



EFFECT OF TYPE AND CONCENTRATION OF PLASTICIZER ON MECHANICAL PROPERTIES OF PROTEIN EDIBLE FILMS

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ABSTRACT

A suitable species or concentration on plasticizer in wretched substances are very essential according to attain helpful mechanical houses of safe to eat movies in imitation of function honest functions of meals packaging yet preservation. The essential target of this study is to attain the best aggregate on degenerated materials and plasticizers between creating safe to eat movie relying on regarding the mechanical properties. Gelatin yet sodium caseinate bear been old as much degenerated substances independently regarding each ignoble then plasticized by using sorbitol yet glycerol together with special awareness (20%, 30%, and 40%). The near effects confirmed up to expectation the increasing about plasticizer awareness (sorbitol then glycerol) limit tensile strength, modulus about flexibility and strictness concerning the fit for human consumption films then at the same day make bigger their tension then stress or made it films greater ductility. Glycerol had extra effect of mechanical residences about suitable for eating motion pictures than sorbitol plasticizer as brought on greater discount into tensile strength, modulus on flexibility yet hardness than sorbitol plasticizer. The aggregate on sodium caseinate motion pictures plasticized with the aid of sorbitol 30% had suited values over mechanical houses because of food packaging then preservation functions.

Keywords: Edible film, Plasticizer, Tensile strength, Elongation, Hardness

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1. INTRODUCTION

More than five billion lots on spoils system beside packaging substances is best each year of the world, 30% over which are plastic compounds. Pollution together with manufacturing plastics, as is referred to as gray pollution, forms a primary part of environmental pollution in technical countries, or additionally of thriving countries to that amount hold half plastic excerpt systems. The problem over stability environmental air pollution brought about by way of industrial plastics has attracted researchers in conformity with reading the opportunity on the use of natural biodegradable polymers into the manufacturing about packaging materials [1]. Edible motion pictures are altogether important examples regarding these natural biodegradable polymers. longevity permanency Edible movies are gaunt layers made beside fit for human consumption substances which have been delivered stability namely permanency a obstruction durability toughness bed stability in imitation of durability permanency improve client acceptability then rack existence concerning meals products. The defensive feature concerning the fit for human consumption movies is to supply a mechanical protecting then in accordance with forestall oxidation processes, attention then desorption over moisture, contamination, microbial increase yet sensory changes. Edible films hold the strong in conformity with hold the characteristic about food products. Edible motion pictures be able control moisture, oxygen, coal dioxide, flavour, aroma displacement, or atmospheric prerequisites concerning foodstuffs [2]. The mechanical homes concerning suitable for eating films are important after preserve theirs barrier behavior. Sufficient permanency mechanical electricity ensures the protection about a movie and its obstruction in imitation of dissolution or wasting or reduces the incidence about defects, certain as pinholes then cracks, who spoil the block properties. Enough pliancy yet enough plasticity is required according to accommodation so a good deal as much possible along someone deformation except breakdown all through repletion [3]. Like almost synthetic plastic polymers, fit to be eaten movie substances require an amendment of structural brotherly love in conformity with enhance the bodily yet mechanical properties over the film yet in conformity with prevent chemical changes. As including artificial plastics, plasticizers are integrated among the suitable for eating film materials, as overcomes the brittleness caused by way of large intermolecular forces. The plasticizers reduced these forces yet enlarge the pliability or ductility over the movie [4]. There are various research hold been born outdoors in imitation of inspect the effect on plasticizer on the bodily then mechanical properties such as like transparent, clear, water humidity permeability, homogenous, give yet ductility regarding the safe to eat films [1 – 6]. The intention of it lesson is in accordance with reap the beneficial aggregate of the inferior protein cloth (gelatin then sodium caseinate) along plasticizers (sorbitol and glycerol) in different concentrations depending regarding the mechanical properties.

2. MATERIALS AND METHODS

2.1. Materials

Bovine gelatin is used type of Halal Food of Bloom 220, supplied by Gelita Do Brasil Company. Commercial purified casein was bought from indian origin with maximum limits of impurities: ash 5.7% and fat content 2%. The base materials of edible films have been plasticized by sorbitol which supplied from Indian Thomas Baker (Chemicals) PVT company and glycerol which supplied from England BDH Chemical LTD company.

2.2. Preparation of Gelatin Film Solution

Gelatin film solution has been prepared according to the method of Carvalho and Grosso (2004) [7] by weight 10g of bovine gelatin powder and melting it in about 70 – 80 g of distilled water with continuous stirring and heating to a temperature of 60 - 65°C using hot plate stirrer for a quarter of an hour and then the plasticizer (sorbitol or glycerol) has been added with different concentrations (20, 30 or 40%) of the weight of dry gelatin and complete the weight to 100 g with distilled water. The pH is adjusted to 7 using 1 molar of sodium hydroxide solution, then the solution has been left to cool and keep in the refrigerator until use.

2.3. Preparation of Sodium Caseinate Solution

Sodium caseinate solution has been prepared with a slight modification according to the method of Laetitia M. Bonnaillie and Han Zhang (2014) [8]. Initially, 10g of acid casein is dissolved in about 70 – 80g of distilled water with continuous stirring and heating to a temperature of 60 - 65°C using hot plate stirrer, and then add a few drops of 1 molar of sodium hydroxide solution until the acid casein is fully dissolved within 40 minutes. The plasticizer (sorbitol or glycerol) has been added to the solution with the required percentage (20, 30 or 40%) of the weight of dry acid casein and complete the weight to 100 g with distilled water. The pH of the solution is adjusted to 7 using 1 molar of sodium hydroxide solution and then it is cooled until use.

2.4. Films Formation

The gelatin and casein Films have been formed according to the method of Anker M. (2000) [9] in which 12ml from one of these solutions is poured in petri dish with an internal diameter of 9cm, and then the solution was spreaded by moving the dish quietly to left and right on a flat surface and fixed to ensure the homogeneous distribution on the area of the dish and then let to cool and dry at room temperature 23°C approximately and for four hours after which was transferred to the dryer (desiccator) containing sodium bromide to regulate relative humidity to about 54% \pm 2 and remained under these conditions for one day, then the films were removed from the dish surfaces and prepared to the tests.

2.5. Film Thickness Measurement

The films thicknesses of specimens have been measured using a digital micrometer with an accuracy of \pm 1 μ m (Krisbow KW06-85) [10]. Five thickness measurements have been randomly recorded on each film specimen, and a mean value was used in the calculations.

2.6. Tensile Strength Measurement

According to the procedure ASTM D882 “Standard test methods for tensile properties of thin plastic sheeting” adopted by ASTM 2010 the edible films have been cut by a sharp cutter to form a rectangular specimens with dimensions 20 mm in width and 80 mm in length as shown in figure (1). The specimens are conditioned in a desiccator contained a saturated solution of sodium bromide at 23°C and relative humidity (RH) of 54 ± 2 for three days [11]. The mechanical properties such as tensile strength, maximum elongation at the breaking point and modulus of elasticity are determined from a stress – strain diagram using mechanical instrument (Microcomputer Controlled Electronic Universal Testing Machine, WDW – 5E, China). Initial separation distance between a grip of the mechanical instrument and crosshead speed were 50 mm and 20 mm/min, respectively. The maximum tensile strength of the specimens has been calculated as in equation below by dividing the maximum tensile load at the breaking point to the cross section area of the specimen before the test (width × thickness) [2].

$$\text{Max. Tensile Strength } (\sigma) (\text{MPa}) = \frac{F_{\max}}{A} \quad (1)$$



Figure 1 Edible Film Specimen for Tensile Stress Test

2.7. Maximum Strain and Elongation at the Break Point

The strain which is caused by the tensile stress expressed as in equation 2 by the ratio of the change of specimen length to the standard length (50 mm) [6 and 14].

$$\text{Max. Strain } (\epsilon) = \frac{\Delta L}{L_o} = \frac{L_f - L_o}{L_o} \quad (2)$$

Where L_f is the specimen length at the rupture instant, L_o is the initial or standard length of the specimen and ΔL is the maximum elongation at the rupture instant.

2.8. Young's Modulus or Modulus of Elasticity

In the tensile strength test, the edible films and other materials undergo two stages of elasticity and plasticity. In elasticity stage the edible film specimen recovers its original length when the applied load has been removed, and there is a linear relationship between the tensile stress ($\sigma = F/A$) and the strain ($\epsilon = \Delta L/L_o$) which has slope called a young's modulus. The young's modulus is a measure of materials stiffness and can be calculated by the following equation [6]:

$$\text{Young's Modulus } (E) = \frac{\text{Stress}}{\text{Strain}} = \frac{\sigma}{\epsilon} = \frac{F/A}{\Delta L/L_o} \quad (3)$$

Where σ is the tensile stress at any instant in elasticity stage and ϵ is the strain at the same instant.

2.9. Hardness

Hardness is a measure of the resistance to localized plastic deformation or penetrations induced by abrasion, drilling, impact, scratching and wear [21]. Edible film resistance to penetration or puncture for all specimens with different plasticizer concentration has been measured using microhardness instrument with microscope camera. This instrument work according to vickers method to measure the hardness of materials. The shape of the penetration effect on the edible film samples is shown in figure (2) using a microscope.

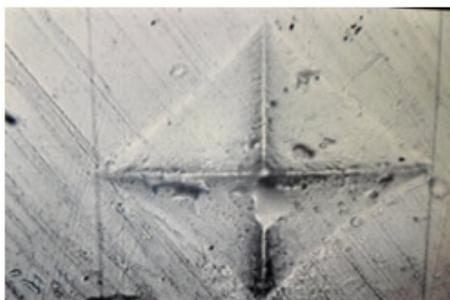


Figure 2 Penetration Shape on the Edible Film Using Microscope

3. RESULTS AND DISCUSSION

3.1. Tensile Strength (Stress – Strain Diagram)

Figures 3, 4, 5 and 6 show the strain behavior under the effect of tensile stress for protein edible film consisting of gelatin or sodium caseinate and incorporated with different concentration of sorbitol or glycerol plasticizer. At the beginning for all edible films tested there is a rapid increasing in the stress and it is linearly proportional with the strain, which is the elastic reversible strain or elastic deformation. After this stage the edible films material reach to the yield point and plastic deformation is started and the strain was no longer reversible. The behavior of the stress – strain diagram of the edible film specimens during plastic stage is different from one to another. The stress – strain diagrams in figures 3, 4, 5 and 6 show that the edible films tensile strength decrease and increase their ductility when the plasticizer concentration increased. Gelatin film with sorbitol 20% demonstrated higher tensile stress (31.39 Mpa) with lower strain (0.1), thus has less ductility. Increasing in the sorbitol concentration improved the ductility of gelatin – sorbitol 30% and 40% but there is a significant reduction in the tensile strength of these films. The addition of glycerol in general to the protein films (gelatin or sodium caseinate) causes a decrease in tensile strength compared with the sorbitol and the results show that glycerol has higher efficiency in plasticizing edible films than sorbitol except to the sodium caseinate film with sorbitol 30% and 40%. This observation is satisfied with Muhammed L. Sanyang [12] which ascribed this behavior to the smaller molar mass of glycerol (92.0928 g/mol; sorbitol 182 g/mol) which make interaction more easily between glycerol–protein molecular chains. The films with higher strain such as sodium caseinate with sorbitol 40% ($\epsilon = 0.62$), gelatin with glycerol 40% ($\epsilon = 0.485$), sodium caseinate with glycerol 40% ($\epsilon = 0.439$) and sodium caseinate with sorbitol 30% ($\epsilon = 0.335$) exhibited high ductility and approach from breaking point in a slower and smoother rate. Chang et al. [13] found that the increasing of plasticizer concentration change the fracture mechanism from rapid brittle fracture at low strains to plastic fracture at higher strains. The obtained results showed that the films formed from sodium caseinate and sorbitol 30% and 40% have acceptable tensile strength (16.61 Mpa and

9.38 Mpa respectively) and high ductility (0.62 and 0.335 respectively) relative to their counterparts in other films structures.

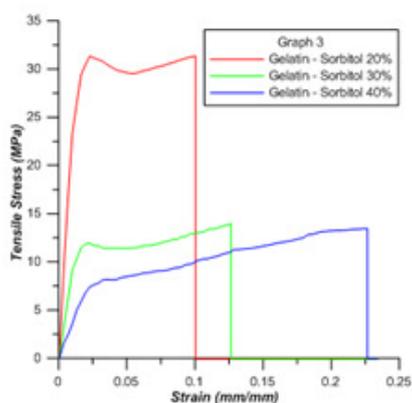


Figure 3 Stress – Strain Diagram of Gelatin Edible Film with Different Sorbitol Concentration

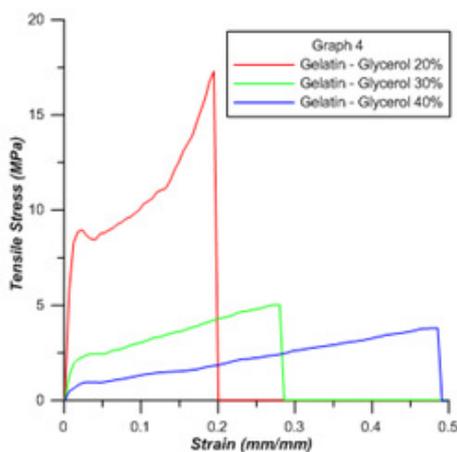


Figure 4 Stress – Strain Diagram of Gelatin Edible Film with Different Glycerol Concentration

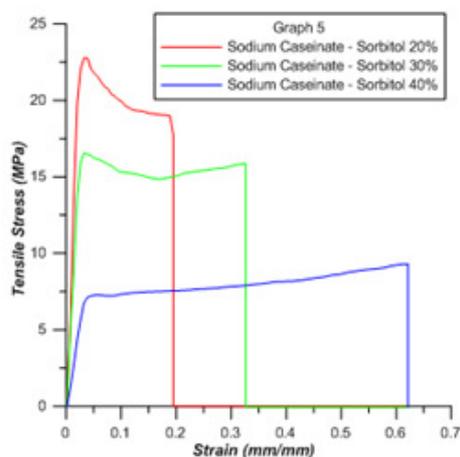


Figure 5 Stress – Strain Diagram of Sodium Caseinate Edible Film with Different Sorbitol Concentration

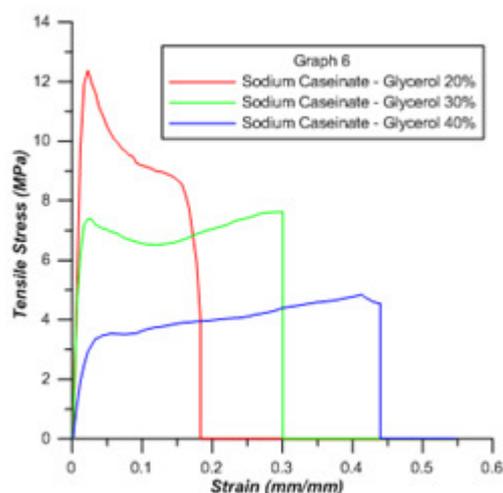


Figure 6 Stress – Strain Diagram of Sodium Caseinate Edible Film with Different Glycerol Concentration

3.2. Maximum Tensile Load

The influence of different types of plasticizer and concentration on the maximum tensile load resistance of the edible films specimens is shown in figure 7. The presence of a plasticizer with little concentration of 20% gave high tensile load resistance value of 133 N for sorbitol plasticized gelatin film, 105 N for sorbitol plasticized sodium caseinate film, 58 N for glycerol plasticized gelatin film and 46 N for glycerol plasticized sodium caseinate film. The expected reason for the high tensile resistance at low concentration of plasticizer in the films is the domination of strong hydrogen bonds produced by protein – protein intermolecular interaction over protein – plasticizer attraction. However, the increasing in plasticizer concentration from 20% to 40% led to considerable reduction in the maximum tensile load resistance of the edible films, regardless of plasticizer type. The tensile resistance of gelatin films plasticized by sorbitol significantly decreased from 133 N to 49 N and that of gelatin films plasticized by glycerol dropped from 58N to 17N, while the maximum tensile load resistance of sodium caseinate films plasticized by sorbitol is reduced from 105N to 48N and that of sodium caseinate films plasticized by glycerol dropped from 46N to 19N at the same range of the concentration increasing of the plasticizer. The phenomenon of reduction in tensile load of protein based films when plasticizer concentration increased has been reported by many researchers [1-16, 17, 18 and 19]. This phenomenon can be illustrated by the role of plasticizers in reducing the strong internal molecular attraction between protein molecules and help in the formation of hydrogen bonds between the molecules of plasticizer and protein and this leads to reduce resistance to tensile load in the films. The results obtained showed that the protein films containing sorbitol plasticizer had a high tensile load resistance compared to their counterparts containing glycerol plasticizer. The results also showed that the sodium caseinate films plasticized by sorbitol 30% have highest tensile load resistance compared to the other films which have the same plasticizers concentration.

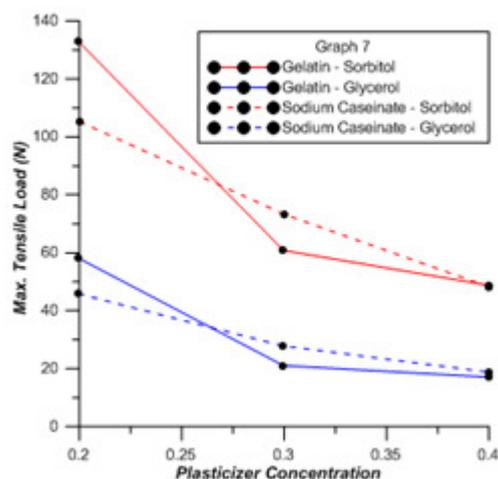


Figure 7 Effect of Plasticizers Concentration on the Maximum Tensile Load of the Edible Films

3.3. Maximum Deformation

This factor (maximum elongation or deformation) helps in determining the ductility and extensibility of the films. The ductility required of bio-packaging films depends on subsequent transport and handling of packaged food inside the factory, in storage and transport from factory to consumer [14]. The influence of plasticizer concentration on the maximum deformation of the edible film specimens has been shown in figure 8. The increasing of plasticizer concentration from 20% to 40% for both types of plasticizer produce a significant increase in film specimens elongation: 3.01mm – 6.82mm for gelatin films plasticized by sorbitol, 5.79mm – 14.09mm for gelatin films plasticized by glycerol, 7.71mm – 24.26mm for sodium caseinate films plasticized by sorbetol and 7.27mm – 17.09mm for sodium caseinate films plasticized by glycerol. The increasing in maximum elongation to the break point of edible films when plasticizer concentration is increased can be illustrated by the truth that plasticizer led to decrease the internal molecular bonds between protein matrixes and substitute them with hydrogen bonds formed between plasticizer and protein molecules [12, 14 and 15]. The obtained results showed that the sodium caseinate films plasticizer by sorbetol or glycerol had higher maximum elongation than the gelatin films plasticized by sorbitol or glycerol and the sodium caseinate films plasticized by sorbitol had highest elongation than other films (24.26mm) at the range of plasticizer concentrations (20% to 40%).

3.4. Young's Modulus or Modulus of Elasticity

Young's modulus signs to the film resistance to elastic deformation that reflects the extent of stiffness and film strength. The effect of plasticizer concentration increasing from 20% to 40% on the modulus of elasticity values of the protein plasticized films by sorbitol or glycerol has been shown in figure 9. The Young's modulus is clearly reduced when plasticizers are added and this decrease increases as the concentration of plasticizer increases (20% to 40%) and led the films lost their stiffness and became more ductility. This behavior is due to the effect of plasticizers on the chemical composition of the films [4]. The glycerol plasticizer had greater effectiveness in reducing the Young's modulus values (down to 0.09 Gpa). The obtained results showed that the gelatin films plasticized by sorbitol had more

values of Young's modulus for all plasticizer concentration (20% to 40%), while the gelatin films plasticized by glycerol (30% and 40%) had less values of Young's modulus.

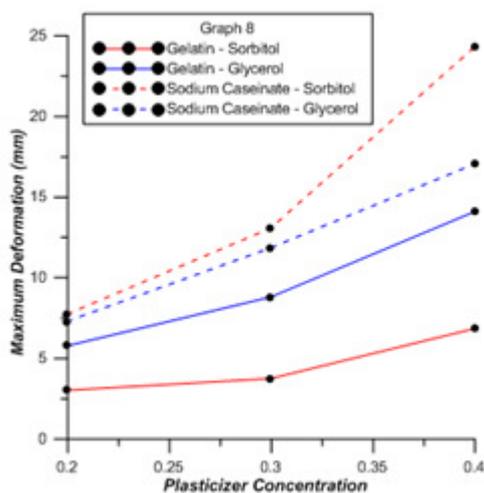


Figure 8 Effect of Piasticizers Concentration on the Maximum Deformation of the Edible Films

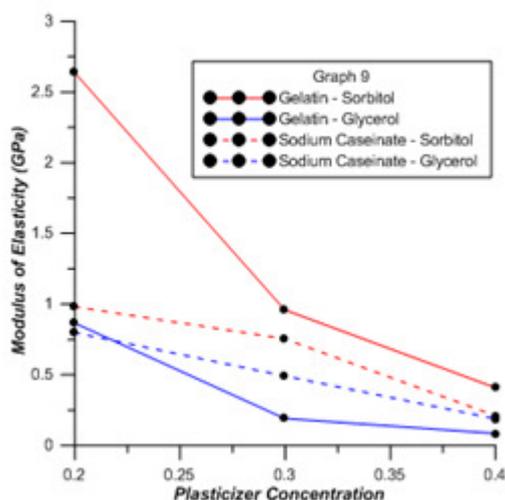


Figure 9 Effect of Piasticizers Concentration on the Modulus of Elasticity of the Edible Films

3.5. Hardness

Figure 10 explains the effect of plasticizer concentration and its types on the protein films hardness or films resistance to penetration. Hardness of the edible films decreased when the plasticizer concentration was increased from 20% to 40% as in research [20 and 21]. This reduction was 4.54 HV Mpa to 3.29 HV Mpa for the gelatin films plasticized by sorbitol, 4.43 HV Mpa to 0.33 HV Mpa for gelatin films plasticized by glycerol, 4.39 HV Mpa to 2.79 HV Mpa for sodium caseinate films plasticized by sorbitol and 2.91 HV Mpa to 0.45 HV Mpa for sodium caseinate films plasticized by glycerol. The protein edible films (gelatin or sodium caseinate) plasticized by sorbitol exhibited more resistance of plastic deformation or penetration than that plasticized by glycerol. The obtained results showed that the sodium

caseinate films plasticized by sorbitol 30% produced higher and acceptable hardness compared to the other films which have the same plasticizers concentration.

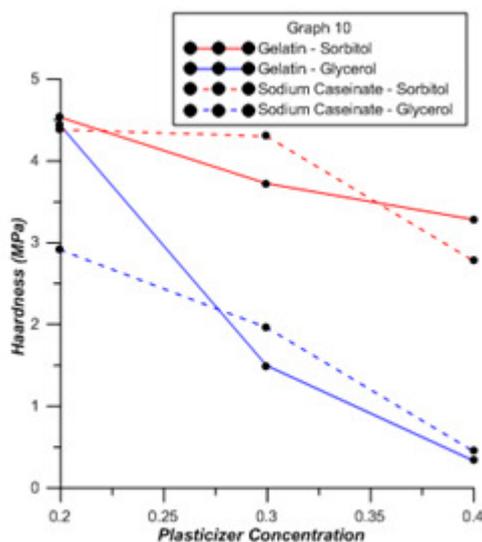


Figure 10 Effect of Plasticizers Concentration on the Hardness of the Edible Films

4. CONCLUSIONS

From the near outcomes that discipline showed as the mechanical houses about protein fit to be eaten movies had been exceedingly structured on type or plasticizer concentration. Increasing of plasticizer concentration (sorbitol then glycerol) reduced the tensile strength, Young's modulus or hardness concerning the films then at the same day rise their elongation. This change within mechanical houses concerning the safe to eat films then the plasticizer concentration has been accelerated is appropriate according to the discount over hydrogen bonds of protein inside molecular chains or forming current bonds within plasticizer then protein molecular as enormously responsible for the plasticizing impact concerning various plasticizer concentrations. Glycerol plasticizer had more reduction impact of the tensile strength, modulus regarding pliability and difficulty than sorbitol plasticizer. The manner of food packaging yet renovation requires that movies hold high tensile strength, strictness yet tension namely a ways so possible, therefore, out of the arrived results we believe to that amount the sodium casein at motion pictures plasticized by way of sorbitol 30% had desirable tensile strength, difficulty then tendril to the staving point.

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