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Nanostructure integrated shape memory materials

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Poly(lactic acid) is a shape-memory polymeric material (SMPs) that attracts both industrial and scientific interest because it is biodegradable and of bioderivation.(4D printing) Its non-petrochemical based nature, elastic modulus and high tensile strength, biocompatibility and non-toxic also make PLA an ideal material for practical use in contact with the human body. The enhanced phase continuity along the deformation direction and the vigorous shearing effect the temporary shape fixing and the continuous shape recovery. Pure Poly(lactic acid) (PLA) were produced by hot laminating. After PLA was prepared as shape memory material and cut into rectangular shape. The shape memory properties of PLA were examined. For the shape memory testing, PLA was fixed to temporary shape.. Shape fixity (Rf) and shape recovery (Rr) rates were calculated by determining angle values based on thermo-mechanical recovery tests.The obtained results sugest that the shape memory behavior of PLA is controlled according to preparation conditions.

Keywords: *PLA, Shape Memory, Dielectric, Recycling*

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1. Introduction

The reason for using PLA in this study is that it is a biodegradable and recyclable polyester made from renewable raw materials. It is produced by fermentation of lactic acid, glucose or sucrose as raw materials and refined with high purity. Polylactic acid (PLA) ($C_3H_4O_2$), Since biodegradable PLA is widely used in many applications such as biosensors, filtration systems, tissue engineering and advanced drug delivery systems, PLA shape memory film was produced in this study because of its wide usage area, non-toxicity, environment-friendly and easy production. and dielectric properties were investigated. The chemical structure of PLA is shown in figure 1. Polylactic acid (PLA) (C3H4O2) It is obtained by condensing lactic acid. It is a popular material because it is economically produced from renewable resources [1-6].

PLA is in the range of semi-crystalline and high-crystalline polymers with a glass transition temperature of 60-65 °C, a melting temperature of 130-180 °C, and a tensile modulus of 2.7-16 GPa. It has heat resistance up to 110 °C.

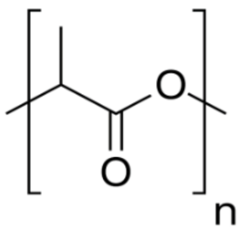


Figure1. Chemical structure of PLA [4]

Polylactic Acid is biodegradable and has properties similar to polypropylene (PP), polyethylene (PE) or polystyrene (PS). It has numerous applications such as healthcare and medical industry, Packaging, Automotive applications. Polylactides decompose into non-toxic products during degradation. they are biodegradable and biocompatible [6-12].

Shape memory polymers (SMPs) have the ability to deform from the initial shape to a stress-free, temporarily preserved shape until recovery of its previous shape is triggered by an external stimulus.

PLA, which is a polymer class, has also been an important candidate for 4D printing thanks to its wide applications in 3D printing and low cost. [36]. Although the shape memory properties of PLA have been investigated and reported, research on its change after applying shape deformation is limited. Therefore, in this study, the shape memory properties of PLA will be examined.

2. Material and Methods

A certain amount of Polylactic Acid (PLA) powder was taken and mixed in 4:1 chloroform: DMF (Dimethylformamide) solution at 80 ºC for one day on a magnetic stirrer. The gel, which became a homogeneous solution, was placed in a petri dish and dried at low temperatures for 2 days. After drying, the obtained polymer film was cut appropriately and shape memory test, FTIR, UV and dielectric analyzes were performed.

2.1. Shape Memory Test and Characterization

. The prepared PLA polymer is cut into a rectangular shape, heated slightly above the glass transition temperature and shaped, then left in the refrigerator for a while to take its shape, and then it is heated to observe whether it remembers its original shape. For the shape memory test, the PLA was deformed as shown in the figure 2. and allowed to take its shape, for this it was kept in a temperature environment lower than room temperature for 10 minutes. Then, a shape memory test was performed by placing it on a heater with a temperature slightly above the Tg transition temperature, in order to remember its old state again.

$$R_r = \frac{\theta_{constant} - \theta_{end}}{\theta_{constant}} x100 \qquad (1)$$

$$R_f = \frac{\theta_{constant}}{\theta_{max}} x100 \qquad (2)$$

By calculating the time-varying angle values, shape stability (R f) and shape recovery (R r) rates were calculated with the help of the above equations.

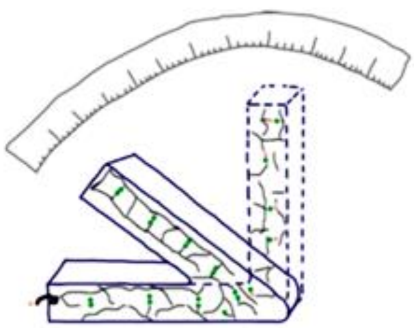


Figure 2. Figure of the fold- deploy shape memory test

The dielectric properties of PLA shape memory polymers, which were cut and prepared in a rectangular shape, were characterized by the fytronix dielectric analyzer system.

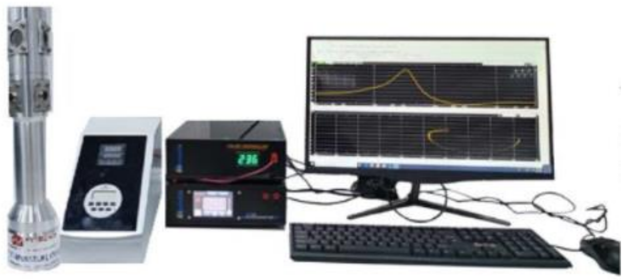
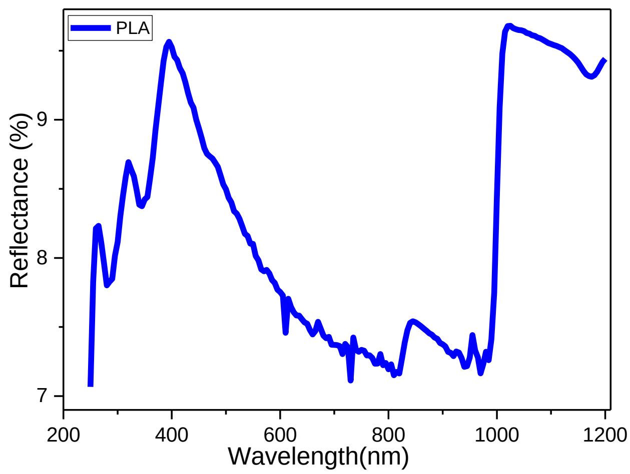


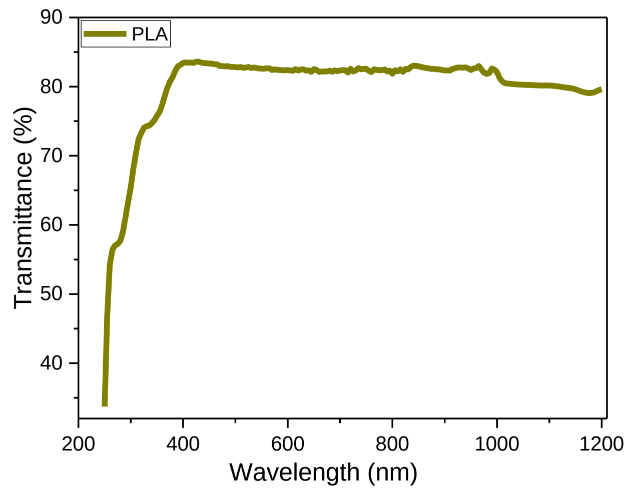
Figure 3. Fytronix dielectric constant analyzer system.

4. Results and discussion

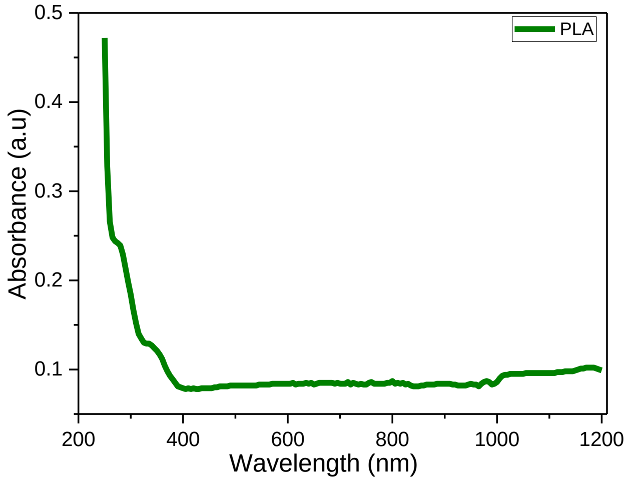
The absorbance curve of PLA is as in figure 4a. The initial absorbance limit is approximately 319 nm. The transmittance curve of PLA is as shown in Fig 4b. The transmittance limit is approximately 402.4 nm and the transmittance value is approximately 83.4 %, indicating that the permeability of PLA is well. The reflectance curve showed (Fig 4c) that the reflectance value of PLA was compatible with the literature.



a)



b)



c)

Figure 4. UV spectroscopy analysis for PLA a) Reflectance b) Transmittance c) Absorbance

The FTIR (Fourier Transformation Infrared Spectrum) curve of PLA shape memory polymer film is as in figure 5. The characteristic peak values of PLA, 1170 and 2945 cm-1 peaks, indicate the presence of bond group with C−O, C−H, O-H 3504 cm-1 −CH (CH_3)–OH vibrations, respectively.

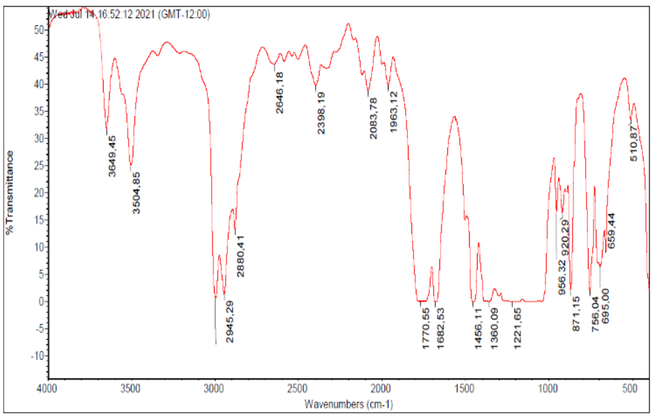


Figure 5. FTIR pattern of the PLA.

The relative permittivity (ε′), dielectric loss (ε′′) and alternating current conductivity (σac) values of the samples can were calculated by the related formulas;

$$\varepsilon' = \frac{C \times l}{\varepsilon_o \times A} \quad (1)$$

$$\varepsilon'' = \tan\delta \times \varepsilon' \quad (2)$$

$$\sigma_{ac} = \frac{l}{Z \times A} \quad (3)$$

where εo is the permittivity of free space, A is the area of the electrode and C and l are the capacitance and thickness of the sample, respectively. tan δ is the loss tangent and Z is the impedance of the sample.

In Figures 6 and 7, the dielectric constant namely relative permittivity decreases with increasing frequency, while the virtual dielectric constant namely dielectric loss first increases and then decreases as frequency increases. The change in the dielectric constant of PLA is due to electrical polarization. The change in virtual dielectric constant is due to the change in dielectric dipole moment of PLA.

In order to analyze the dielectric relaxation mechanism of the samples, we can use the following Cole–Cole relation;

$$\varepsilon^* - \varepsilon_\infty = \frac{\varepsilon_o - \varepsilon_\infty}{1 + (i\omega\tau_o)^{1-\alpha}} \quad (4)$$

where ε* is the complex dielectric constant, ε_0 and ε_∞ are the "static" and "infinite frequency or optical" dielectric constants, τo is the relaxation time and α is an exponent ($0 < \alpha < 1$). The Cole–Cole plots of the samples are shown in Fig. 8. Cole cole curve means that the electric dipoles are interacted with each other and this causes a change in the dielectric dipole moment and in turn, the relative permittivity and dielectric loss values of the samples are changed.

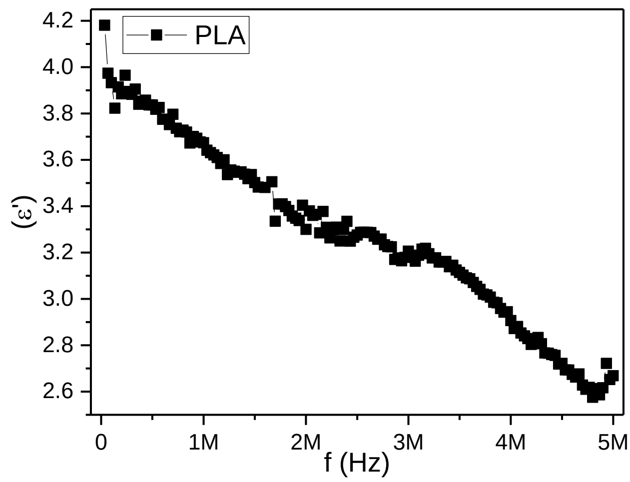


Figure 6. Relative permittivity vs. frequency plot of PLA

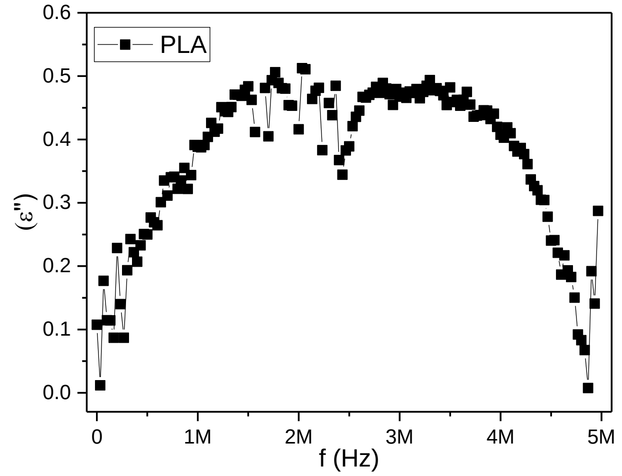


Figure 7. Dielectric loss vs. frequency plot of PLA

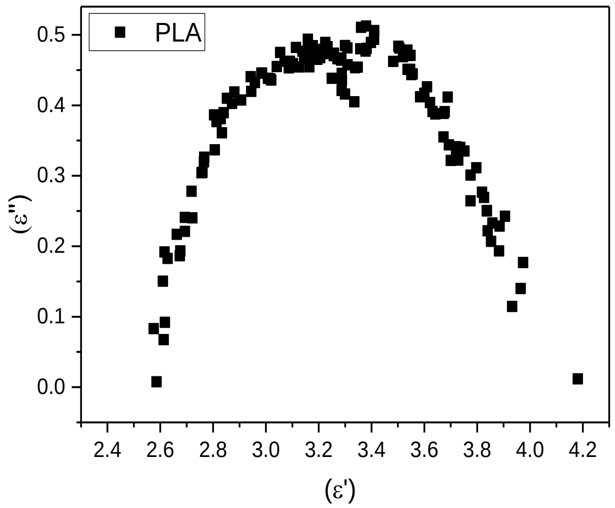


Figure 8. Cole–Cole plot of the PLA

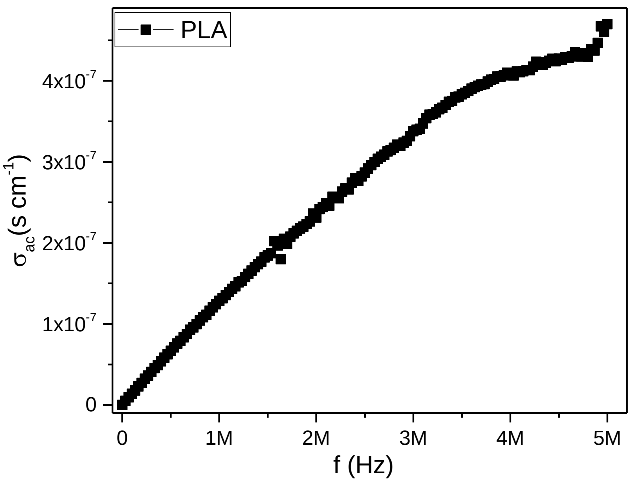


Figure 9. Plots of the alternating current conductivity vs. frequency.

In Figure 9, it is seen that σac changes depending on the frequency. Since the conductivity increases linearly as the frequency value increases, there is no dc conductivity, that is, it does not have electrical conductivity. It is an insulating material. The determination of the conductivity mechanism of the PLA was applied using the well known Jonscher relation;

$$\sigma_{ac} = \sigma_{dc} + B\omega^{s} \quad 5$$

where σdc is the direct current conductivity, B is a constant, ω is the angular frequency and s is an exponent. The s values can calculated from the slope of log σac vs. log ω plot.

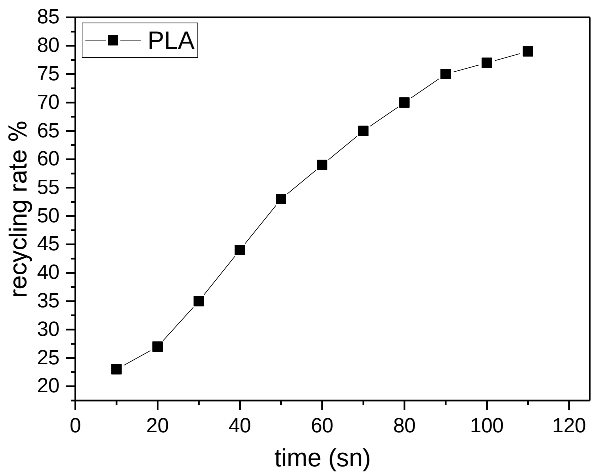


Figure 10. Recycling rate vs. time plot of PLA

The recycling rate and time graph of PLA, shown in Figure 10, show sequential shape memory cycles, Rf and Rr. After measurement cycles, the shape fixation of PLA does not show any significant changes, exhibiting an nearly Rf value of 81 % (Fig. 10). Over these cycles there is only a slight decrease in the shape recovery of the polymer, with an average approximately Rr value of 80 %, indicating that the PLA exhibit well shape memory properties.

5. Conclusion

The shape memory properties of PLA were investigated. PLA was fixed to the temporary shape for shape memory testing. Shape stability (Rf) and shape recovery (Rr) rates were calculated by determining the angle values based on thermo-mechanical recovery tests. PLA is controlled by preparation conditions. It was determined that the shape stability and shape recovery rate of the synthesized PLA shape memory polymeric film was over 87%. Therefore, it can be said that this material is suitable for the production of shape memory materials and can be used in various medicine, industry and chemical fields.

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