Mpa) found to be lower than but almost the same with that of commercial adhesive used as control. These are suggestive of the fact that starch-based adhesive with 20 % PVAc is a good and possess almost equal strength with the commercial adhesive used for standard measurement. The result in Table 3.1 reveals that increasing peeling strength leads to increasing peeling rate and peeling rates are positively correlated to adhesive energy [13], as the adhesive energy required is larger when the cracking velocity increases [14]. It is pertinent to note also, that the values obtained for peeling test agrees with that of the shear modulus. We can find that increasing shear modulus leads to increasing peeling strength. This possible reason is that when shear modulus increases, more energy is needed to peel the adhesive test piece off the substrate.

3.2 CHARACTERISATION OF ADHESIVES USING FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FTIR).

FTIR was used to analyze the structure of graft-copolymerized starch-based adhesives. As shown in Fig. 3.3 a and b, the spectrum of the various adhesives system were characterized by peaks. FTIR was used to confirm the graft modification of starch-based adhesives system. Compared with gelatinized starch, the copolymer showed new characteristic peaks of ester at 1070-1080.9 cm^{-1} in the infrared spectrogram shown in Fig. 3.3b, which indicated the existence of the fatty acid ester group in the grafted derivatives.

3.3 ADHESIVES MORPHOLOGY

Small and poly-dispersed particles are observed in the latex exemplified in the micrographs (figure 3.4 a and b). The surface of the adhesive without Vinyl acetate was not uniform suggesting that the particles might have gathered together. This similar observation was found in the work of Bryn *et al.,* 2007 and Wang *et al.,* 2013 [15][16]. In contrast, incorporation of PVAc in the copolymer in Fig. 3.40b caused appreciable changes as a more uniform distribution of particles and spaces could be observed on the surface of adhesive with 20% PVAc. Evidently the grafting reaction between Starch/PVA and triethylamine greatly improved the component compatibility of the starch based adhesive as well as limited the phase separation between the starch and the polymer. The SEM/EDS revealed that some elements such as Mg, Si, Fe and P which are absent in the absence of modifier are found in the copolymer. These could have resulted in the coupling effect observed in the morphological structure of the adhesive films. It is also found that the atomic and weight concentration of Carbon is higher in the modified adhesive compare to the control adhesives system. This is in agreement with the observation in Fourier-Transform Infrared Spectroscopy resulting in stronger bond.

CONCLUSION

Environmentally friendly adhesive formulated from Ipomea *batatas* starch was developed in this study and characterized using single lap-shear, peeling test, FTIR and SEM/EDS. Modification of adhesive using polyvinyl ester improved the bonding strength of the starch-based adhesive. 20 % incorporation of the modifier into the adhesive formulation reveals that it is comparable to the commercial counterparts that were used as control. The result showed that the adhesive is of good quality and will compete favorably with other starch-based adhesives. The FTIR and SEM/EDX analysis also confirmed that there was polymer blend between the polymer matrixes. The impact of adhesives industries on the environment and public health will be considerably reduced since the materials used to produced the adhesive are environmental friendly and also sustainable. The recyclability, biodegradability, cheapness and stability in price of Ipomea *batatas* starch standout compared to the synthetic counterparts used for adhesive production.

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