# A Comparative Study on the Synthesis and Characterisation of Certain Lactic Acid Based Polyesters and Their Composites

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**Abstract: -** Recently, biodegradable synthetic polyester based food packaging materials have received attention because they are easily susceptible to biological attack and their degradation products are non-toxic and can enter the metabolic cycles of bio-organisms.   Several biopolymers have been exploited to develop materials for eco-friendly food packaging. However, the use of biopolymers has been limited because of their usual poor mechanical and barrier properties, which may be improved by converting them into composites.  Chitosan is a biopolymer which has a wide range of applications due to its biodegradability, biocompatibility, antimicrobial activity and  non-toxicity. Chitosan based films have proven to be very effective in food preservation but it has  poor mechanical and barrier properties.  The main objective of this investigation was the study and characterization of chitosan/lactic acid-based polyester blends which are useful as bio-packaging material for potential food applications. The first part of the investigation was related to the synthesis and characterization of polyesters, PEGLT, PBLT, PEGLSu and PEGLSe by melt polycondensation method. Then, the chitosan/polyester blend films were prepared using acetic acid-acetone solvent system. The synthesized polyesters were characterized by solubility, viscosity, ^{1}H NMR and ^{13}C NMR. Both polymer and composites were characterised by FTIR, DSC, XRD and SEM analysis. DSC results shows that the methylene chain length increases with decresing the glass transition temperature (Tg) value in aromatic polymers PEGLT and PBLT while the methylene chain length decreses with increasing the glass transition temperature (Tg) value in aliphatic polymers PEGLSu and PEGLSe. The analytical results of the synthesised  polyesters are compared with the corresponding   chitosan-polyester   composites   and interpreted.

Keywords: Biopolymer, eco-friendly, composites, Chitosan. glass transition temperature.

## I INTRODUCTION

Biodegradable polymers are extensively used for various applications such as packaging, paper coating, fibers, films, and other disposable articles, as well as in biomedical applications, such as resorbable surgical sutures, implants, and controlled drug delivery devices [1-9].  These polymers need to be biodegradable and non-toxic or, in the biomedical applications, bioresorbable and biocompatible. On the other hand, polymers should have good chemical, mechanical and thermal properties. In addition, in the packaging sector, the raw materials should be annually renewable and the end products should be compostable to reduce the use of fossil resources. Furthermore, the raw materials and the end products should be low cost and the production processes on an industrial scale should be efficient, environmentally friendly and economically competitive [10-13]. However, only a few monomers and polymers can fulfil these demands. Among possible monomers, lactic acid (2-hydroxy propionic acid), which is a non-toxic, naturally occurring, and renewable raw material, fulfils most of these rigorous requirements [14]. Blending of a polymer with other polymer is one of the most straight forward ways to alter physical properties with well-defined phase separated morphologies [15]. Blending of chitosan with lactic acid based polymers are biodegradable modern polymers from renewable resources. Chitosan is the second polymer after cellulose which is used in food packaging material due to its excellent film-forming ability. Due to its hydrophilic nature it is very sensitive to moisture thus blending with hydrophobic polymer material to reduce the sensitivity of moisture.

In this study, Lactic acid basedaromatic/aliphatic copolyester is systematically synthesised and chitosan/polyester blend films were prepared by solvent mixing and film casting method.  The results regarding the structure and morphology as well as the related properties of these blend films are presented here.

## II. EXPERIMENTAL PROCEDURE

### A. Materials

Lactic acid (Merck AR grade), ethylene glycol (Lancaster, AR grade) and 1, 4 butane diol (Merck AR grade) Sebacic acid, Subaric acid and Terepthalic acid (Lancaster AR grade) were recrystallised from deionised water and used. Chitosan (Aldrich), and Titanium tetra isopropoxide, used as catalyst, purchased from Lancaster were used as such.  All the other materials and solvents used were of analytical grade.

B. Synthesis of polyester

The four polyesters are synthesised by two step polycondensation method using Titanium tetra isopropoxide as catalyst as reported in the previous study [16].

## III. RESULTS AND DISCUSSION

A. Intrinsic Viscosity and solubility studies

The inherent viscosity of the copolyesters was measured in chloroform using ubbelhode viscometer. The range is 0.82dL/g and to 0.95dL/g.

### TABLE – 1 INTRINSIC VISCOSITY OF COPOLYESTERS

| Polymers | Inherent viscosity $\eta_{inh}$ (dL/g) |
|---|---|
| PEGLT | 0.82 |
| PBLT | 0.90 |
| PEGLSe | 0.95 |
| PEGLSu | 0.87 |

The synthesized copolyesters are soluble in $CHCl_3$, acetone, DMSO and insoluble in alcohols and water.

B. Fourier- Transform Infrared (FTIR) Spectroscopy

FTIR spectral values of copolyesters PEGLT, PBLT, PEGLSu and PEGLSe are shown in the Figure 2. It shows the values of -C=O Stretching of ester group, -C-O- Stretching of ester group, Aliphatic -CH$_2$ – Stretching and Aliphatic -CH$_2$ – bending.

It was observed that the ester carbonyl, -C=O stretching frequency decreases with increase in the length of the spacer groups. This suggests that the ester carbonyl bond strength decreases with increase in the length of the spacer groups in the repeating unit of the main chain of the polyester.

In polymer composites the main bands in the IR spectrum of chitosan can be observed as follows: a broad and strong overlapped band at around 3443 cm$^{-1}$ (OH and NH stretch); two weak bands at 2924 and 2857 cm$^{-1}$ (CH stretch); two middle strong bands at 1639 and 1584 cm$^{-1}$ (amide I and amide II); 1160, 1094, and 1023 cm$^{-1}$ (saccharide structure) [17].

C. $^1$H NMR spectroscopy

The chemical shift values obtained from $^1$H NMR spectra of the copolyesters are shown in the table.

D. $^{13}$C NMR Spectroscopy

The chemical shift values obtained from $^{13}$C NMR Spectra of the copolyesters are shown in the table.

### TABLE 2.IR ABSORPTION FREQUENCIES AND ASSIGNMENT OF GROUPS

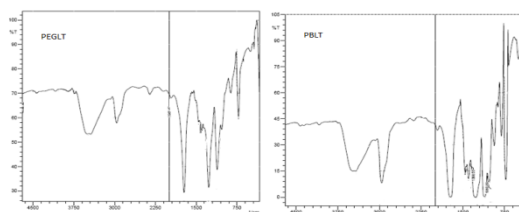| Copolyester | Absorption frequency, cm$^{-1}$ | | | |
|---|---|---|---|---|
| | -C=O Stretching of ester group | -C-O- Stretching of ester group | Aliphatic -CH$_2$ - Stretching | Aliphatic -CH$_2$ - bending |
| PEGLT | 1725.4 | 1060.9,1116.8 | 2933.6 | 920.5 |
| PBLT | 1722.4 | 1035.8,1112.6 | 2940.4 | 963.2 |
| PEGLSu | 1744.7 | 1166.3,1244.5 | 2941.5 | 968.3 |
| PEGLSe | 1734.0 | 1179.5,1263.0 | 2930.9 | 948.0 |



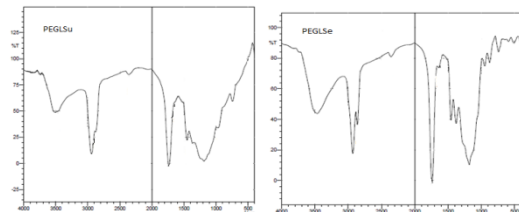Fig . 1.  IR Spectra of copolyesters  PEGLT and PBLT



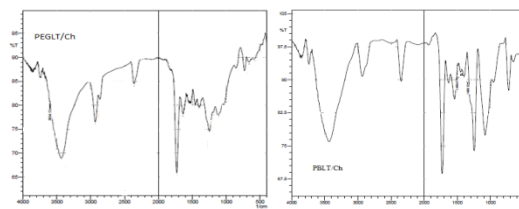Fig . 2.  IR Spectra of copolyesters  PEGLSu and PEGLSe



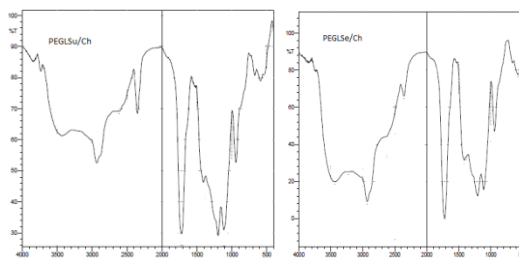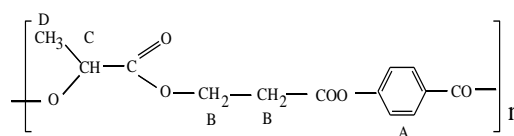Fig . 3.  IR Spectra of polymer composites PEGLT/Ch and PBLT/Ch



Fig . 4.  IR Spectra of polymer composites  PEGLSu/Ch and PEGLSe/Ch

### TABLE 3. $^1$H NMR CHEMICAL SHIFT VALUES OF COPOLYESTERS

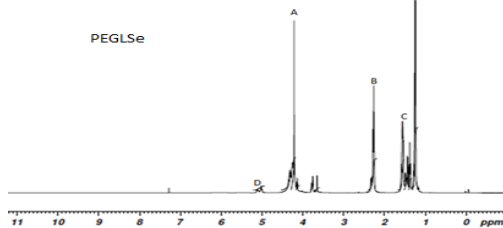| Copolyesters | Chemical shift values, δ (ppm) | | | | |
|---|---|---|---|---|---|
| | Aromatic protons | -CH$_2$O- | O=C-CH$_2$- | Central -CH$_2$ - | Terminal -CH$_2$ |
| PEGLT | 8.10 | 4.10 | 2.56 | 1.29 | 1.74 |
| PBLT | 8.08 | 4.42 | 2.10 | 1.26 | 1.72 |
| PEGLSe | - | 4.21 | 2.26 | 1.24 | 1.55 |
| PEGLSu | - | 4.07 | 2.28 | 1.30 | 1.70 |

Fig . 5. [1] H NMR Spectra of copolyester PEGLT

TABLE 4. ^{13}C NMR CHEMICAL SHIFT VALUES OF RANDOM COPOLYESTERS

| Copolyesters | Chemical Shift ,δ (ppm) | | | | |
|---|---|---|---|---|---|
| | Quaternary Aromatic Carbon | O - C - | -CH$_2$O- | - CO CH$_2$ | Central - CH$_2$ - |
| PEGLT | 134.10 | 172.43 | 64.9 | 29.19 | 25.55 |
| PBLT | 133.82 | 166.3 | 64.8 | 29.91 | 25.18 |
| PEGLSe | - | 1753 | 63.1 | 34.0 | 24.7 |
| PEGLSu | - | 173.0 | 63.6 | 34.1 | 25.3 |



Fig . 6. [1] H NMR Spectra of copolyester PBLT
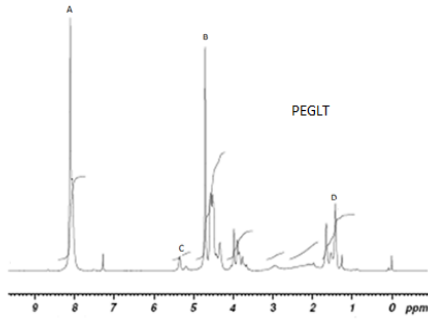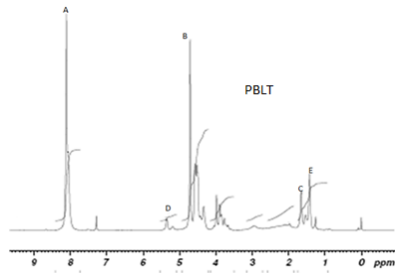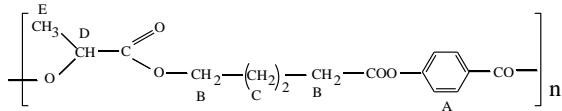


Fig . 9. ^{13}C NMR Spectra of copolyester PEGLT



Fig . 7. [1] H NMR Spectra of copolyester PEGLSu



Fig . 10. ^{13}C NMR Spectra of copolyester PBLT
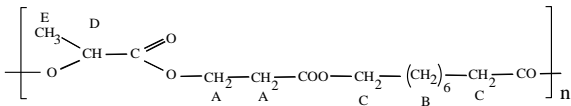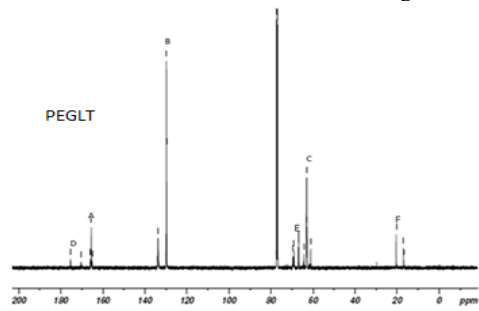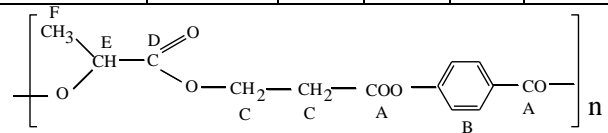


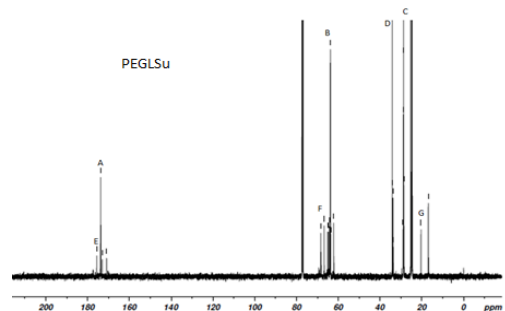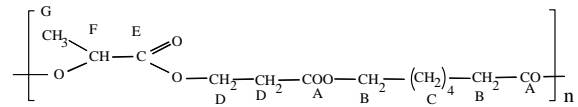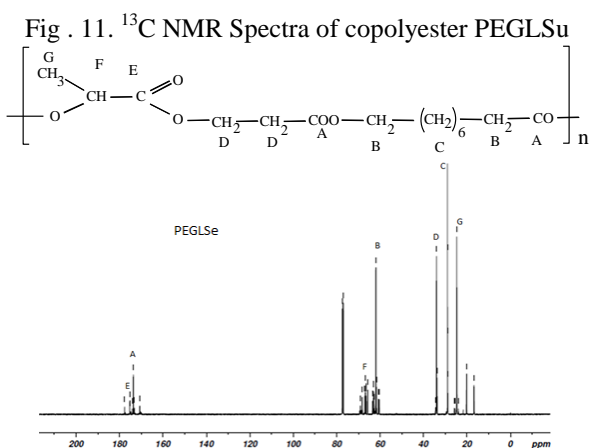Fig . 8. [1] H NMR Spectra of copolyester PEGLSe
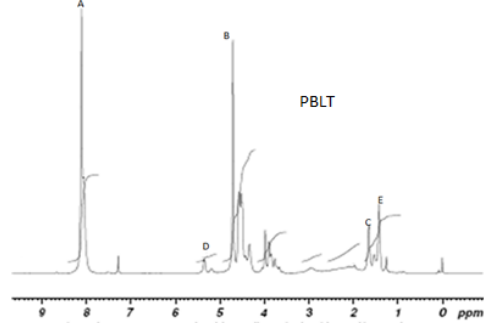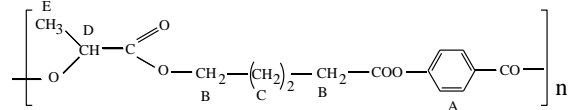
Fig . 11. $^{13}$C NMR Spectra of copolyester PEGLSu



Fig . 12. $^{13}$C NMR Spectra of copolyester PEGLSe

### E. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) Analysis. DSC is a technique for determining the quantity of heat either absorbed or released when a substance undergoes a physical or chemical change. Several parameters could be estimated by performing a DSC scan, such as the glass transition temperature (TG), melting temperature, and decomposition temperature (Td) [18].

The glass transition temperature, $T_{ag}$ of a polymer describes flexibility of the chains because a high $T_{ag}$ is assumed to be related with relatively high barriers of bond rotation [19]. It is observed from the table that the $T_{ag}$ values decrease PEGLT to PBLT in the case aliphatic-aromatic co polyesters. Considering aliphatic - aromatic copolyesters the aliphatic content increases with decreasing the Tg values.

Kari hiltunen et al reported that in the case of aliphatic copolyester series the Tg strongly depends on the molecular weights that are higher the methylene units, higher the molecular weights, and hence, higher the glass transition temperature of these polymers [20]. It was observed from the table that the Tg values increase PEGLSu to PEGLSe.

The melting temperature of aliphatic series, $T_m$, increases with increase in number of methylene groups in the repeating unit of the polymer chain. This trend is just the reverse of aliphatic - aromatic copolyesters as reported by Dimitrios and co-workers [21].

In polymer composites, the glass transition temperature increase with increasing melting temperature, decomposition temperature and melting enthalpy in comparison with the polymers. It is well known fact that the Tg of the composite are affected by chemical cross-linking density and physical interaction between hydroxyl groups of chitosan and ester bonds, terminal-hydroxyl groups and terminal-carboxyl groups in the polymer. The physical interaction in the composites can bring an increase in Tg due to the hindrance of the mobility of the polymer segments [22].

TABLE 5. THERMAL DATA OF COPOLYESTERS

| Copolyester | Tg ($^0$C) | Tm ($^0$C) | Td ($^0$C) | $\Delta Hm$ (J/g) |
|---|---|---|---|---|
| PEGLT | 33.7 | 100.5 | 301.0 | 127.3 |
| PBLT | 31.6 | 98.3 | 281.2 | 164.5 |
| PEGLSu | 14.7 | 61.2 | 288.4 | 214.6 |
| PEGLSe | 21.4 | 92.6 | 295.1 | 55.23 |

TABLE 6. THERMAL DATA OF POLYMER COMPOSITES

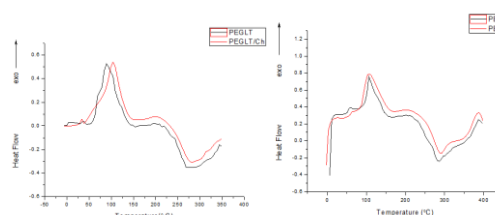| Copolyester/Ch | Tg ($^0$C) | Tm ($^0$C) | Td ($^0$C) | $\Delta Hm$ (J/g) |
|---|---|---|---|---|
| PEGLT/Ch | 34.6 | 103.7 | 303.4 | 129.7 |
| PBLT/Ch | 32.8 | 99.7 | 283.2 | 186.7 |
| PEGLSu/Ch | 17.0 | 60.4 | 291.3 | 235.7 |
| PEGLSe/Ch | 23.8 | 95.6 | 298.5 | 238.9 |



Fig. 13. DSC Thermograms of polymers and composites PEGLT, PEGLT/Ch and PBLT, PBLT/Ch
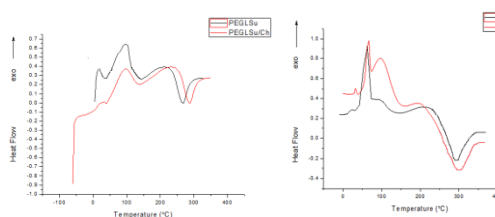


Fig. 14. DSC Thermograms of polymers and composites PEGLSu, PEGLSu/Ch and PEGLSe, PEGLSe/Ch

### F. X-ray Diffraction (XRD)

The XRD pattern obtained for the synthesised copolyesters can be separated into two phases crystalline and amorphous [23]. The X-ray diffractogram was taken for the synthesised polyesters PEGLT, PBLT and PEGLSe. The diffractograms of the synthesised copolyesters, polymer composites and chitosan are presented in Figures 15 and 16.

The comparison of the diffractograms of the aliphatic - aromatic copolyesters reveal that the degree of crystallinity decreases in PEGLT to PBLT which is supported by decrease in the melting point of these polyesters obtained from DSC thermograms.

In aliphatic copolyester, the crystallinity of copolyester increases with the increase in number of methylene groups in the repeating unit of the polymer chain [24].

In comparison of polymers and composites, the polymers have the sharp peaks than in the polymer composites. Hence, the polymers are more crystalline than polymer composites.
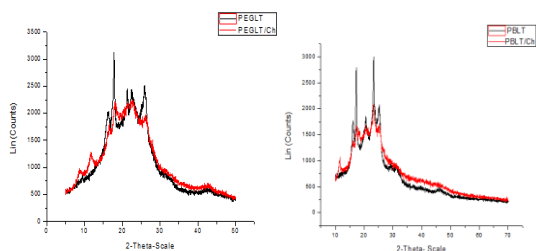
Fig. 15. X-ray Diffraction Patterns of polymers and composites PEGLT,PEGLT/Ch and PBLT, PBLT/Ch
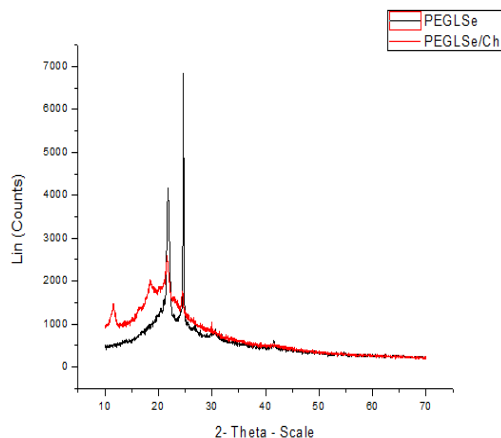


Fig. 16. X-ray Diffraction Patterns of polymer and composite PEGLSe, PEGLSe/Ch

G. Scanning Electron Microscopy

SEM images of the synthesised polymers and their corresponding Chitosan-polymer blends are shown in figures 19-22. SEM images of synthesised polymer blend with chitosan particles indicated much better adhesion.
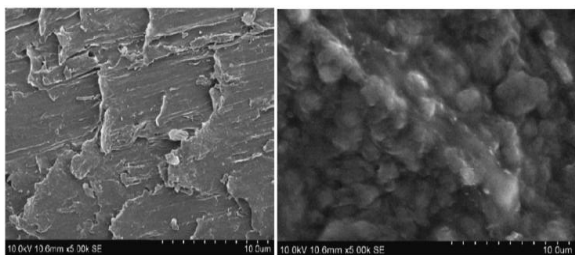


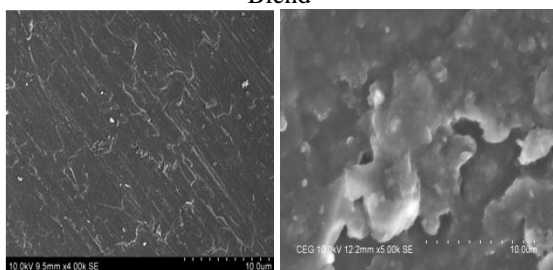Fig. 17. SEM Images of PEGLT and PEGLT /Chitosan Blend



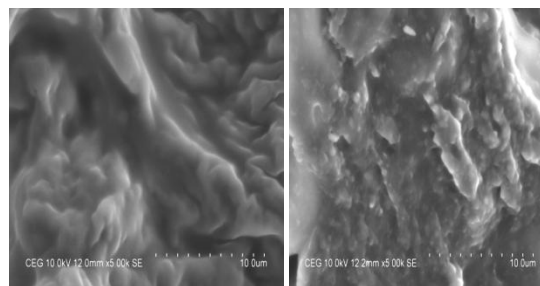Fig.. 18. SEM Images of PBLT and PBLT /Chitosan Blend.



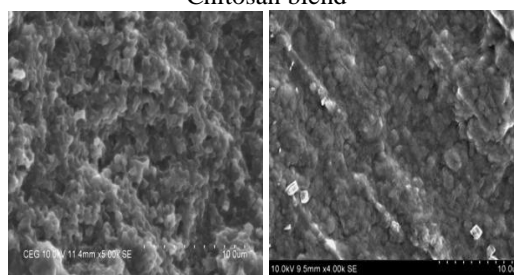Fig. 19. SEM Images of PEGLSu and PEGLSu / Chitosan blend



Fig. 20. SEM Images of PEGLSe and Chitosan/PEGLSe

H. Mechanical Properties

The mechanical property of film was studied based on the parameters; tensile strength (TS), Young's modulus (Y) and ultimate elongation at break (UE). Tensile testing is usually used to evaluate the tensile strength and elongation at break of the polymer composite.

The changes in the molecular structure and crystallinity of the polymer may affect mechanical properties of a composite. It is generally accepted that the modulus may increase with an increasing level of crystallinity. Hence, the composites show increased stiffness and reduced toughness [25].

Mechanical properties are measured for the Chitosan/polymer composite thin films are tabulated in the table 8. As shown in the Table , increasing the methylene chain length in the composite, the tensile strength and the modulus of composites prominently increased, meanwhile, the elongation at break of the composites differ slightly.

TABLE 7. MECHANICAL PROPERTY OF POLYMER COMPOSITES

| Polymer Composite Name | Tensile strength(M Pa) | Young's modulus( MPa) | Elongation at break (%) |
|---|---|---|---|
| PEGLT | 1.075 | 6.41 | 70.4 |
| PBLT | 1.045 | 5.66 | 65.7 |
| PEGLSu | 1.243 | 4.41 | 10.23 |
| PEGLSe | 1.398 | 4.78 | 20.33 |

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## IV CONCLUSION

All the four copolyesters have been synthesised by direct melt polycondensation of common monomer lactic acid with diols and dicarboxylic acids at high temperature and high vacuum. The synthesised copolyesters are blended with chitosan to prepare composites. The synthesized polyesters were characterized by solubility, viscosity, ^{1}H NMR and ^{13}C NMR. Both polymer and composites were characterised by FTIR, DSC, XRD, SEM analysis and mechanical studies.

DSC results show that the glass transition temperature (Tg) decreases with increasing methylene chain length for aliphatic – aromatic copolyesters. Whereas the glass transition temperature increases with decreasing methylene chain length for aliphatic copolyesters. X- ray diffractogram shows that the polymers have more sharp peaks than the corresponding composites which reveals the more crystalline nature of polymer. The mechanical properties of the polymer composite films were evaluated and compared. SEM images of composites show much adhesion between chitosan and synthesised polyesters. Hence, these synthesised nove chitosan/plymer composites have potential applications as moisture resistant biodegradable packaging materials for food items.

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