The 2014 World Congress on
Advances in Civil, Environmental, and Materials Research (ACEM14)
Busan, Korea, August 24-28, 2014

Effect of maleic anhydride on the physical properties of bio-based poly(oxalate - co - urethane)

*Cheng-Chien Wang(1) , Yu-Wen Ho(1), Chuh-Yung Chen(2)

(1) *Department of Chemical and Materials Engineering, Southern Taiwan University of Science and Technology, Tainan, 710, Taiwan*
(2) *Department of Chemical Engineering, National Cheng-Kung University, Tainan, 701, Taiwan*
(1) *ccwang@mail.stust.edu.tw*

ABSTRACT

Bio-based polyoxalates (PBOX) with hydroxyl end group were firstly synthesized by using diethyl oxalate and 1, 4-butandiol. The poly(oxalate - co - urethanes) (PBOX-PU) was polymerized by using PBOX reacting with 4,4`-diphenylmethane diisocyanate and polyethylene glycol 2000. PBOX was a highly crystalline polymer with brittle properties after DSC and XRD measurements. In order to destruct the crystallinity of PBOX, maleic anhydride (MA) was introduced into the PBOX segments, name as PBMA. FTIR spectra of the PBOX and PBMA show the characteristic peaks of –NH and C=O of amide group was assigned at 3400 cm^{-1} and 1750 cm^{-1}, respectively. In addition, the characteristic peak of carbon-carbon double bond at 1645 cm^{-1} appeared when MA was introduced into the PBOX. The thermal properties of the PBOX and PBMA were characterized by DSC, and the result indicated T_m was decreased from 102 °C and 78 °C and the $\triangle H_m$ was shifted from 69 J/g to 47 J/g as MA was added. Moreover, the thermal degradation temperature (T_d) of PBOX was increased from 246 °C to 275 °C as MA was added. Interesting, the T_g of PBMA-PU was higher than that of PBOX-PU and the young's modulus of PBMA-PU was lower than that of PBOX-PU when MA was induced into PU matrix. Moreover, the soil degradation rate of the PBOX-PU films would be enhanced twice times after 2 weeks as MA was induced into PBMA-PU.

1. INSTURCTION

The massive use and burn of petroleum based plastics had been seriously caused the environmental pollution and global warming in past twenty years. To develop materials that are renewable, degradable, and recyclable, better known as "green materials," (Albertsson 1988, Dipa 2001, Gassan 1999, Kesel 1997, Mohanty 2002) as alternatives to the petroleum-based materials become a popularly researches topic in polymer industry. Among them, biodegradable and bio-based polymers have attracted great attention because biodegradable and bio-based polymer are the low carbon footprint product and they decompose harmless ingredients as it is disposed on soil or special environments. For example, on a pound-for-pound basis, the production of bio-based propanediol consumes about 40% less energy than the production of its

---

1) Professor

petroleum-based counterpart. (Dupond Co. Ltd.) Polylactic acid (PLA), a plastic substitute made from fermented plant starch (usually corn), is another popular alternative to traditional petroleum-based plastics.

Polyoxalate, which could synthesized by using oxalate and diol, is also belong to bio-based polymer. Carothers et. al. (1930) were firstly proposed the polyoxalate material which was polymerized by using oxalic acid and ethylene diol. The advantages of oxalic acid can benefit the energy saving as well as carbon dioxide reduction because oxalic salt is existed within most of the herbaceous plant, such as spinach, beet, citrus fruits. Hence, the bio-based poly(ester urethanes) was synthesized by the polymerization of polyoxalate, which is prepared by reacting oxalate and diols, with 4,4`-diphenylmethane diisocyanate (MDI) as the chain extender in this study.

2. EXPERIMENTAL

The melt polycondensation polymerization was employed to prepare the polyoxalate and the poly(oxalate - co - urethanes). The polyoxalate was firstly synthesized by using diethyl oxalate and 1, 4-butandiol via transesterification, the poly(butylene oxalate ester) was named as PBOX. On the other hand, 10 wt.% maleic anhydride was introduced into the polyoxalate to prepare poly(oxalate-co-maleic anhydride ester), named as PBMA. Then, the poly(oxalate - co - urethanes) (PBOX-PU) and poly(oxalate-co-maleic anhydride-co-urethane) (PBMA-PU) were polymerized by using PBOX and PBMA reacting with 4,4`-diphenylmethane diisocyanate (MDI) and polyethylene glycol 2000 in presence of $Ti(OBu)_4$ as catalyst, respectively. The average molecular weights and thermal properties of the resulting PBOX and PBMA were characterized by GPC, TGA and DSC. The characteristic of the bio-based poly(ester urethanes) was measured by using FTIR (MATTSON SATELLLIE 5000) and GPC (HITACHI, SEDEX75). The thermal properties of the bio-based poly(ester urethanes) were also detected by using DSC (Perkin Elmer DSC-7) and TGA (Perkin Elmer TGA-7). The weight and viscosity loss of bio-based polymer were employed to calculate the soil degradation rate of PBOX-PU and PBMA-PU in same oblong shape.

3. RESULTS AND DISSCUSSION

Fig. 1 shows the FTIR spectra of PBOX and PBMA. The characteristic peaks of carboxyl group (-C=O), hydroxyl group (-OH) and –C-O-C- group of PBOX is assigned at 1750 cm^{-1}, 3580~3400 cm^{-1} and 1100 cm^{-1}, respectively. As the maleic anhydride was introduced into PBOX, the characteristic peak of carbon carbon double bond was present on 1680 cm^{-1}. Moreover, the 1H-NMR spectrum PBMA also present a new chemical shift at 6.3 ppm which is assigned at carbon carbon double bond, comparing to that of PBOX. The above reuslt reveals the maleic anhydride segments have successfully introduced into the ester main chain of PBOX.

The molecular weight of PBOX and PBMA were 3,800 Da and 5,100 Da and the polydispsion index were 1.73 and 2.55, respectively, from the GPC measurement.

Fig. 2 presents that the heating (Fig.2 (a)) and cooling (Fig.2 (b)) history curves of PBOX and PBMA, respectively. Obviously, the crystallinity of PBMA is lower than PBOX, because the carbon carbon double bond would inhibit the crystallinity of oxalate ester chain. The crystal enthalpy $\triangle H_c$ of bio-based PU was decreased from 33 J/g to 24 J/g in cooling period and the melting enthalpy $\triangle H_m$ decreased from 69 J/g to 47 J/g in heating period. The thermal degradation temperature (T_d) of PBMA was 275 °C which is higher than that of PBOX at 246 °C.

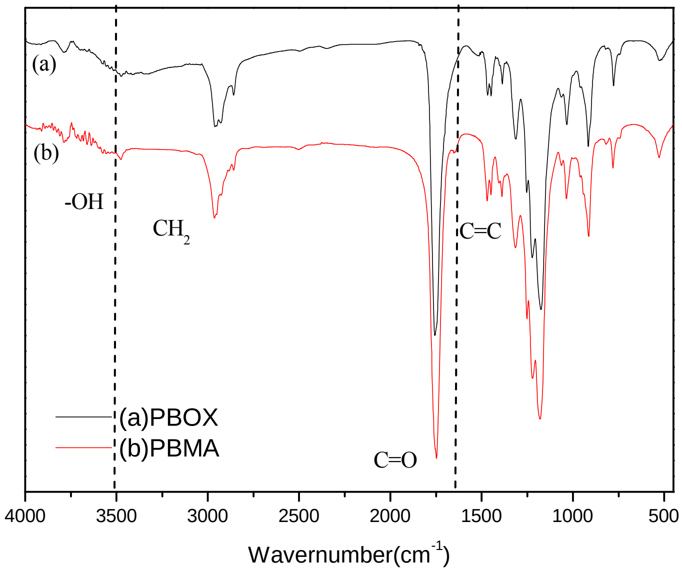
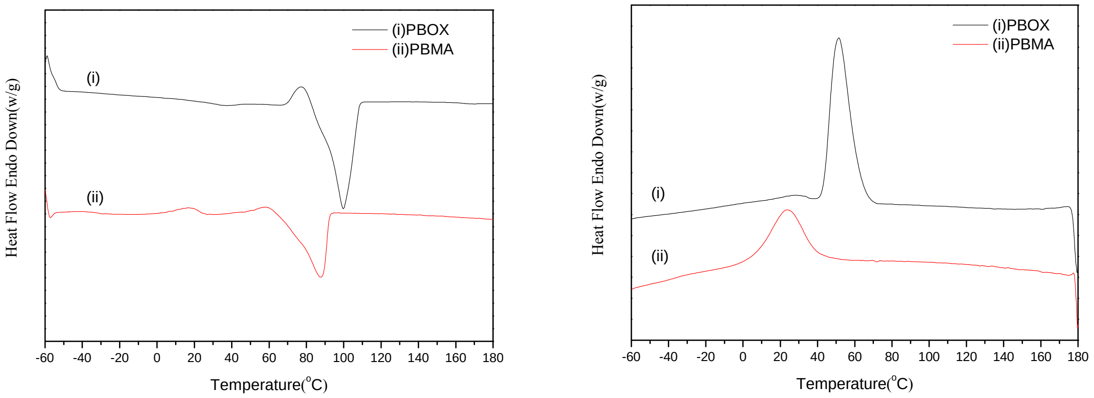


Fig. 1 FTIR spectra of (a) PBOX and (b) PBMA



(a) (b)

Fig. 2 DSC curves of (a) heating and (b) cooling curves of (i)PBOX and (ii)PBMA

Tab. 1 present the viscosity and Tg of PBOX-PU and PBMA-PU. The viscosity of PBMA-PU solution was higher than that of PBOX-PU, which reveals the molecular weight of PBMA-PU was higher than PBOX-PU. In addition, Tg of PBMA was higher than that of PBOX even though the Tg of PBMA is lower than that of PBOX. Furthermore, Tab. 2 shows the mechanical properties of PBOX-PU and PBMA-PU in different polyoxalate ester ratio. When 1.58 mol.% of PBOX was induced into PU polymer, the modulus, tensile strength and elongation at break would be obviously improved. However, the modulus, tensile strength and elongation at break of bio-based PU would be decreased when PBMA was induced into PU. From the above result, the carboxylic acid of MA would seriously influenced on the properties of PU. More maleic anhydride was added, more brittle of PU was obtained. This result may be attributed from the carboxylic acid would form inter- and intra- hydrogen bonding within the domain of PU. There are because why the Tg of PBMA was lower than PBOX, but the Tg of PBMA-PU was higher than that of PBOX-PU.

Tab. 1 Tg and solution viscosity of PBOX-PU and PBMA-PU

Sample	**υ(cp)***	**T_g(°C)**	**Sample**	**υ(cp)***	**T_g(°C)**
0.00 mol% PBOX	2.09	-28	0.00 mol% PBMA	2.09	-28
1.03 mol% PBOX	1.97	-25	0.82 mol% PBMA	2.08	-21
1.58 mol% PBOX	2.19	-11	1.02 mol% PBMA	2.07	-9
3.97 mol% PBOX	1.95	-14	3.31 mol% PBMA	2.05	-11

*****solvent: Choloform; temperature: 30 °C

Tab. 2 The mechanical properties of PBOX-PU and PBMA-PU

Sample	**Young's modulus (MPa)**	**Tensile strength (MPa)**	**Elongation at break (%)**
0.00 mol% PBOX	0.09	5.38	540
1.03 mol% PBOX	0.07	2.68	242
1.58 mol% PBOX	0.11	13.11	1612
3.97 mol% PBOX	0.05	1.41	128
0.82 mol% PBMA	0.09	2.02	50
1.02 mol% PBMA	0.13	1.89	57
3.31 mol% PBMA	0.13	1.85	69

Fig. 3 and Fig. 4 present the weight loss and the viscosity of PBOX-PU and PBMA-PU in soil degradation experiment. We buried the samples of PBOX-PU and PBMA-PU in soil environment and took and analyzed the samples every week. The weight loss tendency of PBOX-PU and PBMA-PU are similarly within two weeks. After that, amount of the weight loss in PBMA-PU is larger than that of in PBOX-PU. In addition, the viscosity of PBOX-PU and PBMA-PU also show a decreasing tendency with the buried times, as shown in Tab. 3. This is attributed from the linearly ester chain was easily degraded in soil environment, thus the molecular weight of PBOX-PU and PBMA-PU was decreased. When MA is introduced into PU matrix, the hydrophility of PBMA-PU would be increased. Higher hydrophilic of matrix means that water and bacteria would be easier penetrate into matrix. Moreover, the thermal degradation temperature of PBOX-PU and PBMA-PU was also decreased with the buried times.

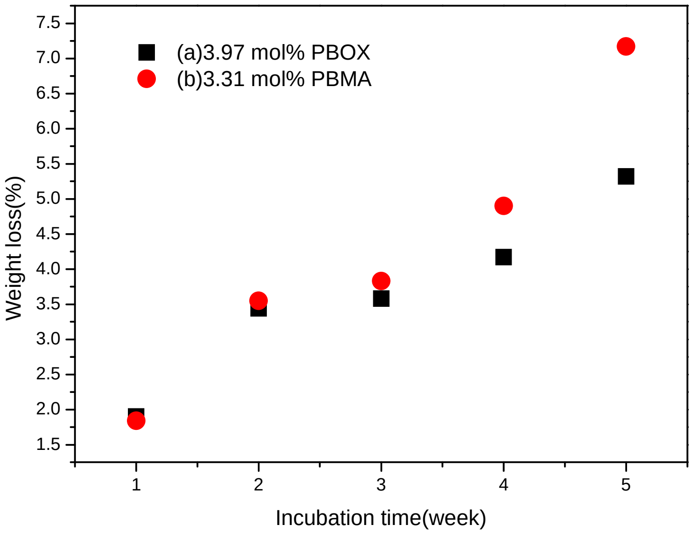


Fig. 3 The weight loss of PBOX-PU and PBMA-PU in soil degradation experiment

Tab. 3 The degradation, viscosity and thermal degradation temperature of PBOX-PU and PBMA-PU samples in soil experiment

Sample	**Degradation rate(%/week)**	**Viscosity(dl/g)**	**T_{d5}(°C)**
3.97 mol% PBOX-1W	1.90	1.93	290
3.97 mol% PBOX-2W	1.72	1.74	287
3.97 mol% PBOX-3W	1.19	1.50	278
3.97 mol% PBOX-4W	1.04	1.46	277
3.97 mol% PBOX-5W	1.06	1.39	268
3.31 mol% PBMA-1W	1.84	2.02	284
3.31 mol% PBMA-2W	1.78	1.84	281
3.31 mol% PBMA-3W	1.28	1.72	273
3.31 mol% PBMA-4W	1.23	1.60	273
3.31 mol% PBMA-5W	1.43	1.53	248

4. CONCLUSIONS

The crystallinity of bio-based the poly(oxalate) was successfully decreased via introducing maleic anhydride segments. When the bio-based poly(oxalate) was introduced into polyurethanes, the physical and mechanical properties of bio-based poly(oxalate - co - urethanes) would be improved. As the maleic anhydride segment was introduced into PU matrix, the physical and mechanical properties of bio-based poly(oxalate - co - urethanes) would be decreased, however, the soil degradation rate would be increased.

ACKNOWLEDGES

The authors would like to thank the Ministry of Economic Affairs of the Republic of China and the Ministry Science and Technology for financially supporting this work under Contract No. TDPA 101-EC-17-A-08-S1-204, NSC100-2221-E-218 -012 -MY2.

REFERENCES

Albertsson A.C., Karlsson S., (1988), "The three stages in degradation of polymers-polyethylene as a model substance", *J. Appl. Polym. Sci.*, **35**, 1289-1302.

Carothers W. H., Arvin J. A., Dorough G. L., (1930), "Studies on polymerization and ring formation. V. glycol esters of oxalic acid, *J. Am. Chem. Soc.* 52(8), 3292-3300

Dipa R., Sarkar B.K., (2001), "Characterization of alkali-treated jute fibers for physical and mechanical properties.", *J. Appl. Polym. Sci.*, **80**, 1013-1020.

Dupont Co. Ltd. http://www.duponttateandlyle.com/our_process.php

Gassan J., Bledzki A.K., (1999), "Alkali Treatment of Jute Fibres: Relationship between Structure and Mechanical Properties", *J. Appl. Polym. Sci.*, **71**, 623-629.

Kesel C.D, Wauven C.V, David C, (1997), "Biodegradation of polycaprolactone and its blends with poly(vinylalcohol) by micro-organisms from a compost of house-hold refuse", *Polym. Degrad. Stab.*, **55**, 107-113.

Mohanty A. K., Misra M., Drzal L.T., (2002), "Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials world", *J. Polym. Environ.* **10,** 19-26.