Synthesis and characterization of glyceryl monooleate-based polyester

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Abstract−A unique biobased polyester poly(succinic acid-glyceryl monooleate) (PSAGMO) was synthesized and characterized from succinic acid (SA) and glyceryl monooleate (GMO). The polyester was characterized by gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic response spectroscopy (NMR). The polyester was used as the plasticizer of poly (vinyl chloride) (PVC). The mechanical properties and the thermodynamic properties of the blends were characterized. The TG-DTA data indicated that the thermal degradation temperature (T_d) of PVC blends plasticized with PSAGMO could increase from 249.3 °C to 255.6 °C. The DMA showed that the glass transition temperature (Tg) of the PVC blends decreased from 49.5 °C to 35 °C. The mechanical properties indicated that the PSAGMO could decrease the tensile strength and increase the elongation at break of the PVC blends. This study may lead to the development of new type of PVC plasticizer based on renewable resource.

Keywords: Polyester, Poly(vinyl chloride), Blends, Thermal Stability

INTRODUCTION

Dioctyl phthalate (DOP) as the primary plasticizer of poly(vinyl chloride) (PVC) products is widely used in a large number of applications such as coatings, films, paints, medical devices, food packing or toys, and its plasticizing efficiency has been the subject of some reviews. The plasticizer contacted with biological fluids accelerates the migration of phthalate ester, which has adverse effects on people's health, especially the "plasticizer event" that happened in Taiwan in May, 2011. The reason is that bis (2-ethylhexyl) phthalate (DEHP) plasticizer that migrated from the food packaging was found in some foods; the DEHP presents cancer and reproductive system disease to the human body. Taiwan has begun to limit the phthalate plasticizer used in medical devices, food packings, toys and plastic products which contact the human body directly [1-5]. In 1999, six phthalate esters (diisononyl phthalate, diisodecyl phthalate (DIDP), DEHP, Dioctyl phthalate (DOP), benzyl butyl phthalate and dinoctyl phthalate) were forbidden to be used in childcare articles and toys that were intended to be placed in the mouths of children under the age of 3 in Europe.

Polyester plasticizers have attracted considerable attention and do show decreased migratory aptitude, increased thermostability, decreased extractability, non-toxicity and environmental friendliness in comparison to low molecular weight phthalate plasticizers [6]. The primary role of the polyester plasticizers is to improve the flexibility and processing of polymers by lowering the second-order transition temperature and the glass transition temperature (Tg). PVC blends with polyester, such as poly (butylene adipate), polycaprolactone and poly (3-hydroxybutyrate-co-3-hydroxyvalerate),

have been reported [7-9]. However, the raw materials are petrochemical and depend on oil resources; with the depletion of fossil resources, the development of "green" of polyester plasticizer from renewable resources is an inescapable trend. Nowadays, there is an increasing interest in the use of nature-based plasticizers such as oleic acid polyester, citric acid-based polyester, castor oil based polyester, aliphatic polyester based on ltaconic acid and rice fatty acid based polyester [10-24].

We synthesized a novel potentially biobased polyester poly(succinic acid-glyceryl monooleate) (PSAGMO) from succinic acid (SA) and glyceryl monooleate (GMO) via direct esterification and polycondensation route using tetrabutyl titanate (TBT) as catalyst. The PSAGMO was used as plasticizer for PVC and the plasticization efficiency was also investigated. To the best of our knowledge, there is no study on the polymers synthesized from a combination of succinic acid (SA) and glyceryl monooleate (GMO) for polyester plasticizers or used as the plasticizer of PVC.

EXPERIMENTAL

1. Materials

Analytical grades of succinic acid (SA), Dioctyl Phthalate (DOP), Glyceryl monooleate (GMO), Calcium stearate, Zinc stearate and tetrabutyl titanate (TBT) were kindly supplied by Nanjing Chemical Reagent Co., China; polyvinyl chloride polymer (PVC) resin was obtained from Hanwha KM-31, South Korea. All of the chemicals were used without further purification.

2. Synthesis of PSAGMO

PSAGMO was synthesized through a two-step procedure of esterification and subsequent polycondensation. 10 g (0.08 mol) SA, 34.74 g (0.097 mol) GMO (M:356.53) and 0.013 g TBT (0.03%, with respect to the total mass of reactants) were put into a 250 ml three-necked round-bottom flask with a water separator, mechanical stirrer and
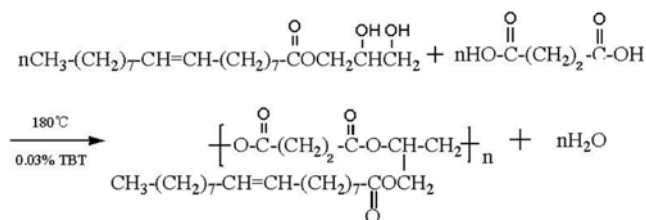
Fig. 1. The idealized reaction scheme for the synthesis of PSAGMO.

N₂ inlet pipe. The mixture was heated to 150 °C and the temperature kept until all the monomers melted completely under N₂ atmosphere. The temperature was slowly increased to 160-180 °C over a period of 6 h while the mixture was stirred to finish esterification, then the condensation was allowed to proceed in vacuum at 180 °C until the acid value remained unchanged. The resulting polyesters were allowed to cool and dissolved in acetone and reprecipitated from water. The dissolution and reprecipitation were repeated three times and the polyester products were air dried for 36 h and finally dried at 60 °C in vacuum for 24 h. The process of reaction is depicted in the Fig. 1.

3. Preparation of Blends

The PVC was pretreated by drying at 60 °C for 20 h to eliminate possible absorbed water on the surface of particle. Blends were melt processed at 165 °C for 5 min at 50 rpm using Poly Lab Torque rheometer (Hakke Insturment Crop., Germany). Dumbbell-shaped samples of blends were molded on a MiniJetII Micro-injection molding machine (Hakke Insturment Crop., Germany) according GB/T 17037.1-1997 (China). Mounding conditions were set at 165 °C for 5 min at 550 bar. The formulation used for preparing plasticized PVC blends is shown in Table 1.

4. Intrinsic Viscosity

Intrinsic viscosity of polyester was measured by using NDJ-1 rotary viscometer at 30 °C.

5. Esterification Ratio

Acid value (Av) was determined according GB/T 1668-2008 (Plasticizer-Determination of acid value and acidity, China).

6. ¹HNMR Spectroscopy

Chemical structures and composition of polymers were characterized by AV500 NMR spectrometer (Bruker Instrument Crop., Switzerland) at ambient temperature; CDCL₃ and tetramethylsilane (TMS) were used as the solvent and the internal standard, respectively.

7. FT-IR Spectrum

The FTIR studies were carried out using a Nicolet iS10 FT-IR (Nicolet Instrument Crop., America). The spectra were acquired in the range of 4,000 to 650 cm⁻¹ at a resolution of 4 cm⁻¹.

8. Gel Permeation Chromatography

The molecular weights and polydispersity indices of the polymers were determined by permeation chromatography at 35 °C with a Model 1515 GPC (Waters Instrument Crop., America) using polystyrene as a standard. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 ml/min, and the sample concentration was 25 μl. The polyester was characterized at the polycondensation time of 6 h, 8 h and 10 h, respectively, and total polycondensation time was 10 h.

9. TG-DTA

TGA was carried out in a TG209F1 TGA thermal analysis instrument (Netzsch Instrument Crop., German) in N₂ atmosphere (50 ml/min) at a heating rate of 10 °C/min. The samples were put into platinum pans and scanned from ambient temperature to 600 °C.

10. DMA

The dynamic mechanical property was examined via a DMTA Q800 (TA Instruments, USA). The oscillatory frequency of the dynamic test was 1 Hz; the temperature increased at a rate of 3 °C/min in the range of −100-100 °C.

11. Tensile Test

Tensile modulus, tensile strength, and elongation at break were determined according GB/T 1040.1-2006 (China) under ambient conditions, using an E43.104 Universal Testing Machine (MTS Instrument Crop., China). The reported values were the average of at least.

RESULTS AND DISCUSSION

1. ¹H NMR Spectroscopy

The ¹H NMR spectra of PSAGMO are shown in Fig. 2. The peak value of chemical shift 5.35 ppm was the '-CH=CH-' from the GMO; the peaks around 4.1-4.3 ppm were assigned to the methylene protons of the polyester backbones connected to the ester structure (-CH₂-O-C=OCH₂-). While the peaks around the 2.6 ppm and 5.15 ppm were corresponding to the '-CO-CH₂-CH₂-CO-' and '-O-CH=' from SA, the peaks around 0.85 ppm and 1.29 ppm obviously attributed the methylene and methy from GMO. The peak at about 1.65 ppm is most likely from the beta carbon next to the C=O in
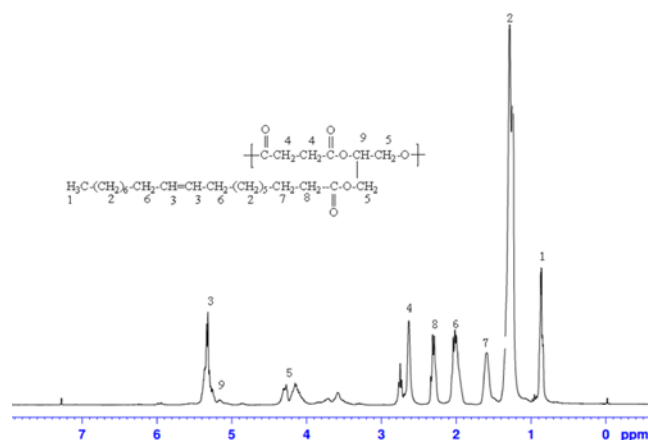
Table 1. Formulations used for preparing plasticized PVC blends

Formulation (g)	PVC-20	PVC-25	PVC-30
PVC	100	100	100
DOP	30	30	30
PGAGMO-3	20	25	30
Calcium carbonate	10	10	10
Thermal stabilizers	2	2	2
Calcined clay	10	10	10

Fig. 2. The ¹H NMR spectra of PSAGMO.

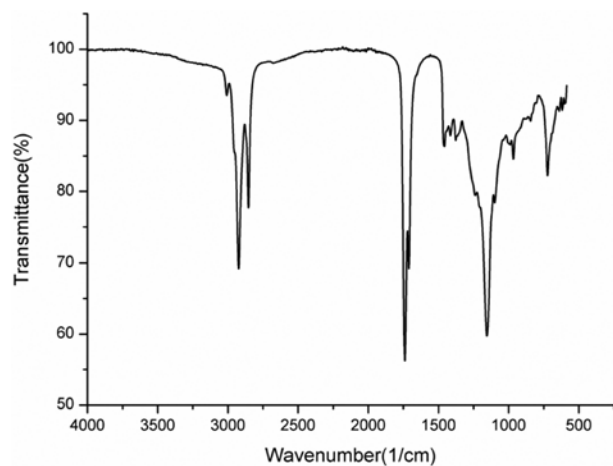Fig. 3. FT-IR Spectrum of PSAGMO.

Fig. 4. TG-DTA curves of PVC-20%.

the pendant chain. All of the results suggested that PSAGMO-3 molecular chain was synthesized successfully.

2. FT-IR Spectrum

FT-IR was used to determine the functional groups of the optional polyester. The FT-IR spectra are shown in Fig. 3; from the FTIR spectra, the appearance of the broad C-H band at 2,920.12 cm^{-1} in the polyester samples was observed. The most intensive peaks at 1,737.96 cm^{-1} belong to the C=O valence vibration; the peaks at regions 1,154.77 cm^{-1} and 723.11 cm^{-1} correspond to the C-O bond and C-C of polyester was noted. All of the characteristic peaks are important evidence of ester structure existing in the products.

3. Gel Permeation Chromatography and Intrinsic Viscosity

The number molecular weight (Mn), weight average molecular (Mw) and viscosity of PSAGMO were characterized by GPC and NDJ-1 rotary viscometer at different reaction time, and the results are given in Table 1. According to Table 2, the Mn, Mw and viscosity increase obviously with the extension of the reaction time; the slight shifting of polydispersity index of PSAGMO was mainly caused by the shifting vacuum degree, which was difficult to control at the same value in different operation of the lab experiment.

4. TG-DTA

The blends of PSAGMO-3 and PVC were a melt process at 165 °C for 5 min at 50 rpm using Poly Lab Torque rheometer according to the formulations (Table 1) for injection molding soft products. The obtained TG-DTA curves of PVC-20%, PVC-25% and PVC-30% are in Fig. 4, Fig. 5 and Fig. 6. From the TG-DTA curves, we can see that there is a two-step mechanism for the thermal degradation of PVC blends. The temperature of the maximum decomposition rate is around 280 °C in the first step and 470 °C in the second step. The thermal ability of plasticized PVC is increasing
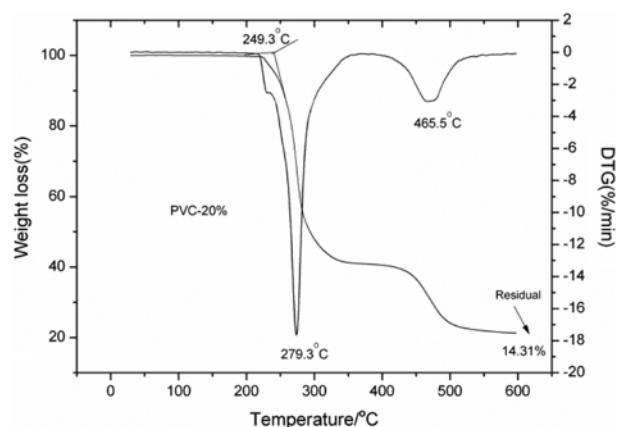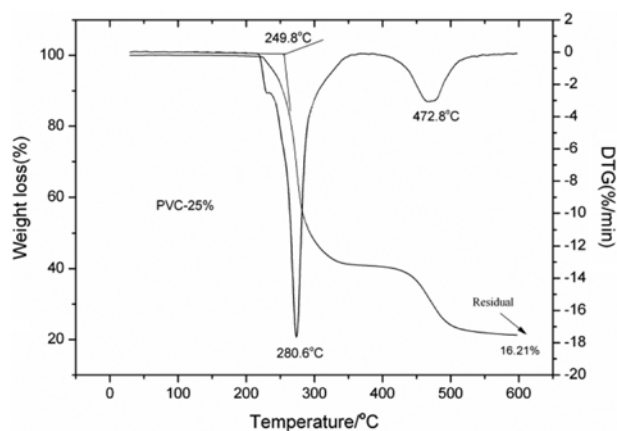

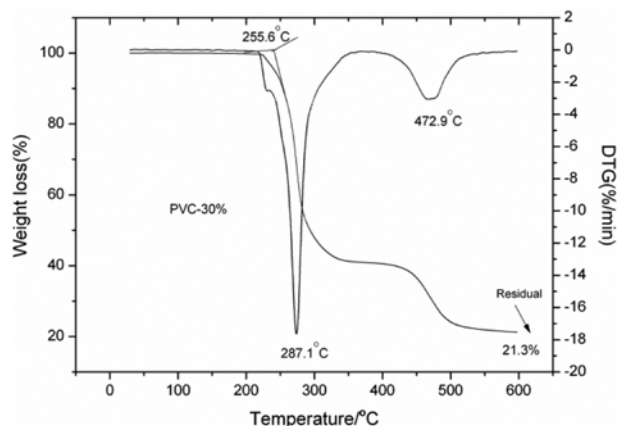Fig. 5. TG-DTA curves of PVC-25%.

Fig. 6. TG-DTA curves of PVC-30%.

Table 2. The GPC properties and viscosity of PSAGMO

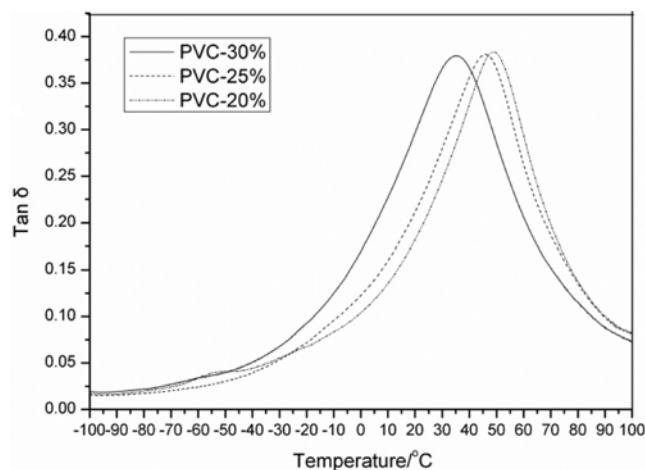| Sample	Polycondensation time (h)	Viscosity (Pa·s)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Distribution index
PSAGMO-1	6	3.3	9987	11522	16375	1.32
PSAGMO-2	8	3.5	12173	14685	21031	1.22
PSAGMO-3	10	3.9	14223	18263	27505	1.41

Fig. 7. DMA curves of PVC blends.

with the addition of PSAGMO-3; the decomposition temperature (T_d) is determined as the temperature of 5% thermal weight loss; the T_d values of PVC-20%, PVC-25% and PVC-30% are 249.3 °C, 249.8 °C and 255.6 °C and were analyzed. The PVC-20% showed a lower thermal stability than PVC-25% and PVC-30%, because the PVC-20% easily started thermal degradation. The residue rate of PVC-20%, PVC-25% and PVC-30% is 14.31%, 16.21% and 21.3% with the addition of PSAGMO-3 at 600 °C; the high residual rate is caused by PSAGMO-3.

5. DMA

The glass transition temperature (Tg) of the PVC blends was characterized by DMA, and the DMA curves are in Fig. 7. Only a tan δ peak in every DMA curve could be observed, which indicated that compatibility of the PVC and polyester plasticizer is excellent. The DMA data indicated that the tan δ peak shifts to lower temperature with the decreasing content of plasticizer. From Fig. 6, with the addition of PSAGMO-3 the Tg of PVC-20%, PVC-25% and PVC-30% is 49.5 °C, 46.2 °C and 35 °C; the decrease of Tg indicated that the chain mobility of PVC increased. The change of Tg of PVC is in agreement with the common rule that the plasticizer can decrease the Tg of PVC. The reason is that PSAGMO-3 could interact with PVC molecular and increase the mobility of PVC chain segment.

6. Tensile Test

The tensile strength, elongation at break and tensile modulus of PVC blends were tested using the E43.104 Universal Testing Machine; the obtained mechanical properties are shown in Table 3. From the Table 3, we can see that the PVC blends show different mechanical properties when adding different mass of PSAGMO-3: the PVC-30% with a concurrent decrease from 22.32 MPa to 18.22 MPa in the tensile strength and increasing in the elongation at break with

Table 3. Mechanical properties of PVC

Sample	PVC-20	PVC-25	PVC-30
Tensile strength (MPa)	22.32	20.35	18.22
Elongation at break (%)	270.19	301.34	310.29
Tensile modules (MPa)	89.86	29.91	20.99

decreasing in tensile modulus compared to PVC-20%. It is in accordance with the common rule that the plasticizer can increase the elongation at break and decrease the tensile strength and tensile modulus.

CONCLUSIONS

A novel, potentially biobased polyester poly(succinic acid-glyceryl monooleate) (PSAGMO) was synthesized from succinic acid (SA) and glyceryl monooleate (GMO) via direct esterification and polycondensation route. The polyester was characterized by GPC, FTIR and ^{1}HNMR. Furthermore, the molecular weight of PSAGMO polyester was governed by the polycindensation time. The obtained polymer has the expected chemical structure. The blends of PSAGMO-3 and PVC were melt process for injection molding soft products. The TG-DTA data indicated that the thermal degradation temperature (T_d) of PVC blends plasticized with PSAGMO could increase from 249.3 °C to 255.6 °C. The DMA showed that the glass transition temperature (Tg) of the PVC blends decreased from 49.5 °C to 35 °C. The mechanical properties indicated that the PSAGMO could decrease the tensile strength and increase the elongation at break of the PVC blends. This work suggests a new research area for synthesis and application of renewable resource to produce a functionalized plasticizer, which will expand the application range of PVC plasticized with PSAGMO materials.

ACKNOWLEDGEMENT

REFERRENCES

1. A. Marcilla, S. Garia and J. C. Garcia-Quesdad, *J. Anal. Appl. Pyrol.*, **7**, 457 (2004).
2. G. Latini, C. D. Felice and A. Verrotti, *Reprod Toxicol.*, **19**, 27 (2004).
3. G. Ltini, *Biology of Neonat*, **78**, 269 (2000).
4. J. H. Li and Y. C. Ko, *Kaohsiung J. Med. Sci.*, **28**, 17 (2012).
5. Y. H. Chen, S. H. Fu and J. K. Huang, *J. Food Drug. Anal.*, **21**, 242 (2013).
6. M. Hakkarainen, *Adv. Polym. Sci.*, **211**, 159 (2008).
7. F. C. Chiu and K. Min, *Polym. Int.*, **49**, 223 (2000).
8. B. L. Shah and V. V. J. Shertukde, *Appl. Polym. Sci.*, **90**, 3278 (2003).
9. C. Soonja and C. Yoon-Jong, *Polymer*, **36**, 4977 (1995).
10. M. M. Sander, A. Nicolau and R. Guzatto, *Polym Test*, **31**, 1077 (2012).
11. M. A. D. Silva, M. G. A. Vieira and A. C. G. Macumoto, *Polym. Test*, **30**, 478 (2011).
12. Y. Li, C. M. Wang and G. J. Wang, *J. Wuhan Univ. Technol.*, **2**, 100 (2008).
13. Y. M. Wu, Q. W. Xie and C. H. Gao, *Polym. Eng. Sci.*, (2013), DOI: 10.1002/pen.23798.
14. I. Djordjevic, N. R. Choudhury and N. K. Dutta, *Polymer*, **50**, 1682 (2009).
15. P. S. Sathiskumar and G. Madras, *Polym. Degrad. Stabil.*, **96**, 1695 (2011).

16. U. Edlund and A. C. Albertsson, *Adv. Polym. Sci.*, **157**, 67 (2002).
17. M. G. A. Vieira, M. A. Silva and L. O. Santos, *Eur. Polym. J.*, **47**, 254 (2011).
18. L. M. Espinosa and M. A. R Meier, *Eur. Polym. J.*, **47**, 837 (2011).
19. K. Sudesh, H. Abe and Y. Doi, *Prog. Polym. Sci.*, **25**, 1503 (2000).
20. M. T. Isa, A. S. Ahmed and B. O. Aderemi, *Composites: Part B*, **53**, 217 (2013).
21. J. Salimon, N. Salih and E. Yousif, *Arab. J. Chem.*, **5**, 135 (2012).
22. P. Bordes, E. Pollet and L. Avérous, *Prog. Polym. Sci.*, **34**, 125 (2009).
23. V. Sharma and P. P. Kundu, *Prog. Polym. Sci.*, **31**, 983 (2006).
24. S. C. Chua, X. B. Xu and Z. Guo, *Process Biochem.*, **47**, 1439 (2012).