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PLASTICIZATION EFFECTS OF ETHALINE DEEP EUTECTIC SOLVENT VERSUS GLYCEROL ON THERMOPLASTIC STARCH FILMS FROM CASSAVA PEELS

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ABSTRACT

The plasticization efficiency evaluation of deep eutectic solvent (DES), based on choline chloride (CC) and ethylene glycol has been performed on the extracted starch from cassava peels as compared to the conventional plasticizer glycerol in the production of thermoplastic starch (TPS) (bioplastic films). In this work, Deep eutectic solvents (Ethaline) was evaluated as plasticizer and it's plasticization effect was compared with glycerol at varying concentrations (0, 5, 10, 15, 20, 25 and 30 wt%). The mechanical testing portrayed that Ethaline plasticized thermoplastic starch (TPS) exhibited higher tensile strength of 3.9 MPa at low concentrations (15 wt%) compared to glycerol 3.1 MPa, while maintaining acceptable elongation. At higher concentration (>20 wt%), Ethaline enhanced flexibility but reduced tensile strength similar to glycerol. Water absorption studies revealed that Ethaline plasticized-TPSs absorbed less moisture than glycerol counterpart, suggesting improved barrier properties. Overall, Ethaline has a good potential of plasticization and inhibits the migration of plasticizer from the polymer matrix, compare to conventional ones like glycerol, as it improves the performance of bioplastic films (TPSs) in both mechanical and barrier properties.

Keywords: Plasticization, Thermoplastic Starch, Deep Eutectic Solvent, Ethaline, Glycerol

INTRODUCTION

Starch is an annual renewable polysaccharide. Owing to its abundance and biodegradability, researches are geared towards the synthesis of starch based polymer as an alternative to petroleum plastics. The desire for a waste crop with abundant starch signifies cassava peels as one of the best alternatives. Therefore, the predicament encountered due to incessant disposal of cassava waste peels after processing will be tackled with a projection of converting waste to wealth (Liu *et al.,* 2019).

Starch Limitations and Plasticization

However, the brittleness of neat starch polymer is a hiccup. It can be overcome by use of additives such as plasticizer. Plasticizer results in increasing the mobility of macromolecular chains of starch polymer by reducing the intermolecular forces in the starch polymer (Romero-Bastida *et al.,* 2015). Water is one of the common starch plasticizer, but the starch based polymer got dehydrated after short period of time (Zhang *et al.,* 2018). Low molecular weight substances such as Polyols (like glycerol, ethylene glycol), urea and organic acids are most commonly used starch plasticizers (Nafchi *et al.,* 2018). But they tend to migrate from starch matrix after sometimes, posing serious issue and bring about limitation in their application (Özeren *et al.,* 2020). The ideal plasticizer is expected to be of good solvent power with low volatility as well as tendency to remain bonded to the plasticized materials (Lewis., 2021). These characteristics cannot be met when choosing the plasticizer simultaneously without compromise (Wilpiszewska and Skowrońska., 2023). Overall efficiency of plasticizer can be evaluated on the basis of rheology, thermal and mechanical performances. The mechanism of plasticization can be explained on theories of classical, lubricity, gel and free volume. However for perfect understanding of plasticization process, combined idea from various theories is a must since none of them is exhaustive (Wilpiszewska and Skowrońska., 2023). The plasticizer breaks the centers of attraction and increasing chain mobility (Marcilla and Beltrán., 2017).

DES as Plasticizer

Currently, group of media which are novel, known as deep eutectic solvents (DES), cheap and more environmentally friendly alternative to conventional plasticizers, have been tested as starch plasticizing agents (Zdanowicz *et al.,* 2018). DES is a mixture of two or more components (containing hydrogen bond donor and acceptor) where it's melting temperature (Tm) is much lower than the (Tm) of the individual components (Abbott *et al.,* 2013). So far, mainly choline chloride (CC) based DES with urea (Abbott *et al.,* 2012, Ramesh *et al.,* 2012, Leroy *et al.,* 2012 and Zdanowicz *et al.,* 2011), glycerol (G) (Leroy *et al.,* 2012), carboxylic acids and imidazole (Zdanowicz *et al.,* 2016) have been tested as starch plasticizers. One way to improve mechanical and barrier properties as well as to increase the hydrophobicity of starch materials is by the use of most efficient plasticizer like DES. This work aimed to evaluate the plasticizing efficiency Ethaline DES systems (choline chloride: ethylene glycol) on cassava peels starch as compared to conventional plasticizer (glycerol).

MATERIALS AND METHODS

Experimental

Cassava peel's starch, Ethylene glycol (technical pure). Choline chloride (CC) was a product of Sigma-Aldrich

Preparation of Cassava Peels and Starch Extraction

Cassava peels were sourced from Garri processing area in Anyigba metropolis Dekina L.G.A Kogi state Nigeria. The peels were washed with clean water before shredded to small pieces and sun dried before being powdered by onion chopper to facilitate starch extraction. The starch was extracted from cassava peel based as follows: 600 g of grounded sample was mixed with 400 mL distilled water in small bucket to form solution and the solution was stirred frequently for 30 min. Then, the solution was filtered using 20 µm sieve into a beaker. The filtrate was allowed to stand for 2 h until the entire starch being settled down and then the supernatant was decanted. The extracted starch was rinsed with distilled water

and dried in an oven at 50 ºC for 24 h. The dried starch was crushed for further drying at a temperature of 30 ºC in an oven for 2 days. Finally, the dried starch was stored in polyethylene bag for film preparation was characterized to entails; 8.43% moisture, 0.53% protein and 0.23% ash. The amylose/amylopectin ratio was 20.63/79.37 wt%.

Preparation of Deep Eutectic Solvent

Deep eutectic solvent was prepared by stirring the components (mole ratio 1:2) at 98 ºC (CC:EG) until the homogenous clear liquid was obtained

Characterization of Deep Eutectic Solvent

The assessment of this DES as new plasticizer to replace the conventional ones requires knowledge about its fundamental properties. Thus, the physicochemical properties such moisture content, viscosity, density, thermal conductivity, surface tension and refractive index of the synthesized DES were determined.

Moisture Content Determination of the Synthesized DES

Before evaluating the attributes of DES, the amount of water within them was determined, because it could interfere with DES physicochmithermal properties. A Metrohm 831 Karl Fischer coulometric titrator, according to ASTM D6304 procedures was used for moisture content analysis of the synthesized DES

Viscosity Determination of the Synthesized DES

Viscosity was measured using rotating NDV intelligent viscometer (Model number 1909N59) made in Shanghai, China according to ASTM-D445. Each reading was repeated three times with the average value calculated. The viscosity of the synthesized DES was measured at atmospheric pressure from 25 to 60 ºC.

Surface Tension and Density Determination of the Synthesized DES

Surface tension and density were measured using tensiometer and densimeter with model number sigma 702 and serial number of 72296 by Bionic scientific according to ASTM D1331-20 and ASTMD 1298 procedures. Each reading was repeated three times with the average value calculated. The Surface tension and density of the synthesized DES was measured at atmospheric pressure from 25 to 60 ºC.

Conductivity and Refractive Index Determination of the Synthesized DES

The conductivity of the DES investigated in this work was measured according to ASTMD1125-14 using Jenway 4510 (Eutech Cyber Scan Con 11 hand-held meter) conductivity meter at Biology department ABU Zaria. Refractive index of the synthesized DES was measured using Bausch and Lamb Abbe-3L Refractometer (Rochester, NY). Deionized water was used for calibration before each experiment. The average uncertainty of the measurements was estimated to be ± 0.00. All measurements were carried out at room temperature (28 ºC ± 1)

Fourier Transform-Infrared Spectroscopy (FT-IR) of the Synthesized DES

The intermolecular vibrational modes of the ions that make up the materials are frequently very sensitive to their local potential energy environment. FTIR analysis of the synthesized DES was done using Schimadzu FTIR-8400S model between an intensity range of 4000 to 600 cm^{-1} by placing the sample on the plate and then inserted into the infrared barrel.

Preparation of DES and Glycerol Plasticized-TPS (Bioplastic Film)

Starch 10 g was placed in a flask with distilled water 100 ml and stirred for 10 min at 90 ºC. Subsequently, the proper amount of DES or glycerol plasticizer (0, 5, 10, 15, 20, 25 and 30 wt%) was added and mixed until homogeneity. The obtained mixture was poured into a rectangular container with dimension of 10 cm × 5 cm. The mixture was then dried in a heating oven at 60 °C for 24 h. The formed films were peeled out of the casting plates and stored in desiccator prior to the characterization processes.

Characterization of Plasticized-TPS (Bioplastic Film)

The bioplastics obtained were then characterized by mechanical (tensile strength, young modulus and elongation at break**)** and barrier (water absorption) testing

Tensile Strength Test

Tensile strength was measured with GoTech Universal Testing Machine using the standard of ASTM D882-91. Tensile strength testing uses universal tensile strength using both ends of the bioplastics sheet clamped to the testing machine. The measurement results in the form of force (F) and sample extension are included in equation 1. It was represented by calculating the average of three replicates

$$\text{Tensile strength (MPa)} = \frac{\text{Force (F)}}{\text{Surface area (A)}} \quad (1)$$

Elongation at Break Test

Elongation at break is an indication of bioplastics flexibility and is expressed as a percentage. Elongation at break estimated using the standard of ASTM D882-91 and was calculated as shown in equation 2. It was represented by calculating the average of three replicates

$$\text{Elongation} = \frac{\text{Final gage length – initial gage length}}{\text{Initial gage length}} \times 100 \quad (2)$$

Modulus Young Test

The relationship between tensile strength and elongation results in line with standard of ASTM D882-91. It was represented by the average of three replicates as calculated using equation 3

$$\text{Young Modulus} = \frac{\text{Tensile strength (MPa)}}{\text{Elongation}} \quad (3)$$

Water Absorption Test

Water absorption test was carried out according to ASTM - D570. Sample size of 1 cm x 3 cm with 0.028 cm thickness was prepared for the water absorption test and dried in oven at 50 °C for 2 hours. Bioplastics humidity absorption capacity was acquired by soaking the sample for 24 hours in water. Next, the sample was instantly dried using cloth and weight. Bioplastics water absorption capacity can be calculated as in Equation 4, in which the average of three replicates was represented.

$$\text{Water Absorption (\%)} = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \times 100 \quad (4)$$

Statistical Analysis

Using descriptive analysis, the data obtained were analyzed using Statistical Package for Social Science (SPSS) software ver. 20.0. The p value of mechanical and barrier tests were analyzed and $p < 0.05$ was considered as significant. The information is represented in mean ± standard deviation.

RESULTS AND DISCUSSION

The FT-IR of the developed Ethaline and its components which are choline chloride and ethylene glycol is presented and investigated in figure 1. The formation of hydrogen bonding between the chloride anion of choline chloride and ethylene glycol is the main force for the formation of Ethaline. According to the FT-IR spectra, the broad band at 3294 cm^{-1} related to the stretching vibration of the O–H group in ethylene glycol shifted to 3303 cm^{-1} in Ethaline. This shift towards higher wavenumber with the incorporation of choline chloride and ethylene glycol was due to the decrease in the extent of intermolecular hydrogen bonding between ethylene glycol molecules. The spectrum of Ethaline was dominated by ethylene glycol, however, an additional characteristic band at 953 cm^{-1} originating from choline chloride was observed. This new band was attributed to the C–N^+ stretching. In addition, Ethaline presented vibrational bands at 2938 cm^{-1} and 2875 cm^{-1} referring to C−H stretching, 1478 cm^{-1} to the CH_2 bending of an alkyl group, and 1084 cm^{-1}, 1036 cm^{-1}, and 882 cm^{-1} to functional groups, namely C−O stretching, C−C−O asymmetric stretching, and C−C−O symmetric stretching. Delgado-Mellado *et al.* 2018**,** recorded similar results. Thus, indicated the successful synthesis of ethaline.

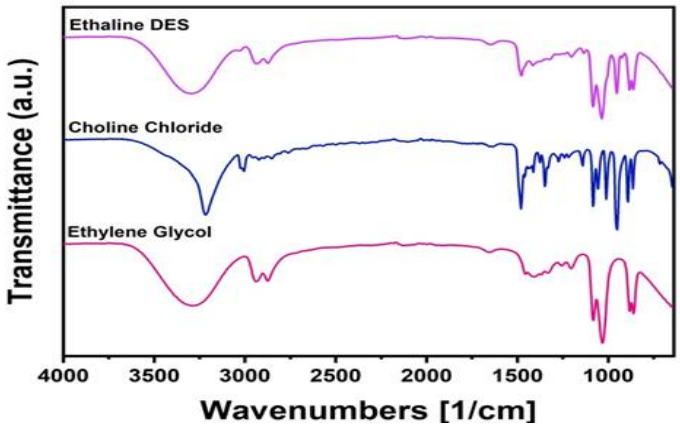

Figure 1: The FT-IR of the Developed Ethaline and its Components (Choline Chloride and Ethylene Glycol)

Density is an important characteristic property of any liquid. Generally, deep eutectic solvent possess high density. The density is often higher than both the material that form the DES (Lo and Ting., 2019). The density values of the developed DES within the temperature range from 25 ^{0}C to 60 ^{0}C were measured using densimeter with model number sigma 702 and serial number of 72296 by Bionic scientific. From the Figure 2, the density of the synthesized DES (Ethaline) moderately reduces as the temperature increases from 25 ^{0}C to 60 ^{0}C, this is owing to fact that, increase in temperature of the mixture weakens the nanostructure of the components and promote their disintegration. García *et al.,* 2015, reported that rate of decrease densities, depends on the molecular structure and intermolecular bonding strength of the DES components.

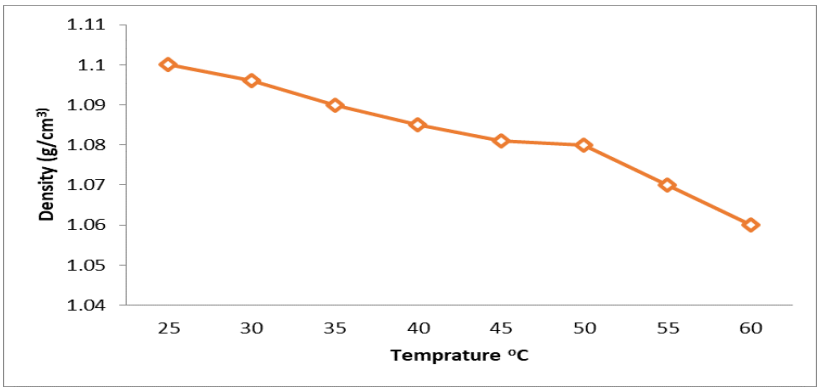

Figure 2: Effect of Temperature on the Density of the Synthesized DES (Ethaline)

Viscosity is an important factor in the application of solvents, and high viscosity is one of the limiting factors with its use as a bulk solvent. Viscosity is an important property on DES, since it affects the mass transport phenomena quite strongly; besides, liquids with lower viscosities have a wider potential window for industrial application (Azhar *et al.,* 2019). The viscosity of the developed DES was measured without water addition using a similar method by Yan *et al.,* 2014 in a rotating viscometer (Model number of 1909N59), NDV intelligent viscometer made in Shanghai, China at temperature range of (25 – 60 ^{0}C) using thermostatic water bath with model number (HH-501,XMTE-206) at atmospheric pressure. Each reading for viscosity was repeated three times with average value reported. Figure 3, shows the temperature effects on viscosities for the synthesized DES (Ethaline).

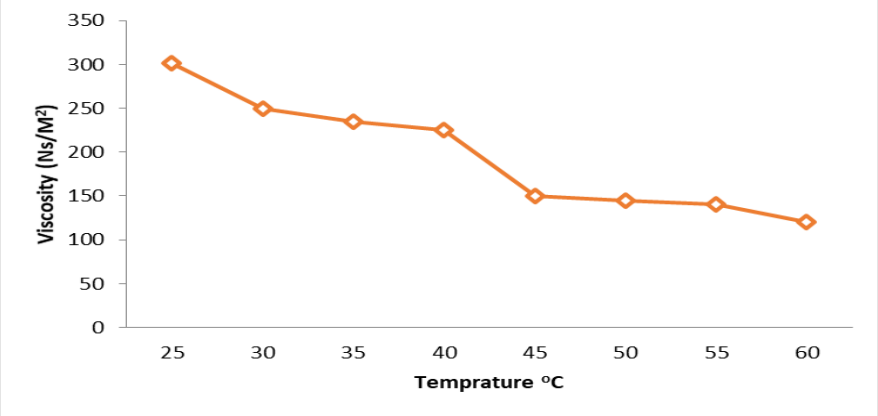

Figure 3: Effect of Temperature on the Viscosity of the Synthesized DES (Ethaline)

The results from figure 3, shows that as temperature increases, the viscosities of the DESs decreases. The synthesized DESs have higher viscosities at room temperatures, and is mainly due to the hydrogen bonding between the HBDs and HBA. The intense interaction and bonding between the material would reduce the mobility of the system, thus increase the viscosity of the DES (Lo and Ting., 2019). In the same vein, viscosity of the fluids is also affected by the size of the holes in them. At low temperature, the size of the holes is smaller, and the size of the ions becomes relatively big, and the hole size becomes bigger at high temperature. Thus, under low temperature, it becomes harder for the ions to move into the vacant places (the "availability" of the holes is low), which means the ion mobility was reduced, and the viscosity becomes higher consequently (Lo and Ting., 2019). At high temperature, (35 ^{0}C to 60 ^{0}C), the situation is vice versa. Castro *et al.*, 2018, also obtained similar pattern in their works, where viscosity decreases as temperature increases. According to Ameri (2017) and Castro *et al.*, 2018**,** the degradation of DES starts at the temperatures between 200 ^{0}C to 324 ^{0}C, and the operating temperatures of bioplastics synthesis is between 80 ^{0}C to 100 ^{0}C (Nur *et al.*, 2021), hence stability of the developed DES for plasticization is glaringly ascertained.

Surface tension is one of the important and crucial properties of liquid characterization that is required in many industries and it affects the reactivity of DES. It is a measure of the cohesive forces at the liquid's surface. It is also is measured of the energy required to increase the surface area of a liquid by a unit of area (Abbott *et al.*, 2011). In DES, it's influenced by, hydrogen bonding strength, viscosity and molecular interactions between HBA and the HBD (Leron *et al.*, 2012). The surface tension of the developed DES was measured at atmospheric pressure from 25 ^{0}C to 60 ^{0}C using a tensiometer with model number sigma 702 and serial number of 72296 by Bionic scientific. Each reading was repeated three times with the average value reported as shown in figure 4. From the figure as the temperature increases from 25 °c to 60 °c, surface tension decreases across, this is because, the increase in thermal motion is disrupting the intermolecular forces, reducing hydrogen bonding strength and enhancing molecular mobility (Tang and Row., 2013).

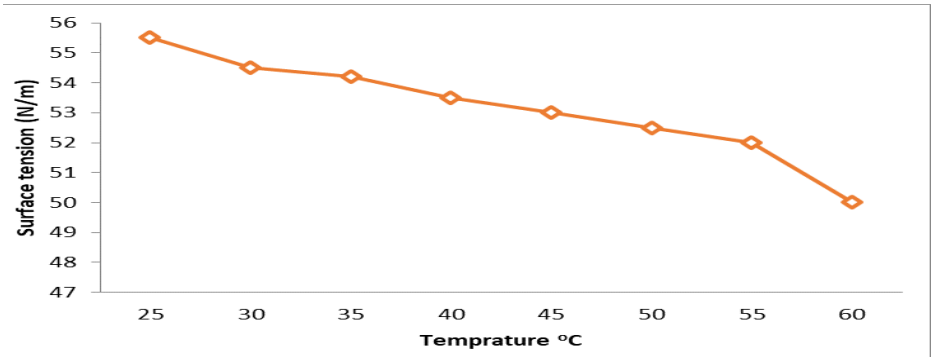

Figure 4: Effect of Temperature on the Surface Tension of the Synthesized DES (Ethaline)

Conductivity of a solvent is important for its applications in electrochemistry. The conductivity of deep eutectic solvents is strongly affected by the compositions of DES (Abbott *et al.*, 2011). The developed DES (Ethaline) has the conductivity of 0.980563 $WK^{-1}m^{-1}$, these results are in moderate agreement with the work of El-hoshoudy *et al.*, 2019**,** who obtained 0.75 $WK^{-1}m^{-1}$. Refractive index is the ratio of the velocity of light of a specified wavelength in air to its velocity in the examined substance. Is a key property for optical applications, solute concentration measurements, and characterizing molecular interactions in DES (Luan *et al.*, 2023). The refractive index was measured at room temperature. The refractive index result of the DES is 1.48, and is in good agreement with work of Luan *et al.*, 2023.

Tensile strength is a mechanical testing that aims at determining the material response of a construction, component or fabrication assembly when subjected to a load. It is also to ensure the determination of bio-film ability to withstand the load given until it breaks (Andahera *et al.*, 2019). The effects of plasticizing agents (ethaline (DES) and glycerol) concentrations on the tensile strength of cassava peels starch TPSs are presented in figure 5. It was found that TPS with lower concentrations of plasticizer from 5 to 15wt%, demonstrated moderate increase in tensile strength,

with 15 wt% be the highest (3.8Mpa for DES and 3.3Mpa for Glycerol) as compared to other concentrations of plasticizers added. This was owing to the dominance of strong hydrogen bonding within starch-starch intermolecular interaction without much disruption by starch-plasticizer interaction at lower concentrations of plasticizer (Ng *et al.* 2021). Furthermore, it expected that DES form new hydrogen bond with starch hydroxyl groups, reinforcing cohesion while still reducing brittleness (Tarique *et al.*, 2021, Masdar *et al.*, 2022, Wilpiszewska and Skowrońska, 2023), necessitating the actual increase up to 15 wt% as compared to control and other concentrations of plasticizers added. Meanwhile, there was significant decrease in tensile strength as increase concentrations of the plasticizers from 15 to 30 wt%. These results were in line with those of Wilpiszewska and Skowrońska (2023) and Ng *et al.* (2021) where authors reported that increase of plasticizer concentrations resulted in a decrease of tensile strength of TPSs. From figure 5, the tensile strength of DES (ethaline) plasticized-TPS reduced from 3.9 to 1.2 Mpa where that of glycerol plasticized films decreased from 3.1 to 1.1 Mpa as the concentrations was increased from 15 to 30%. This phenomenon according to Ballesteros-Martinez et al. (2020) occurred due to the effect of plasticizing agents weakened the strong inter-molecular attraction within the starch polymer chain. Meanwhile, plasticizer ensured the formation of hydrogen bonds between starch and plasticizer molecules. As a result, the tensile strength cassava peels starch TPSs in this study decreased due to the disruption and weakening of hydrogen bonds between the starch polymer chains (Ng *et al.*, 2021). In comparing the effect of plasticization of plasticizers, it was observed that, at the same concentration, the glycerol plasticized-TPS showed lower tensile strength as compared to DES counterpart. This is because DES forms stronger hydrogen-bonding networks with polymer chains, leading to tighter intermolecular interactions and reduced chain mobility, while glycerol increases flexibility but weakens mechanical strength (Stettler *et al.*, 2024, Masdar *et al.*, 2022). The tensile strength profiles presented in figure 5, were consistent with the findings of Stettler et al. (2024) whereby authors reported that DES plasticized films were highly resistance to breakage compare to those plasticized by convectional plasticizers (glycerol, urea e.t.c) at the same concentration. In the same vain DES at 15% resulted in higher tensile strength than unplasticized firm, this is because DES also acts as a structural stabilizer, forming strong hydrogen bonds with hydroxyl groups in starch cellulose, which increases cohesion and tensile strength compared the unplasticized, (Andahera *et al.*, 2019, Masdar *et al.*, 2022, Wilpiszewska and Skowrońska, 2023)

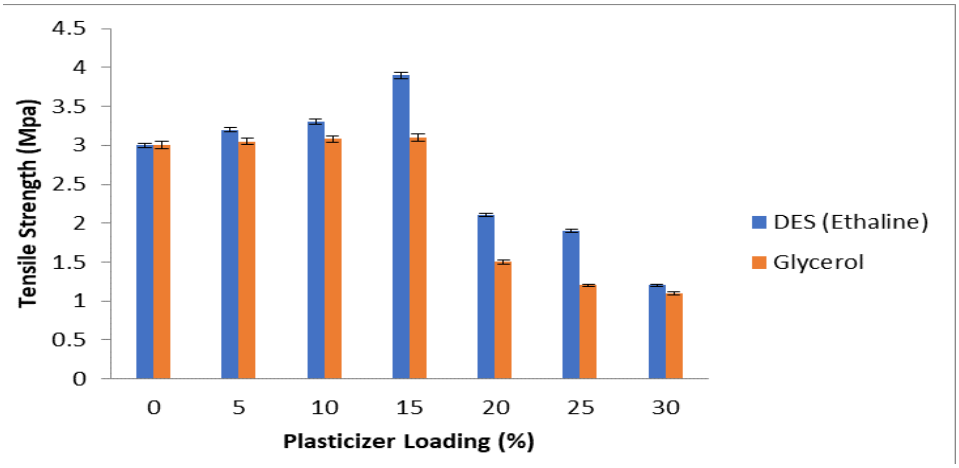

Figure 5: Effect of Plasticizers Loading on the Tensile Strength of TPSs Note: All Data are Presented in mean ± Standard Deviation, n=3. MPa is a Unit for Tensile Strength

On the other hand, elongation at break is known as the extendibility of plastic film starting from initial length to the maximum break point. It also indicates the stretchability and flexibility of plastic film. The results of elongation for the plasticized TPSs in this study were in opposite trend to the tensile strength. As shown in figure 6, the elongation of the produced TPSs increased along with increase in concentration of plasticizers. This phenomenon as explained by Ballesteros-Martinez et al. (2020), is due to the reduction in intermolecular bonds between glucosidic units (amylose and amylopectin) of the starch matrix owing to plasticization. This led the formation of hydrogen bonds between the plasticizer and starch matrix. Thus, crystallinity reduces and flexibility of TPS enhanced. In comparing the effect of plasticization, it was observed that, at the same concentration, the glycerol plasticized-TPS showed higher elongation at break as compared to DES counterpart. This is due to the small molecular and high hydrophilic nature of glycerol. Thereby penetrating fast into glucosidic unit, reducing the intermolecular bonding and increases the chain mobility, which translate to more flexibility, thus increase in elongation (Stettler *et al.*, 2024). In the same vain, DES forms stronger hydrogen-bonding networks with polymer chains, leading to tighter intermolecular interactions and reduced chain mobility, while glycerol increases flexibility (elongation) but weakens mechanical strength (Stettler *et al.*, 2024, Masdar *et al.*, 2022).

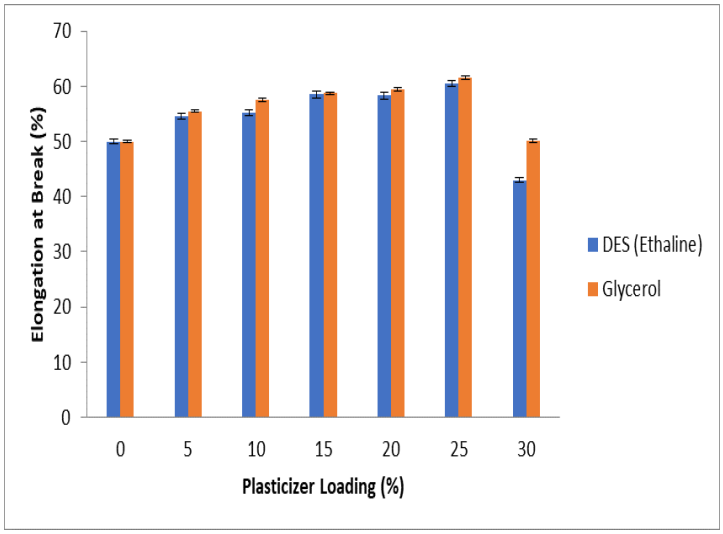

Figure 6: Effect of Plasticizers Loading on the Elongation at Break of TPSs

Figure 7, depicts the results of Young's modulus which is a pivotal parameter that implying the flexibility and brittleness of plastic film. The results from this study, revealed the indirect proportionality of increase in concentration of plasticizers to reduction in Young's modulus of the TPS. The unplasticized TPS recorded the highest Young's modulus of 6.0 Mpa, showcasing its high brittleness. In comparing the effect of plasticizers, both plasticized-TPSs recorded the highest Young's modulus at plasticizer loading of 5%. The value of the Young's modulus keeps dropping as the plasticizers loading concentrations increases up to 30%. This reduction trend of Young's modulus proved that addition of plasticizers enhanced the flexibility and durability of the TPSs which resulted in lower rate towards the fracture point. This finding is in line with work of Masdar et al. (2022), who reported that the presence of plasticizer modified the starch's fracture mechanism from swift brittle fracture at low train to elastoplastic fracture at high strain.

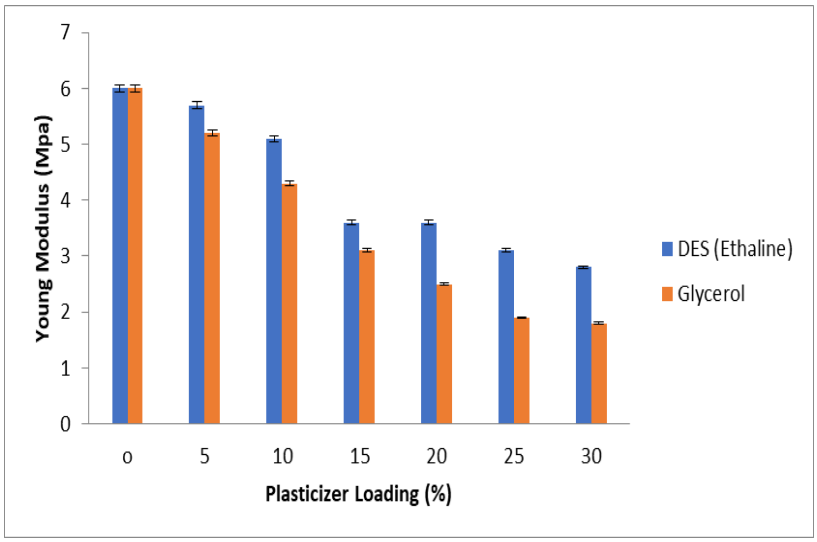

Figure 7: Effect of Plasticizers Loading on Young Modulus of TPSs Note: All Data are Presented in mean ± Standard Deviation, n=3.MPa is a Unit for Young Modulus

One of the major concerns of TPSs is the resistance and diffusivity when in contact with water molecules. In this study, water absorption test was performed for 24hours at room temperature of which increase in mass of the tested bioplastic films were noted and recorded bihourly. This testing is important to investigate the stability of TPS under humid and moisture conditions. To investigate the effect of hydrophilic nature of plasticized TPSs on the varied concentrations of plasticizing agents, all the TPSs were immersed in water. Upon immersion in distilled water, water molecules diffused into the fabrics (network chain) of the films. This resulted to the absorption of water and swelling of the TPSs. At the beginning, the mass of the films increased gradually due to high availability of vacant sites of the active hydroxyl groups of the TPSs. This absorption of water continues until equilibrium state established where the bioplastic films could not absorb any more water molecules due to saturation of active sites (Ng *et al.*, 2021).

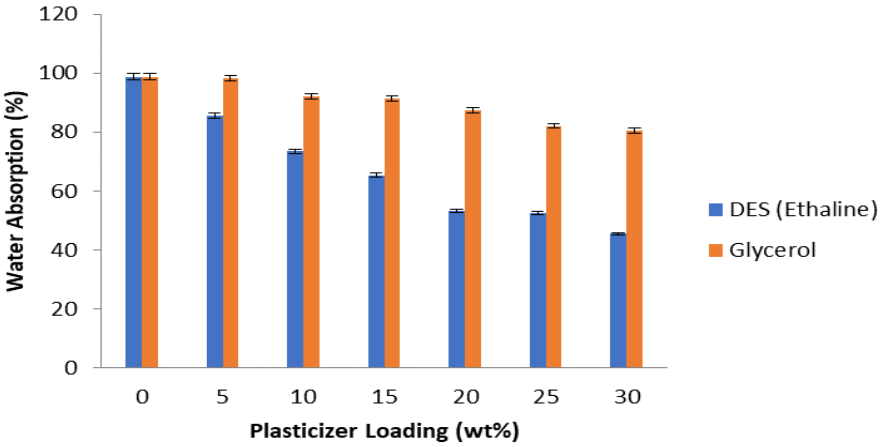

Figure 8: Effect of Plasticizers Loading on Water Absorption of TPSs Note: all Data are Presented in Mean ± Standard Deviation, n=3. The mean Different is Significant at P < 0.05 by one- way ANOVA.

The figure 8, shown the water absorption of all the TPSs produced using plasticizers at different concentrations. The results showed that the ability to absorb water reduced accordingly, when concentration of plasticizers were increased, with 0% plasticized film demonstrated high water absorption rate due to high nature of hydrophilicity exhibited by unplasticized TPS. The results proved that the addition of plasticizer depleted the hydrophilicity of TPSs.

CONCLUSION

The synthesized choline chloride – ethylene glycol deep eutectic solvent exhibited favorable physicochemical properties including stable viscosity, density, and surface tension across 25 to 60 °C as well as strong hydrogen bonding interactions confirmed from FTIR and conductivity analysis. When applied as a plasticizer for thermoplastic starch, DES outperformed glycerol in terms of tensile strength, modulus and water resistance. While both plasticizers increased elongation at higher concentrations, DES provided a more balanced improvement in mechanical and barrier properties. These findings highlight ethaline as a promising alternative to conventional plasticizer like glycerol, offering enhanced mechanical strength and reduced moisture sensitivity in TPS films. This study demonstrates that tailoring DES concentration is critical to optimizing bioplastic performance, paving the way for sustainable starch-based materials in packaging and related applications. The preliminary results obtained in the present study provide insights into the future work to focus specifically on study of others DES as plasticizers to produce bioplastics that demonstrate the required characteristics for a specific application (packaging, food services, agriculture and horticulture). As well, biodegradability tests are suggested to ascertain the veracity of its effect on the DES plasticized films.

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