DEVELOPMENT OF CARDANOL-BASED PHENOLIC RESIN AS NATURAL ADHESIVE FOR UNITING FOSSIL (METACARPAL BONE OF BOVIDAE FAMILY) FRAGMENTS

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Abstract - Cardanol, an organic compound contained in Cashew Nut Shell Liquid (CNSL) has been consider as one of natural resources to produce adhesive material. It could have been extracted from CNSL by simply liquid-liquid extraction method. Due to its chemical structure, cardanol has been easily converted to be phenolic resin through polymerization reaction with formaldehyde. Regarding to the necessity in reversible adhesive for initial fossil identification by archeologist and paleontologist, the obtained cardanol-based phenolic resin was then used to reunite fossil bone fragments of Metacarpal Bovidae. Identification of fossil's compound contents conducted by X-Ray Fluorescence (XRF) showed that the fossil majorly contained CaO (56%), Fe_2O_3(15.33%), P_2O_5 (11.85%), MnO (11.17%), SiO_2 (2.05%), MgO (1.47%), Al_2O_3 (0.67%) and other compounds (1.46%). The very hard bone fossil was firstly cut into several pieces and jointed to be three pairs using twodifferent resins, those were commercial epoxy resin, and cardanol-based phenolic resin. Those adhered fragments were then tested using Universal Testing Machine (UTM) in term of examining the strength of each resin. Different strength of both resins commercial epoxy resin and cardanol-based phenolic resin measured were 177.1, and 104 N/mm^2, respectively. Although cardanol-based phenolic has the lower strength among resins, but it is reversible and practically the easier one to be applied.

Keywords - Adhesive, Fossil, Cardanol, Resin

I. INTRODUCTION

Synthetic resins are widely used by conservators. These resins are polymers constructed of a chain or network of repeating singleunits, called monomers, that combine with themselves or with other similar molecules or compounds to form polymers. Resins can be divided into two types of polymers: thermoplastic resins and thermosetting resins [1-2].

Thermoplastic resins are polymers in which the monomeric units are linked together to form two-dimensional linear chains that are soluble in a range of solvents. They remain permanently fusible and soluble; however, some thermoplastic resins may form insoluble, infusible resins after long exposure to light or heat. Such exposure may cause chemical bonds or links, referred to as cross linking, which become established between linear chains to form three dimensional networks characteristic of thermosetting resins [3].

Thermosetting resins are characterized by monomeric units that are linked together by chemical bonds to form three-dimensionalnetworks that are infusible and insoluble in all solvents. The three-dimensional network will not allow solvents to flow between the chains, so thermosetting resins remain permanently insoluble. However, some solvents may cause the resins to swell, forming a gel. There are innumerable thermosetting epoxy resins on the market with many varied properties and special characteristics. Each conservator, through experience, has his or her own favorites. Epoxy resins make excellent adhesives, consolidants, and gap-fillers [4-5]

There are cold-setting thermosetting resins that set up with the addition of a catalyst. This is in contrast to all the thermoplastic resins that set through the evaporation of a solvent, thereby undergoing some degree of shrinkage. The main disadvantages of epoxies are that they areessentially irreversible and often discolor with age. As a general rule, epoxy resins should be avoided; however, epoxies are occasionally required by conservators because nothing else has the necessarystrength. They are excellent when a very strong, permanent bond is required. Epoxies are often used in reconstructions of wooden and glass artifacts and are used extensively in all aspects of casting. Epoxy resins are cured by the addition of ahardener (usually an aliphatic amine or amide) rather than a catalyst. The hardener itself reacts with the resin and must therefore be mixed correctly [6-7].

Cashew nut shell liquid (CNSL) as a waste could be utilized as an alternative source of phenols and its derivatives for the variety of applications ranging from the production of pol ymers and resins. The presence of phenolic –OH group, aromatic ring and side chains such as long alkylene chain in cardanol, could be utilized for various chemical transformations. In general, the cardanol will be ready to polymerize with chemical agent aditon to form phenolic resin based cardanol that very prospective as adhesive agent [8-9].

In this study, two types of resin, commercial epoxy resin and cardanol-based phenolic (CP) resin were used as adhesive for Metacarpal bone fossil of Bovidae family conservation. The work of resins has been monitored from their strength on bonding the

fossil fragments. Reversibility and practical use were also considered as particular parameters for adhesive.

II. DETAILS EXPERIMENTAL

2.1 Synthesize Cardanol-based phenolic resin (CP)

Cardanol-based phenolic resin (CP) was synthesized by the condensation reaction of cardanol and formaldehyde with molar ratio cardanol to formaldehyde 1:0.5 using 1 wt% citric acid based on weight of cardanol as catalyst. Cardanol was taken into a 100 mL three-necked round bottom flask fitted with a condenser, thermometer and mechanical stirrer. The temperature was raised until 120 ºC along with the addition of catalyst. Formaldehyde was then added drop wise in batches for 30 minutes. The mixture was vigorously stirred and kept at 120 ºC for 5 hours. The system was allowed to cool down after the reaction finished [10]. Obtained product was characterized using FTIR.

2.2 Applying Resin to Fossil

Metacarpal bone fossil of Bovidae family was firstly characterized using XRF to determine the chemical compound's composition. The bone's fossil was then cut in to four pieces to build up two pairs of fossil fragments. One pair was adhered by commercial epoxy resin and left over night. While, CP resin-adhered fossil was dried (T=70 C) for 12 hours. Each fossil was then tested using UTM to determain strength of the adhesive.

III. RESULT AND DISCUSSION

3.1 Characterization of Resin Using FTIR

Cardanol-based phenolic (CP) resin was synthesized through polycondensation reaction where the reaction scheme showed at Figure 1. Characterization of CP resin using FTIR showed that aliphatic chain has not been affected by addition of formaldehyde. It was confirmed by the remain adsorption around 3077 cm^{-1} and 3010 cm^{-1} of C-H alkenes [11]. Then, the presence of adsorption peak at 1709 cm^{-1} and the occurrence of wave number shift from 1074 cm^{-1} at cardanol (standard) became 1111 cm^{-1} at resins emerged methylolation of cardanol due to substitution of C-O grup from CH_2OH as explained by previous research [12]. Adsorption intensity around 1592 cm^{-1} (C=C stretching), 3010 cm^{-1} (C-H alkenes stretching) dan 779 cm^{-1} (C-H deformation out-of-plane) almost unaffected by addition of formaldehyde. Then it was assumed that substitution CH_2OH did not through double bond of side chain but aromatic group [13]. FTIR analysis showed sharp adsorption at 870 cm^{-1} dan 779 cm^{-1} which was assumed as benzene nuclei substituted at para and ortho position, respectively.

3.2 Determination of Fossil's Chemical Compound

Metacarpal bone fossil of Bovidae's familiy was analyzed using XRF to determine its chemical composition. Several recorded major components were provided as a graphic at **Fig. 1.** The highest percentage compound was Calcium oxide (CaO) around 56% and followed by Fe_2O_3 (15.33%), P_2O_5 (11.85%), MnO (11.17%), SiO_2 (2.05%), MgO (1.47%), Al_2O_3 (0.67%), and other small compounds (1.46%). Calcium and Phosphor contributed to the hardness of the bone. In the other hand, the alteration of bone to fossil was identified from the high content of Iron (Fe) and Manganese (Mn).

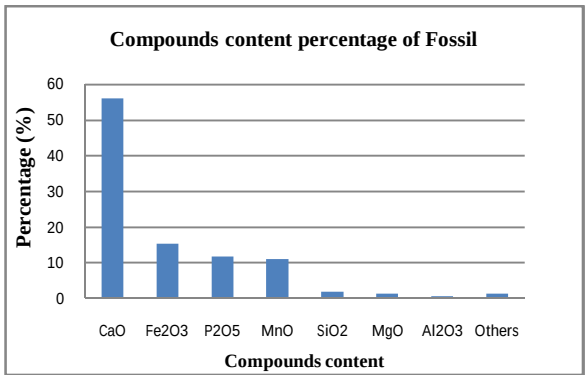
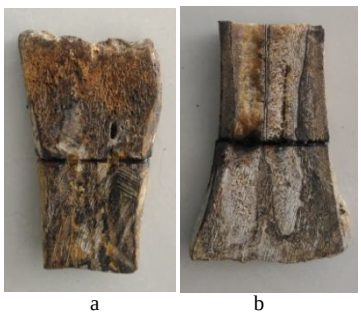


Fig. 2 Chemical content percentage graphic of Fossil

3.3 Analysis of Adhesive Strength

In order to investigate the capability of CP resin on adhering the fossil fragments, the adhered fragment's pair was then tested using UTM and compared to another fragment's pair adhered with commercial epoxy resin. The tensile strength of each pair was 104 and 177.1 N/mm^2, respectively. The requirement of resin is based on necessity. In this case, for initial archeological research and identification, the reversible and practical resin is needed. Although cardanol-based phenolic has lower strength than commercial epoxy resin, but it practically easier to be applied and so is . In the other hand, cardanol, the main material was collected from waste, so it is convenient to the principle of sustainable resources. The adhered fossils were showed at Fig. 3 (a and b).



a b

Fig. 3 Adhered bone fossil of Bovidae Family using a) Commercial epoxy resin; b) CP resin

CONCLUSIONS

Cardanol-based phenolic (CP) resin has showed reasonable results to be applied as conservation utility of metacarpal bone fossil of Bovidae's family. It provided quite good tensile strength, practical and reversible uses.

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