Research Article

CHEMICAL MODIFICATIONS OF EXISTING POLYMERS: AN ATTEMPT TO INCREASE BIODEGRAD ABILITY

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ABSTRACT

Polymers are a highly diverse class of materials. The applications of polymers are in almost all fields including agricultural (mulching films, green house films, etc), medical (syringes, capsules, medicine packaging, urine bags, etc), and transport (car bumpers, wheel covers), etc. Some polymers are of vital importance however their applications are limited due to non-biodegradability. Polymer possesses a number of reactive functional groups in their structure such as hydroxyl, amino and carboxylic acid group. The chemical modifications using these functionalities may be useful to increase biodegradability and hence the acceptance for pharmaceutical and biomedical use. The aim of the present research was to improve the biodegradability of existing non-biodegradable polymers by chemical modifications.

The polymer blends of polymethyl methacrylate (PMMA) and polyvinyl chlorides (PVC) were prepared separately with chitosan (CS). The prepared blends were characterized for thin layer chromatography (TLC), Fourier transform infrared spectroscopy (FTIR), Differential scanning colorimetry (DSC), Nuclear magnetic resonance (NMR) and hydrolytic and enzymatic degradations. The TLC, FTIR, DSC and NMR analysis revealed the successful formation of PMMA-CS and PVC-CS blend. In the hydrolytic degradation study, the polymer exhibited progressive mass loss over the 8 week period ranging from 1.90% to 45.66%. Similarly, the enzymatic degradation study demonstrated 0.6-4.8% degradation of PMMA-CS blend and 0.3-3% degradation of PVC-CS blend. Thus, chemical modifications could be a promising approach to improve the biodegradability of polymers.

INTRODUCTION

A polymer is a big molecule made up of monomers, which are connected repeating subunits in a chain or ring. Polymers of various kinds are employed in pharmaceutical compositions. Biodegradable polymers are those that degrade when exposed to certain environmental conditions. Starch, cellulose, collagen, gelatin, polyhydroxyalkanoates (PHAs), natural rubber etc. are natural biodegradable polymers and polyamides, polyurethanes, polyureas, polyanhydrides, polyvinyl alcohol (PVA), etc. are some of the synthetic biodegradable polymers. Non-biodegradable polymers are those that do not degrade in the environment. Polyethylene, poly (methyl methacrylate) polyester, polycarbonate, polyamide (nylon), and polyurethane are examples of non-biodegradable polymers. Increased white pollution is caused by non-biodegradable polymers.

They have serious environmental consequences, including as harming marine life, causing land infertility, and causing health problems in animals that ingest them, etc. Using biodegradable polymers instead of non-biodegradable polymers can reduce the harmful effect on environment. Biodegradable polymers can break down easily and rapidly into organic materials as they are synthesized from natural sources as plants. So, it is necessary to convert non-biodegradable polymers into biodegradable polymers [1-5].

There are various factors such as degree of hydrophilicity, chemical structure, stereochemistry, crystallinity, degree and type of branching, and other variables considered for conversion of non-biodegradable polymers into biodegradable polymers. If the molecular weight of polymers is high i.e., 400-500 daltons then, degradation of polymers become very

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difficult. Molecular weight of biodegradable polymers is less so, they get easily degraded.

Increase in the hydrophilicity of polymer leads to deep penetration of microbes into the polymer. Chemical structure of polymer has most significant effect on its biodegradability. Biodegradable nature of polymer is dependent on functional groups of polymers. Presence of amphiphilic diblock copolymers/ hydrolysable links, oxidisable functional groups enhances biodegradability of polymers. Biodegrability of functional groups increases in order: Methylene <Aliphatic ether <Carbamate <Aliphatic ester, Peptide bond. Alteration in stereochemistry can cause enzymatic degradation of polymers. By reducing the melting point and crystalline nature of polymers by structural modification can enhance the biodegradability of polymer. Polymer break down can be improved by modifications to branching groups. The presence of ester moieties facilitates in the hydrolytic breakdown of polymers, both enzymatically and non-enzymatically. Amino acids can introduce into polymers to make them biodegradable. As the branching becomes complex/ more the biodegradability of the polymer reduces. So, less branching will be beneficial for the biodegradability of polymer [6-15]. Present research work was aimed to synthesize biodegradable polymer using non-biodegradable polymers via chemical modifications.

MATERIAL AND METHODS

Materials

Polymethylmethacrylate and Polyvinyl chloride (PVC) were procured from Mylan Pvt. Ltd. Hyderabad (A. P.), India. Chitosan was purchased from Sigma Aldrich, Mumbai. Tetrahydrofuran was purchased from Molychem, Mumbai.

Methods

Preparation of polymers blend

The polymethyl methacrylate (PMMA) and chitosan (CS) reaction were carried out at the ratio of 1:1. Acetone was used as a common solvent for preparing polymer solutions of PMMA and CS. Briefly, PMMA and CS (1:1 mmol) were dissolved in 10 mL acetone by stirring and reaction mixture was stirred continuously on magnetic stirrer for 24 hrs. The TLC of reaction mixture was taken after every half hour. After completion of reaction, the acetone was evaporated to dryness. The PVC and CS blend was prepared in the similar manner using tetrahydrofuran (THF) as a solvent. After completion of reaction, the PVC and CS mixture was subjected for THF evaporation using rotary evaporator at 60^0C temperature. Finally, the product obtained was subjected for FTIR, NMR and DSC analysis.

Characterization of prepared blends

TLC analysis

TLC was performed using silica gel. The different spots of reactant and product were applied and allowed to run in the mobile phase composed of n-Hexane and ethyl acetate (95:5). Finally the spots were detected either by iodine staining.

FTIR analysis

FTIR spectroscopy was used for structural analysis of the samples. The FTIR spectra of samples were recorded using an Agilent FTIR spectrophotometer (Agilent, Alpha 100508) over the wavenumber 4000 to 400 cm^{-1}.

DSC analysis

The glass transition of samples was determined using DSC. The analysis was performed under nitrogen atmosphere and using 5-10 mg of samples at the flow rate of 30 mL/min by a Mettler DSC 30 instrument. The glass transition temperatures were measured from the inflection point of the thermograms relevant to the second heating cycle. Indium and gallium samples were used as calibration standards.

NMR analysis

NMR spectroscopy was also used for the structural analysis of the samples. The ^{1}H NMR spectra of the samples were recorded by dissolving them in DMSO using FT-NMR Bruker 300 Avance (300 MHz). The tetramethylsilane (TMS) was used as an internal standard.

Hydrolytic degradation tests

Polymer degradation in phosphate buffered saline (PBS) was characterized over 8 week period at 37ºC. Briefly, the polymer was weighed and immersed in 10 mL PBS of pH 7.4 at 37ºC temperature. Samples were taken every week and weighed after washing with fresh PBS and then drying in a freeze dryer for 4 days [16-21]. The weight remaining was calculated as weight remaining (%) = $100 \times$ W2/W1

Where W1 and W2 are the weights of polymer before and after degradation, respectively.

Enzymatic Degradation

The degradation of polymers blend was studied in the presence of lipase enzyme using Phosphate buffer solutions (PBS) of pH 7.5. Briefly, PBS of pH 7.5 was prepared by mixing known amounts of Na_2HPO_4 and KH_2PO_4 solutions in a fixed ratio. Buffered enzyme solution was prepared by adding a fixed amount of enzyme to these buffer solutions. Enzyme concentration used was 250 units per 10 mL. The weighed polymer blends were immersed in enzyme solution at room temperature (30^0C) and were intermittently aerated. The films were removed after 1, 3, 5 days, washed well with water and dried in hot air oven to complete dryness and weighed [22].

RESULT AND DISCUSSION

Preparation of polymers blend

PMMA and CS polymer blend as well as PVC and CS polymer blend were prepared at 1:1 molar ratio using acetone and THF solvent respectively. The proposed interaction between PMMA and CS as well as PVC and CS is represented in Figure 1A and 1B.
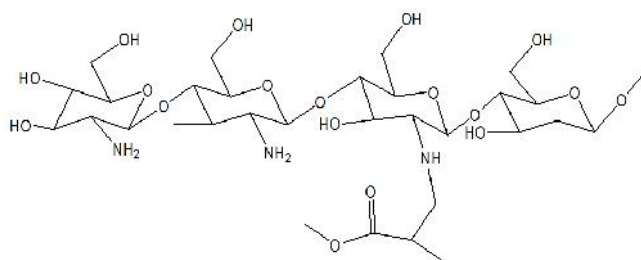

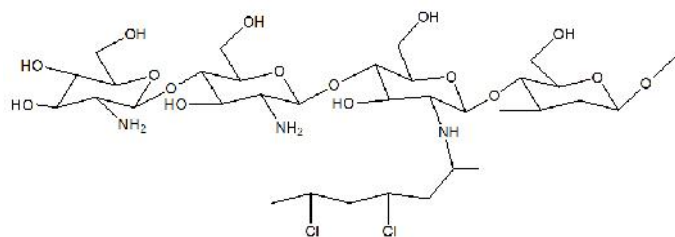**Figure 1 A** Proposed interaction between PMMA and CS

Figure 1B Proposed interaction between PVC and CS

Characterization of polymers blend

TLC

The TLC analysis confirmed the synthesis of reaction product. We observed different spots for the reactants and products. The R_f values CS, PMMA, PVC, PMMA-CS conjugate and PVC-CS conjugate was found to be 0.36, 0.64, 0.83, 0.45 and 0.57 respectively. This confirmed the formation blends. The R_f values of compounds are depicted in table 2.

Table 1 R_f values of different compounds

Compound	Rf value
CS	0.36
PMMA	064
PVC	0.83
PMMA-CS	0.45
PVC-CS	0.57

FTIR

The polymers blends were characterized by using FTIR across wave number range of 4000 to 650 cm^{-1}. The FTIR spectra of PMMA-CS and PVC-CS blend is shown in figure 2A and 2B. In FTIR spectra of PMMA-CS blend (Figure 2A), the peak observed around 1700-1500 cm^{-1} confirms the presence of C=O of ester. The peak observed around 1050-1150cm^{-1} and 1250-1020cm^{-1} are corresponding to the presence of C-OH and C-N groups respectively.

The FTIR spectra of PVC-CS blend (Figure 2B) displayed the peak at 1400cm^{-1} which is attributed to the C–H aliphatic bending and the peak observed around 1250cm^{-1} confirms bending of C-H near Cl. Moreover, the peaks in the range of 1100-1000 cm^{-1} which is corresponding to the C–C stretching bond of the PVC backbone chain. Furthermore, the C-Cl gauche bond is represented by peaks in the 600–650cm^{-1} range.
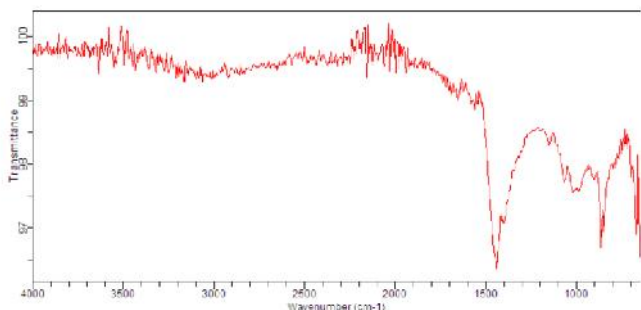

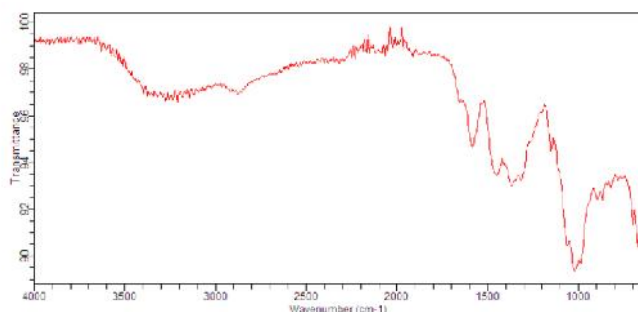**Figure 2A** FTIR Spectra of PMMA-CS blend

Figure 2B FTIR Spectra of PVC-CS blend

NMR

The polymers blends were also characterized by using ^{1}H NMR (400 MHz, DMSO-d6). The NMR spectra of plain PMMA, PVC, CS, and PMMA-CS blend and PVC-CS blend are shown in Figure 3. In the ^{1}H NMR spectra of PMMA-CS blend (Figure 3D), the peaks between 2.93 and5.18 ppm are ascribed to the protons of glucosamine unit and the peak at 3.24 ppm is assigned to the methoxy protons in the ^{1}H NMR spectrum of chitosan. Compared with the peaks of chitosan, the ^{1}H NMR spectrum of PMMA-CS derivative displayed the prominent peak of –OCH3 proton at 3.67 ppm along with the resonance peaks at 2.73 and 1.24 ppm corresponding to the hydrogen atoms on the methyl and methane of methyl acrylate moiety. In ^{1}HNMR of PVC (Fig. 3B), -CH$_3$, -CH$_2$ and –CH proton showed signals at 1.59, 1.77 and 3.64 ppm respectively. When PVC grafted with CS, only slight change in chemical shift values of PVC moiety was observed.
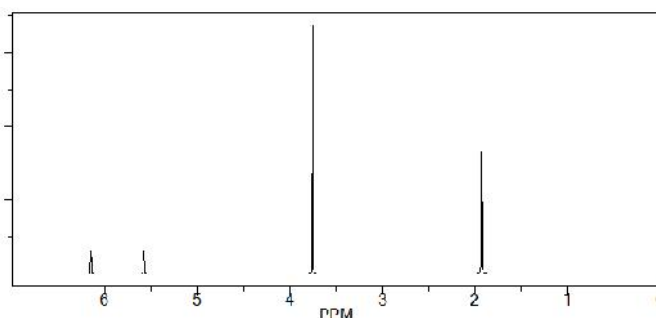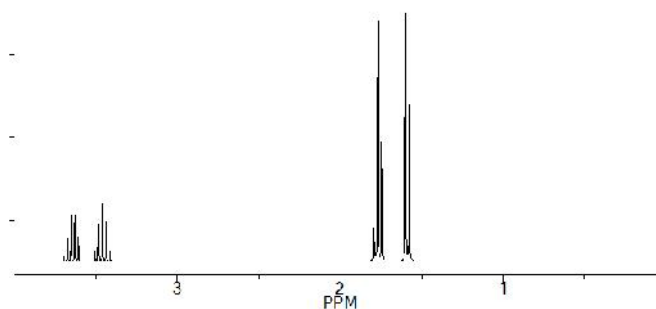

Figure 3A NMR spectra of PMMA
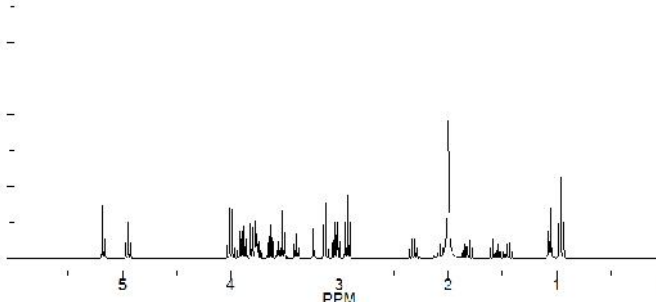

Figure 3B NMR spectra of PVC

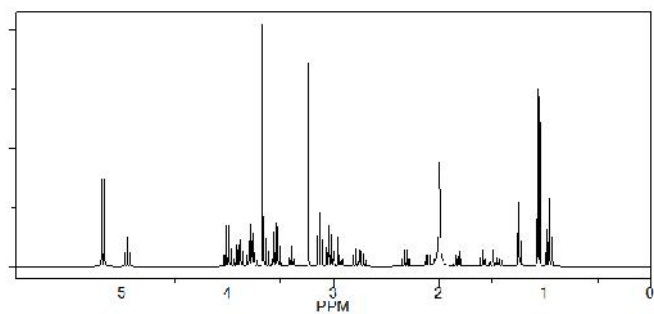**Figure 3C** NMR spectra of Chitosan

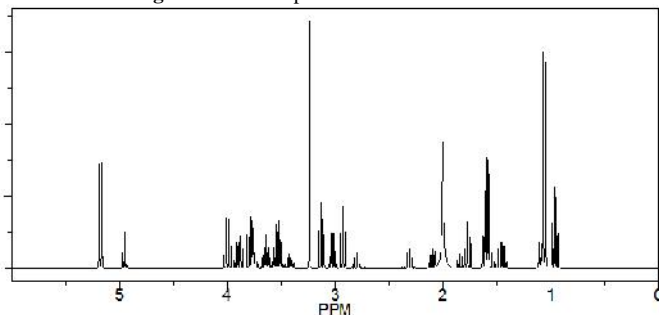25249

Figure 3D NMR spectra of PMMA-CS blend

Figure 3E NMR spectra of PVC-CS blend

DSC

DSC is an important tool for the determination of glass transition and melting behaviour of polymers. DSC thermogram of PMMA (Fig. 4A) exhibited an endothermic peak at 77.66°C that may be correlated to elimination of loosely bound water in the PMMA. The thermogram showed two exothermic peaks at 225°C and 280°C that were due to pyrolysis reaction in the sample. DSC thermogram of PVC (Fig. 4B) exhibited an endothermic peak at 55.14°C that may be due to loss of water in the sample. The thermogram exhibits exothermic peaks at 245°C-308°C due to dehydrochlorination reaction in the sample. In this reaction, polyene radicals and unsubstituted aromatics are released. DSC thermogram of CS (Fig. 4C) sample did not exhibit any glass transition temperature which was mainly associated with its rigid crystalline nature and occurrence of strong inter/intra molecular hydrogen bonding. DSC thermogram of chitosan exhibited a broad exothermic peak at 250°C. This exothermic peak can be correlated to decomposition of amine units of the CS.

In the DSC thermograms of PMMA-CS blend (Fig. 4D), the degradation commenced at around 215°C and terminated at around 219°C. The PMMA lost 20.20% of its weight at 215°C and 12.05 % of its weight at 219°C. In the TGA-DTG thermograms of PVC-CS blend (Fig. 4E), the degradation commenced at around 215°C and terminated at around 276°C. Thus, degradation revealed improved degradability of both polymers (PMMA and PVC) on blending with CS.
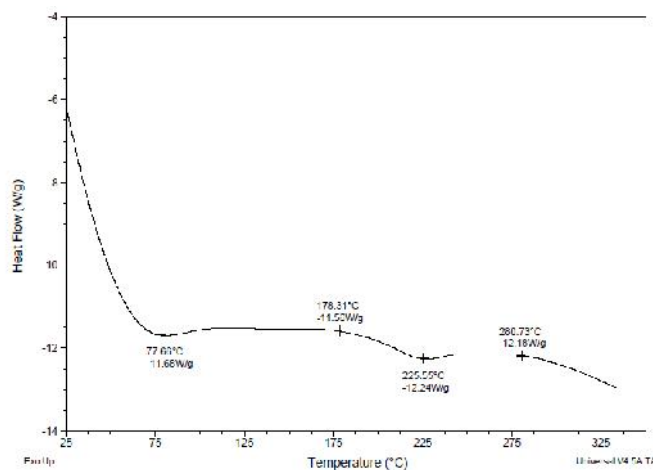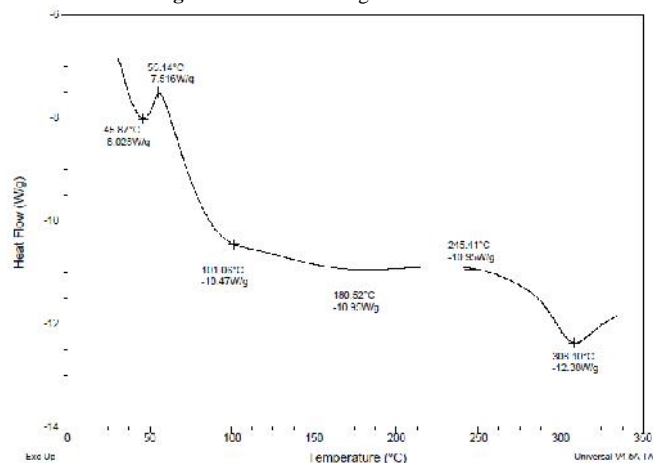

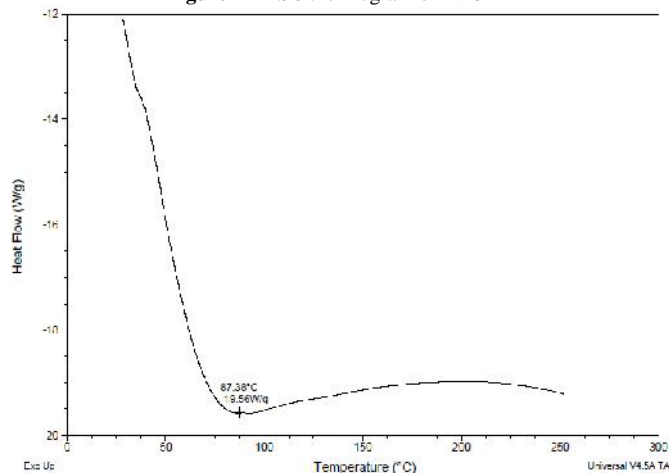**Figure 4A** DSC thermogram of PMMA

Figure 4B DSC thermogram of PVC
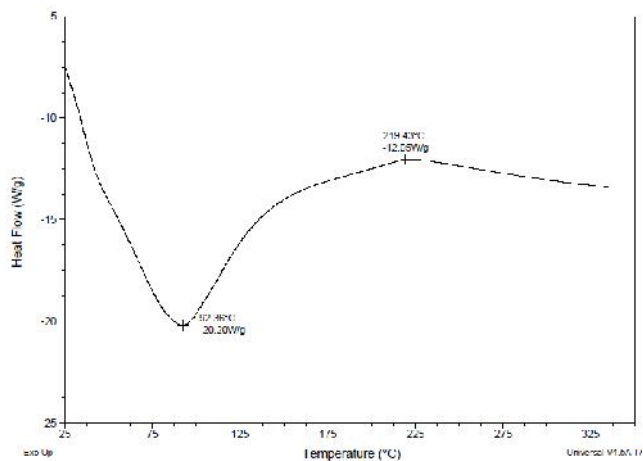

Figure 4C DSC thermogram of CS

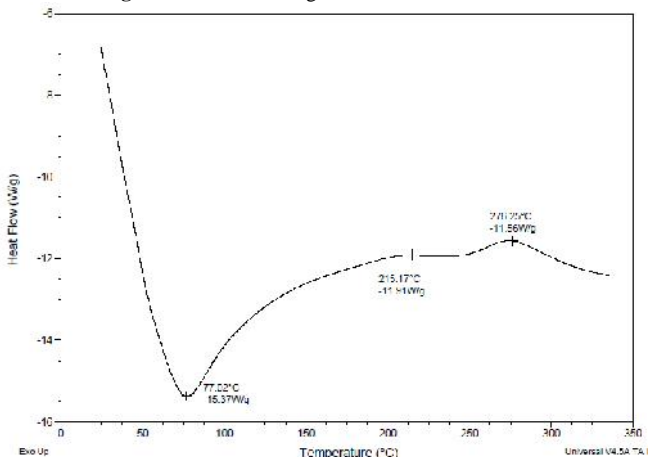**Figure 4D** DSC thermogram of PMMA-CS blend

Figure 4E DSC thermogram of PVC-CS blend

Hydrolytic degradation tests

The hydrolytic degradation rates of both chemically modified PMMA and PVC were determined by measuring its weight loss during its hydrolytic degradation. The hydrolytic degradation of chemically modified PMMA and PVC at 37 ℃ is shown in Figure 5. The polymer exhibited progressive mass loss over the 8 week period ranging from 1.90% to 45.66%. It was said that the hydrolytic degradation rate of these polymers depend on the morphological structure, crystallinity, size and form of the crystallite, *etc*. [23]. Since water molecules can diffuse into the amorphous area of the polymer without difficulty, the hydrolytic degradation happens in the amorphous area rather than the crystalline area. It was found that the presence of chitosan in these polymers caused the improvement of its hydrolytic degradation.
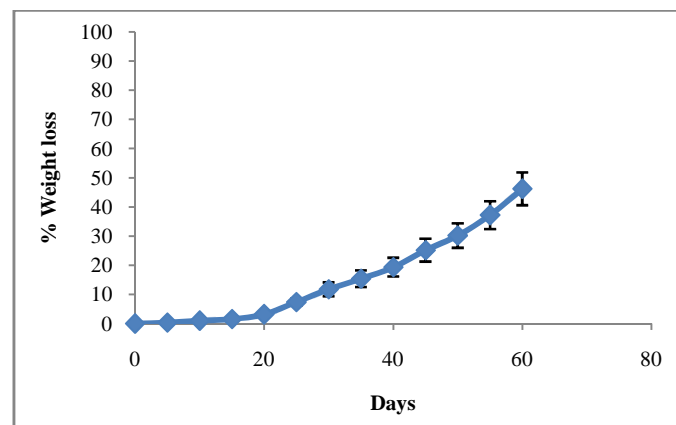

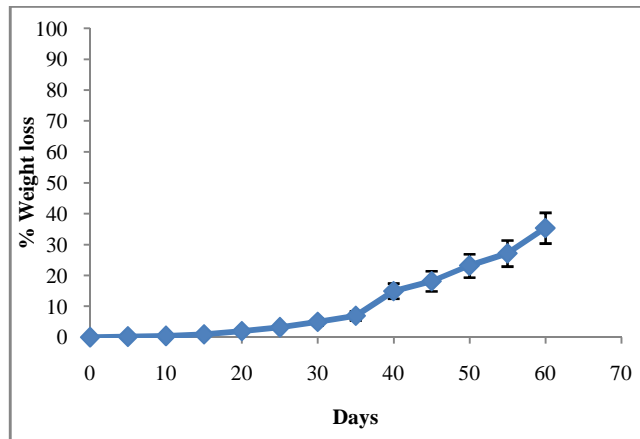**Figure 5A** %Weight loss of PMMA-CS blend during hydrolytic degradation at 37 ℃

Figure 5B %Weight loss of PVC-CS blend during hydrolytic degradation at 37 ℃

Enzymatic Degradation

The enzymatic degradation of the polymers blends were tested by using lipase enzyme. This method is frequently used for quickly evaluating the biodegradability of polymers, although it does not exactly reflect degradation under natural conditions. The time dependent enzymatic degradation was observed with both PMMA-CS blend and PVC-CS blend. In case of PMMA-CS blend the degradation was observed between 0.6-4.8% while PVC-CS blend demonstrated degradation between 0.3-3%. The enzymatic degradation was observed with both PMMA-CS blend and PVC-CS blend is shown in Figure 6.

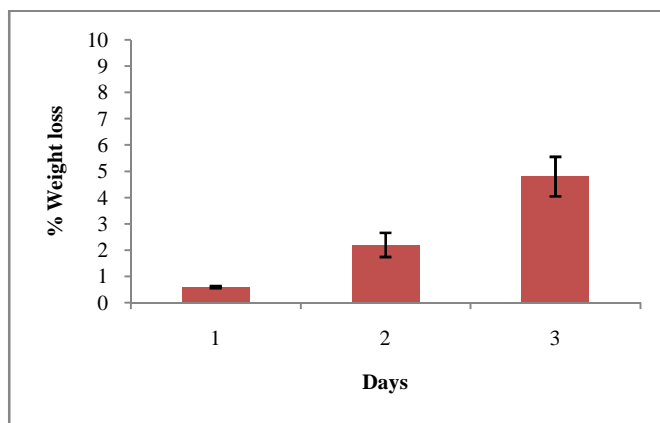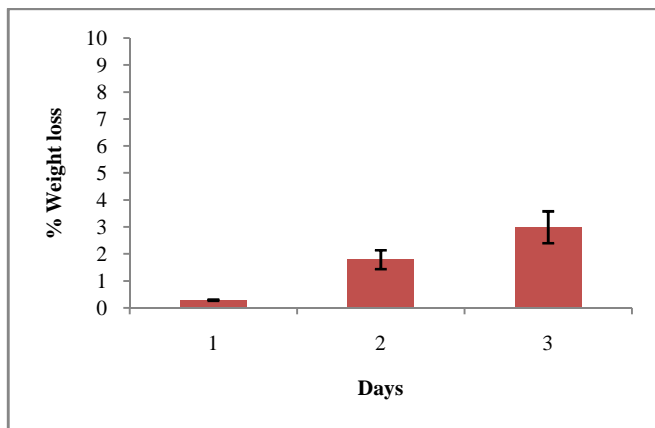**Figure 6A** Degradation of PMMA-CS blend in enzyme solution

Figure 6B Degradation of PVC-CS blend in enzyme solution

CONCLUSION

As the non-biodegradable polymers has major drawbacks in the environment so, the present research work aimed to

convert non-biodegradable polymers to biodegradable polymers to improve the biodegradability of existed polymers and physic chemical characterization of newly synthesized polymers by chemical modification using suitable a reaction strategy. New chemical methods to improve the biodegradability of polymers CS, PMMA, PVC were explored. Prepared blends were characterized by using TLC, FTIR, NMR, DSC, hydrolytic degradation tests, enzymatic degradation. The TLC, FTIR, NMR and DSC analysis exhibited synthesis of biodegradable blends of PMMA and PVC. Both blends demonstrated effective hydrolytic and enzymatic degradations. The inclusion of CS in these polymers was discovered to enhance their hydrolytic breakdown.

Competing interest

The authors declare that they have no competing interests.

References

1. Lu, T.S., Sun, Y.M., Wang, C.S. Novel copolyesters containing naphthalene structure. II. Copolyesters prepared from 2, 6-dimethyl naphthalate, 1, 4-dimethyl terephthalate, and ethyleneglycol. *J. Polym. Sci. A* 1995, 33, 2841-2850.

2. Raquez, J.M., Nabar, Y., Narayan, R., Dubois, P. Novel high-performance talc/poly[(butylenes adipate)-co-terephthalate)] hybrid materials. Macromol. Mater. Eng. 2008, 293, 310-320.

3. Ulery, B.D., Nair, L.S., Laurencin, C.T. Biomedical applications of biodegradable polymers. *J. Polym. Sci. Part B* 2011, 49, 832-864.

4. Seyednejad, H., Ghassemi, A.H., van Nostrum, C.F., Vermonden, T., Hennink, W.E. Functional aliphatic polyesters for biomedical and pharmaceutical applications. J. Control. Release 2011, 152, 168-176.

5. Vert, M. Aliphatic polyesters: Great degradable polymers that cannot do everything. Biomacromolecules 2005, 6, 538-546.

6. Bezwada, R. S., Jamiolkowski, D. D., Lee, I.Y., Agarwal, V., Persivale, J., Trenka- Benthin, S., Erneta, M., Suryadevara, J., Yang, A., Liu, S. Monocryl® suture, a new ultrapliable absorbable monofilament suture. Biomaterials 1995, 16 (15), 1141-1148.

7. Nair, L. S., Laurencin, C. T. Biodegradable polymers as biomaterials. Progress in Polymer Science 2007, 32 (8–9), 762-798.

8. Estey, T., Kang, J., Schwendeman, S. P., Carpenter, J. F. BSA degradation under acidic conditions: a model for protein instability during release from PLGA delivery systems. *Journal of Pharmaceutical Sciences* 2006, 95 (7), 1626-1639.

9. Gisha E.L. Novel approaches to biodegradable polymers: Synthesis and biodegradation studies 2006; 3-25.

10. Wendy A., Allan A., Brian T. Polymer International Vol.47 No.2,1998: A Review of Biodegradable Polymers, 108-112.

11. Phatale, T., Agnigotri, J., A. Khale. Technical advancement in biodegradable polymers and their recent patents. International Journal of Sciences and Research, 2014,37-39, 42,43.

12. Zhong, Y., Zeberl, B.J., wang, X., Luo, J.. Combinatorial approaches in post-polymerization modification for rational development of therapeutic delivery systems, Acta Biomaterialia (2018), 45-48.

13. Stefani, F. B. Delivery systems using preformed biodegradable polymer compositions and methods WO 2001060335 A2(2001).

14. Daniel, S. K. Methods, devices, and systems for on-demand ultrasound-triggered drug delivery, US 20130041311 A1, (2013).

15. Andreas, B., Drug delivery device with biodegradable plastic components. US20130023830 A1(2013).

16. You, Y., Min, B.M., Lee, S.J., Lee, T.S., Park, W.H. In-vitro degradation behavior of electrospun polyglycolide, polylactide, and poly (lactide-co-glycolide). Journal of Applied Polymer Science. (2005) 95 (2):193-200.

17. Guelcher, S.A., Srinivasan, A., Dumas, J.E., Didier, J.E., McBride, S., Hollinger, J.O. Synthesis, mechanical properties, biocompatibility, and biodegradation of polyurethane networks from lysine polyisocyanates. Biomaterials. (2008) 29 (12):1762-1775.

18. Lipika, V.T., Konga, J.F., Chattopadhyaya, S., Widjajaa, L.K., Liowa, S.S., Venkatramana, S.S. Thermoplastic biodegradable elastomers based on e-caprolactone andL-lactide block co-polymers: A new synthetic approach. Acta Biomaterialia. (2010) 6:4261–4270.

19. Grad, S., Kupcsik, L., Gorna, K., Gogolewski, S., Alini, M. The use of biodegradable polyurethane scaffolds for cartilage tissue engineering: potential and limitations. Biomaterials. (2003) 24 (28):5163-5171.

20. Middleton JC, Tipton AJ. Synthetic biodegradable polymers as orthopedic devices. Biomaterials. (2000) 21 (23):2335-2346.

21. Patel, H., Bonde, M., Srinivasan, G. Biodegradable polymer scaffold for tissue engineering. trends in biomaterials and artificial organs. (2011) 25 (1):20- 29.

22. Krishna, B., Selva, K. Biodegradability of PMMA blends with some cellulose derivatives. *J Polym Environ* (2006) 14:385-392.

23. Atkins, K. M., Lopez, D., Knight, D. K., Mequanint, K., Gillies, E. R. A versatile approach for the syntheses of poly (ester amide)s with pendant functional groups. *Journal of Polymer Science Part A: Polymer Chemistry* 2009, 47 (15), 3757-3772.