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FORMULATION AND CHARACTERIZATION OF FILM USINGPOLYLACTIC ACID AND ESSENTIAL OIL FOR PACKAGING APPLICATION

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***Abstract*—** Biopolymers are the material derived from living organism which reduces environmental impact when compared to other synthetic polymers. The futuristic packaging of a product will bank on the biodegradable and renewable source and it depends upon materials which are eco-friendly. As an alternative to conventional plastic material, the synthesis of the film was carried out by amalgamating Poly Lactic-acid and essential oils (cardanol, Coconut) as plasticizers through solvent casting method. The formulation was accomplished by blending the materials under offbeat percentage. The film characteristics like mechanical, thermal and optical properties were analysed and comparative results were produced. The test like FTIR, contact angle, TGA, tensile strength, elongation, colour and opacity were studied. It shows that the tensile strength is reduced whereas elongation is improved with the addition of essential oil. Colour and opacity of the film changes with the addition of essential oil and contact angle also increased stating that it's hydrophobic. FTIR tells the elements present in the film and TGA gives a comparative result on the thermal stability of the composition of film.

***Keyword*— Poly lactic-acid, Essential oils, FTIR, TGA, elongation, optical properties.**

INTRODUCTION

Mostly plastics pose threat to nature as they are not biodegradable and the increasing synthetic plastic wastes forced the packaging industry to develop alternate biodegradable packaging materials. The focus is now being given to the development of bio-based materials in the packaging field, as it could reduceenvironmental impacts and at the same time givingprotection against physical, chemical and microbiological effects to the packaged product. Polylactic acid (PLA) can be considered as a sustainable replacement for synthetic plastic because of its potential commercial applications.

PLA is a kind of versatile, biodegradable thermoplastic material that can be derived from renewable resources such as sugar beet and potato starch. The properties of PLA can be improved by adding essential oil in order to enable them to competewith other plastic films.

Active compounds like essential oils can be incorporated into biodegradable polymer films toimprove their functional properties such as mechanical properties, antimicrobial and barrier properties. For instance, the essential oils from cashew nut shell and coconut kernel have attracted great attention due to their potential as antioxidant and antimicrobial agents. The plant essential oils are categorized as GRAS by the US Food and Drug Administration for materialsintended to be in contact with food stuff. The blend of essential oil into PLA film is an interesting way to improve their industrial applications. In the previous research carried out it shows that the enhancement of polymer properties not only depends on the type and concentration of essential oil, but also depends on the compatibility between polymer matrix and essential oil. There are few reports available to compare the effects of different types of essential oil on the improvement of mechanical, thermal, and antimicrobial properties of PLA films.

Therefore, the present work was carried out with the main objective of preparing PLA/essential oil (Cardanol oil, coconut oil) blend films and to investigate the effects of essential oil on the mechanical optical, thermal properties of the fabricatedPLA-based blend films.

EXPERIMENTAL WORK

A. Materials

PLA plastic or polylactic acid is a vegetable-based plastic material, which commonly uses corn starch as a raw material was provided in form of pellets by Natur-Tec®. The cardanol and coconut oils were bought from oil mill from Cuddalore (Panruti) and Trichy respectively.

B. Formulation of PLA and PLA/CA/CO blend

PLA (4.0g) was completely dissolved in chloroform (100ml) by vigorous mixing for an hour on a magnetic stirrer at room temperature. Finally, the resultant solution was poured evenly onto the petri dish plates. Then the solvent was allowed to evaporate at room temperature. After 12 hours of drying, the films were stripped off from the trays.

PLA (4.0g) was completely dissolved in chloroform (100ml) by vigorous mixing for an hour on a magnetic stirrer at room temperature. Different proportion of Cardanol oil and coconut oil was added to the PLA solution and stirred for varying time duration to determine the complete blending of oil in the polymer solution. The resultant solution was poured evenly onto the petri dish plates. Then the solvent was allowed to evaporate at room temperature. After 12 hours of drying, the films were stripped off from the trays.

CHARACTERIZATION STUDIES

A. *Wettability study*

Contact angle measurement was carried outby taking a unit of water drop on to the samples by following ASTM D5946-17. 2 mL of pre-calibrated water drop was released on to the surface of PLA and PLA/CA/CO blend dumbbells. Contact angle apparatus, which is equipped with a CCD camera was operated at an acquisition speed of 50 frames per second.

B. *Colorimetric study*

The property possessed by a film of producingdifferent sensations on the eye as a result of the way it reflects or emits light. The CIELAB color space also referred to as *L*a*b** is a color space defined by the International Commission on Illumination. A spectrophotometer measures the spectral reflectance, transmittance, or relative irradiance of a color sample.

C. *Study of Opacity*

Opacity is the ability of a thin, transparent material to hide the surface behind. It is also sometimes referred to as contrast ratio and hiding power. Opacity is expressed as the ratio of the reflectance when the material is backed by a black substrate to the reflectance when it is backed by a white substrate. A spectrophotometer measures the spectral reflectance, transmittance, or relative irradiance of a color sample by following ASTM D1003. A spectrocolorimeter is a spectrophotometerthat can calculate tristimulus values.

D. *Fourier transform infrared spectroscopy (FT-IR)*

Fourier transform infrared spectroscopy (FT- IR) of the films was performed by a PerkinElmer FT- IR/NIR Frontier spectrometer by following ASTM E1252 standard. The PLA/CA, PLA/CO, PLA/CA/CO and PLA samples were measured by cutting it to 1 x 1cm. The measurements were acquired between 4000 and 550 cm^{-1} with a resolution of 4 cm^{-1} using the arithmetic average of four scans.

E. *Thermal stability study*

Thermal degradation is the study of mass of a substance which is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program. The study was carried out in the range of 30° – 500°C at constant heating rate of 10°C/min, using thermo-gravimetric analyser (TGA), Perkin Elmer Frontier (TL-4000) by following ASTM 3850-2000.

F. *Mechanical study*

Tensile strength and elongation at break were calculated on a Tinius olsen Universal Testing Machine by following ASTM D-882 standard. The samples were cut to a size of 12 × 2 cm, at the initial grip separation of 10 cm with a testing speed of 50 mm/min for the tensile test of each combination of PLA/CA/CO blend and neat PLA.

RESULTS AND DISCUSSION

A. *Wettability study*

The contact angle is a measure of the ability ofa liquid to wet the surface of a solid. The shape that a drop takes on a surface depends on the surface tension of the fluid and the nature of the surface.

Table1: Contact angle for the formulation

Formulation	Left angle	Right angle
Neat PLA	63°	67°
PLA/CA/CO(75/22/3)	68°	81°
PLA/CA/CO(75/19/6)	77°	89°
PLA/CA/CO(75/17/8)	69°	84°

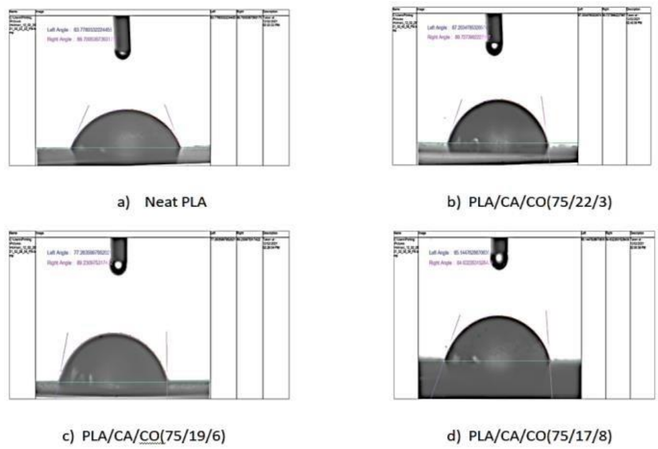

Fig 1: Wettability study for the formulation

The contact angle was measured for the formulation to know whether the surface is hydrophobic and the Neat PLA has an angle of 63° and 67° on left and right respectively. The formulation PLA/CA/CO(75/19/6) has a good contact angle of 77° and 89° on left and right respectively. This depicts that its hydrophobicity is better than the Neat PLA.

B. *Colorimetric study*

The colour of the film is studied for the formulation using spectrophotometer. The neat PLA has whiteness value of 85.626 (L*) which tells that the film is transparent and white in colour with a* and b* values -0.25 and 1.136 respectively. The formulation PLA/CA/CO (75/22/3) is brown in

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colour and has whiteness value low (L*=53.406) compared with PLA. Thus it has colour difference of ΔE =50.975. The formulation PLA/CA/CO (75/19/6) is pale brown incolour and has whiteness value low (L*=54.998) compared with PLA. Thus, it has colour difference of ΔE =48.486. The formulation PLA/CA/CO (75/17/8) is pale brown in colour and has whiteness value low (L*=49.332) compared with PLA. Thus it has colour difference of ΔE =48.264.

C. *Study of Opacity*

The opacity of the film was studied for the formulation using spectrophotometer. The neat PLA has opacity value of 5.3% which tells that the film is transparent. The formulation PLA/CA/CO (75/22/3) is brown in colour and has opacity value of 49.88% compared with PLA. The formulation PLA/CA/CO (75/19/6) is pale brown in colour and has opacity value of 36.58% compared with PLA. The formulation PLA/CA/CO (75/17/8) is pale brown in colour and has opacity value of 45.30% compared with PLA.

D. *Fourier transform infrared spectroscopy (FT-IR)*

The FTIR was carried out to understand the elements and functional group present in the sample. The FTIR spectrum of neat PLA has C=O stretching at 1746cm-1 and C-O stretching at 1100-1300cm-1 and C-H bending at 1300-1500cm-1. The spectrum of PLA with cardanol oil shows the presence of CA. It can be confirmed by the appearance and increased intensity of the bands at 3300 and 1590 cm−1, attributed to the asymmetric stretching of phenolic O−H bond and the stretching of the aromatic C=C bonds.

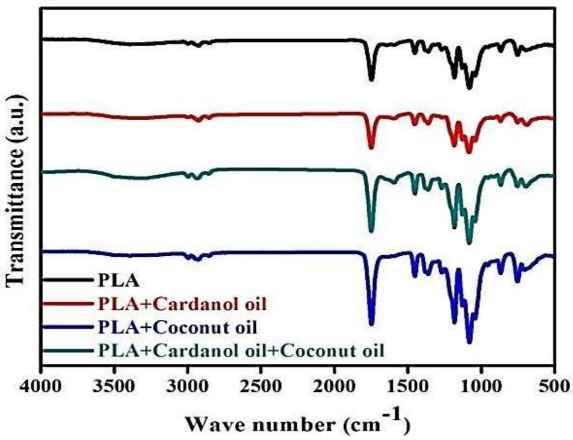

Fig 2: Fourier transform infrared spectroscopy (FT-IR) for the formulation

The FTIR spectrum of coconut oil with PLA has a wavenumber of 2920 cm-1 showing the stretched C-H bond. The typical absorption from triglycerides also appears at wavenumber of 1740 cm-1 which is an absorption of C=O ester

E. *Thermal study*

In order to evaluate the thermal stability of PLA and PLA blends, TGA (Thermo-gravimetric Analysis) was performed and the graph was obtained and the values are tabulated. The addition of essential oil has led to the reduction in thermal stability than Neat PLA and out of the three formulation carried out the onset and end-set temperature of mass reduction for the formulation PLA /CA/CO(75/19/6) was found to becloser to Neat PLA with the residual percentage of 1% at final degradation temperature.

Table 2: TGA values for the formulation

Formulation	Temp onset (°C)	Temp endset (°C)	Residual atFDT (%)
Neat PLA	230	320	2
PLA/CA/CO(75/22/3)	200	305	0.5
PLA/CA/CO(75/19/6)	215	317	1
PLA/CA/CO(75/17/8)	205	310	3

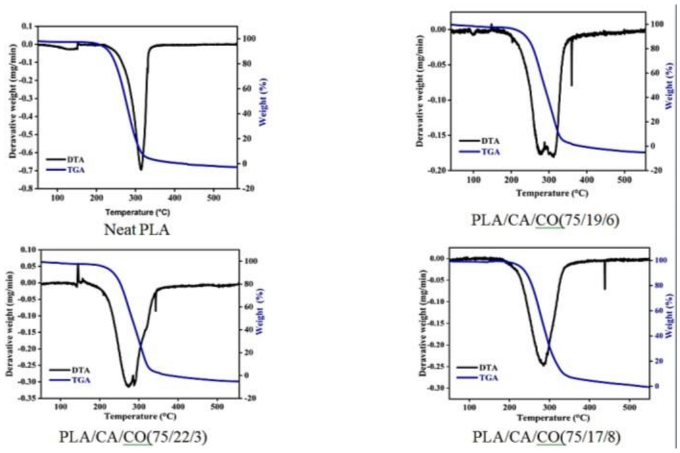

Fig 3: Thermal study for formulation by TGA

F. *Mechanical study*

The mechanical study was performed for the formulation by measuring the tensile strength and elongation at break on tinius olsen universal testing machine. The tensile strength of Neat PLA was found to be 22.833MPa and the formulation PLA/CA/CO(75/22/3) has tensile strength of 5.047MPa with a tensile strength reduction of 77.89 %, the formulation PLA /CA/CO(75/19/6) has tensile strength of 7.088MPa with a tensile strength reduction of 68.95 % and the formulation PLA /CA/CO(75/17/8) has tensile strength of 10.43MPa with a tensile strength reduction of 54.32 %.

Table 3: Mechanical parameters extracted from stress-strain graph

Formulation	Thickness (mm)	Tensile strength (MPa)	Elongation (%)	Reduction of Tensile strength (%) against Neat PLA	Increase in Elongation (%) against Neat PLA
Neat PLA	0.210	22.833	11.90	-	-
PLA/CA/CO (75/22/3)	0.210	5.047	37.19	77.89	212.52
PLA/CA/CO (75/19/6)	0.210	7.088	28.783	68.95	141.87
PLA/CA/CO (75/17/8)	0.210	10.43	23.06	54.32	93.78

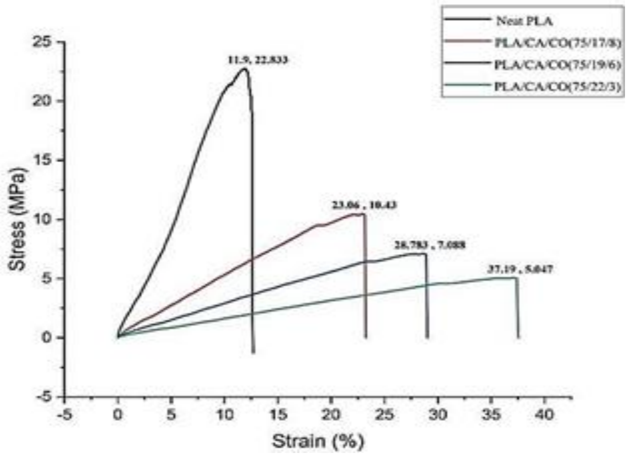

Fig 4: stress-strain curve for the formulation

The tensile test also gives the elongation value of Neat PLA as strain percentage of 11.90 % and the formulation PLA /CA/CO(75/22/3) has elongation value as strain percentage of 37.19% with an improvement of 212.52%, the formulation PLA

/CA/CO(75/19/6) has elongation value as strain percentage of 28.783% with an improvement of141.87% and the formulation PLA /CA/CO(75/17/8) has elongation value as strain percentage of 23.06% with an improvement of 93.78%.

CONCLUSION

It could be seen that the addition of essential oil changes the characteristics of Neat PLA as follows. The addition of essential oil improves the mechanical and optical property of the Neat PLA film. The tensile strength of the formulation PLA /CA/CO(75/19/6) has a value of 7.088MPa against Neat PLA with a tensile strength reduction of 68.95 % and elongation value (strain percentage) of 28.783% against Neat PLA with an improvement of 141.87% and with opacity of 36.58%. The addition of essential oils tends to reduce the thermal stability of the film produced. However, the onset and end-set temperature of mass reduction of the formulation PLA /CA/CO (75/19/6) was found to be closer to Neat PLA with the residual percentage of 1% at final degradation temperature. Thus, among the three formulations done, the PLA/CA/CO (75/19/6) shows better characteristics such as opacity, thermal stability, reasonable tensile strength and very good elongation against neat PLA for the flexible pack application.

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