Malaysian Journal of Fundamental and Applied Sciences Vol.10, No.1 (2014) 33-36

MJFAS Malaysian Journal of Fundamental and Applied Sciences UTM
ISSN:2289-5981 e-ISSN:2289-599X

Effect of different solvents on the thermal, IR spectroscopy and morphological properties of solution casted PLA/starch films

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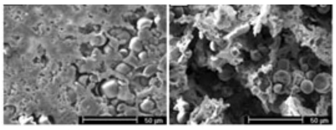
Article history :
Received 2 January 2013
Revised 19 June 2013
Accepted 1 July 2013
Available online 2 August 2013

GRAPHICAL ABSTRACT



ABSTRACT

PLA/starch films were prepared by using three different solvent which is consist of chloroform, acetonitrile, and tetrahydrofuran. Similarly, composite films prepared using co-solvent of choloroform-acetonitrile (C-Ac) and choloroform- tetrahydrofuran (C-THF) were also investigated. Their properties were characterized by using TGA, DSC, IR spectroscopy and SEM. It was found that the acetonitrile casted biodegradable film achieved superior properties compared to films prepared by Ac, THF, C-Ac and C-THF.

Keywords: Polylactic acid, Starch, Morphological, Thermal, Film

http://dx.doi.org/10.11113/mjfas.v10n1.67

1. INTRODUCTION

Polylactic acid (PLA) is a thermoplastic, high-strength, high-modulus polymer that can be made from renewable materials for either industrial field or medical device market [1]. It is also widely used as a biodegradable and renewable plastic [2]. While its biodegradability ranges from several months up to two years compared to synthetic polymers which take 500-1000 years [3].

Starch is a natural polymer, inexpensive, abundant, renewable, thermo-processable, and is often used as filler for the replacement of synthetic polymers [4,5]. It is totally biodegradable which will hydrolyze at the acetal link by the actions of enzymes [6]. Commercial starches are obtained from grains such as corn and rice or from tubers like tapioca and potato.

Since PLA is expensive due to complicated process [5], the modification of PLA favors a cost effective process, for example the blending of PLA with starch as a filler. The introduction of starch to polyester-starch blends can maintain the great physical properties of the polyester, at the same time, reducing cost [5,7,8]. Besides that, the addition of starch to PLA can boost moisture absorption, thus, improving fragmentation and biodegradation of the film [7,9].

In addition, PLA also has better thermal processability compared to other biopolymers and can be processed by extrusion, injection moulding, blow moulding, thermoforming, fiber spinning, and film forming [10,11]. Solvent casting technique has been a widely used technique to prepare film. This technique involves solubilization, casting and drying [11].

PLA is soluble in most organic solvents for example acetonitrile, chloroform, dichloromethane, and tetrahydrofuran [11]. Hughes et.al. (2012) reported series of PLA films casted by mixing dichloromethane with various percentage of acetonitrile. They found that the addition of acetonitrile up to 50% gave the most thermally stable film [12]. At the same time, a study done by Byun et.al. (2012) also found PLA film casted with dichloromethane: acetonitrile (50:50 v/v%) to be the most thermally stable film compared to chloroform and dichloromethane alone [13]. However, none had form PLA blended with starch films. It is the objective of this research to investigate the effect of starch on the PLA film and mainly to investigate the effect of different solvents on the PLA/starch film.

2. EXPERIMENTAL

2.1 Materials

PLA resin (3052D) with injection molding grade was purchased from NatureWorks, LLC (MN). Tapioca starch with food grade was purchased from ThyeHuat Chan Sdn. Bhd. (M). The solvents, chloroform, acetonitrile and tetrahydrofuran were purchased from J.T Baker (USA).

2.2 Film preparation

The films were prepared by using solvent casting method. PLA and starch were premixed by 80:20w/w% ratios in a beaker before solvents or co-solvents were poured into the beaker. The solvents used in this study were chloroform, acetonitrile and tetrahydrofuran, while the co-solvents were chloroform-acetonitrile (C-Ac) and chloroform-tetrahydrofuran (C-THF). The co-solvents were mixed by 50:50 v/v% ratios. Then, the mixtures were stirred for 12 hours before casting. The casted films were dried at ambient temperature for 12 hours before were peeled from the casting surface. Detail information of the films is listed in Table 1

Table 1. PLA films designations, materials and solvents.

Films	Materials (w/w%)	Solvents/co-solvents (v/v%)
PLA (control)	PLA (100)	Chloroform (100)
PLA80	PLA/starch (80/20)	Chloroform (100)
PLA-Ac	PLA/starch (80/20)	Acetonitrile (100)
PLA-THF	PLA/starch (80/20)	Tetrahydrofuran (100)
PLA-C-Ac	PLA/starch (80/20)	Chloroform-Acetonitrile (50/50)
PLA-C-THF	PLA/starch (80/20)	Chloroform- Tetrahydrofuran (50/50)

2.3 Thermal analysis

The thermogravimetry analysis (TGA) analysis of the films was done on Perkin Elmer TGA 7 under nitrogen environment at a rate of 20 mL min^{-1}. Approximately 20 mg of each sample was analyzed from ambient temperature up to 650°C at a heating rate of 10°C min^{-1}.The differential scanning calorimetry (DSC) analysis of the films was done on Perkin Elmer DSC 7. Around 5 mg of each sample were sealed in an aluminium pan and heated from 10°C to 200°C at 10°C min^{-1}.

2.4 Fourier-transform infrared spectroscopy (FTIR)

FTIR spectra of the PLA/starch films were obtained from Perkin Elmer Spectra GX. The spectra were collected within 4000 – 400 cm^{-1} region with resolution of 8 cm^{-1} and 32 scans. Automatic smooth and baseline correction were applied for all spectra.

2.5 Scanning electron microscope (SEM)

SEM images of the films were taken by Hitachi Tabletop SEM TM3000. Prior to analysis, each sample was sputter-coated with gold in order to prevent electrical discharge.

3. RESULTS AND DISCUSSIONS

3.1 Thermal analysis

Thermal stability of the PLA films was investigated by using TGA. The thermograms are illustrated in Figure 1 and it is obvious that PLA80 and PLA-C-Ac loss approximately 5% of their weight in the beginning of the heating process. This is due to the removal of entrapped solvent within the films during casting process. The thermograms also showed that PLA-Ac has the highest onset temperature (degradation temperature, T_D) which is 363°C compared to other films, thus is the most thermally stable film. The T_D values for each film can be found in Table 2.

Table 2 T_m, ΔH_m and T_D values of PLA films.

	PLA-c	PLA80	PLA-Ac	PLA-THF	PLA-C-Ac	PLA-C-THF
T_m (°C)	135	135	135	136	136	136
ΔH_m (J/g)	10	13	24	7	8	10
T_D (°C)	315	300	363	257	346	350

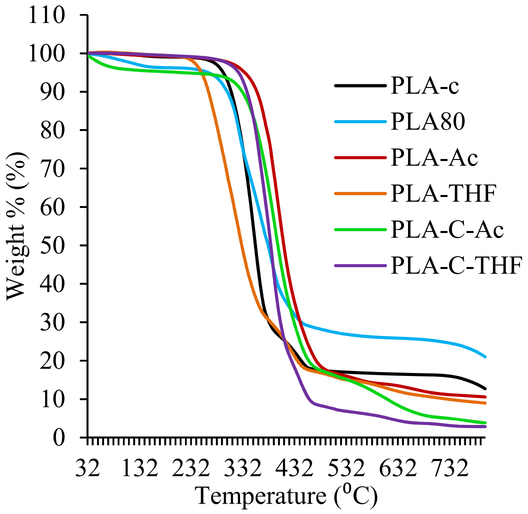


Fig. 1 TGA thermograms of PLA films with different solvents.

Thermal transition properties for each film were examined by using DSC and the results are showed in Figure 2 and Table 2. The DSC thermograms in Figure 2 showed three obvious peaks for each thermogram except for PLA-c film with only two peaks. First peak appeared approximately at 90°C which is assumed to be the melting temperature (T_m) of additive within PLA, while the second peak appears to be the T_m of starch. Apparently, T_m and ΔH_m of starch is influenced by different casting solution as in Table 3. It seems that chloroform has low interaction with starch since it has the lowest T_m and ΔH_m. On the other hand, acetonitrile and tetrahydrofuran have great interaction with starch with their elevated T_m and ΔH_m. It appears that tetrahydrofuran has stronger interaction with starch than chloroform given that its ΔH_m is higher than that chloroform. There is a small decrease in ΔH_m when co-solvent C-Ac and C-THF were used. This is probably chloroform disrupts the interaction between acetonitrile and tetrahydrofuran with starch

The third peak is the T_m of PLA film. There is no significant change on T_m with different solvent during casting process. This is in agreement with Rhim et.al. (2006) and Vasanthan et.al. (2011) [11,15].However, there are great differences in ΔH_m as in Table 2. Between PLA-c and PLA80 small difference is observed, 10 J/g and 13 J/grespectively. This small increase is due to small interaction between PLA and starch within PLA80. A drastic increase in ΔH_m for PLA-Ac (24 J/g) is observed. This data is coincides with high ΔH_m of starch in acetonitrile (Table 3) and thus, proves acetonitrile has great intermolecular interaction with PLA and starch. But, compared to PLA-C-Ac, a huge difference is observed where its ΔH_m is far much smaller (8 J/g) than PLA-Ac. This further proved that chloroform interrupts the interaction between acetonitrile, PLA and starch. On the contrary, PLA-THF and PLA-C-THF have similar very small ΔH_m values, 7 J/g and 10 J/g respectively. The small increase observed in PLA-C-THF value shows that there is some interaction between chloroform and tetrahydrofuran that promotes more interaction with PLA.

Table 3 T_m and ΔH_m values of starch within PLA films.

Starch in PLA films	PLA-c	PLA80	PLA-Ac	PLA-THF	PLA-C-Ac	PLA-C-THF
T_m (°C)	N/A	96	110	110	110	110
ΔH_m (J/g)	N/A	0.74	1.18	1.28	1.04	0.71

3.2 Fourier-transform infrared spectroscopy (FTIR)

FTIR spectroscopy was used to investigate the structural changes of PLA during casting with different solvent used. FTIR spectra are illustrated in Figure 3. There are four common peak bands can be seen, 3300, 3000, 2950, and 1750 cm^{-1} corresponding to OH stretching, CH stretching (doublet) and C=O carbonyl stretching [14]. It is clear that the transmittance of OH stretching is increasing from PLA-c to PLA-C-THF. This shows that PLA-C-THF film has the ability to absorb more moisture than other films. Aside from that, C=O stretching for PLA-Ac film seems to be dull. This most probably that acetonitrile interacts more with carbonyl group within PLA. Acetonitrile reacts with a base (hydroxyl group, most likely contributed by moisture trapped within the film) with an α-hydrogen at an α-carbon to produce a carbanion, a nucleophile (an electron-rich compound). This reactive carbanion nucleophile is then attacks the electrophile (an electron deficient compound) which is produced from electron delocalization of a carbonyl group within PLA, as illustrated in Figure 4.

3.3 Scanning electron microscope (SEM)

SEM was done to investigate the morphology of the solvent casted films. The micrograph images are illustrated in Figure 5. It is clear that each images show different type of morphology, as in PLA-C-Ac and PLA-C-THF there are big pores and holes across the surfaces. These explain the high transmittance at 3300 cm^{-1} in FTIR spectra where these pores and holes entrapped a lot of moisture. Quite smooth surfaces can be observed on PLA-c, PLA80 and PLA-THF, and rough on PLA-Ac. The smooth surface probably contributed from only PLA chains while the rough surfaces probably contributed from the interaction of PLA chains with starch chains. Fairly the same phenomenon can be seen on PLA-C-Ac and PLA-C-THF surfaces.

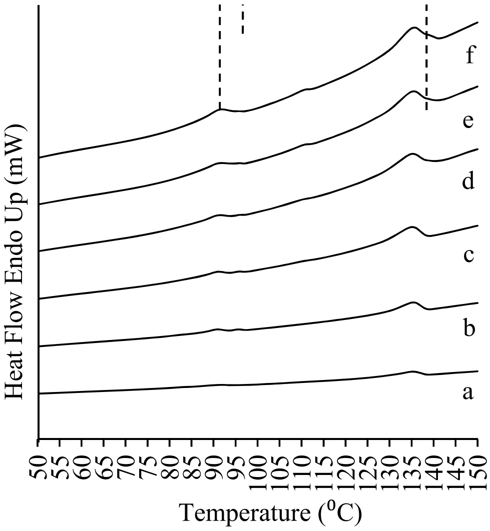


Fig. 2 DSC thermograms of PLA films with different solvents. a) PLA-c b) PLA80 c) PLA-Ac d) PLA-THF e) PLA-C-Ac f) PLA-C- THF.

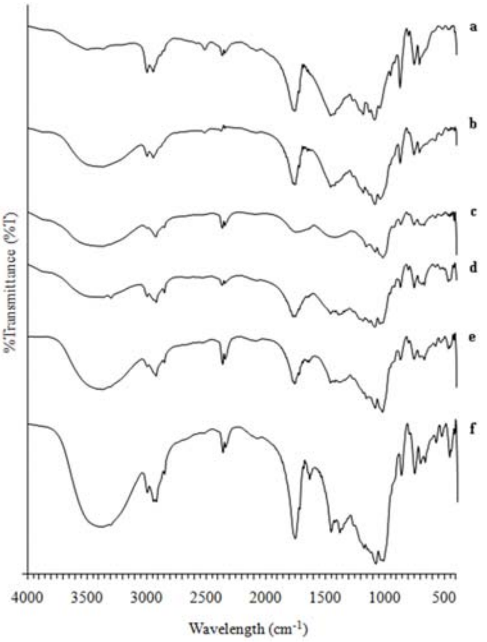


Fig. 3 FTIR spectra of solvent casted PLA films. a) PLA-c b) PLA80 c) PLA-Ac d) PLA-THF e) PLA-C-Ac f) PLA-C-THF.

Apart from that, it is also clear that the starch granules for each film are different in shape and size. A more uniform shape and size can be observed on the film casted with acetonitrile, tetrahydrofuran and their co-solvents. This is consistence with the DSC data on starch T_m (Table 3) where starch interacts more with acetonitrile, tetrahydrofuran and their co-solvents.

Table 4 Peak band assignment for PLA films FTIR spectra.

Peak	Peak band (cm^{-1})	Peak assignment
a	3300	-OH stretch
b	3000, 2950	-CH- stretch (doublet)
c	1750	-C=O carbonyl stretch

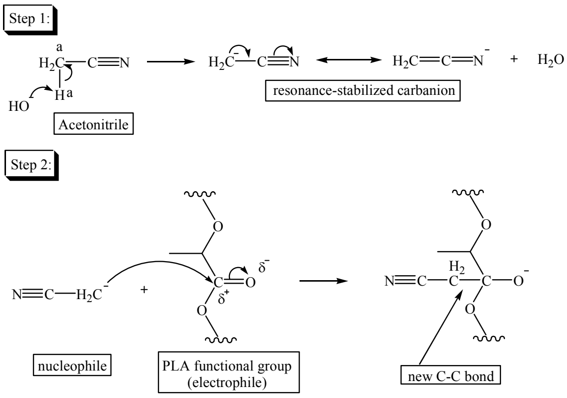


Fig. 4 Suggested interaction between acetonitrile with PLA carbonyl functional group.

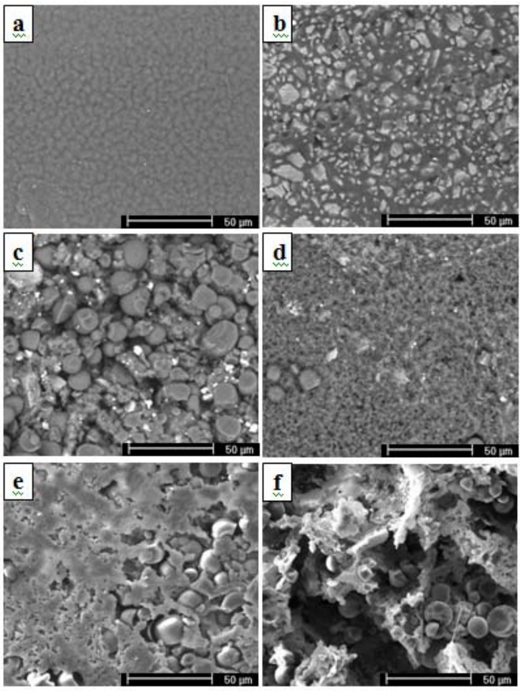


Fig. 5 SEM micrograph images of the solvent casted PLA/starch films. a) PLA-c b) PLA80 c) PLA-Ac d) PLA-THF e) PLA-C-Ac f) PLA-C-Ac.

4. CONCLUSION

It is obvious that the properties of PLA/starch films not only rely on the solvent used but also the filler (starch) used for solvent casting method. The interaction between PLA, solvents, and starch is important to ensure improved properties of the films. PLA-Ac film had the highest T_D, T_m, and ΔH_m values by having the most interaction between PLA, acetonitrile, and starch. Conclusively, the properties of PLA films can be altered by changing the solvent and the filler to the desired applications.

ACKNOWLEDGEMENT

The authors thank the Department of Polymer Engineering, Faculty of Chemical Engineering, Faculty of Mechanical Engineering, and Ibnu Sina Institute, Universiti Teknologi Malaysia, Johor for instrumentations as well as to Malaysian Government (GUP) vot 00H07 for funding the project.

REFERENCES

[1] D. Garlotta. J. Polym. Env. 9 (2001), 63.
[2] Q. Fang, and M.A. Hanna. J. Ind. Crops Prod. 13 (2001) 219.
[3] H. Wang, X.Z. Sun, and P. Seip. J. Appl. Polym. Sci. 82 (2001) 1761.
[4] D. Garlotta, W. Doane, R. Shogren, J. Lawton, and J.L. Willett. J. Appl. Polym. Sci. 88 (2003) 1775.
[5] S.Y. Lee, and M.A. Hanna.J. Appl. Polym. Sci. 110 (2008) 2337.
[6] I. Spiridon, M.C. Popescu, R. Bodarlau, and C. Vasile. Polym. Degrad. Stab. 93 (2008) 1884.
[7] G.H. Yew, A.M. Mohd Yusof, Z.A. Mohd Ishak, and U.S. Ishiaku. J. Polym. Degrad. Stab. 90 (2005) 488.
[8] L.Yu, E. Petinakis, K. Dean, H.Liu, and Q. Yuan. J. Appl. Polym. Sci. 119 (2011) 2189.
[9] J.L Willet and R.L Shogren Polymer 43 (2002) 5935.
[10] R. Auras, B. Harte, and S. Selke. Macromol. Biosci. 4 (2004) 835.
[11] J-W. Rhim, A.K. Mohanty, S.P. Singh, and P.K.W. Ng. J. Appl. Polym. Sci. 101 (2006) 3736.
[12] J. Hughes, R. Thomas, Y. Byun, and S. Whiteside. J. Carb. Polym. 88 (2012)165.
[13] Y. Byun, S. Whiteside, R. Thomas, M. Dharman, J. Hughes, and Y.T. Kim. J. Appl. Polym. Sci. 124 (2012) 3577.
[14] J-T. Yeh, C-H. Tsou, Y-M. Li, H-W. Xiao, C-S. Wu, W-L. Chai, Y-C. Lai, and C-K. Wang. J. Polym. Res. 19 (2012) 9766.
[15] N. Vasanthan, H. Ly, and S. Ghosh. J. Phys. Chem. B. 115 (2011) 9556.