

## Effect of Glycerol and Stearic Acid as Plasticizer on Physical Properties of Benzylated Wheat Straw

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**ABSTRACT:** The wheat straw as abundant lignocellulosic resource was successfully undergone in a benzylation reaction and plasticized with different contents (2.5, 3, 5 and 7 wt. %) of glycerol and stearic acid. The effect of type and concentration of plasticizers on the mechanical, thermomechanical, morphological and water absorption properties of Benzylated Wheat Straw (BWS) was investigated by tensile, Dynamic Mechanical Thermal Analysis (DMTA) measurements and Scanning Electron Microscopy (SEM), respectively. The experimental results show that addition of plasticizer may increase the elongation at break, and may decrease the tensile strength for the sheet plasticized with 5% or 7% stearic acid and 3% or 5% glycerol. The addition of 7% glycerol or 3% stearic acid make increase both tensile strength and elongation at break. These films are stronger but less tough compared to unplasticized BWS film. The porosity at the surfaces of samples from the SEM micrographs showed good correlation with the mechanical properties of the blends. On addition of plasticizer, it is observed that there is a decrease in the size of micro-pores and for higher concentration, it no longer exists. Compared with glycerol, the water absorption of the BWS films plasticized with stearic acid was significantly lower. Glycerol is soluble in water and removed from films after floating in water. The film plasticized with 2.5% both glycerol and stearic acid had better water resistance than others. As usual, glass transition temperatures of samples were decreased by addition of plasticizers according to DMTA results.

**KEY WORDS:** Lignocellulosic resource, Benzylation, Wheat straw, Stearic acid, Glycerol.

### INTRODUCTION

Nowadays, thermoplastic polymers are widely used in various aspects of human life. They have several properties e.g. excellent chemical resistance, good mechanical properties and low cost that makes them suitable for numerous applications [1].

Due to increase in environmental pollutions, researchers have tried to produce biodegradable polymers

using natural resources. The use of renewable resources as raw materials for production of biodegradable polymers is an interesting field investigated by researchers in the past decade [2]. Wood and straw of annual plants such as wheat and rice are materials composed mainly from cellulose offering many possible applications [3, 4]. Cellulose also has some undesirable

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properties. One of major drawbacks of natural polymers is the rigidity of their chains. The  $\beta$ -D-glucose rings, the main chain of cellulose as well as the strong hydrogen bonds among their hydroxyl groups, harden the processing of these polymers. The traditional procedures of thermoplastic polymers cannot be implemented for their processing without modification of the process or material [5]. There are some ways to improve its chemical or physical properties such as alkylation, acylation and benzylation.

benzylation reaction has been employed to produce thermoplastic derivatives. Products can be obtained, having different degree of substitution, by employing different reaction times or particular experiment conditions [6-8]. Benzylation of cellulose was initially performed to manufacture a useful thermoplastic cellulose derivative in order to expand the application area for cellulose [9, 10].

There are studies where benzylation of raw lignocellulosic materials and characterization of the thermoplastic product have been investigated [11-20]. The benzylation and acetylation of poplar and beech woods and also rice straw were carried out in our previous studies [21-24]. In these studies, the focus point was on reaction parameters, degree of substitution and mechanical properties of products. All of these studies have been conducted on wood residues and rice straw with no attempt on modification of wheat straw as alternative cheap and available lignocellulosic resource.

In the present study, wheat straw was selected as a lignocellulosic resource to obtain the thermoplastic material. The benzylated lignocellulosic fibers are usually brittle polymers and this fact makes the polymers hard to form in different shapes [15]. To improve the mechanical properties of the BWS, stearic acid and glycerol were used as most plasticizer and their effect on the tensile, morphological and mechanical-thermal properties and also water absorption of the products has been investigated. The main objective of this study is to use cost effective natural resource in a biopolymer production as an alternative for molding applications.

## EXPERIMENTAL SECTION

### Materials

Wheat Straw (WS) was obtained from Khalkhal of province of Ardabil, Iran. After drying at 60°C in an oven

for 24 h, the straw was crushed to pass through a 40 mesh screen. The composition (% w/w) of the straw is cellulose 38.0%, hemicelluloses 30.0%, lignin 16.5%, ash 5.5% and 10.0% other components on a dry weight basis [25]. Benzyl chloride, ethyl acetate, methanol and sodium hydroxide, all obtained from Merck, Germany, and used as received. Glycerol and stearic acid as plastisizers were purchased from commercial sources.

### Methods

#### Benzylation of Wheat Straw

The benzylation was carried out according to a method derived from the literature [13]. Wheat straw powder was dried at 105°C prior to application. 180 g of Wheat straw powder (mesh 40) was placed in a 2.5 L glass reactor, then 1L benzyl chloride and 1L sodium hydroxide solution 40% by weight were added. The flask, equipped with a condenser and an overhead stirrer (Model Heidolph, Germany), was placed into an oil bath. Reaction was carried out at 120°C with gentle stirring at 400 rpm for 5h. After this period, the liquor was decanted and solid mass was refluxed twice with methanol (to remove unreacted benzyl chloride). The resulting product was washed with hot and cold water successively and dried at 60°C. As a result, 297.3 g Benzylated Wheat Straw (BWS) was obtained.

#### Film Forming

Product sheets were prepared using solutions of plasticizer and Benzylated Wheat Straw (BWS). Plasticizers (glycerol and stearic acid) were used in various proportions. Amounts of plasticizers (2.5–7% of solids, w/w) were weighed and dissolved into ethyl acetate and followed by adding BWS to obtain a uniform solution. The film forming solution was heated while being stirred by a magnetic stirrer and manually by a glass rod, to above 65°C to obtain the solution. The solution was then poured on aluminum foil until the solvent was completely evaporated at room temperature. 8 g from each blended film was grinded and molded by a hot press at 130°C and 30 bar pressure for 10 min. and 100 bar for an additional 15 min. until a uniform sheet with a thickness of 0.338 mm was obtained. Compositions of various BWS/plasticizer blends are shown in Table 1.

**Table 1: Compositions of the various BWS/Plasticizer blends.**

Blend compositions for Benzylated Wheat Straw (BWS) and plasticizers				
Sample Code	BWS (%)	Glycerol (%)	Stearic Acid (%)	Total (g)
S1	100	-	-	8
S2	97	3	-	8
S3	95	5	-	8
S4	93	7	-	8
S5	97	-	3	8
S6	95	-	5	8
S7	93	-	7	8
S8	95	2.5	2.5	8

#### FTIR spectra

The infrared spectroscopy was performed using a Bruker instrument (Bruker, Equinox 55LS 101 series, Germany) with a resolution of 4 cm<sup>-1</sup> (averaging 50 scans) for determination of polymer functional groups.

#### Tensile Test

A micrometer was used to monitor sheet thickness. An average of 3 measurements was recorded. To measure the tensile properties of samples, the dumbbell-shaped test pieces were cut from 0.338 mm thick sheets and subjected to tensile test on a universal testing machine (Model Gotech) at a cross-head speed of 1mm/min. Testing protocols followed ASTM standard D412. At least 5 tests specimens of every composition were tested. Conditions during testing were at 23°C and 50% relative humidity. Tensile strength was calculated at the maximum force used during measurement. The elongation at break was calculated by measuring the maximum extension of the sheet between the initial and final grip separation. *E*- Modulus was calculated from the slope of initial linear region of the stress-strain curve.

#### Dynamic Mechanical Thermal Analysis (DMTA)

The dynamic thermomechanical properties of the sheets were measured with Exstar (model SII DMS6100) analyzer. The bending (dual cantilever) method was used with a frequency of 5 Hz, the strain level of 0.04%, within the temperature range from 25 to 200°C. The heating rate was 10°C/min. The test was performed by using rectangular bars measuring approximately

30 \* 10 \* 3 cm. The samples were prepared in a hydraulic press, at a temperature of 220°C and pressure of 250 bar, for a time period of 5 min. The exact dimensions of each sample were measured before the scan.

#### Scanning Electron Microscope

The morphology of the surface area of each blend was studied using a scanning electron microscope (SEM, Philips, Model XL-30, Eindhoven, The. Netherlands). Prior to examination, each sample was coated with gold using a sputter coater. The gas pressure was less than 50 mtorr, and the current was about 40 mA.

#### Water Absorption

Water absorption was determined by mean of the ASTM Standard D570-81. A given piece of each sample (0.338 mm thick, 12 mm wide and 50 mm long) was initially dried to a constant weight and then immersed in water at different time intervals. Each sample was removed from the water container, dried and subsequently weighted. Water absorption of all samples was calculated by following equation:

$$M_t(\%) = \frac{W_t - W_0}{W_0} \times 100 \quad (1)$$

Where  $M_t$  is the amount of water absorbed at time  $t$  and  $W_t$  and  $W_0$  are the weight of the samples at time  $t$  and initial weight of the sample, respectively.

## RESULTS AND DISCUSSION

The color of Benzylated Wheat Straw (BWS) was orange. After intensive mixing of the plasticizers and

benzylated wheat straw in cast solution technique, the resulting blends exhibited a range of color from light orange to yellow, depending on the amount of BWS present in the product.

The plasticizers have various contents of glycerol or stearic acid. The blends contain 93-100 parts of BWS and 0-7 parts of glycerol or stearic acid. Compositions of various plasticized BWS blends are shown in Table 1.

Fig. 1 shows FT-IR spectra of BWS samples with and without plasticizers (glycerol and/or stearic acid). The FT-IR spectrum was used more as a qualitative analysis. Since the values of plasticizer in polymeric sheets are practically negligible, their signals in FT-IR spectrum are very weak and interactions between polymer and plasticizer cannot be detected from the spectrum. The most significant signal is observed in the FT-IR spectrum is C-O etheric bond at  $1050\text{ cm}^{-1}$ .

### Tensile Properties

Fig. 2 shows the tensile strength of the BWS films plasticized with different levels of plasticizers. The BWS sheet without plasticizer has a tensile strength of 32.82 MPa. This compound is brittle, but addition of stearic acid (5% or 7% Wt) and glycerol (3% or 5% wt) as plasticizer decreased the tensile strength causing a softer BWS films. The formation of hydrogen bonds between the unreacted cellulose hydroxyl groups and plasticizers weakened the inter- and intra-hydrogen bonds among cellulose molecules, leading to reduced tensile strength. With plasticizer levels  $>3\%$  of BWS, samples plasticized with stearic acid showed lower tensile strength than samples plasticized with glycerol. Addition of 3% stearic acid and 7% glycerol shows an increase in tensile strength compared to unplasticized film. As presented in Fig. 2, the addition of 2.5% stearic acid and 2.5% glycerol together has no effect on the tensile strength of blend. This may be due to esterification of glycerol with stearic acid under temperature and pressure of pressing process that leads to decrease of their plasticizing effects [26].

Fig. 3 shows the elongation at break for unplasticized and plasticized BWS blends. Interestingly, the addition of glycerol or stearic acid in all proportions shows an increase in elongation at break as compared to unplasticized BWS film. The presence of plasticizer causes a reduction of interaction force between BWS

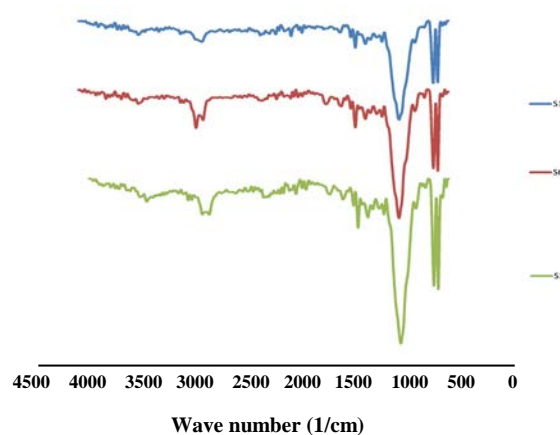


Fig. 1: FTIR spectra of BWS samples without and with plasticizers (glycerol and stearic acid).

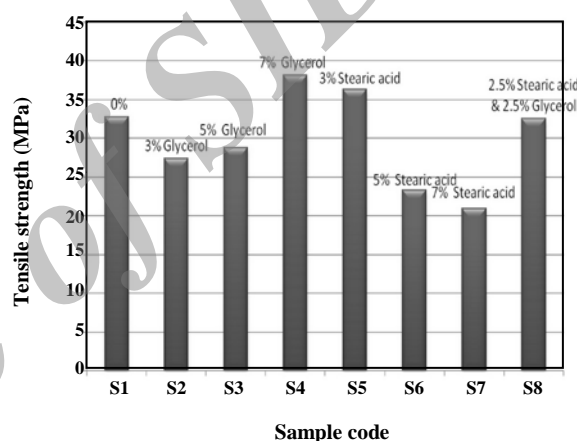


Fig. 2: Tensile strength of the BWS films plasticized with different levels of plasticizers.

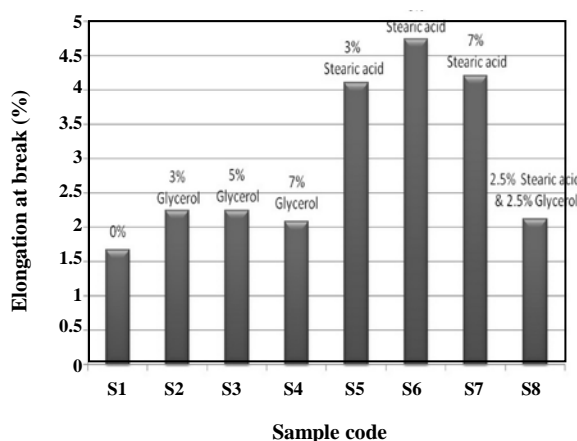


Fig. 3: Elongation at break of the BWS films plasticized with different levels of plasticizers.

chains and an increase in the movement of macromolecules [27, 28], leading to increase in the films elongation at break.

Combining the data from Figs. 2 and 3 shows that addition of 7% glycerol or 3% stearic acid increases the tensile strength and elongation at break of BWS blend. These films are stronger but less tough compared to the unplasticized BWS films. It means glycerol and stearic acid does not exhibit the conventional effect of common plasticizers at 7% and 3% concentrations. The differences in tensile strength and elongation at break of the plasticized films, with several plasticizers suggested that the appropriate plasticizer for an individual BWS film system depends on the nature, size and the structure of plasticizer as well as the compatibility between BWS molecules and plasticizers.

Fig. 4 shows the *E*-Modulus of the BWS sheet. It decreases with the addition of 3% glycerol to 1.68 GPa and with 5% glycerol to 1.82 GPa. However, the *E*-Modulus for film plasticized with 7% glycerol was higher than usual. It may be because of high tensile strength of this sample. On the other hand addition of stearic acid decreases the *E*-Modulus of samples in a common way.

An important way of assessing mechanical characteristics of materials is the stress-strain curve obtained from an extensimeter [29]. The stress-strain curves of BWS films with different levels of glycerol or stearic acid are shown in Figs. 5 and 6, respectively. The stress-strain curve of pure BWS film has an elastic region, without showing a yield point and a transition to ductile or plastic region. This clearly demonstrates that BWS film without glycerol or stearic acid was brittle. The results from stress-strain curves agreed with Schiling *et al.* [30], who found that the stress-strain curves exhibited progressively greater deviations from linearity as the concentration of plasticizer increased.

The results of comparing BWS films plasticized with glycerol and with stearic acid show that mechanical properties of stearic acid are higher than those of glycerol.

#### Dynamic Mechanical Thermal Analysis (DMTA)

The prepared blends were studied by the DMTA in temperatures close to their glass transitions. Fig. 7 shows the  $T$ - $\tan\delta$  curves for sample without plasticizer and with 5% stearic acid and 5% glycerol. The maximum of  $\tan\delta$  peak,

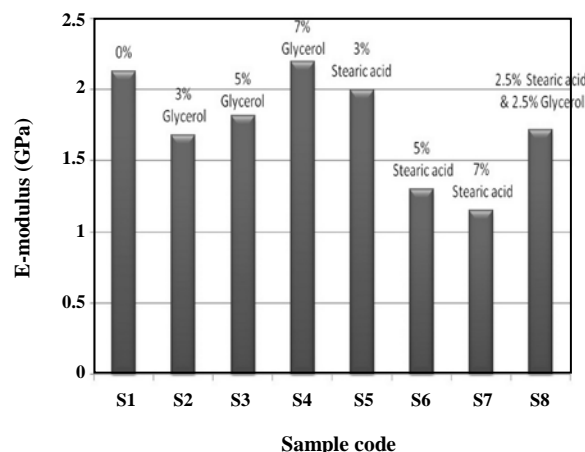


Fig. 4: Stiffness of blends, pure BWS compared with blends with different levels of plasticizers.

which corresponds to the glass transition, is ca. 84.5°C for BWS (S1), 81.1°C for BWS plasticized with 5% glycerol (S3) and 73°C for BWS with 5% stearic acid (S6). The elongation at break is larger in samples plasticized by stearic acid and *E*-Modulus of BWS and glycerol samples are higher. It shows that stearic acid samples are softer than others and it also is clear in DMTA results.

#### Morphological examination of the surface area

The morphological behavior strongly influences the properties of polymer blends [31]. Figs. 8a-8h shows the SEM micrographs of BWS films with and without the plasticizers at different levels. The SEM micrographs from surface area of samples show good correlation with the mechanical properties of the blends. The BWS film without plasticizer has some imperfections in the film indicated as some black spots in the micrograph (Fig 8a). These black spots are micro-pores which can be sites for micro-crack formation and propagation that lead to fracture.

The cracks and voids in the structure of BWS films without plasticizer may explain the lower values of elongation at break. Comparison of the surface morphology of BWS films plasticized with 3%, 5%, and 7 % glycerol show a marked change in the surface properties of the thin films on addition of plasticizer. It is observed that there is a decrease in the size of micro-pores with increasing glycerol. In the case of 7% glycerol, this decrease no longer exists. This indicates that introduction of glycerol into BWS film induces the rich adhesive or interaction of surfaces.

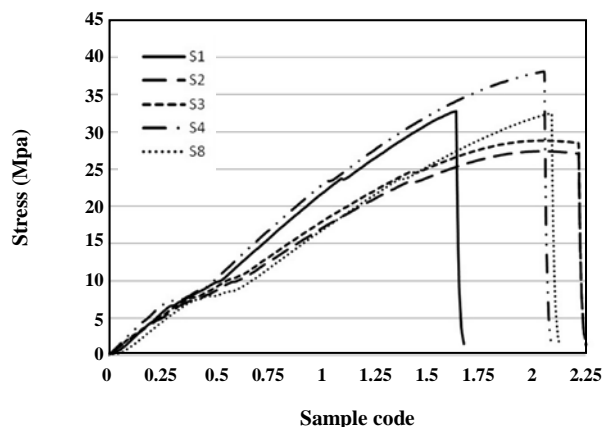


Fig. 5: The stress-strain curves of BWS films plasticized with different levels of glycerol: S1: Unplasticized, S2: 3% Glycerol, S3: 5% Glycerol, S4: 7% Glycerol, S8: 2.5% Glycerol & 2.5 % Stearic acid.

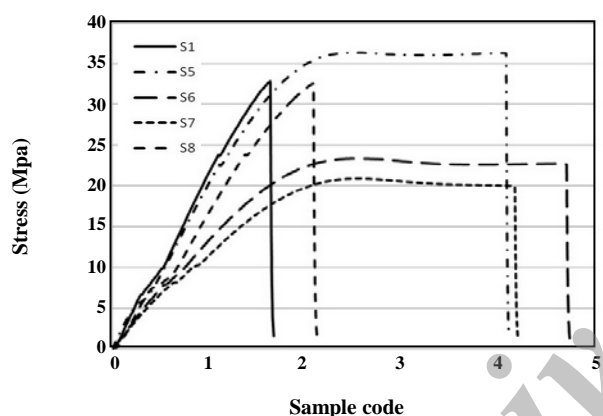


Fig. 6: The stress-strain curves of BWS films plasticized with different levels stearic acid: S1: Unplasticized, S5: 3% Stearic acid, S6: 5% Stearic acid, S7: 7% Stearic acid, S8: 2.5% Glycerol & 2.5 % Stearic acid.

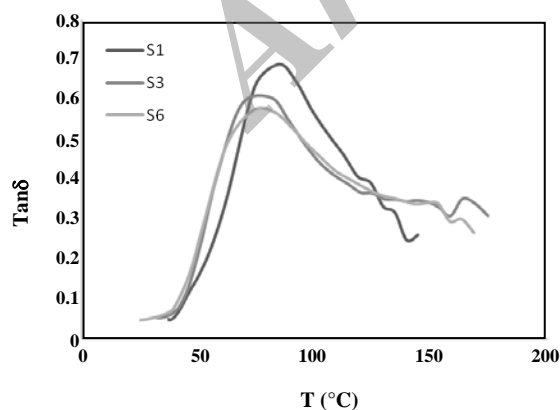


Fig. 7: T-tan $\delta$  curves for BWS and BWS plasticized with 5% glycerol and stearic acid.

Figs. 8(e), 8(f) and 8(g) present the SEM micrographs of the BWS films plasticized with 3%, 5%, and 7 % stearic acid, respectively. It can be observed that good morphology with a decrease in the size of micro-pores could be obtained using 3% or 5% stearic acid. This morphology is a good evidence of compatibility of stearic acid with BWS compared to glycerol. From Figure 8(g), it was found that utilization of 7% stearic acid leads to more lubrication of film surface compared with the samples plasticized with 3% or 5%. The stearic acid crystallization could be observed visually from the white regions appearing on the surface of film plasticized with 7% stearic acid.

The SEM micrograph of the porosity surfaces of BWS film plasticized with 2.5% glycerol and 2.5% stearic acid is displayed in Fig. 8(h), which indicates the presence of voids in the matrix resulting in lowering the elongation at break of the blend.

#### Water Absorption Behavior of Blends

Fig. 9 shows the percentage of water absorption as a function of time for BWS films with and without the plasticizers at different levels. Permeability of materials is influenced by the hydrophobic or hydrophilic nature of the material [32, 33], and the existence of voids or cracks [34]. As can be observed in Figure 9, the water absorption and hydrophilicity of unplasticized pure BWS film via substitution of H-atom of hydroxyl group with benzyl group was remarkably decreased. This was completely consistent with our previous research on chemical modification of beech wood. The chemically modified wood had low hydrophilicity and water absorbency [22]. It is interesting to note that both BWS blends plasticized with stearic acid and glycerol absorbed appreciable amount of water compared to the BWS films without the plasticizer.

The water absorption of the BWS blended with 3% or 5% glycerol increases as the amount of plasticizer increases. Since glycerol is hydrophilic, an increase in its concentration from 3% to 5% enhanced the absorption of water to the network and increases the percentage of water absorption.

In contrast, BWS blended with 7% glycerol shows an unusual decrease in the water absorption amount. The investigation of mechanical and morphological tests showed that the BWS network structure plasticized

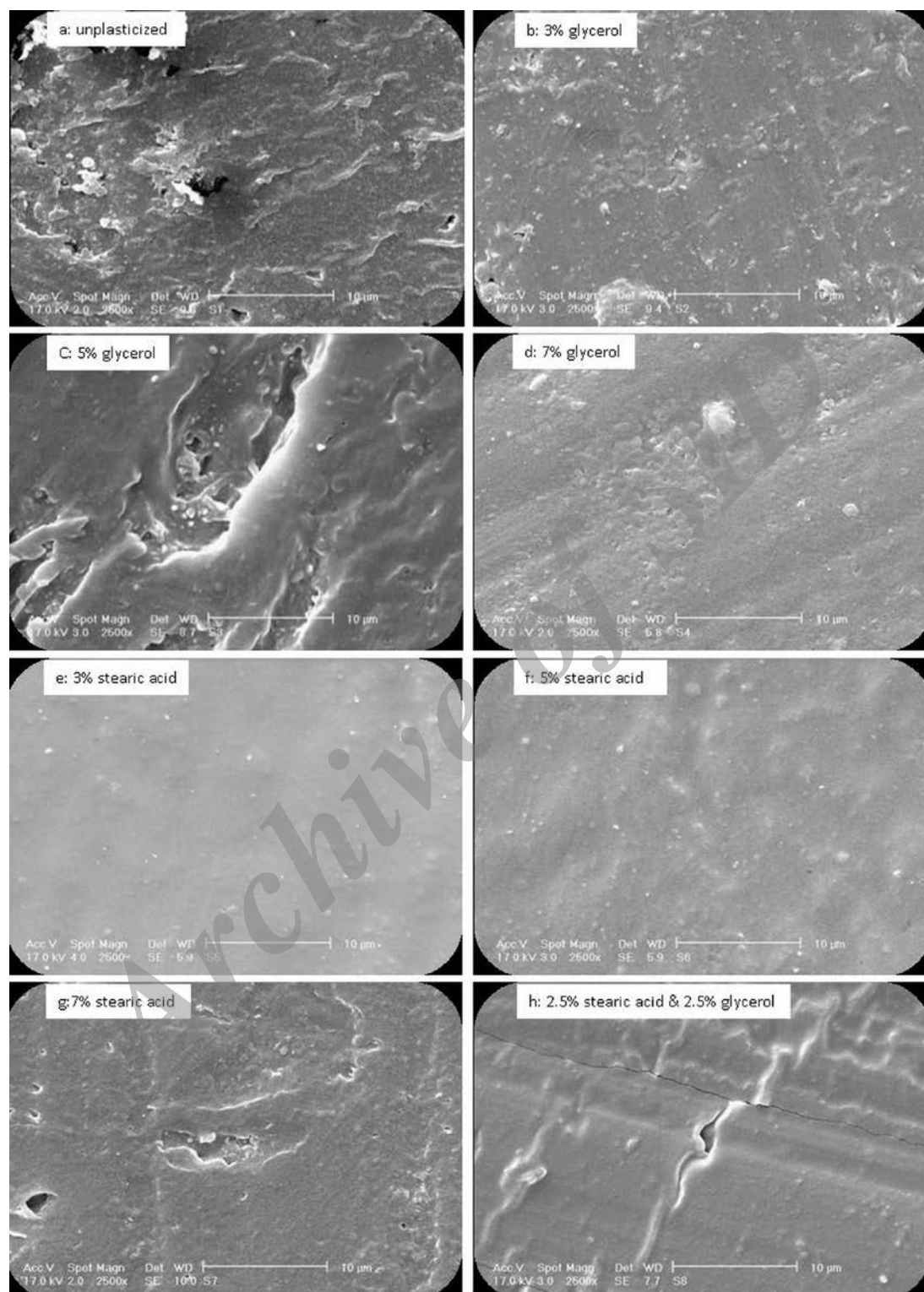


Fig. 8: SEM micrographs of plasticized BWS films with various proportions of stearic acid and glycerol plasticizers.



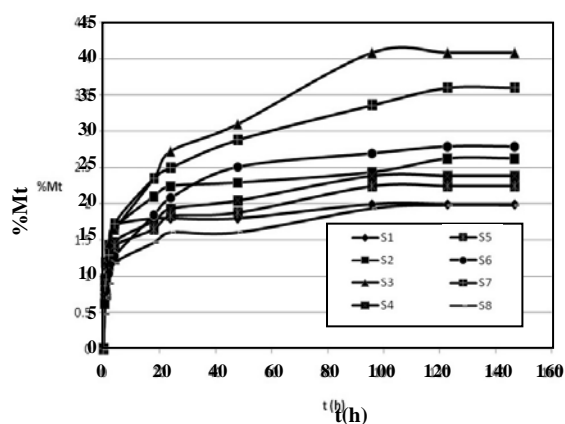


Fig. 9: Water absorption curves for BWS and BWS plasticized with stearic acid or glycerol.

with 7% glycerol was more dense and impermeable. Also, the BWS plasticized with 7% glycerol undergoes the facial migration of plasticizer into water leading to some weight loss, and subsequently decreases the water absorption of BWS blend.

Addition of stearic acid influenced the structure as to becoming more hydrophobic and compact, thus absorbing less water [31]. The hydroxyl group of stearic acid interacts with water molecule and helps the facial introduction of water into the plasticized blends. For this reason, the utilization of stearic acid as plasticizer leads to a regular increase of the water absorption. Because of partial solubility of stearic acid in water, BWS plasticized with 7% stearic acid do not show any decrease in water absorption compared to the sample plasticized with 7% glycerol. Since glycerol has three hydroxyl groups that easily interact with water molecules, the BWS plasticized with 3% or 5% glycerol shows the high water absorption compared to that plasticized with 3% or 5% stearic acid.

Interestingly, the water absorption of BWS plasticized with 2.5% stearic acid and 2.5% glycerol is very low compared to the sample plasticized with 5% stearic acid or glycerol. This decrease of water absorption may be associated with the interaction of glycerol hydroxyl groups with carboxyl group of stearic acid leading to decrease of available hydroxyl groups for interaction with water molecules.

## CONCLUSIONS

The utilization of stearic acid in different levels exhibited relatively good plasticization of BWS films and good resistance against water absorption compared

to glycerol. The addition of plasticizers decreased the tensile strength and increased the elongation at break of BWS films, which was due to the formation of intermolecular hydrogen bonds between the plasticizers and BWS, which weakened the hydrogen bonds among the BWS molecules. The films plasticized with stearic acid resulted in surfaces less or without micro-pores may help in resistance against fracture. Compared to glycerol, the plasticizing effect of stearic acid was increased as the amount of plasticizer increased. However, the resistance against water absorption was enhanced significantly and was increased with the increase of the level of stearic acid. The results indicated that application of stearic acid is more influential than glycerol. The films containing 5% stearic acid-BWS showed lower water absorption and also weaker tensile strength, but larger percents of elongation at break compared with films containing 5% glycerol-BWS. These materials can be used for the preparation of films, sheets and other molding systems.

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