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Polylactic acid (PLA) viscoelastic properties and their degradation compared with those of polyethylene

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Polyethylene (PE) films are widely used in packaging. PE is a thermoplastic manufactured from nonrenewable petroleum resources. Due to its non-biodegradability, its films have posed serious pollution problems e.g. visual pollution, blockage of gutters and drains, choking of animals etc. Suitable replacements for PE films especially for single use only, are the starch based thermoplastics such as Polylactic acid (PLA) which are fully biodegradable. This paper reports a comparison of the viscoelastic properties of commercially obtained PLA and PE films, and the degradation of the same under a composting environment. The storage and loss moduli of PLA and PE films were determined using the Dynamic mechanical analyzer (DMA) model 2980. The elastic modulus of PLA was found to be 2222.87 MPa at 50°C and amplitude of 10 µm. This is higher than that of PE which was found to be 236.69 MPa at the same temperature and amplitude. Analysis of composting samples over a time span of 36 days indicated a rapid loss of storage modulus of PLA with that of PE remaining fairly constant. Overall, the results suggest that PLA is a suitable substitute for PE in as far as technical performance and degradability is concerned.

Key words: Polylactic acid, polyethylene, modulus, biodegradable, degradation.

INTRODUCTION

Environmental conservation is undoubtedly one of the top priorities in the world today. According to composters, the top contaminant in feed stocks is plastic with plastic bags being an integral part of waste collection infrastructure (Biocycle, 2008). Over 60% of plastic waste is produced by households, most of it as single use packaging (Scott, 1999). Polyethylene (PE) is the major packaging plastic

and is the main constituent of plastic waste most of which ends up in landfills (Swift, 1993). PE bags are light and have good barrier properties against water and water-borne organisms. These properties make them suitable for protecting commodities from the environment. They also offer protection against corrosive or toxic chemicals (Conrad et al., 2003). PE is a tough, semi-rigid plastic with a

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high modulus between temperatures of -85 and 136°C. Compared to glass, PE bags have superior impact resistance and resilience, resulting in reduced product losses during transport. Energy requirements for production of PE as compared to other materials such as aluminium, steel, glass and paper are much lower. Also, the effluents emitted e.g. sulphur (iv) oxide, oxides of nitrogen, Carbon (ii) oxide, and dust during manufacture of paper bags from trees compared to PE are much higher (Scott, 1999).

There are however major drawbacks associated with the extensive use of PE. Due to their non-biodegradability, littered PE bags result in visual pollution, cause blockage of gutters and drains and choke domestic, wild and marine animals. When disposed on farm lands, they reduce the fertility of the soils, resulting in reduced agricultural productivity. Littered PE bags also provide conducive breeding grounds for mosquitoes. At the other end of the durability scale, there is the probability of over stabilization (Scott, 1999). Consequently, banning of thin PE bags has taken place in many countries such as Kenya, Botswana, Tanzania amongst others, while some countries such as Australia, South Africa and Taiwan amongst others have strongly discouraged their use by taking measures such as tax impositions (Plastic Bags – World Report, 2012; Kimilu, 2007).

A lot of research and development is being directed towards development of environment friendly bags. Such a bag must possess all the mechanical properties of PE and disintegrate within a reasonable time frame leaving no toxic substances or visible traces. In other words, it should be strong yet biodegradable. The use of natural or synthetic photo and biodegradable polymers is promising (Shumigin et al., 2011). They are compostable, aiding solid waste management.

Poly(lactic acid) (PLA) is a biopolymer which has been 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 (Ajioka et al., 2005). 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 (Reddy et al., 2008).

There have however been restraints of high cost and insufficient technical performance of lactic acid produced in this way (Jones-Hulfachor, 2000). In an effort to address

these restraints, researchers such as Suszkiw (2008) 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 (Jones-Hulfachor, 2000). Amyolytic 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 (Reddy et al., 2008).

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 to 80% compared with oil based plastic (European Environment and Packaging Law Weekly, 2008). PLA polymer was first used as biodegradable sutures in the 1960's (Jones-Hulfachor, 2000). According to a polymer data sheet by Mat Base (2009), PLA has a Young's modulus of between 350 megapascals (MPa) and 2800 MPa and a glass transition temperature (T_g) of between 45 and 65°C. Its degradation period is between 18 to 24 months. It is however brittle and has a slight milkiness (Sukano News, 2005). Its brittleness can be overcome by incorporation of biodegradable additives which have seen its Young's modulus values reduce to a range of between 375 and 2307 MPa, values that are very comparable to polypropylene and low density polyethylene at between 2000 and 1900 MPa and 303 to 255 Mpa respectively (Kurt, 2010).

PLA has mainly been used in biomedical applications (Marc, 2006). It is suitable for medical products in orthopedic fixation (pins, rods, ligaments etc.), cardiovascular applications, dental applications, intestinal applications, and sutures (Dayachi and Kaffashi, 2015). Other potential applications include packaging for cereals, snack foods, dairy products, food container and candy wraps (Jamsidian et al., 2010). 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.

Polymers such as PLA due to their chain-like structure exhibit a viscoelastic response (Chang, 2006). 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 (Cowie, 1991). 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. The strain can be described in terms of its angular frequency (ω) and the maximum amplitude (ϵ_0) using complex notation, by

$$\epsilon^* = \epsilon_0 \exp(i\omega t) \quad (1)$$

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

$$\sigma^* = \epsilon^* E^*(\omega) \quad (2)$$

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

$$E^*(\omega) = E'(\omega) + iE''(\omega) \quad (3)$$

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

$$E = |E^*| \quad (4)$$

hence,

$$E = \sqrt{(E')^2 + (E'')^2} \quad (5)$$

and,

$$E = \sqrt{(E'^2 + E''^2)} \quad (6)$$

Equation 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.

The fundamental measurement of the DMA 2980 is sample stiffness K and the sample's modulus E is then calculated as follows

$$E = Kx(GF) = K \cdot x \left(\frac{L}{A} \right) \quad (7)$$

Where, GF for a sample of rectangular cross-section is the geometric factor which is related to the dimensions of the sample as per Equation 8.

$$GF = \frac{\text{Length}}{\text{Cross-sectional-area}} \quad (8)$$

Hence, the sample modulus is directly proportional to the sample stiffness, that is $E_s \propto K_s$. In dynamic mechanical experiments, the DMA 2980 measures the raw signals of force, amplitude of deformation, and phase angle. The drive force for this apparatus ranges between 10^{-4} N and 18 N. It uses the amplitudes to calculate the complex stiffness K^* which is used with the phase angle to calculate the storage and loss stiffness (K' and K''). The apparatus automatically calculates the GF using Equation 8. It then calculates the storage and loss moduli by multiplying the raw stiffness measurements by the appropriate geometry factors GF using Equation 7. The dynamic mechanical analysis utilized in this study, offers a versatile method, and has been used extensively for analyzing the viscoelastic properties of polymers and their changes (Gibson and Plunkett, 1976; Carey et al., 2009; Mano and Reis, 2004; Tanner, 2010; Weber, 2008; Shumigin et al., 2011).

PLA films are stable up to temperatures of around 60°C (Kurt, 2010). Due to this, the mechanical properties, in particular the elastic modulus of PLA films is compared with that of PE at a temperature of 50°C and an amplitude range of between 10 to 20 μm using DMA, with the primary aim of establishing whether it can substitute PE for single use purposes and in the manufacture of disposable items.

MATERIALS AND METHODS

PLA and PE samples

PLA films of thickness 20 μm were obtained from Polyfilms limited,

France, while PE films of the same thickness were sourced from Pii, Kenya Ltd. Rectangular strips of dimensions 30 mm x 5 mm x 0.02 mm of PE and PLA were cut out from the films. These dimensions are suitable for the tension film clamp of the DMA apparatus. However, the exact length of the samples was provided by the DMA apparatus, which automatically calculates it after the samples have been clamped.

Determination of modulus of dry samples

The TA Instruments DMA 2980 machine was set to the Multisrain mode (DMA 2980 Operator's Manual). The samples were clamped using the tension film clamp. 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°C using a ramp rate of $3^\circ\text{C}/\text{min}$ and a fixed frequency of 1 Hz and over an amplitude range of between 10 to 20 μm .

Determination of modulus of wet samples

The storage modulus of the wet samples was determined at a temperature of 50°C using a ramp rate of $3^\circ\text{C}/\text{min}$. The first

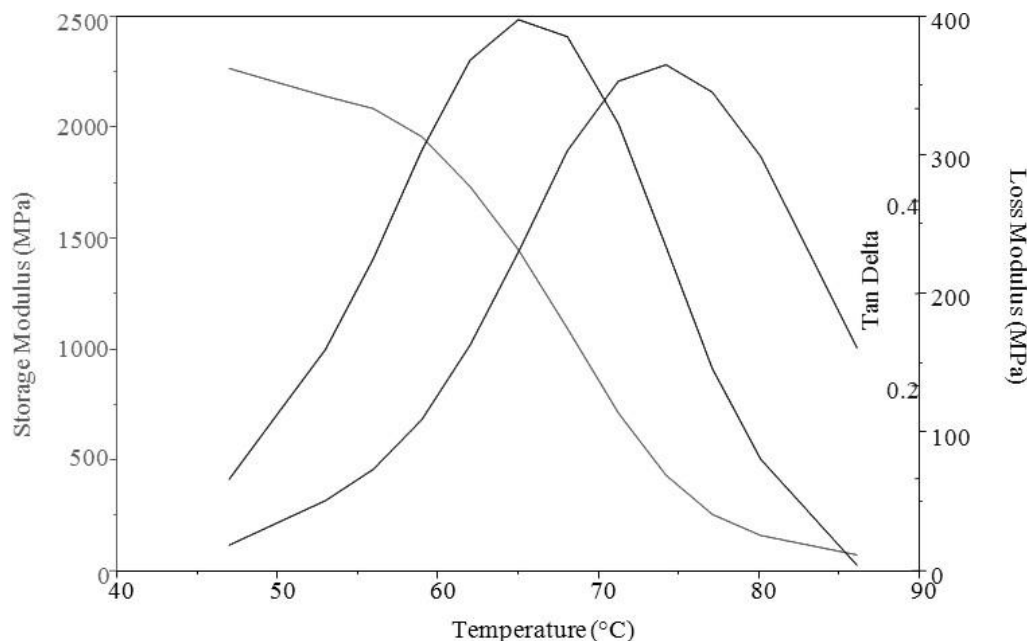


Figure 1. Viscoelastic behavior of PLA, obtained from DMA, recorded at a frequency of 1 Hz, amplitude of 20 μm , an oscillating force of 0.01 N and a ramp rate of 3°C/min. At $T_g = 65^\circ\text{C}$, the loss modulus for PLA forms a peak.

measurement was taken on the first day before immersion in a wet mixture of green and dry leaves to encourage biodegradation. The green leaves are high in nitrogen needed to activate the heat process in compost. They also introduce the moisture needed in the process of biodegradation. The brown leaves are high in carbon and serve as the fiber for the compost. The next measurements were taken after every 48 h within 36 days.

RESULTS AND DISCUSSION

Viscoelasticity of PLA and PE

Figure 1 displays the viscoelastic behavior of PLA, obtained from DMA, recorded at a frequency of 1 Hz, amplitude of 20 μm , an oscillating force of 0.01 N and a ramp rate of 3°C/min. It is evident that PLA is in the glassy state, and at $T_g = 65^\circ\text{C}$, the loss modulus for PLA forms a peak. In the glassy region there are no molecular motions, and only vibrational motions are possible. The glass transition region can be interpreted as the onset of long-range coordinated molecular motion and the glass transition temperature varies widely with the polymer structure as well as other parameters (Sperling, 2006).

Figure 2 displays the viscoelastic behavior of conventionally processed PE, obtained from DMA, recorded at a frequency of 2 Hz, amplitude of 50 μm and an oscillating force of 0.01 N. Below 60°C, the storage modulus (E') of PE as well as its loss modulus (E'') are steadily falling. PE is in the rubbery plateau, which occurs after glass transition. In this viscoelastic region, the

polymer exhibits long-range rubber elasticity (Sperling, 2006). The data sampling intervals were higher in this case. However, it should be noted that the Tan Delta data at temperatures above 90°C does not fit well into a smooth curve, and this might imply that some aspects of these samples modulus data prediction may be suspect at these temperatures.

From the foregoing, it is evident that at 60°C and lower temperatures towards room temperature, PLA and PE are in different polymer viscoelastic regions. PLA is in its glass state and hence stiffer while PE is in the rubbery plateau region.

For a better comparison of the viscoelastic properties of PE and PLA, we choose three amplitudes for the oscillating force, a single temperature point, 50°C and measure the properties for periods not more than 10 min. Figures 3 and 4 show the storage modulus curves for PLA and PE respectively.

The storage modulus (E') of PLA and PE were also determined as a function of temperature, at a temperature range of 48 to 51°C. The storage modulus of PLA and PE is found to be 2220.00 MPa and 232.50 MPa respectively at the same temperature of 50°C and amplitude of 10 μm as shown in Figure 5.

The storage modulus (E') gives information about the elasticity of a material. According to Equation 3 it is almost equal to the elastic modulus especially if the value of the loss modulus is low. Using Equation 3, the elastic modulus of PLA is found to be 2222.87 MPa while that of PE is found to be 236.69 MPa. The elastic modulus is

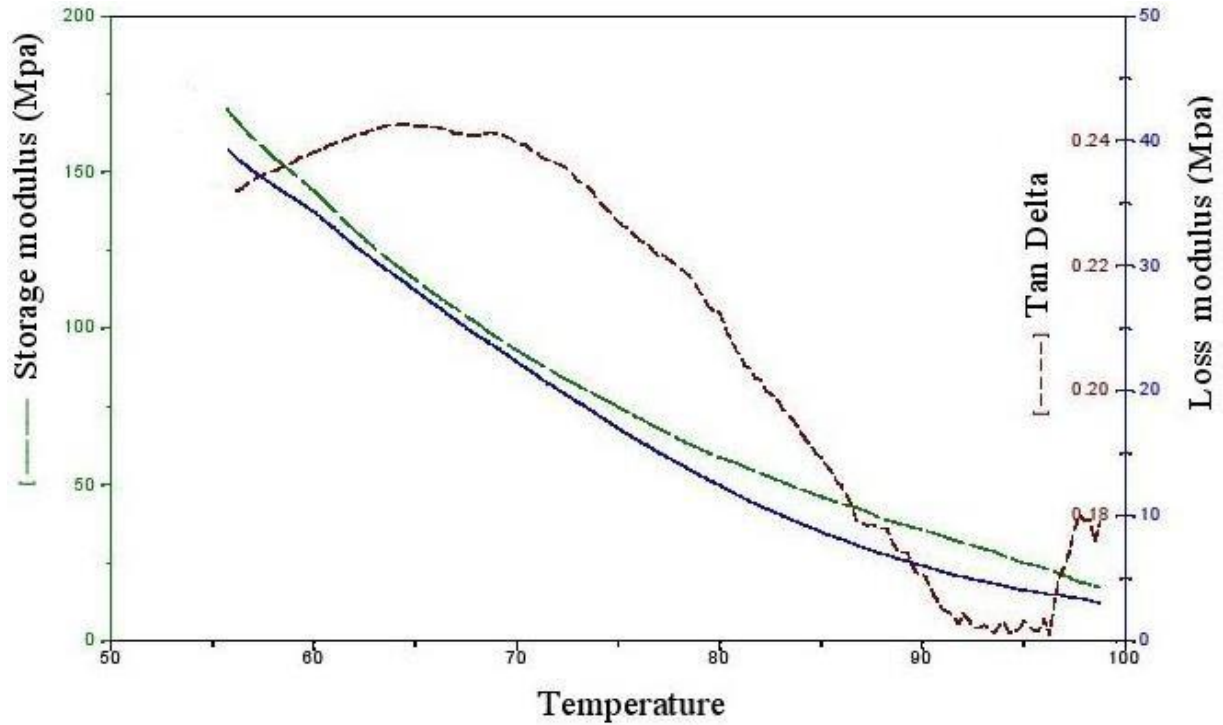


Figure 2. Viscoelastic behavior of conventionally processed PE, obtained from DMA, recorded at a frequency of 2 Hz, amplitude of 50 μm and an oscillating force of 0.01 N.

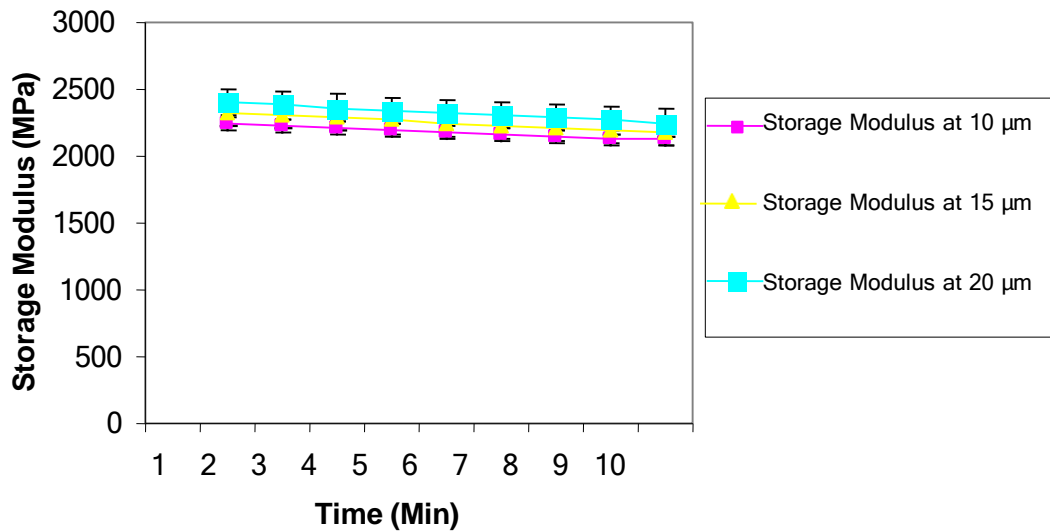


Figure 3. E' of PLA measured at amplitudes 10, 15 and 20 μm and at a frequency of 1 Hz.

also directly proportional to the stiffness of a material as per Equation 7. As compared to PE, PLA is stiffer and has a much higher elastic modulus at 50°C. This indicates that PLA is stronger and tougher than PE at this temperature.

The loss moduli (E'') of PLA and PE were also

compared as a function of temperature, and for a temperature range of 48 to 51°C (Figure 6). The loss modulus for PLA is found to be 112.9 MPa at 50°C while that of PE is found to be 44.33 MPa at the same temperature and amplitude of 10 μm . The loss modulus of PLA is found to be much higher than that of PE at 50°C.

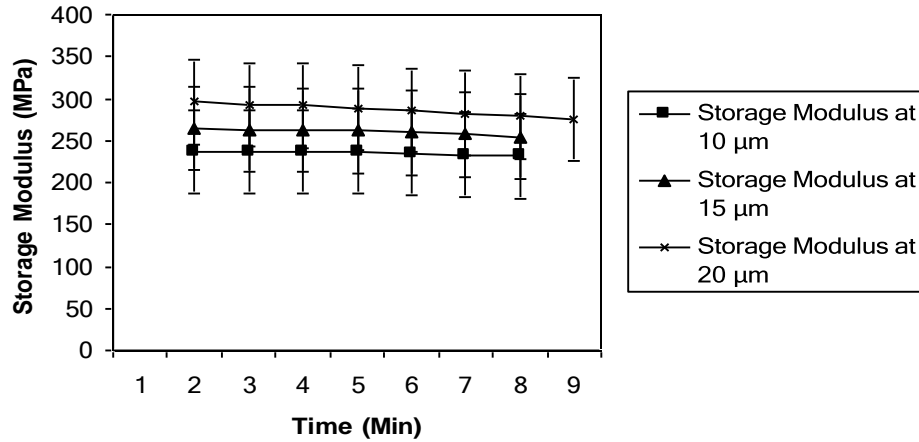


Figure 4. E' of PE measured at amplitudes 10, 15 and 20 μm and at a frequency of 1 Hz.

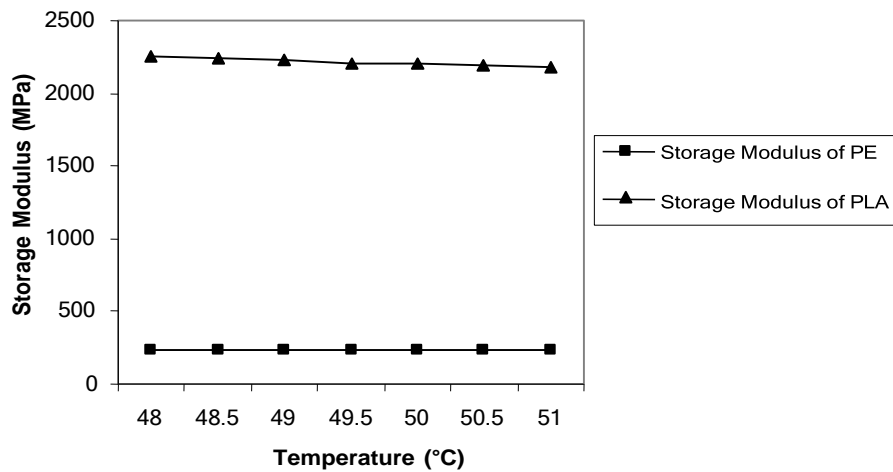


Figure 5. E' of PLA and PE as a function of temperature, heated at a ramp rate of 3°C/min. At 50°C, PLA has an E' value of 2220.00 MPa which is higher compared to that of PE- 232.50 MPa. Both moduli are measured at amplitude of 10 μm and at a frequency of 1 Hz.

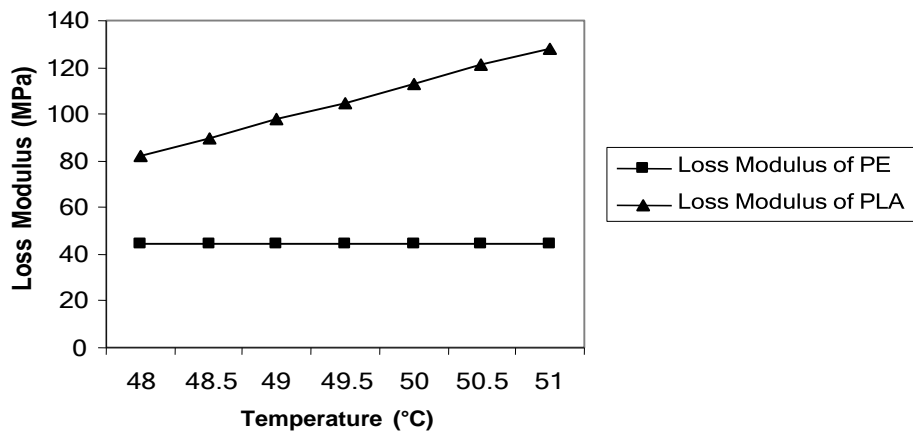


Figure 6. E'' of PLA and PE as a function of temperature, heated at a ramp rate of 3°C per min. At 50°C PLA had an E'' value of 112.9 MPa which is higher compared to that of PE- 44.33 MPa. Both moduli were measured at amplitude of 10 μm and at a frequency of 1 Hz.

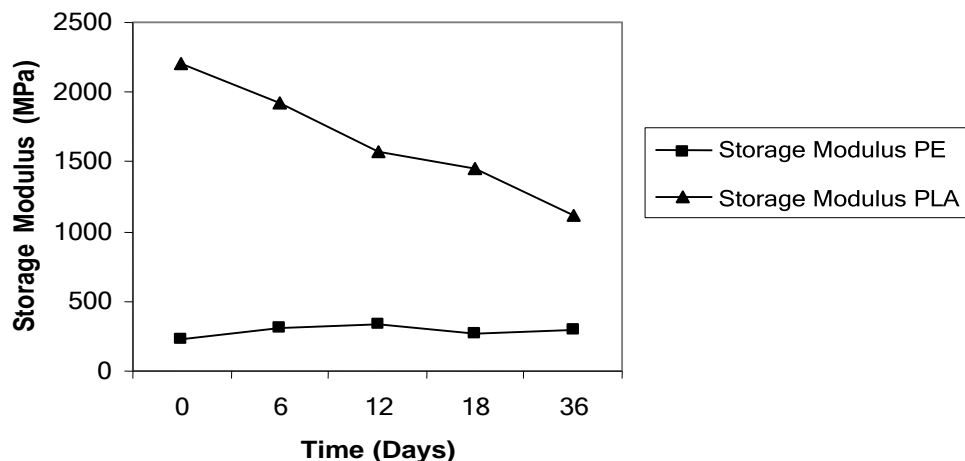


Figure 7. E' of PLA and PE samples treated in a composting environment and storage modulus recorded at 0th, 6th, 12th, 18th and 36th days.

Degradation of viscoelasticity of PLA compared to PE

This study also endeavored to compare the degradation of viscoelastic properties of PLA as the materials are exposed to a degradation enhancing environment. The samples were immersed into a wet mixture of dry and green leaves to encourage biodegradation. The storage modulus was determined at a temperature of 50°C and amplitude of 10 μm . The E' measurements were conducted in pre-determined intervals of 48 h, and Figure 7 shows the following days of analysis: 6, 12, 18, 24, 30 and 36 days.

The storage modulus for PLA reduces steadily by 49% within 36 days as compared to PE, whose storage modulus actually increases by 29% by the 36th day. The decrease of storage modulus of PLA is suggestive of chain scission degradative processes, whereas the increase of the storage modulus of PE at these conditions is indicative of cross-linking processes (Gottlieb et al., 1981). The reduction in the storage modulus of PLA is correlated with the deterioration in its mechanical properties. This would lead to its fragmentation, which make it easier for de-polymerization or attack by microbes (Andrady, 2015). These two processes ultimately lead to elimination of the material from the environment within a comparatively reasonable time frame as compared to PE which seems to become even more stable within this time period.

Conclusions

The values for the elastic moduli of the conventionally processed samples of PLA and PE were found to be 2222.87 and 236.69 MPa respectively at a temperature of 50°C. PLA is therefore stronger and stiffer than PE at this

temperature. On immersion in a composting environment, the modulus values were 1133.36 and 305.33 MPa for PLA and PE respectively, after a period of 36 days. PLA undergoes rapid degradation as compared to PE. This is indicated by the decrease in the modulus values of the wet samples of PLA as compared to those of PE whose modulus value remains largely unchanged, and in fact, registers a slight increase. PLA films were found to be of superior mechanical strength as compared to PE and can replace it in single use packaging. As expected, their initial mechanical properties reduced as they biodegraded. PLA would compost after use and address the pollution problem caused by PE.

Conflict of Interests

The authors have not declared any conflict of interests.

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