DETERMINATION OF GLASS TRANSITION TEMPERATURE AND MODULUS OF PLA FILMS USING DYNAMIC MECHANICAL ANALYSIS AT 50ºC AND AMPLITUDE OF 10 μm

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ABSTRACT
Polylactic acid (PLA) is an environment friendly biodegradable thermoplastic produced by microorganism synthesis through the fermentation of starch. It can be used in the manufacture of thermoplastic films used to produce packaging material in place of those produced from fossil fuels. It may reduce consumption of petroleum, which releases Carbon IV Oxide, a greenhouse emission, unburned carbon fragments and other compounds that give rise to smog and air pollution on burning. It is also compostable, aiding solid waste management. In this study, the mechanical properties of PLA were determined over a temperature and amplitude range to establish whether it can be used in production of packaging material for single use purposes and disposable items. The storage ($E^{'}(\omega)$) and loss ($E^{''}(\omega)$) moduli as well as the Loss Tangent ($\tan\delta$) and glass transition temperature (T_g) of PLA films were determined using the Dynamic Mechanical Analyzer (DMA) model 2980, used in the Multistrain mode. At 50ºC and amplitude of 10 μm the storage modulus of PLA was 2220.00 MPa, while loss modulus was 112.90 MPa. Consequently, elastic modulus E of PLA was 2222.87 MPa, indicating that PLA is strong and tough at this temperature. From the peak of the loss modulus graph the T_g was 65ºC. T_g from variation of loss tangent with temperature occurred at 74.3ºC.

Key words: *Dynamic mechanical analysis, Packaging materials, Polylactic acid*

INTRODUCTION
Environmental conservation is undoubtedly one of the top priorities in the world today**.** There are major drawbacks associated with the extensive use of plastics manufactured from fossil fuels due to their stability in both photochemical and environmental conditions. According to a report by UNEP/Grid-arendal [1], plastics take over one million years to biodegrade. According to composters, the top contaminant in feed stocks is plastic with plastic bags being an integral part of waste collection infrastructure[2]. Over 60% of plastic waste is produced by households, most of it as single use packaging. Polyethylene (PE) is the major packaging plastic and is therefore one of the top environment pollutants.

Littered PE bags result in visual pollution, cause blockage of gutters and drains and choke domestic, wild and marine animals. They also result in a reduction in agricultural productivity while providing breeding grounds for mosquitoes[3].

A lot of research and development is being directed towards development of environment friendly bags which should be strong yet biodegradable [4]. These can be manufactured from biopolymers. The introduction of biopolymers will reduce the consumption of petroleum, which releases Carbon (IV) Oxide, a greenhouse emission, unburned carbon fragments and other compounds that give rise to smog and air pollution on burning. They are also compostable, and disintegrate within a reasonable time frame leaving no toxic substances or visible traces, aiding solid waste management. According to the American society of testing and materials (ASTM D6400-04) and the European standards (EN 13432) a compostable material should biodegrade such that Carbon is converted to Carbon (IV) Oxide to the level of between 60% and 90% over a period of 180 days[5].

Polylactic acid (PLA) is a biopolymer which can be used to manufacture thermoplastic films. Lactic acid is one of the most important organic acids produced by lactic acid bacteria (LAB). LAB consists of bacterial genera within the phylum Firmicutes comprised of about 20 genera. These genera include Lactococcus, Lactobacillus and Streptococcus amongst others. Lactobacillus is the largest genera comprising about 80 species. LAB can produce either l (+PLLA) or d (−PDLA), which are optically active, or a racemic mixture of lactic acid [6]. The first step in the production of lactic acid involves pretreatment by gelatinization and liquefaction of cheap raw materials such as whey, molasses, starch waste, sugar beet, cane sugar and other carbohydrate rich materials. This is followed by enzymatic saccharification to glucose. The glucose is then converted to lactic acid by Lactobacillus fermentation[7]. There have however been restraints of high cost and insufficient technical performance of lactic acid produced in this way[8]. In an effort to address these restraints, researchers such as Suszkiw[9] reveal that sugar beet can be turned into biodegradable filler material for PLA making it a cheaper alternative to petroleum-based thermoplastics. Also, PLA's former filler was corn sugar removed from the kernels. By finding ways to use starch from the entire plant, farmers would be able to sell the corn as produce and the remaining plant for plastic[8]. Amylolytic lactic acid producing bacteria have the ability to convert starchy biomass to lactic acid in single step fermentation. This will eliminate the two step process to make it economical[7].

Sugar alcohol, sorbitol is used to plasticize the pulp. The pulp is reshaped into particulate matter, melted into PLA and processed through a twin-screw extruder to produce composite material for subsequent remolding. They are fully biodegradable and result in carbon savings of 30-80% compared with oil based plastic [10]. PLA polymer was first used as biodegradable sutures in the 1960's [8]. PLLA is a semi crystalline polymer exhibiting high tensile strength and low elongation with high modulus. According to a polymer data sheet by Mat Base[11] , PLA has a Young's modulus of between 350 MPa and 2800 MPA and a T_g of between 45^0C and 65^0C. Its degradation period is between 18 – 24 months. It is however brittle and has a slight milkiness[12].

PLA has mainly been used in biomedical applications [13]. It is suitable for medical products in orthopedic fixation (pins, rods, ligaments etc.), cardiovascular applications, dental applications, intestinal applications, and sutures. Other potential applications include packaging for cereals, snack foods, dairy products, food container and candy [2]. PLA is degradable in soil, water or compost. When PLA is incinerated, the heat of combustion is half or less compared with conventional plastics such as PE. In dynamic mechanical methods for locating T_g, a rapid change in modulus is indicative of the glass transition. Below T_g a polymer behaves like a stiff spring storing all the available energy in stretching as potential energy, when work is performed on it and has a high modulus. The elastic modulus for glassy polymers just below the T_g is constant over a wide range of polymers having the value of approximately 3000 MPa [14]. As the temperature of a polymer rises, molecular motion increases and it begins to behave like a viscous liquid if no degradation occurs. With a further rise in temperature, a transition from glass to rubber-like state takes place. There is a rapid change in stiffness as shown in Figure 1.1 which indicates a transition and T_g is located within this region.

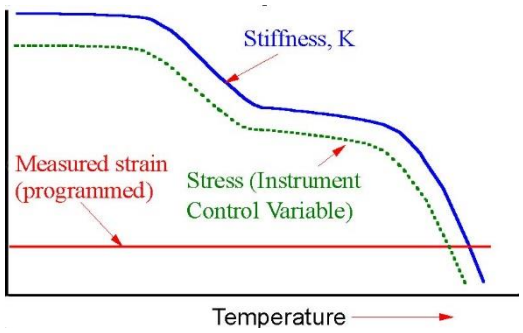

Figure 1.1: Stiffness against temperature. Source: DMA User Manual

As Stiffness and Modulus are directly proportional, a rapid decrease in modulus is also indicative of a transition and T_g is located within this region. For the loss modulus and loss tangent graphs, T_g is located at the peak of the graphs. For all polymers, T_g from the loss tangent graph occurs several degrees higher than from the loss modulus graph. Changes in the physical properties, such as hardness and elasticity are observed. The temperature at which T_g is observed depends largely on the chemical nature of the polymer chain. T_g has an important bearing on the potential application of a polymer. After the transition from the glassy to the rubbery state, typical polymers acquire modulus values of approximately 200 MPa [14].

Polymers such as PLA due to their chain like structure exhibit a viscoelastic response [15]. A stress results in an instantaneous strain, which continues to increase more slowly with time. It is this delay between cause and effect, that is, the stress and strain respectively, which is fundamental to the observed viscoelastic response resulting in creep, stress relaxation and dynamic response. The system is then said to be in a viscoelastic state and exhibits a 'delayed elasticity'. A Maxwell model can be used to explain the dynamic response. It consists of a Maxwell element which consists of a purely elastic spring and a purely viscous damper connected in series [16]. The application of a sinusoidal stress to a Maxwell element produces a strain with the same frequency as, but out of phase with, the stress. This is illustrated in Figure 1.2 where δ is the phase angle between the stress and the strain. The strain can be described in terms of its angular frequency ω and the maximum amplitude ϵ_o using complex notation, by

$$\varepsilon^* = \varepsilon_o \exp(i\omega t) \qquad (1.1)$$

Where, $\omega = 2\pi\nu$, ν is the frequency. The alternating stress and strain have the following relationship

$$\sigma^* = \varepsilon^* E^*(\omega) \qquad (1.2)$$

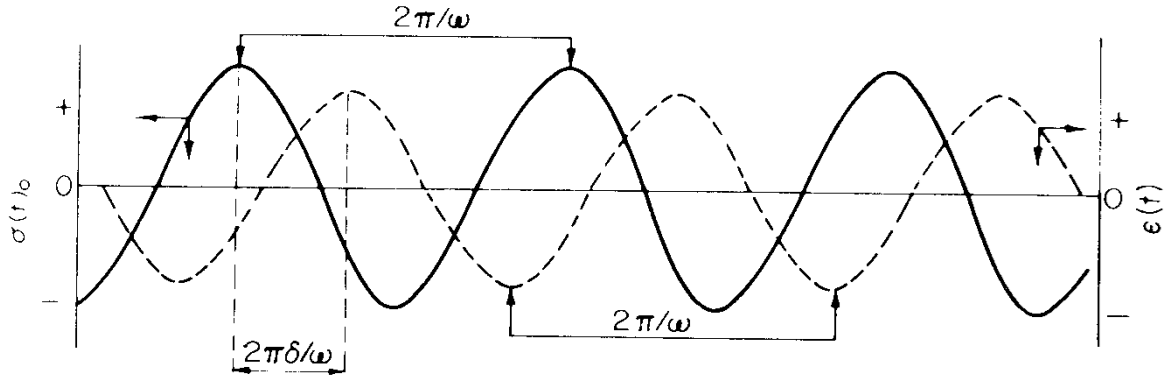

Figure 1.2: Harmonic oscillation of a Maxwell model. Source: Cowie (1991)

$E^*(\omega)$, is the frequency dependent complex dynamic modulus given as

$$E^*(\omega) = E'(\omega) + iE''(\omega) \qquad (1.3)$$

Where $E'(\omega)$ is the storage modulus which measures the amount of energy stored instantaneously. $E''(\omega)$ is the loss modulus which lags behind the storage modulus and grows with time. It is defined as the ratio of the component 90°

out of phase with the stress to the stress itself. It measures the amount of energy dissipated in the material. The elastic modulus E and the dynamic modulus $E^*(\omega)$ have the following relationship;

$$E = |E^*| \quad (1.4)$$

hence,

$$E = \sqrt{\left((E^*)(E^*)^*\right)} \quad (1.5)$$

and,

$$E = \sqrt{\left(E'^2 + E''^2\right)} \quad (1.6)$$

Equation 1.6 shows that the elastic modulus is almost equal to the storage modulus, depending on the value of the loss modulus. It is slightly smaller depending on the value of loss modulus. In this study the mechanical properties of PLA in particular the Storage and Loss Moduli, Loss Tangent and Glass Transition Temperature are determined over a temperature and amplitude range using Dynamic Mechanical Analysis.

2.0 EXPERIMENTAL SECTION

2.1 Samples

PLA films of A4 size and thickness 20 μm were obtained from Polyfilms limited, France. Rectangular strips of dimensions 30mm x 5mm x 0.02mm were used. However, the exact length of the samples was provided by the DMA, which automatically calculates it after the samples had been clamped.

2.2 Determination of the glass transition temperature (T_g)

The DMA machine was set to the Multistrain mode using the tension film clamp. The recommended combination for a single-frequency temperature ramp of a frequency of 1 Hz and ramp rate of $3\,^{\circ}C$ per min was used. The glass transition temperature was recorded at a temperature of $50\,^{\circ}C$ using a ramp rate of $3\,^{\circ}C$ /min , a fixed frequency of 1 Hz and over an amplitude range of between 10 – 20 μm.

2.3 Determination of Modulus

Using the tension film clamp the DMA machine was set to the Multisrain mode. The real (storage) modulus E' and the imaginary (loss) modulus E'' components of the complex modulus E*, for a specimen of each sample were recorded at a temperature of $50\,^{\circ}C$ using a ramp rate of $3\,^{\circ}C$ /min , a fixed frequency of 1 Hz and over an amplitude range of between 10 – 20 μm.

3.0 RESULTS AND DISCUSSION

3.1 Glass transition temperature of PLA

Figure 3.1 shows the variation of the storage modulus of PLA with temperature at amplitude of 10 μm. The storage modulus of PLA decreased gradually within the temperature range of 47 – 60 ^0C from 2270 MPa – 1882 MPa. Between temperatures of 60 – 76 ^0C the decrease was rapid from 1882 MPa – 285 MPa. The storage modulus then decreased between the temperatures 76 – 85 ^0C from 285 – 75 MPa. This shows that a transition takes place within the 60 - 76 ^0C temperature range.

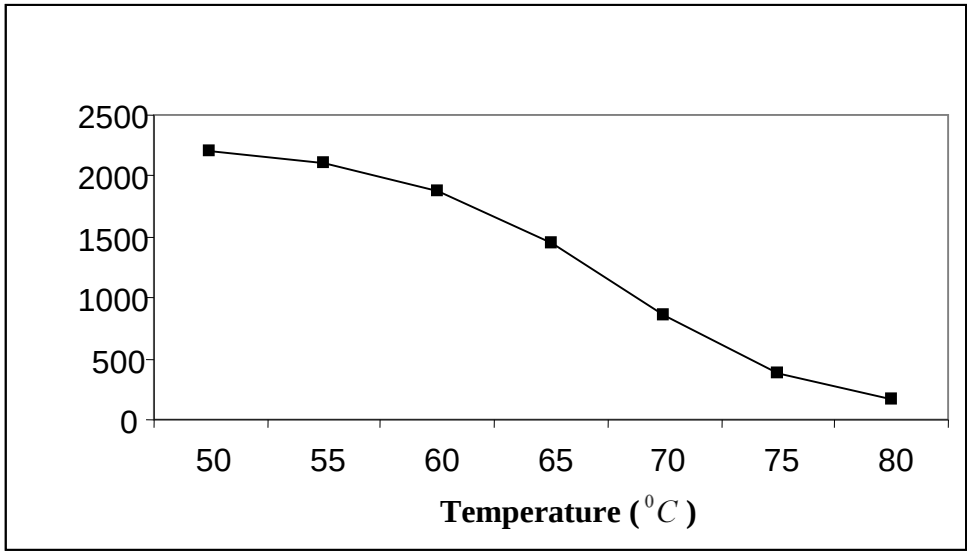

Figure 3.1 Storage modulus of PLA against temperature

For the variation of Loss modulus with temperature and amplitude of 10 μm, Figure 3.2 was obtained. From the peak of the loss modulus graph the T_g of PLA was found to be 65 ^0C . T_g from the variation of loss tangent with temperature occurred at 74.3 ^0C as per Figure 3.3.

Figure 3.4 shows the variation of storage and loss modulus as well as loss tangent with temperature for PLA at amplitude of 10 μm. The loss tangent graph is slightly shifted to the right and hence gives a T_g which is slightly higher than the loss modulus graph. Also, the region within which the storage modulus decreases rapidly coincides with the region where the peaks of the loss modulus and loss tangent arise. PLA is in the glassy state below 65 ^0C according to the loss modulus graph and below 74.3 ^0C according to the loss tangent graph. It has a storage modulus of 2220 MPa at 50 ^0C . It is therefore quite stiff below these temperatures. After the glass transition, its storage modulus comes down to 285 MPa at 76 ^0C .

The storage modulus of PLA at 50 ^0C and amplitude of 10 μm was found to be 2220.00 MPa. The loss modulus for PLA was found to be 112.90 MPa at the same temperature and amplitude. Consequently, the elastic modulus of PLA was found to be 2222.87 MPa. The elastic modulus is directly proportional to the stiffness of a material. PLA is therefore stiff because it has a high elastic modulus at 50 ^0C . This indicates that PLA is strong and tough at this temperature.

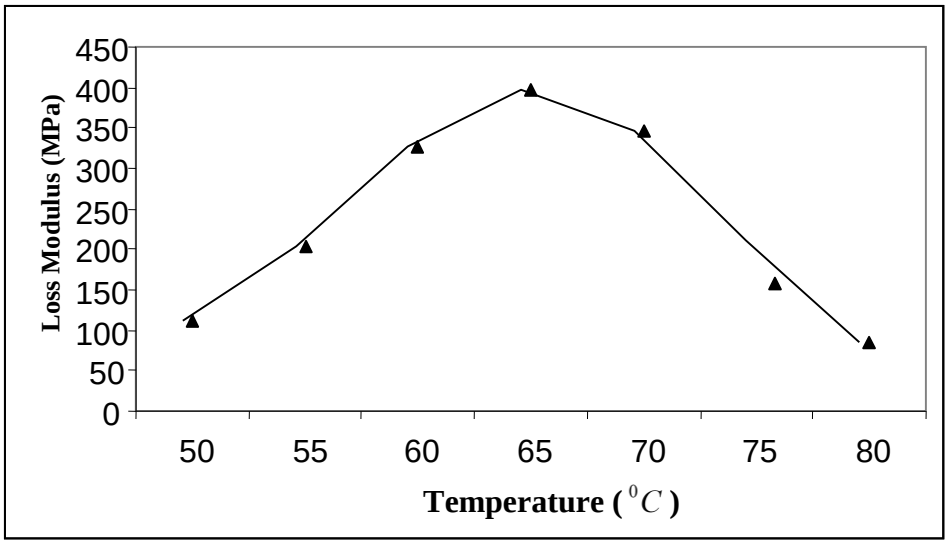

Figure 3.2 Loss modulus of PLA against temperature

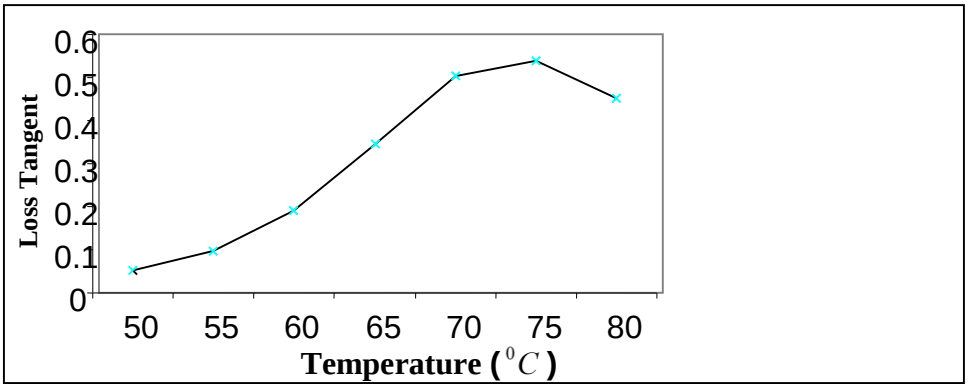

Figure 3.3 Loss Tangent of PLA against temperature

Figure 3.5 shows the variation of Storage and Loss modulus as well as Loss tangent against temperature for one of the samples of PLA at amplitudes of 10 – 20 μm.

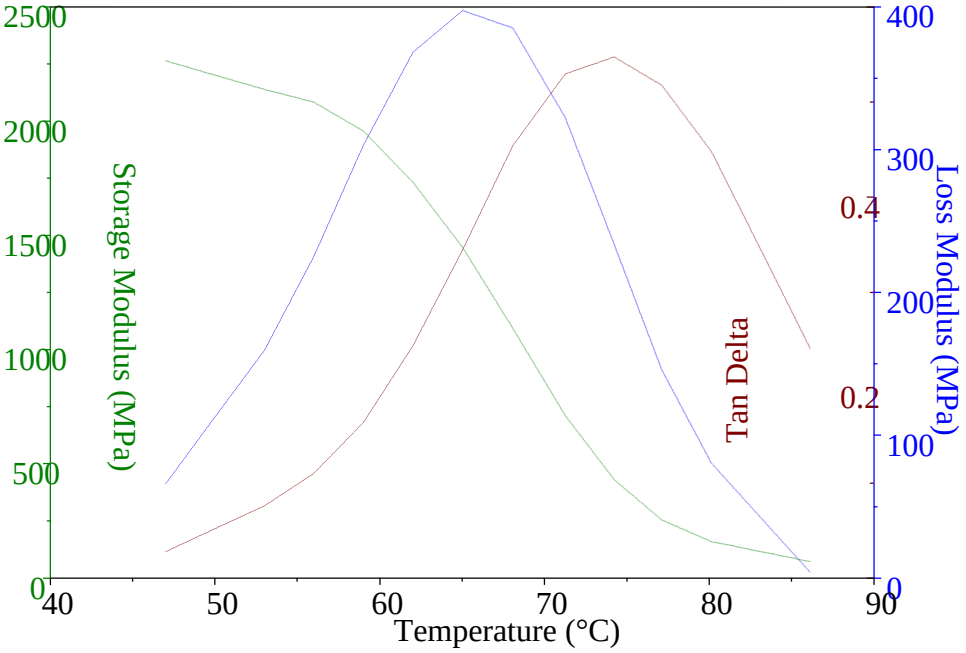

Figure 3.4 Storage and Loss modulus and loss factor against temperature for PLA

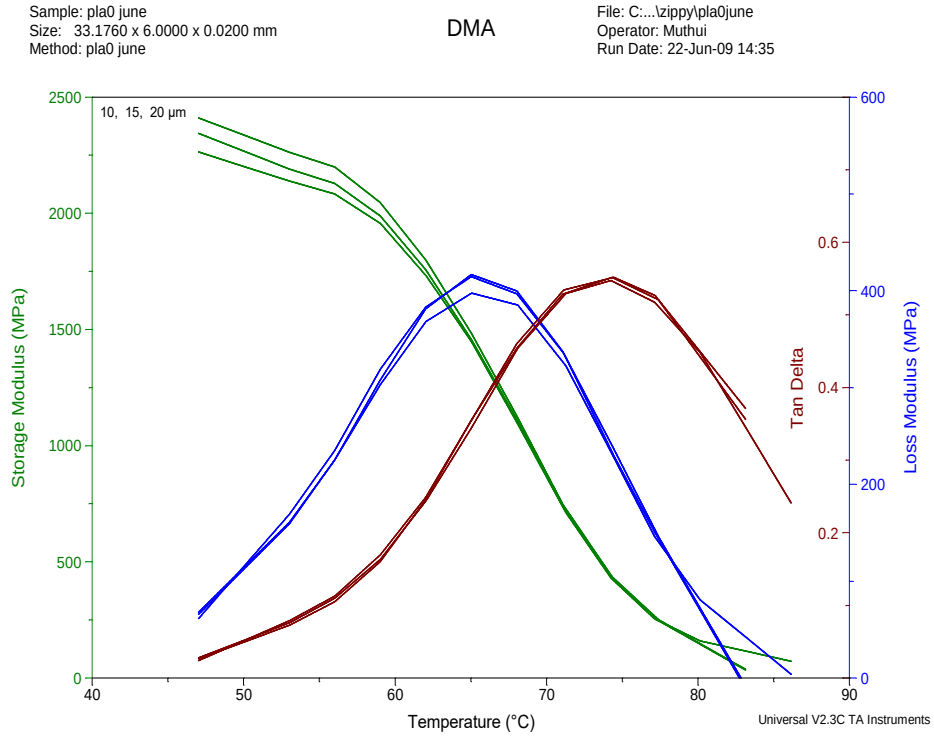

Figure 3.5 Graph of storage and Loss modulus as well as Loss tangent against temperature for PLA at amplitudes of 10 – 20 µm

Storage and Loss modulus as well as Loss tangent for PLA was measured against temperature for a fixed frequency of 1 Hz. and at amplitude of 10, 15 and 20 µm. The values are quite close as indicated in Figure 3.5. These indicated independence of the measured quantities on the amplitude.

4.0 CONCLUSION

From the loss tangent curves, the glass transition temperature of PLA occurred at 74.3^{o}C while from the Loss modulus curve it occurred at 65^{o}C. PLA is therefore in its glassy state at 50^{o}C and is therefore quite stiff**.** Above T_g PLA acquires a much lower modulus and therefore becomes more flexible.The elastic modulus of PLA is found to be 2222.87 MPa. at 50^{o}C. This is quite high as expected of a polymer in the glassy state. Above T_g PLA acquires a much lower storage modulus of 285 MPa at 76^{o}C. These results indicate that PLA is a high modulus Polymer at room temperature and would therefore be suitable for use as a packaging material. Its flexibility would increase if exposed to higher temperatures of between 65 – 75^{o}C and these property changes should therefore be taken into account. Since it is a biodegradable polymer, it would serve as a suitable alternative to the current materials obtained from fossil fuels as it is environment friendly and would decompose after use.

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