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Shear Rheology and Molecular Properties of Biobased Adhesives Through Molecular Dynamics Simulation

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Abstract

The study of shear rheology and molecular architecture through molecular dynamics simulation of starch-based and gelatin-based adhesives formulated from Eleusine coracana, and cow hide has been successfully achieved. This research has revealed that esterification of natural dextrins with 20 % polyvinyl acetate (PVAc) will yield adhesives product with improved gel properties suitable for applications. Method of extraction, production of the adhesives by varying the quantity of fatty acid ester and quality assessment was performed and 20% PVAc incorporation found to be suitable for application. The physical features of the macromolecular complexes formed by the synergistic interaction of starch/gelatin and PVAc in the presence of tetraethylamine (TEA) has been studied from the rheological point of view. On examining the impact of the molecular structure and electronic properties of the adhesive molecules on the adhesive efficiency, quantum chemical calculations were carried out. Rheological analysis shows the adhesives are consistent and the computed free energy obtained from molecular dynamics simulation reveals that the adhesive molecules are spontaneous, hence efficient.

Keywords: Rheology; Biobased adhesive; Molecular Structure; Simulation

I. INTRODUCTION

Adhesives are used to join surfaces, typically by changing their phase from liquid to solid. Sometimes this is triggered by a temperature change (hotmelt adhesives), in other cases the glue hardens at ambient conditions (contact adhesives) e.g. due to solvent evaporation or due to the humidity of the surrounding air. There are also reactive and multi-component adhesives, which harden by mixing two or more components that chemically react with each other, and one-part adhesives, which harden via a chemical reaction when an external energy source, such as radiation or heat, is applied [1]. Adhesives are found in nature, like pitch (from wood), bitumen, beeswax, starch (from plants) or gelatin (from animals). Adhesives must flow smoothly onto surfaces to ensure both wetting and adhesion. For this reason, testing viscosity as a function of temperature with a rheometer is essential for ensuring proper performance. By knowing the rheological characteristics of a given adhesives, its suitability for a given task can be determined, or its formulation can be modified to customize it for a specific application.

Molecular rheology is the missing link between the macromolecular structure of polymeric materials and their viscoelastic properties in the melt state. It complements the engineering or continuum mechanics aspects of rheology, which generally ignores the molecular details of the objects under study [2]

Most adhesive manufacturers list the viscosity of the uncured adhesive on their literature to help engineers determine which product is most suitable for a specific application and can be integrated into their production line most effectively. Temperature and shear (stirring or agitating) can affect adhesive viscosity and flow behavior, therefore it is important to take these factors into consideration when selecting an adhesive product.

Viscosity is the measure of resistance to gradual deformation by stress. For the purpose of liquid adhesives, viscosity corresponds to the thickness of the liquid. Water has a viscosity of 1 cP (or mPa.s) at 20 °C. Liquids that have a viscosity less than water are mobile liquids and those with viscosity higher than water are viscous liquids.

Rheology (or Non-Newtonian fluid mechanics) is the study of the flow of matter primarily in the liquid state. Today, rheology is used to predict behavior in application processes such as coating, calendering, and extrusion; to follow adhesive cure and aging; and to characterize bond performance.

The shape of a molecule affects its rheological response, two important parameters, the effective length of the molecule and its degree of branching; ultimately dictate its response [3]. A molecular dynamics simulation study may be conducted to shed light on the effect of molecular shape and structure on the rheological properties. Measurements of linear viscoelasticity are rapid and well established for the characterization of the small strain properties of materials and so, they are commonly used to study the effect of the dynamics of stickers in the literature. Part of this article's focus is however, on the essential role played by the non-linear rheology in controlling the adhesive properties of the materials used in the formulation [4].

Naturally occurring polysaccharides from plant exudates and gelatin from animal sources have been in use from many decades in immense quantities. The commercial value and end use of adhesive is determined by appearance and properties hence, modify viscosity and consistence becomes critical for application in the industries.

Starches are naturally occurring polymers of glucose with the empirical formula of $(C_6H_{10}O_5)_n$, where the exact value of n is unknown. Starch has a more intricate structure than cellulose because its molecules have two distinct areas: 75% has a branched amylopectin molecular structure and 25% has a linear amylose molecular structure. The exact percentages of amylose and amylopectin for each starch are largely responsible for its working properties. Amylose and amylopectin have different properties, both as dry films and in solution. The highly regular linear structure of amylose allows it to dry from solution to form strong films. Amylopectin, being more amorphous, forms weak films". During paste-making the amylose and amylopectin areas of the molecule behave very differently. The amylose fraction is responsible for the internal strength of a starch, many of its working properties, and for its degree of stiffening upon cooling. Thus, the amylose is responsible for gelatinization.

Gelatin is a protein obtained by boiling skin, tendons, ligaments, and/ or bones with water. It is an irreversibly hydrolyzed form of collagen, wherein the hydrolysis reduces protein fibrils into smaller peptides; depending on the physical and chemical methods of denaturation. It is brittle when dried and gummy when moist. Both gelatin and starch are natural polymers and can be used for adhesive formulation. For effective bonding, the adhesive must intimately wet the surface of each substrate being joined together. In addition, a chemical bond must form between the surface of the adhesive and the substrate. To satisfy these conditions, the surface of the substrate must be clean, reasonably smooth, and chemically receptive to the chosen adhesive. The substrate could be metal or non-metal materials such as wood, leather etc. [5].

The focus of this study is on the analysis of the rheological results in combination with theoretical techniques, based upon ab initio quantum mechanics (QM) and molecular dynamics (MD) simulations. The computational QM and MD investigations were carried out to obtain a detailed electronic/atomic scale insight into the experimentally found observations; in particular, the chain−chain interactions governing the behavior of Eleusine coracana (ECS)/ PVAc systems. These techniques allow us to attain microscopic view of adhesives characteristics and to elucidate new information, such as inter/intramolecular hydrogen bonds, interaction energy and correlation between ECS/ PVAc or BGT/ PVAc, which cannot be achieved through experimental efforts.

II. FORMATION OF ADHESIVE FROM NATURAL RESINS

One hundred and fifty (150 cm^3) of de-ionized water was poured into a beaker and 2 g of PVAc was dissolved in the water, with continuous stirring. The mixture was heated to boiling at 60 °C for about 1800 seconds with the aid of heating mantle (solution A).

About 10 g of starch and 0.5 g of Borax were also weighed and transferred into a separate beaker containing 100 cm^3 of NaOH and as well stirred thoroughly at the temperature of 60 ^0C (1800 s) to obtain a homogenous dispersion (solution B).

The boiled solution B was then quickly poured into solution A with continuous stirring. Immediately gelation occurred the temperature was kept constant for five minutes and the resulting viscous solution was stirred thoroughly. Further stirring brought the adhesive produced to its maximum viscosity.

The beaker was removed from the heating mantle, after which about 2 cm^3 of triethylamine and 0.2 g of citric acid were added. In order to achieve better adhesive formulations, the modification was carried out by varying the concentration of polyvinyl acetate (esterification). Similarly, the procedures were repeated for gelatin-based adhesive formulations [6]

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A. *Adhesive Rheology Test*

The rheological properties of the starch-based and gelatine-based adhesives were studied to determine its kinematic viscosity(η) and shear rate (γ). Concentrations of adhesive emulsion was prepared by weighing 8.0 g, 10.0 g, 12.0 g, …18.0 g of dry gelatine-based adhesive into six separate 100 cm3 beaker and 20 cm^3 of de-ionize water was added to each. The beaker containing the mixture was placed in a water bath at 70 ^0C with continuous stirring until the glue was completely dissolved and the solution became homogeneous. The viscometer bath was then set to heat at a temperature of 40 ^0C for 1800 s. 10 cm3 of concentration adhesive was filled into the lower bulb of a u-tube viscometer. The u-tube viscometer was immersed into a viscosity water bath and allowed to stay for 1800 s, after which the pipette filler was used to suction the adhesives solution to top mark of the upper bulb and allowed to flow to the lower bulb. A stop watch was used to observe the time taking to flow from the top mark of the upper bulb to the bottom mark of the upper bulb and the time taken to flow from the top mark to bottom mark was recorded and multiplied by the u-tube viscometer factor to determine the kinematic viscosity. The step was repeated for all the various concentrations of the formulated adhesives and the time taken for the solution to flow down was recorded in triplicates respectively [7].

B. *Quantum Molecular Simulations*

On examining the impact of the molecular structure and electronic properties of the adhesive molecules on the adhesive efficiency, quantum chemical calculations were carried out utilizing density functional theory (DFT) adopting the B3LYP function with the 6-31G + (d, p) basis set for all molecules, using the Hyperchem. Key parameters, for example, the energy of the LUMO (ELUMO) and the HOMO (EHOMO), the energy gap (**Δ**E) between the LUMO and the HOMO, the dipole moment (m), the electronegativity (w), the softness (s) and the hardness (Z) of the molecules, the energy distinction between electron exchange of the molecule and back-donation starting with the atom ($\boldsymbol{\Delta}E_{\text{Back Donation}}$), the chemical potential (p) and the number of transferred electrons (DN) were obtained from the optimized structures in the gas phase. It should be noted that doing the theoretical calculations in the gas phase is a useful method because the results obtained in the gas phase show no significant variation from those obtained in the aqueous phase, while at the same time the time required for the calculation can be significantly decreased [8].

III. THEORETICAL STUDIES

A. *Quantum Chemical Calculations*

To examine the impact of electronic and molecular structure on the adhesive molecules, quantum chemical calculations have been performed. The optimized structures, lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of the respective adhesive system are shown in Fig. 1.

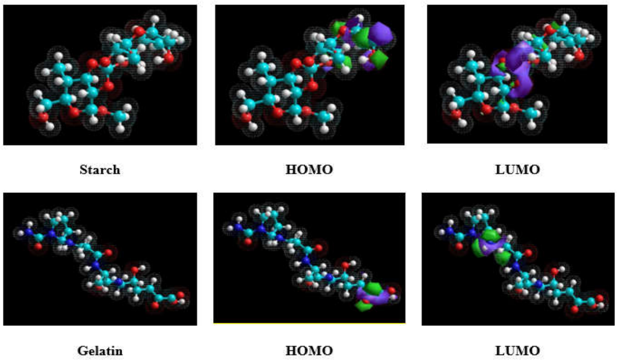

Fig. 1. Optimized structures and frontier molecular orbital density distributions (HOMO & LUMO) obtained by the DFT/B3LYP/6-31G + (d, p) method of starch and gelatine analogue.

All of the computed parameters were computed separately according to the following equations:

$$\Delta E = E_{LUMO} - E_{HOMO} \qquad (1)$$

$$\eta = \frac{1}{2}(E_{LUMO} - E_{HOMO}) \qquad (2)$$

$$\chi = -\frac{1}{2}(E_{LUMO} + E_{HOMO}) \qquad (3)$$

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} - \eta_{inh})} \qquad (4)$$

$$\sigma = \frac{1}{\eta} \quad (5)$$

$$\Delta E_{Back\ Donation} = -\frac{\eta}{4} \quad (6)$$

$$\pi = -\chi \quad (7)$$

ELUMO and **Δ**E (energy gap between HOMO and LUMO) were computed in Fig. 1. A lower value of ELUMO describes a propensity towards the acceptance of electrons from the substrate, while a higher value of EHOMO shows a tendency of the molecule to give electrons to the substrate with empty molecular orbitals. Moreover, a lower value of the energy gap **Δ**E (ELUMO — EHOMO) will result in good adhesive efficiencies, since the energy required to remove an electron from the most recently involved orbital will be minimized. A higher value of the number of transferred electrons (**Δ**N) demonstrates a higher capacity to give electrons to the substrate surface. The electro-$negativity$ (χ) parameter can be used to illustrate the electron holding ability of the molecule. The higher the value of χ, the lower the electron transfers by the adhesive molecules. Electron donation from the adhesive to the substrate increases with increasing softness (σ) and decreases with increasing hardness (η) of the adhesive molecules. A higher value of p $(\chi = -p)$ demonstrates better performance for an adhesive.

Where χ inh and χ Fe represent the electronegativity of the adhesive molecule and substrate, respectively. ηinh and ηFe represent the hardness of the molecule and substrate, respectively. A value of 7 $eVmol^{-1}$ has been taken for χ_{Fe} , and at the same time 0 $eVmol^{-1}$has been taken for χ_{Fe}, as per Pearson's electro-negativity scale 38. σ is the softness value of the molecules and η is the chemical hardness of the adhesive molecule.

Taking every computed parameter and the molecular structures into account, the polysaccharide-based adhesive system seems to be more efficient than the gelatin-based adhesive. This observation is in agreement with the experimental results reported elsewhere [1]. However, since the molecules change extensively under specific condition, any of them might exert a dominant impact; for example, if the examination conditions change, specific characteristics might in turn be upgraded or alternatively suppressed, which may result in a change in the adhesives performance.

Also, Gibbs free energy, denoted G, combines enthalpy and entropy into a single value. The change in free energy, **Δ**G, is equal to the sum of enthalpy plus the product of the temperature and entropy of the system. **Δ**G can predict the direction of the chemical reaction under two conditions: constant temperature and constant pressure. If **Δ**G is positive, then the reaction is non-spontaneous (i.e., an input of external energy is necessary for the reaction to occur) and if it is negative, then it is spontaneous (occurs without external energy input) [11]. Therefore, table II computed values reveal that the adhesives system studied in the current work will undergo reaction spontaneously on contact with substrate.

TABLE I CALCULATED QUANTUM CHEMICAL PARAMETERS OF GELATIN AND STARCH ANALOGUE OBTAINED FROM THE DFT/B3LYP/6-31G + (D, P) METHOD IN THE GAS PHASE.

Adhesive Molecules	starch-based	gelatin-based
E (HOMO) (eV)	-10.710	-0.114
E (LUMO) (eV)	-1.449	-9.159
ΔE (eV)	-12.159	-9.054
Π (Debye)	2.805	4.061
ΔN (e)	0.194	-0.2613
$\Delta E_{\text{Back Donation}}$ (eV)	-1.519	1.130625
η (eV)	6.079	-4.5225
Σ (eV^{-1})	0.164	-0.22112
X (eV)	4.630	4.6365

χ = electronegativity, σ = softness of the molecule, η = hardness of the molecule, $\Delta E_{\text{Back Donation}}$ = back donation, ΔN = number of transferred electrons, π = Dipole moment.

TABLE II TOTAL ENERGY OF THE MOLECULES (*AT 300 K):

Adhesive Molecules	Total Energy (Kcal/mol)	Free Energy (Kcal/mol)	RMS Gradient
starch-based	-124135	-124135	0.08941
gelatin-based	-122891	-122891	19.43

B. Rheology of the Adhesives Formulation

Polymer solutions, dispersions, and melts are usually non-Newtonian liquids. This means their apparent viscosity depends on the applied shear rate and increase rapidly with increasing molecular weight (number of repeat units). Thus, the viscosity of a polymer melt is always larger than that of the corresponding monomer. This is due to entanglement and intermolecular forces between polymer molecules [9]. This phenomenon is not different from the general observation in all the adhesives systems formulated in this research work. This is indicative of the fact that the chemically modified adhesives produced in this work have shear-thinning behavior, that is they belong to pseudo-plastic polymer class and not a shear-thickening class (dilatants) as can be observed with corn starch in water and nano-particles dispersed in a polymer solution. Fig. 2 shows the viscosity graph of kinematic viscosity (ɳ) plotted against shear rate (γ) which yielded a linear curve plotted point that obeys oswalde – de- whaele power index relationship for non-Newtonian fluid and expresses as $\eta = k\gamma^{n}$. According to [10], the power index for non-Newtonian fluid value ranges from 0 to 1, hence the power index of the entire starch-based and gelatin-based adhesives viscosity curve was determined from the slope in the graph to be between 0.015 - 0.086 respectively while that of consistence k of the free flow is revealed in the graph to be between $1.944 - 2.126$ and $2.056 - 2.078\ m^2$. There is no marginal difference of these values obtained with that of the commercial counterparts ($n = 0.072, k = 2.548$) (see Fig. 4). This indicates that the fluid flow behavior of the gelatin concentration at 40 ^{0}C tends to be consistent which give the formulated adhesives its intermolecular weight distribution pattern for mechanical bonding of substrate [10]. However, the power index of that starch-based formulation from Eleusine coracana is higher than the gelatin-based adhesives in this research work.

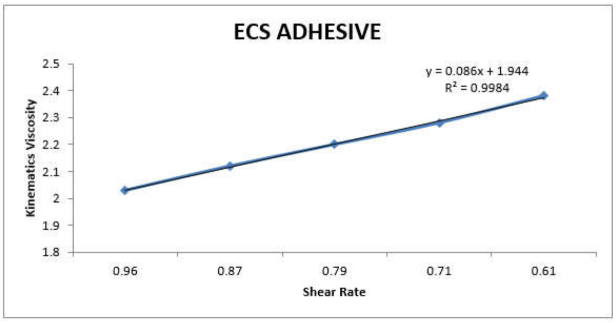

Fig. 2 Rheological analysis of starch-based adhesive formulated from Eleusine coracana.

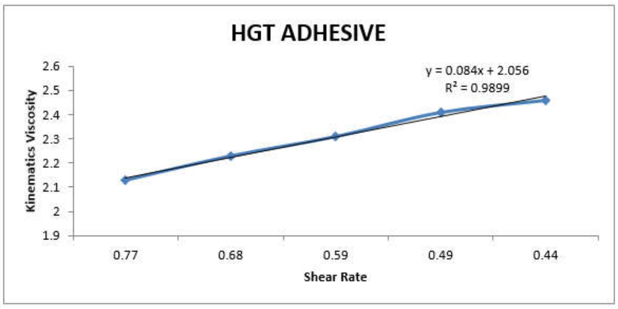

Fig. 3 Rheological analysis of gelatine-based adhesive formulated from cow hide.

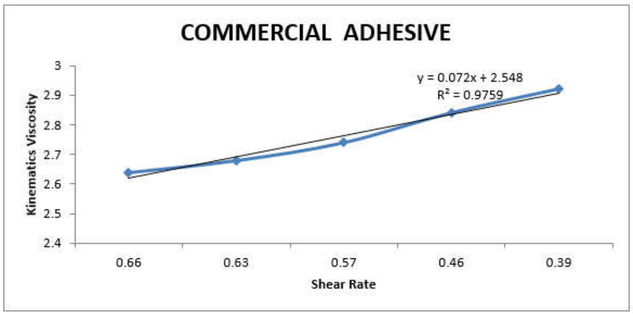

Fig. 4 Rheological analysis of commercial-based adhesive.

Fig. 3 shows the plotted graph of viscosity against concentration which interprets the behavior of the viscosity of natural adhesives with respect to its concentration. The positive curve line indicates that starch/ gelatin viscosities reduce with increase in concentration of starch/ gelatin solution which probably affects the weight distribution of the adhesives on a substrate and consequently reduce the bonding strength performances on the substrate.

IV. CONCLUSION

The aim of this research work, which is the study of shear rheology and molecular architecture through molecular dynamics simulation of starch-based and gelatin-based formulated and modified adhesive from Eleusine coracana, and cow hides has been successfully achieved. Method of extraction and production of various formulation of the adhesive by varying the quantity of fatty acid ester, as well as quality assessment was performed and 20% PVAc incorporation found to be suitable for application in the formulation. Rheological analysis shows the adhesives are consistent and the molecular dynamics simulation reveals that the adhesive molecules are spontaneous, hence efficient.

CONFLICT OF INTEREST

There is no conflict of interest.

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