



Thermal, Morphological and Biodegradable Properties of PVAc/PLA Bioblends

SANJAY K. SINGH*, PRASHANT ANTHONY and ABHISHEK CHOWDHURY

Department of Chemistry, Sam Higginbottom University of Agriculture, Technology & Sciences, Allahabad-211 007, India

*Corresponding author: E-mail: sanjay86in@gmail.com

Received: 24 April 2018;

Accepted: 29 May 2018;

Published online: 31 July 2018;

AJC-19017

In this work, PVAc/PLA blends films were prepared by solution casting methods. The characteristics of PVAc/PLA blend films were analyzed for thermal properties by thermogravimetric analysis, morphology of blends film by scanning electron microscope. The biodegradability of blend films were analyzed under controlled condition of soil burial test. The degradability of films was analyzed by visual observation, measuring weight loss and by morphological analysis.

Keywords: Bioblends, Polyvinyl acetate, Polyvinyl alcohol, biodegradation.

INTRODUCTION

Polymer blending is one of most attractive and convenient method to develop new polymeric material with effective desired properties at low cost [1-4]. The property of blends depends on proper miscibility of the polymers. The miscibility of polymers depends on the specific interaction between the polymer constituent [5]. The completely miscible polymers have better properties as compared their constituent polymers. Polyvinyl acetate (PVAc) is an atactic, branched thermoplastic, formed by polymerization of vinyl acetate monomers. It is semi-crystalline, partially hydrophilic copolymer of vinyl alcohol and vinyl acetate. The glass transition temperature (T_g) of PVAc is very low at room temperature and shows good resistance to oxidation and UV-radiation. It is sticky above T_g and brittle below it. It has good adhesion, high tensile strength and hardness and brittleness varies with the molecular weight [6]. It is used mainly in paint industry [7,8] and also used in medical field for drug delivery [9]. In this work we prepared the PVAc/PLA blends by solution casting methods. The thermal stability of blends film was characterized by TGA, morphology of blends film was analyzed by SEM and biodegradability observed by soil burial methods.

EXPERIMENTAL

Polylactic acid (PLA) was prepared in lab. *p*-Xylene, tetrahydrofuran (THF), polyvinyl acetate (PVAc) *i.e.*, methanol

and ethanol were purchased from Central Drug Houses (CDH) and other reagents were of analytical grade and were used without further purification.

Preparation of PVAc/PLA blends: The homogeneous solution of PVAc and PLA was formed in tetrahydrofuran solvent in three different ratios 7:3, 6:4 and 5:5. The solution of PVAc and PLA were mixed at normal temperature after soaking for 12 h. The blends solution was left for 2-3 h and casted onto mould. The solvent was allowed to evaporate at normal condition. The blend films were peeled off from mould and dried in oven at 50 °C for 24 h [10,11].

Soil burial method: The biodegradation of polymeric films were examined by soil burial test method. The prepared soil composition was taken in a suitable container and environmental condition was maintained at 30 ± 2 °C with 20 to 30 % relative humidity. The initial weight (w_0) of specimens was taken on an analytical balance. The test specimens were buried in the prepared soil at least 12.5 cm deep. The weight loss of film samples were studied after a definite interval of time (1 month), washed with water and dried at 85 °C. The degree of biodegradability was assessed by total weight loss of film samples with respect to initial weight of samples.

Scanning electron microscopic: ZIESS (EVO MA 15) scanning electron microscopic (SEM) was used to observe the surface morphological characterization of PVAc/PLA blends films. The specimens were fractured in liquid N_2 and coated with gold before measurement.

Thermogravimetric analysis: The thermal stability of blends sample was analyzed by thermogravimetric analysis. The weight of sample was taken approximately 10-15 mg. The sample was heated from 30 to 600 °C at a heating rate of 50 °C/min.

Soil burial test: The degradation of polymer was characterized by ASTM G 160-98 method. The soil and specimen of polymer film was prepared according to ASTM G 160-98 method.

Weight loss: The weight loss of PVAc and its blends with different constituent of PLA was determined by the % weight loss equation:

$$\text{Weight loss (\%)} = \frac{W_o - W_t}{W_o} \times 100$$

where W_o is the initial weight before buried in soil and W_t after interval burial time t .

RESULTS AND DISCUSSION

PVAc/PLA blends: The PVAc and PLA blends were formed by solution casting method in different ratios of PVAc/PLA such as 7:3, 6:4 and 5:5. Good intermolecular interaction between two polymers revealed the formation of miscible blends. Morphology, thermal stability and biodegradability were analyzed by SEM, TGA and visual observation.

Morphology of PVAc/PLA blend: The SEM micrographs of both pure PVAc and the different blends with PLA are shown in Fig. 1. On observing SEM images of the pure PVAc films and its blends with PLA, the PVAc films have a smooth and uniform surface. But in the blends films we observe

several very small domains of PLA dispersed phase in PVAc matrix distributed in the homogeneous pattern indicating miscible blends formed. The formation of these homogeneous small domains in PVAc matrix indicates strong interfacial interaction force between PVAc and PLA layer leading to no phase separation and hence miscible blends was formed [2,12-14].

Thermal properties of PVAc/PLA blends: The TGA is used to inspect the kinetic parameter such as order of reaction and activation energy and thermal decomposition polymers. On the basis of this parameter the thermal stability of polymer can be determined. According to Zulfiqar & Ahmad [15] and Sivalingam *et al.* [14] like PVC the thermal decomposition of PVAc was also completed into two stages. First stage complete near about 300 °C temperature with elimination of acetic acid by deacetylation process and after deacetylation the stable products polyolefin formed. In the second stage several reactions such as structural degradation, *cis-trans* isomerization, aromatization and cross-linking occurs and produced stable aromatic product like benzene, toluene and naphthalene and aliphatic hydrocarbon. The thermal properties of pure PVAc and its blends were analyzed by the TG graph given in Fig. 2 and TG data given in Table-1 shown the thermal stability of blends decreased with the increases of PLA content in blends. The results indicated the thermal stability of PVAc/PLA blends gradually decreases as compared to pure PVAc.

According to Sivalingam *et al.* [14] the two peaks observed in DTG graph revealed that thermal decomposition of PVAc is complete in two stages. First peak correspond due to elimination of acetic acid by deacetylation process. Second peak

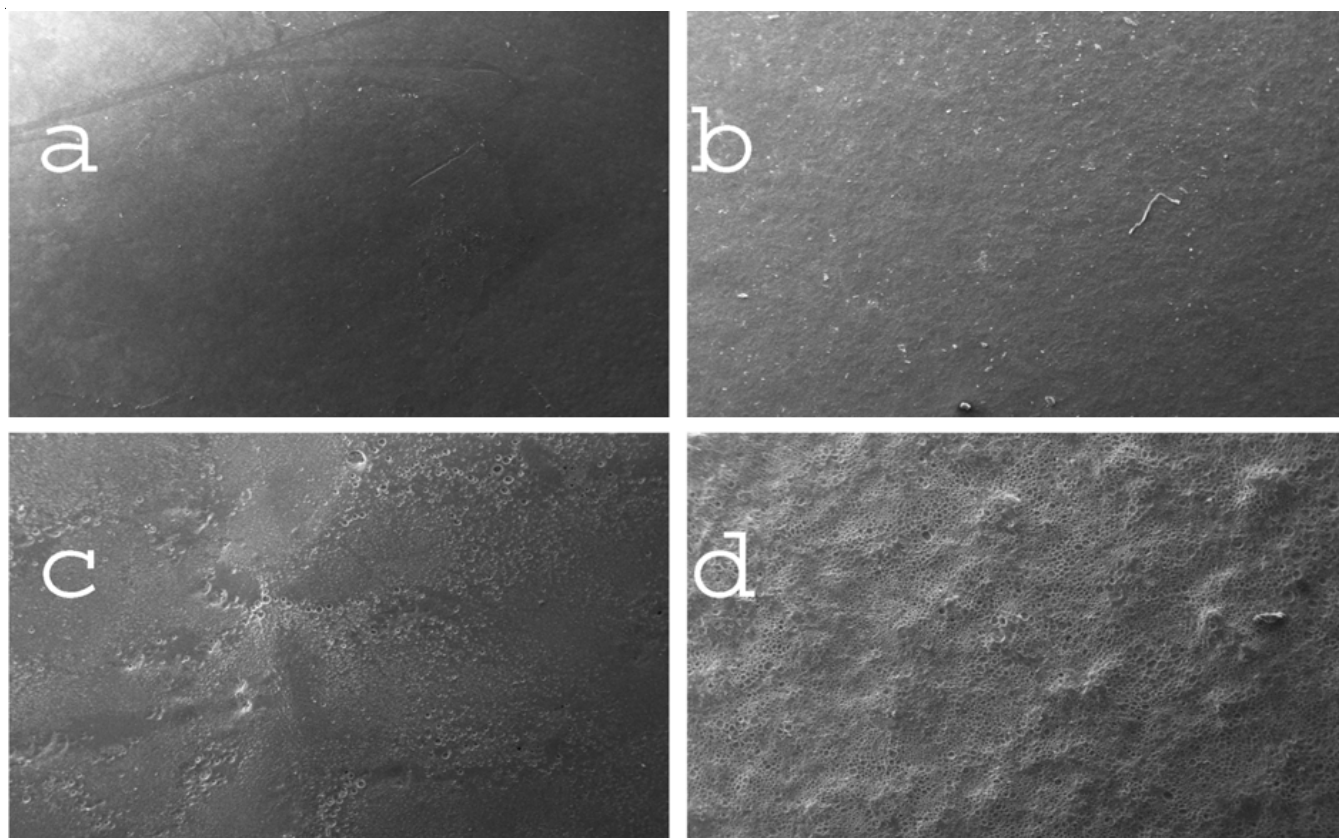


Fig. 1. SEM images (a) pure PVAc (b) PVAc/PLA blend in 7:3 ratio (c) PVAc/PLA blend in 6:4 ratio (d) PVAc/PLA blend in 5:5 ratio

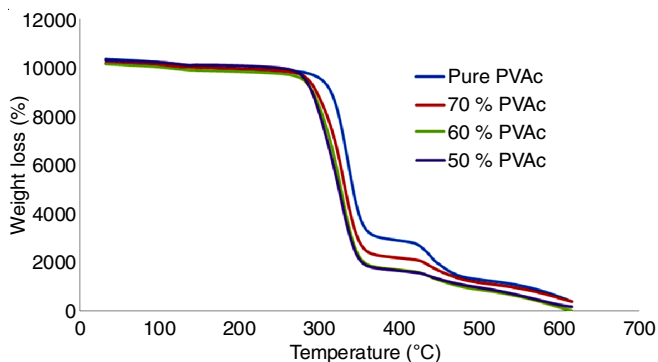


Fig. 2. TG graph of pure PVAc and its blends with different PLA content

PVAc/PLA blends	Temperature (°C) at different weight loss				
	10 %	50 %	70 %	75 %	90 %
100/0	300	325	365	420	500
80/20	278	322	361	415	490
70/30	271	320	358	411	488
60/40	268	317	353	408	485
50/50	261	314	349	405	479

correspond due decomposition of polyolefine into aromatic and aliphatic hydrocarbon. In this study on comparing the DTG Fig. 3 of Pure PVAc with its different blends with PLA it was observed that the corresponding peaks of blend decreased with the increase of PLA content in blends indicated that thermal stability of blends decreases.

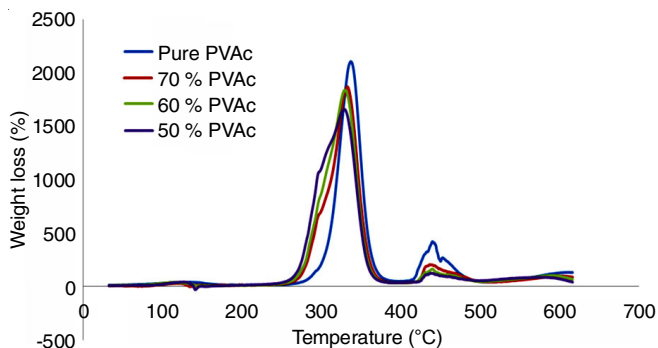


Fig. 3. DTG graph of pure PVAc and its blends with different PLA composition

Visual observation: Many researchers [16-18] in their studies have indicated that the degradation rate of degradable and non-degradable polymers blends increased with increase of biodegradable polymer content. PVAc do not degrade easily by action of microorganism. The degradation of PLA provided a pathway to the disruption of the interfacial interaction between PLA and PVAc and microorganism could easily get diffused into blend by the way of disrupted part of blend films. The several cracks and holes were formed in blend due to the degradation of PLA. Therefore the degradation of PVAc also started with the passage of time period as shown in Fig. 4 and Table-2. After about 8 months the polymeric blend film of 5/5 composition was degraded 56.73 %, the film of 6/4 composition degrade 47.25 %, the film of 7/3 composition degrade 35.42 %. On observing the degradation rate of different

blends composition it was found that when the % of PLA increased in polymeric blend the degradation rate was also found to increase.

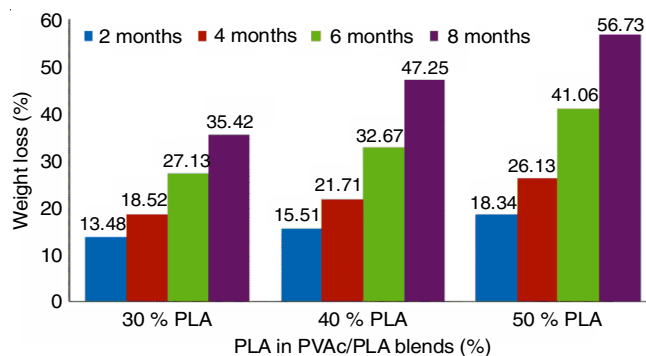


Fig. 4. Weight loss (%) of pure PVAc and its PVAc/PLA blends with different PLA content for different time duration in soil

PVAc/PLA	Weight loss (%)			
	2 months	4 months	6 months	8 months
70/30	13.43	18.52	27.13	35.13
60/40	15.51	21.71	32.67	41.06
50/50	18.34	26.13	47.25	56.73

Morphology of biodegradable blends films: The morphological changes in pure PVAc and blends of PVAc/PLA films before biodegradation and after biodegradation were analyzed by scanning electron microscopy the SEM micrographs are shown in Figs. 1 and 5. In the pure PVAc film, there was no significant change observed on the surface of film after 8 months under the soil. On the other hand in PVAc/PLA blends the degradation commenced due to presence of PLA. The disruption at the surface of blend was observed after degradation by soil burial method. There some erodes, holes and cracks were observed on the surface of PVAc/PLA blends films. The degree of disruption of blend surface also increases gradually with the increasing degradation time. With an increase of PLA composition in blends the cracking at the surface of blends increased. With the passing degradation time the microbes and water molecule penetrate into a blend through these holes and cracks, which increased the contact area between blends surface, microbes and water and accelerates the degradation.

Conclusion

In this work we prepared PVAc/PLA blends by solution casting methods. The thermal properties of blends was analyzed by thermogravimetric analysis and the results revealed that the PVAc thermally degrade in two stage, first stage deacetylation process and second stage structural degradation, *cis-trans* isomerization, aromatization and cross-linking process occur. The thermal stability of blends decreased with the increases of PLA content in blends *i.e.* the thermal stability of pure PVAc more as compared to PVAc/PLA blends. Another hand on observing the biodegradability of pure PVAc and its blends with PLA, the results indicate that the degradation of blends film increased with increases of PLA content in blends.

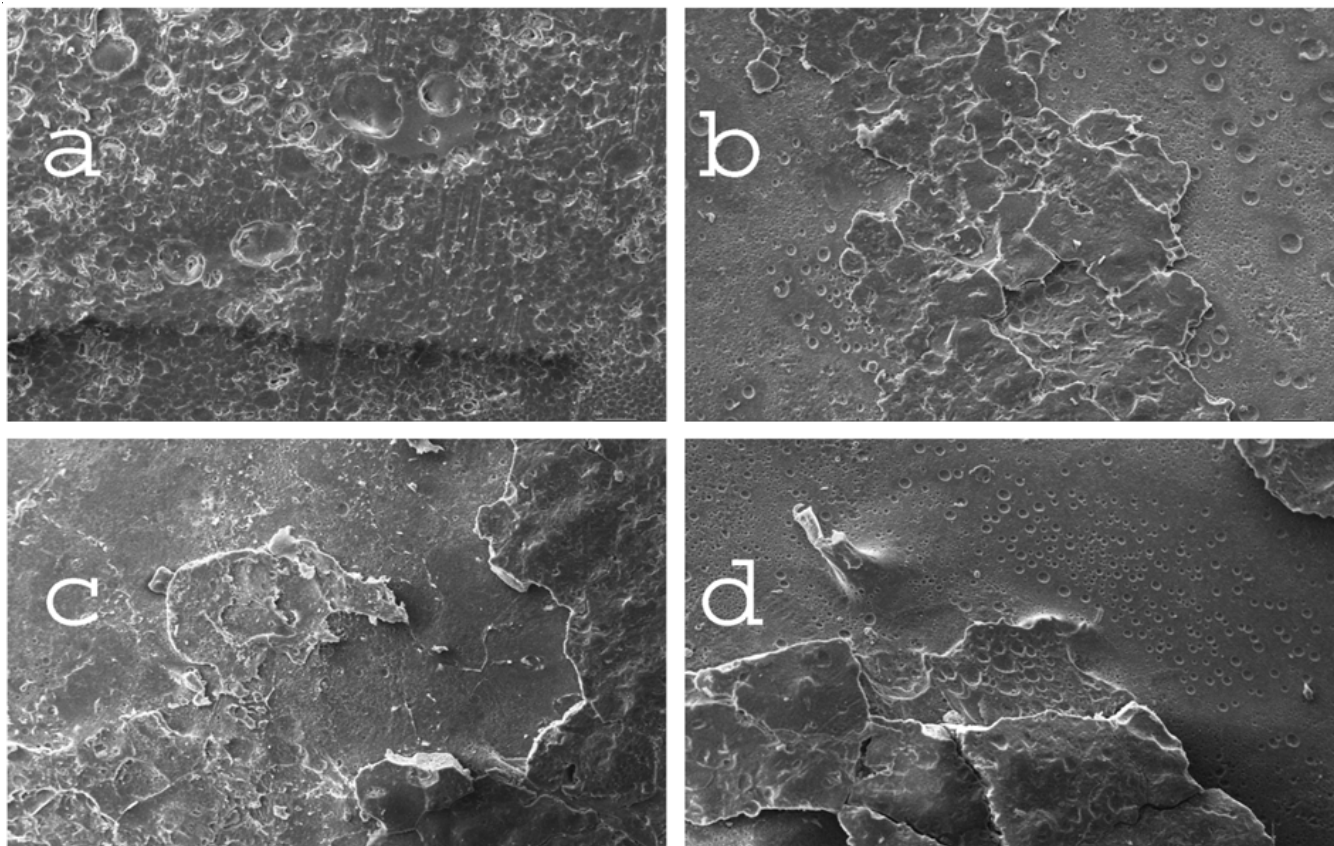


Fig. 5. SEM images after degradation of pure PVAc and its blends in different PVAc/PLA ratios (a) 10/0 (b) 7/3 (c) 6/4 and (d) 5/5

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. R.M. Ahmed, *Int. J. Photoenergy*, **Article ID 150389** (2009); <https://doi.org/10.1155/2009/150389>.
2. J. Gao, H. Bai, Q. Zhang, Y. Gao, L. Chen and Q. Fu, *Express Polym. Lett.*, **6**, 860 (2012); <https://doi.org/10.3144/expresspolymlett.2012.92>.
3. M. Peesan, P. Supaphol and R.J. Rujiravanit, *Appl. Polym. Sci.*, **105**, 1844 (2007); <https://doi.org/10.1002/app.26341>.
4. R. Baskaran, S. Selvasekarapandian, N. Kuwata, J. Kawamura and T. Hattori, *Solid State Ion.*, **177**, 2679 (2006); <https://doi.org/10.1016/j.ssi.2006.04.013>.
5. A. Azmar, F. Saaïd and T. Winie, *Mater. Today*, **4**, 5100 (2017); <https://doi.org/10.1016/j.matpr.2017.05.014>.
6. P. Sedivka, J. Bomba, M. Bohm and P. Boska, *BioResources*, **10**, 3999 (2015); <https://doi.org/10.15376/biores.10.3.3999-4010>.
7. J. Bentley and G.P.A. Turner, *Introduction to Paint Chemistry and Principles of Paint Technology*, London, Chapman & Hall, edn 4, pp. 91-187 (1998).
8. L. Qiao and A.J. Easteal, *Pigment Resin Technol.*, **30**, 79 (2001); <https://doi.org/10.1108/03699420110381599>.
9. F. Zhang and J.W. McGinity, *Drug. Dev. Ind. Pharm.*, **26**, 931 (2000).
10. S. Chattopadhyay, *J. Appl. Polym. Sci.*, **77**, 880 (2000); [https://doi.org/10.1002/\(SICI\)1097-4628\(20000725\)77:4<880::AID-APP23>3.0.CO;2-3](https://doi.org/10.1002/(SICI)1097-4628(20000725)77:4<880::AID-APP23>3.0.CO;2-3).
11. S.R. Vashishtha, N. Chand and S.A.R. Hashmi, *Indian J. Chem. Technol.*, **9**, 316 (2002).
12. A.M. Gajria, V. Dave, R.A. Gross and S.P. McCarthy, *Polymer*, **37**, 437 (1996); [https://doi.org/10.1016/0032-3861\(96\)82913-2](https://doi.org/10.1016/0032-3861(96)82913-2).
13. E.S. Park, H.K. Lee, H.J. Choi, D.C. Lee, I.J. Chin, K.H. Lee, C. Kim and J.S. Yoon, *Eur. Polym. J.*, **37**, 367 (2001); [https://doi.org/10.1016/S0014-3057\(00\)00120-8](https://doi.org/10.1016/S0014-3057(00)00120-8).
14. G. Sivalingam, R. Karthik and G. Madra, *Polym. Degrad. Stab.*, **84**, 345 (2004); <https://doi.org/10.1016/j.polymdegradstab.2004.01.011>.
15. S. Zulfiqar and S. Ahmad, *Polym. Degrad. Stab.*, **71**, 299 (2001); [https://doi.org/10.1016/S0141-3910\(00\)00179-8](https://doi.org/10.1016/S0141-3910(00)00179-8).
16. C.S. Wu, *Polym. Degrad. Stab.*, **80**, 127 (2003); [https://doi.org/10.1016/S0141-3910\(02\)00393-2](https://doi.org/10.1016/S0141-3910(02)00393-2).
17. U. Riaz, A. Vashist, S.A. Ahmad, S. Ahmad and S.M. Ashraf, *Biomass Bioenergy*, **34**, 396 (2010); <https://doi.org/10.1016/j.biombioe.2009.12.002>.
18. I. Kaur, B.N. Misra, M.S. Chauhan, S. Chauhan and A. Gupta, *J. Appl. Polym. Sci.*, **59**, 389 (1996); [https://doi.org/10.1002/\(SICI\)1097-4628\(19960118\)59:3<389::AID-APP2>3.0.CO;2-L](https://doi.org/10.1002/(SICI)1097-4628(19960118)59:3<389::AID-APP2>3.0.CO;2-L).