Investigation of the Interaction between Poly(trimethylene Carbonate) and Various Alcohols

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Article

Investigation of the Interaction between Poly(trimethylene Carbonate) and Various Alcohols

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Abstract: The interaction of poly(trimethylene carbonate) (PTMC) with alcohols were investigated as a model for polymer blending with polysaccharides. While 1-butanol, 2-butanol, ethylene glycol, 1,2-cyclohexanediol showed almost no detectable interaction with PTMC at both of solution state with ^{1}H NMR and solid states of FT-IR, glucose and cellobiose suggests slight change of spectral pattern in FT-IR analysis. The thermal properties of the blending samples of PTMC and these alcohols were also investigated. Although the blend of PTMC with 1-butanol, 2-butanol, and ethylene glycol did not influence on thermal degradation behaviors due to the low boiling points to maintain the structure at blend sample preparation, however, the blend with PTMC and glucose or cellobiose tend to increase thermal resistances and increase glass transition temperature, hence, showed an existence of interaction through hydrogen bonding.

Keywords: poly(trimethylene carbonate); interaction; alcohols; glucose

1. Introduction

Poly(trimethylene carbonate) (PTMC) is a biodegradable polymer that has garnered significant attention in the field of biomedical application [1] due to its unique combination of biodegradability [2,3] and mechanical properties [4]. PTMC and its derivatives were synthesized through the ring-opening polymerization of trimethylene carbonate (TMC) and its derivatives [5–7] and exhibits a range of applications, including tissue engineering scaffolds, drug delivery systems, and medical implants [8]. The polymer's ability to degrade into non-toxic by-products that can be safely absorbed or excreted by the body makes it particularly attractive for temporary biomedical applications [9]. PTMC has been known to degrade in vitro and in vivo by surface erosion in contrast to the bulk degradation behavior shown by other polyesters [10], as well as the recent study of biodegradation mechanism by macrophage-mediated erosion [11]. However, PTMC application is limited because of its soft properties as bulk materials, probably due to its low glass transition temperature (T_g) at around − 20 ◦C [5].

Many efforts have been addressed the improvement of polymer properties by blend of PTMC and the other polymers [12]. For example, poly(adipic anhydride) [13] and poly(glycolic acid) (PGA) [14], which are the similar chemical structures as PTMC, were employed for blend with PTMC. It has been reported many blend studies using polylactide (PLA). The blend of PLA and PTMC were used as loading agents for essential oil [15] and cinnamaldehyde [16], as well as an application of biodegradable medical adhesives [17] and ultrathin membrane [18]. By blending with PLA and PTMC, various applications were also achieved, like drug eluting nanocomposite [19], packaging film [20], prevention of postoperative adhesions [21], and control of protein loading [22]. Sometimes, the copolymer of PLA and PGA were used for the blend with PTMC [23–25], which can tune of the

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polymer properties and freely controllable ratio of PLA and PGA. Poly(ε-Caprolactone) (PCL) was also well employed for blend with PTMC [26,27]. As the other examples, the electrons spinning techniques for blending with PTMC [28,29] and crosslinking reaction after the blending [30,31] were applied. However, the mechanism of polymer interaction with PTMC when it was blended has not been well-investigated.

Under the situation, it is crucial to understand the detailed polymer interactions between PTMC and the partner polymers for optimizing its performance in specific applications. One of the critical structures of PTMC might be the carbonyl groups, flanked with two oxygen atoms within its polymer backbone [32]. One of the primary interactions involving the carbonyl group is hydrogen bonding [33]. The oxygen atom in the carbonyl group can act as a hydrogen bond acceptor, interacting with hydrogen donors [34]. The strength of the hydrogen bonding could be different from ester compounds. The hydrogen bonding strength of the carbonyl group in the carbonate group would be expected to exhibit a larger interaction compared to that of the carbonyl group in the ester group. This is because the carbonyl carbon in the carbonate group is flanked by two oxygen atoms, which may result in a greater dipole moment of the carbonyl group compared to the structure of the ester group, where the carbonyl carbon is flanked by one carbon atom and one oxygen atom. Therefore, the investigation with low molecular compounds with PTMC should contribute to consider the mechanism of the interaction with PTMC at blend materials.

Low molecular compounds are a good model to understand interaction of polymers, because the low molecular size can occupy intermolecular spaces between polymer chains, decreasing secondary forces among them. Sometimes such a low molecular compounds were used as a plasticizer, like addition to poly(vinyl chloride) [35], and numerous studies have been reported [36,37]. As examples of the plasticizer, natural-based compounds were applied for biopolymer films [38]. The plasticizers themselves were recently considered for their environmentally friendly nature, like biodegradable ones for poly(3-hydroxybutyrate) [39]. The role of water against protein are also considered as plasticizers [40].

Among these plasticizers, one of the promising compounds for PTMC is alcohol compounds, because the carbonyl groups of PTMC could be well interacted with alcohols. Generally, alcohol compounds are well-known to work as plasticizers for polymers. For example, ethyl acrylate [41] and dodecyl methacrylate [42], as well as PLA [43], were soften by various alcohols, interacting with carbonyl groups. Alcohol compounds were also employed for plasticizer to poly(vinyl alcohol) [44] bearing hydroxyl groups. As practical use, alcohols were utilized as plasticizers to various biocompatible polymers, such as alginate [45], starch [46,47], and lipid bilayer [48]. However, to the best of our knowledge, there have been no studies on blending PTMC with low molecular weight alcohols. This is likely because PTMC already has a low glass transition point, reducing the need for plasticizer research. However, analyzing the mixture of low molecular weight alcohol compounds and PTMC could provide valuable information on the interactions with the polymer backbone of PTMC.

In this study, we investigated the interaction between PTMC and various alcohols as models of interacting polymer candidates, by observing chemical structures and thermal properties after addition. The present study will contribute to find the effective blend modification with PTMC.

2. Materials and Methods

2.1. Materials

Poly(trimethylene carbonate) (PTMC, viscosity 1.75 dL/g) was purchased from Sigma Aldrich (St. Louis, MO, USA). 1-butanol, 2-butanol, and d(+)-glucose was purchased from Fujifilm Wako Pure Chemical Co. (Chuo-ku, Osaka, Japan) while ethylene glycol, 1,2-cyclohexanediol (*cis* and *trans* mixture), and cellobiose were purchased from Tokyo Chemical Industry (Chuo-ku, Tokyo, Japan. Chloroform-*d* was purchased from Cambridge Isotope Laboratories (Andover, MA, USA).

2.2. Preparation of Solution Mixture for ^{1}H-NMR Measurement

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PTMC and various alcohols except glucose and cellobiose were prepared based on 1:1 mole ratio. Each alcohol and PTMC was then mixed in $CDCl_3$ inside ^1H NMR tube and sonicate for 5 mins before measured with JEOL ECX-400P (JEOL Corporation, Japan) at 400 MHz.

2.3. Preparation of Melt Blending

PTMC and various alcohols except glucose and cellobiose were prepared based on 1:1 mole ratio. PTMC was pre-melt into thin film inside Teflon sheet at 150°C for 5 mins before each alcohol was added into PTMC film using Small-heat-press machine HC300-01 (As One Corporation, Japan). The mixture was then melt-press at 150°C for 15 mins (except 20 mins for glucose and 30 mins for cellobiose) with film reshaping every 5 mins. The same procedure was prepared for PTMC-glucose 16/1 (mol/mol) and PTMC-cellobiose 17/2 (mol/mol) except using at 170°C for 20 mins. The mixture is referred to below as blend samples.

2.4. Fourier Transform Infrared Spectroscopy (FTIR)

Attenuated total reflection infrared (ATR-IR) spectra were obtained by IRAffinity-1S (Shimadzu Corporation, Japan). A total of 64 to 1024 scans were accumulated in transmission mode with a resolution of 4 cm^{-1}. The spectrum was obtained from a range of 4000 to 400 cm^{-1}.

2.5. Thermogravimetric Analysis (TGA)

TGA tests were carried out by using a TGA-50 (Shimadzu Corporation, Japan). The samples, approximately 5-6 mg in aluminum pan, were heated to 500°C at a heating rate of 10°C/min under nitrogen atmosphere.

2.6. Differential Scanning Calorimetry (DSC)

DSC (DSC-60Plus Shimadzu, Japan) measurements were performed in the temperature range from −50 to 200°C at a rate of 10°C/min under nitrogen flow. Samples (5-6 mg) were cooled from RT to −50 before heated from −50 to 200°C at a heating rate of 10 °C/min and held at 200°C for 5 min to eliminate the thermal history (first heating scan), then they were cooled to −50°C at 10 °C/min and reheated under the same conditions (second heating scan).

3. Results and Discussions

3.1. Interaction Study of Mixed Solution

Model interaction between PTMC and various alcohols was shown as in Figure 1. 1-butanol (**1**) and 2-butanol (**2**) were chosen due to similar carbon number with TMC monomer and the possible effect of primary and secondary alcohol in the molecular interaction. Ethylene glycol (**3**) and 1,2-cyclohexanediol (**4**) were selected to investigate the effect of diol with PTMC, while glucose (**5**) and cellobiose (**6**) showed more complex model and more hydroxyl group that potentially interact with PTMC, expecting with the future blending with polysaccharides. Previously, the interactions of alcohols with carbonyl group of ethyl methacrylate have been reported [41], which revealed that the proton donating ability or tendency of complex formation of alcohols increases with alkyl chain length. They mentioned that primary alcohols have relatively more tendency of complex formation than the secondary and tertiary alcohols.

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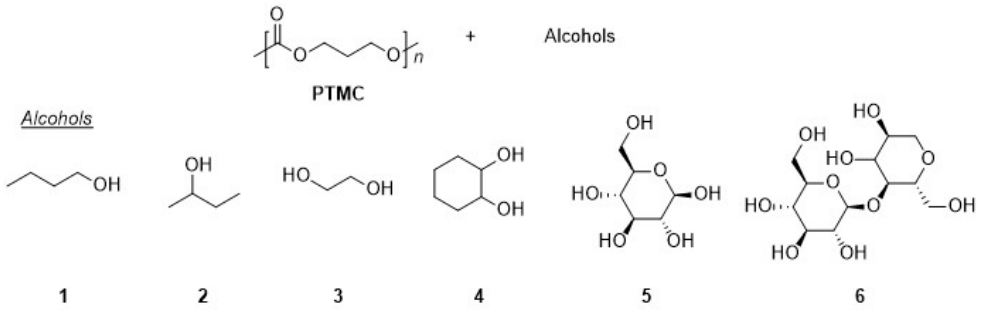

Figure 1. Model interaction of PTMC with various alcohols, using 1-butanol (**1**), 2-butanol (**2**), ethylene glycol (**3**), 1,2-cyclohexanediol (**4**), glucose (**5**), and cellobiose (**6**).

Molecular interaction between PTMC and various alcohols was first investigated through ^{1}H NMR as shown in Figure 2. The PTMC signals corresponding to the repeating OCH_2 and -CH_2 groups in polymer backbone were observed at 4.241 ppm and 2.054 ppm, respectively (Figure 2a). Solution mixture of PTMC with **1**, **2**, **3**, and **4** did not show any significant peak change in ^{1}H NMR spectra at around 4.241 ppm and 2.054 ppm (Figure 2b-2e). This finding implied that ^{1}H NMR measurement was unable to detect molecular interaction between PTMC and alcohols in solution mixture. Full comparison of ^{1}H NMR spectra for all solution mixtures are available (Supporting Information, Figure S1). **5** and **6** were excluded in ^{1}H NMR measurement due to insolubility in $CDCl_3$. Then, we moved to analyze the blend samples without solution samples as a solid state.

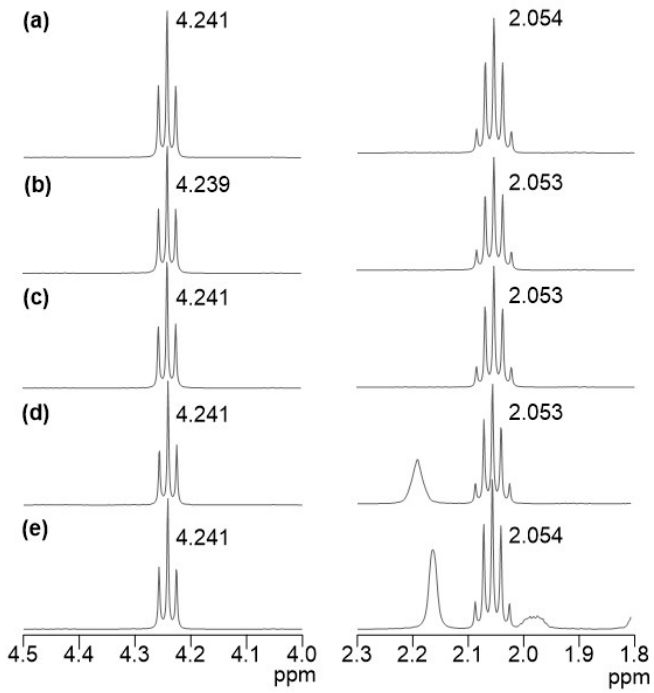

Figure 2. ^{1}H NMR spectra of PTMC (**a**), PTMC with **1** (**b**), **2** (**c**), **3** (d), and **4** (e) (400 MHz, in $CDCl_3$, r.t.).

3.2. Interaction Study of Blend at Solid State

Further investigation of interaction was conducted through melt blending PTMC with various alcohols in 1:1 mole ratio. All melt blending samples were then analyzed for chemical properties. To investigate the interaction between PTMC and various alcohols, we focused on comparing two main regions of PTMC in FT-IR spectra which were hydroxyl (O–H) and carbonyl (C=O) stretch. The

 doi:10.20944/preprints202408.1521.v1

content of O–H and the formation of the hydrogen bond directly affects the peak shape, peak position, and peak area of O–H stretching vibration wave [49]. The stretching of hydroxyl groups of **1** at 3316 cm^{-1}, **2** at 3335 cm^{-1}, and **3** at 3300 cm^{-1} seemed to be disappear in the blend samples, due to the evaporation during sample preparation at 150 °C for 15 mins. The boiling points (b.p.) of **1**, **2**, and **3** are 117°C, 100°C, and 196°C respectively (Figure 3a-3c). Previous work also found out that alcohols have low boiling temperature and volatile behavior, hence not suitable for thermal processing in the starch matrix [46].

In addition, the stretching of hydroxyl groups of **4**, **5**, and **6** slightly shift in the blend samples (Figure 3d-3f). The slightly shift hydroxyl peaks to higher wavenumber from **3**, **4**, **5**, and **6** in the samples might imply a reduction amount of hydrogen bonding, or changes of hydrogen bonding from OH/OH to OH/C=O. The peak intensity decrease on hydroxyl stretches might also show a possible penetration of alcohols into PTMC surface. Similar phenomena on peak-intensity change in hydroxyl stretch have been observed when studying temperature-responsive of poly(dodecyl methacrylate) [42]. The increased OH-absorbance results from an increased ethanol concentration at the sensing surface and increased temperature in 3350 cm^{-1} of poly(dodecyl methacrylate) showed ethanol penetration, thus, enable polymer to swell [42]. All of the stretching of carbonyl groups of the blend of PTMC with **1**, **2**, **3**, **4**, and **5**, however, showed at 1736 cm^{-1} (Figure 3g-3k), although the blend of PTMC and **6** shifted slightly to 1738 cm^{-1} (Figure 3l).

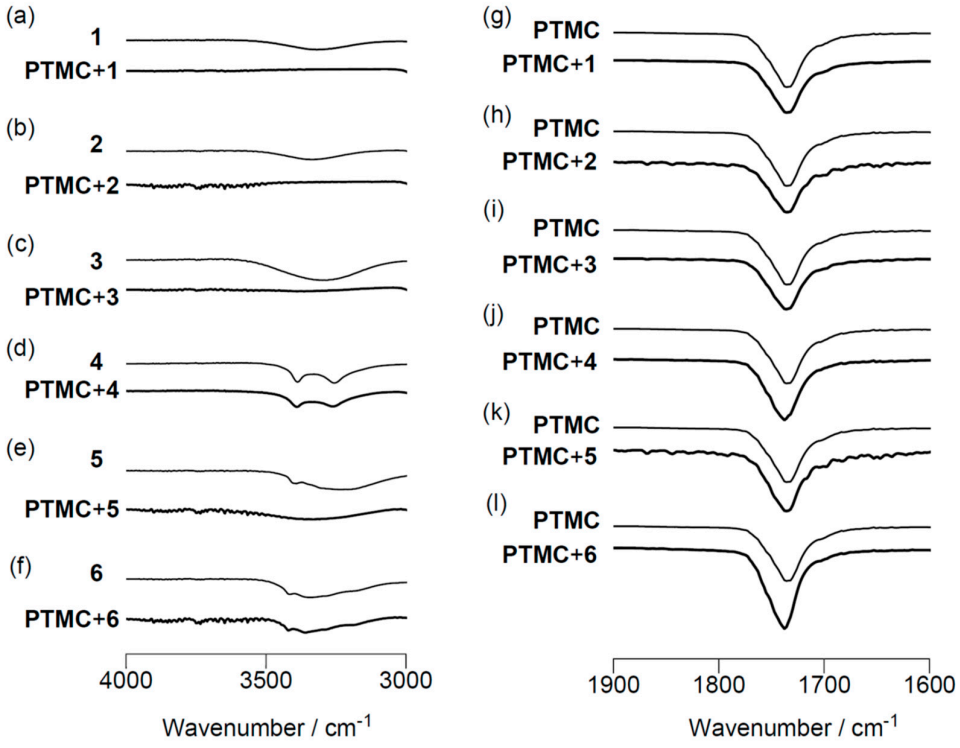

Figure 3. FT-IR spectra of hydroxyl groups of PTMC with 1 (a), 2 (b), 3 (c), 4 (d), 5 (e), and 6 (f). FT-IR spectra of carbonyl groups: PTMC with 1 (g), 2 (h), 3 (i), 4 (j), 5 (k), and 6 (l).

Based on two main regions of PTMC in FT-IR spectra, we consider the possibilities that there was a reduction of the hydrogen bonding from both hydroxyl group and the carbonyl groups. These observations might indicate a possibility of complex formation between free hydroxyl group of alcohol and carbonyl group of PTMC. Similar finding was also found out in alcohol and ethyl methacrylate mixtures.[41] They found out the formation of 1:1 complex between free hydroxyl group of alcohol and carbonyl group of ethyl methacrylate (i.e.,) (O H···O=C) due to increase of the free O-H band intensity and half-band width with increasing alcohol concentration but at the same time the reverse trend is observed for the carbonyl absorption band. Another researcher also found

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out that the hydrogen bonding interactions by ethanol were observed with the carbonyl groups of lipid bilayer through the combination of two-dimensional NOESY spectra and molecular dynamics simulations [50]. To examine the interactions of blend with TMC and alcohols, we next analyze thermal properties of blends.

3.3. Interaction Effects on Thermal Properties

The thermal properties of the blends with PTMC and various alcohols were analyzed through TGA measurement, which were prepared by melt blending method for the homogeneous sample preparation. The thermal decomposition temperatures of samples at which 10% weight loss (T_{10}) were used for a comparison, as well as chart patterns. Compared with PTMC only (Figure 4a), the mixing with **1** and **2** in PTMC with 1:1 mole ratio slightly reduced T_{10} of PTMC from 302°C to 301°C and 288°C (Figure 4b and 4c). Since the FT-IR spectra (Figure 3) showed a possible evaporation of **1**, **2**, and **3** through disappearing of hydroxyl peak, most of alcohols don't exist in the mixtures, that is why only slight change would be observed. However, it is possible to have interactions of PTMC with **3** and **4** due to reduction of T_{10} from pure PTMC.

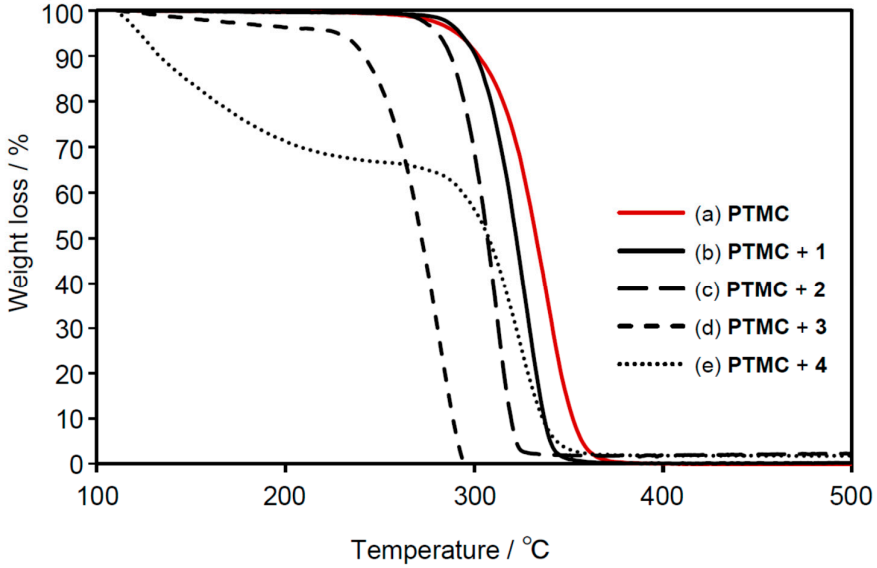

Figure 4. TGA charts of PTMC (**a**) PTMC with **1** (**b**), **2** (**c**), **3** (**d**), and **4** (**e**).

Apparent decrease of T_{10} values were observed with the addition of **3** and **4** from 302°C to 242°C and 123°C, respectively (Figure 4d and 4e). These results implied that 1:1 mole ratio of PTMC and diol derivatives influenced on the polymer-polymer interactions, possibly inside PTMC. Further investigations were conducted by increasing PTMC mole ratio for **5** and **6** samples. The thermal properties of T_{10}, T_g, T_m, and ΔH_m of **5** and **6** samples, obtained from a second heating, were summarized in Table 1.

Table 1. Thermal properties of blend PTMC with **5** and **6**.

Sample	T_{10} (°C)	Tg (°C)	T_m (°C)	ΔH_m (J/g)
PTMC	302	-22.4	80	-97
PTMC and 5 (1:1)	239	-18.5	56	-0.42
PTMC and 5 (17:2)	310	-17.3	46	-0.64
PTMC and 6 (1:1)	270	-19.6	66	-4.56
PTMC and 6 (16:1)	307	-16.1	63	-7.84

TGA curves of PTMC showed one step thermal decomposition process (Figure 5a), while **5** showed two steps thermal decomposition processes (Figure 5b), which are the first thermal decomposition temperature (T_d1st) at 218°C and the second thermal decomposition temperature

 doi:10.20944/preprints202408.1521.v1

(T_d2nd) at 276°C. Previously, it was reported that the first decomposition of pure **5** is related to start losing of its crystalline structure while the second is related to decomposition of the stronger chemical bonds after the complete loss of crystalline structure [51–53]. Interestingly, the T_d1st of the blend of PTMC with **5** (17/2, mol/mol) looks disappeared and the T_{10} increased to 310°C, whereas only PTMC showed T_{10} at 302°C (Figure 5c). This improvement of thermal properties suggests the interaction of PTMC and **5**. When it was compared with degradation temperature at approximately at 55% loss of weight, blend of PTMC with **5** (1/1, mol/mol) showed at 339 °C as well as the blend of PTMC with **5** (17/2, mol/mol), despite low values of 318°C and 331°C for **5** and PTMC, respectively. This result implied that slight interaction between PTMC and **5** possibly occurs.

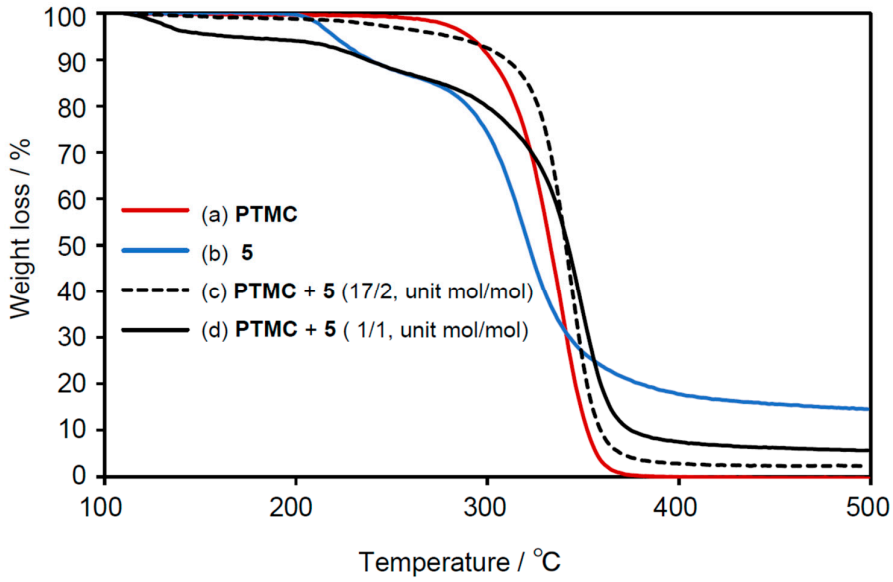

Figure 5. TGA charts of PTMC (**a**), **5** (**b**) PTMC/**5** (17/2, mol/mol) (**c**) PTMC/**5** (1/1, mol/mol) (**d**).

More clearly, the phenomena were also observed in the blend of PTMC with **6** (16/1, mol/mol), which showed the T_{10} values at 307°C improved from 302°C in the case of only PTMC (Figure 6a and 6c). When it was compared with degradation temperature at approximately at around 34% loss of weight, both blend samples showed similar temperature of 351°C that above either **6** of 336°C or PTMC of 339°C. This result also suggested the possibility of interaction between PTMC and **6**.

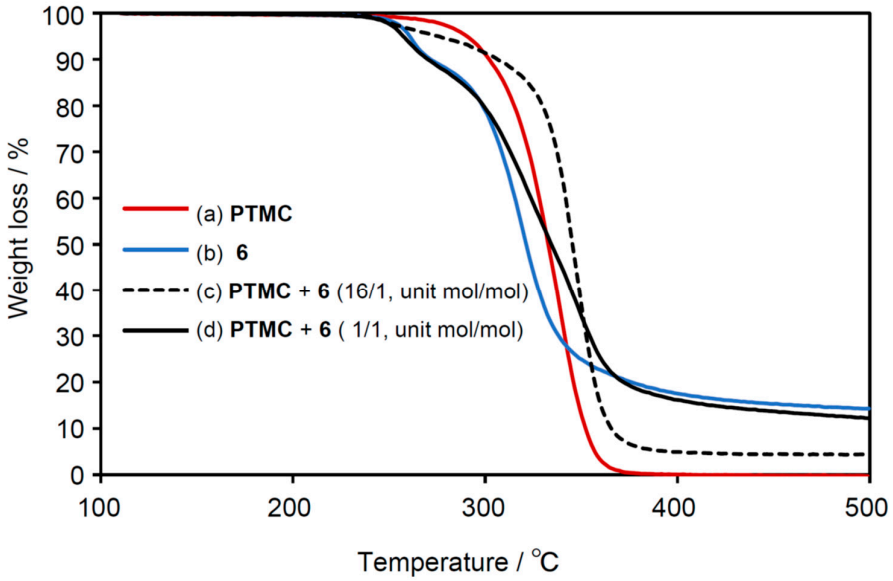

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Figure 6. TGA charts of PTMC (**a**), **6** (**b**) PTMC/**6** (16/1, mol/mol) (**c**) PTMC/**6** (1/1, mol/mol) (**d**).

The investigation with DSC on a possible polymer-polymer interactions inside PTMC was conducted for blend PTMC with **5** and **6**. The T_g of PTMC was slightly decreased from -22.4°C into -18.5°C and -19.6°C for blend of PTMC with **5** and **6**, respectively (Table 1). Increasing PTMC mole ratio for **5** and **6** samples showed higher effect on T_g. These results imply that the interactions between PTMC chains and alcohols would elevate the T_g values. Additionally, it is considered that the weakened interactions between the PTMC polymer chains themselves led to a decrease in the T_m.

While we are not certain what causes this peculiar behavior, we can offer a possible explanation. Based on previous FT-IR spectra, hydrogen bonding possibly occurs between hydroxyl group of alcohols and carbonyl group of PTMC. This interaction between PTMC and alcohols gives a positive effect on thermal properties of samples. Previous research also found out that plasticizers and polymers can interact externally which means it do not attach chemically to the polymer by primary bonds. Even though there are physical interactions between plasticizer and polymeric chains, they attach to the polymer by hydrogen bonding which is a type of dipole–dipole attraction between molecules [38]. The present results would contribute to the design of polymer blending materials as a model interaction.

4. Conclusions

Interaction between PTMC with various alcohols (**1**, **2**, **3**, **4**, **5**, and **6**) has been studied in solution and solid state blend samples using ^{1}H NMR, FT-IR, TGA, and DSC analyses. The solid state blend samples seemed to be a better method than solution mixture to investigate the interaction, resulting in the slightly different spectral pattern in FT-IR at carbonyl group. The possible interaction effected on TGA chart pattern and DSC chart pattern of blend PTMC with **5** and **6**, resulting in higher thermal decomposition temperature and T_m. The presented findings on the interaction between PTMC and alcohols hints an existence of interaction through hydrogen bonding that can contribute to find the effective blend modification with PTMC in the future.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, Figure S1: ^{1}H NMR spectra of (**a**) PTMC; PTMC with various alcohols: (**b**) **1**; (**c**) **2**; (**d**) **3**; (**e**) **4** (400 MHz, in $CDCl_3$, r.t.).; Figure S2: TGA charts: (**a**) PTMC; (**b**) **4**; (**c**) PTMC with **4**.

Author Contributions: Conceptualization, H.A.; methodology, H.A. and A.A.; software, H.A. and A.A.; validation, H.A. and A.A.; formal analysis, A.A.; investigation, A.A.; resources, H.A.; data curation, A.A.; writing—original draft preparation, A.A.; writing—review and editing, H.A.; visualization, A.A.; supervision, N.C and H.A.; project administration, H.A.; funding acquisition, H.A. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data that support the findings of this study are available from the corresponding author, H.A., upon reasonable request.

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Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Fukushima, K. Poly(Trimethylene Carbonate)-Based Polymers Engineered for Biodegradable Functional Biomaterials. *Biomater. Sci.* **2016**, *4*, 9–24.
2. Pêgo, A.P.; Van Luyn, M.J.A.; Brouwer, L.A.; Van Wachem, P.B.; Poot, A.A.; Grijpma, D.W.; Feijen, J. In Vivo Behavior of Poly(1,3-Trimethylene Carbonate) and Copolymers of 1,3-Trimethylene Carbonate with D,L-Lactide or ε-Caprolactone: Degradation and Tissue Response. *J. Biomed. Mater. Res. A* **2003**, *67*, 1044–1054.

 doi:10.20944/preprints202408.1521.v1

3. Zhu, K.J.; Hendren, R.W.; Jensen, K.; Pitt, C.G. Synthesis, Properties, and Biodegradation of Poly (1,3-Trimethylene Carbonate). *Macromolecules* **1991**, *24*, 1736–1740.
4. Pêgo, A.P.; Grijpma, D.W.; Feijen, J. Enhanced Mechanical Properties of 1,3-Trimethylene Carbonate Polymers and Networks. *Polymer* **2003**, *44*, 6495–6504.
5. Tempelaar, S.; Mespouille, L.; Dubois, P.; Dove, A.P. Organocatalytic Synthesis and Postpolymerization Functionalization of Allyl-Functional Poly(Carbonate)s. *Macromolecules* **2011**, *44*, 2084–2091.
6. Nederberg, F.; Lohmeijer, B.G.G.; Leibfarth, F.; Pratt, R.C.; Choi, J.; Dove, A.P.; Waymouth, R.M.; Hedrick, J.L. Organocatalytic Ring Opening Polymerization of Trimethylene Carbonate. *Biomacromolecules* **2007**, *8*, 153–160.
7. Tempelaar, S.; Mespouille, L.; Coulembier, O.; Dubois, P.; Dove, A.P. Synthesis and Post-Polymerisation Modifications of Aliphatic Poly(Carbonate)s Prepared by Ring-Opening Polymerisation. *Chem. Soc. Rev.* **2013**, *42*, 1312–1336.
8. Yu, W.; Maynard, E.; Chiaradia, V.; Arno, M.C.; Dove, A.P. Aliphatic Polycarbonates from Cyclic Carbonate Monomers and Their Application as Biomaterials. *Chem. Rev.* **2021**, *121*, 10865–10907.
9. Amsden, B. In Vivo Degradation Mechanisms of Aliphatic Polycarbonates and Functionalized Aliphatic Polycarbonates. *Macromol. Biosci.* **2021**, *21*, 2100085.
10. Zhang, Z.; Kuijer, R.; Bulstra, S.K.; Grijpma, D.W.; Feijen, J. The in Vivo and in Vitro Degradation Behavior of Poly(Trimethylene Carbonate). *Biomaterials* **2006**, *27*, 1741–1748.
11. Wu, L.; Wang, Y.; Zhao, X.; Mao, H.; Gu, Z. Investigating the Biodegradation Mechanism of Poly(trimethylene carbonate): Macrophage-Mediated Erosion by Secreting Lipase. *Biomacromolecules* **2023**, *24*, 921-928.
12. Nag, A.; Arifianti, A.E.; Khankhuean, A.; Ajiro, H. Polymer Blends Using Poly(Trimethylene Carbonate). *Eur. Polym. J.* **2024**, *214*, 113146.
13. Edlund, U.; Albertsson, A.C. Copolymerization and Polymer Blending of Trimethylene Carbonate and Adipic Anhydride for Tailored Drug Delivery. *J. Appl. Polym. Sci.* **1999**, *72*, 227–239.
14. Qi, J.; Feng, S.; Liu, X.; Xing, L.; Chen, D.; Xiong, C. Morphology, Thermal Properties, Mechanical Property and Degradation of PLGA/PTMC Composites. *J. Polym. Res.* **2020**, *27*, 387.
15. Liu, D.; Li, H.; Jiang, L.; Chuan, Y.; Yuan, M.; Chen, H. Characterization of Active Packaging Films Made from Poly(Lactic Acid)/Poly(Trimethylene Carbonate) Incorporated with Oregano Essential Oil. *Molecules* **2016**, *21*, 21060695.
16. Qin, Y.; Yang, J.; Xue, J. Characterization of Antimicrobial Poly(Lactic Acid)/Poly(Trimethylene Carbonate) Films with Cinnamaldehyde. *J. Mater. Sci.* **2015**, *50*, 1150–1158.
17. Zhang, S.; Li, H.; Yuan, M.; Yuan, M.; Chen, H. Poly(Lactic Acid) Blends with Poly(Trimethylene Carbonate) as Biodegradable Medical Adhesive Material. *Int. J. Mol. Sci.* **2017**, *18*, 2041.
18. Terao, K.; Miyake, J.; Watanabe, J.; Ikeda, Y. Surface Properties of Ultra-Thin Membrane Composed of Polycarbonate and Polylactide. *Trans. Mater. Res. Soc. J.* **2011**, *36*, 557–560.
19. Zhang, X.; Geven, M.A.; Wang, X.; Qin, L.; Grijpma, D.W.; Peijs, T.; Eglin, D.; Guillaume, O.; Gautrot, J.E. A Drug Eluting Poly(Trimethylene Carbonate)/ Poly(Lactic Acid)-Reinforced Nanocomposite for the Functional Delivery of Osteogenic Molecules. *Int. J. Nanomedicine* **2018**, *13*, 5701–5718.
20. Liu, D.; Li, H.; Zhou, G.; Yuan, M.; Qin, Y. Biodegradable Poly(Lactic-Acid)/Poly(Trimethylene-Carbonate)/Laponite Composite Film: Development and Application to the Packaging of Mushrooms (Agaricus Bisporus). *Polym. Adv. Technol.* **2015**, *26*, 1600–1607.
21. Qin, Y.; Yuan, M.; Li, L.; Quo, S.; Yuan, M.; Li, W.; Xue, J. Use of Polylactic Acid/Polytrimethylene Carbonate Blends Membrane to Prevent Postoperative Adhesions. *J. Biomed. Mater. Res. B Appl Biomater* **2006**, *79*, 312–319.
22. Terao, K.; Miyake, J.; Watanabe, J.; Ikeda, Y. Regulation of Protein Loading on Poly(Trimethylene Carbonate), Poly(l-Lactic Acid), and Their Copolymer: Effect of Surface Enrichment by Polymer Crystallinity. *Mater. Sci. Eng. C* **2012**, *32*, 988–993.
23. Qi, J.; Zhang, Y.; Liu, X.; Zhang, Q.; Xiong, C. Preparation and Properties of a Biodegradable Poly(Lactide-Co-Glycolide)/Poly(Trimethylene Carbonate) Porous Composite Scaffold for Bone Tissue Engineering. *New J. Chem.* **2020**, *44*, 14632–14641.
24. Qi, J.; Xiao, J.; Zhang, T.; Zhang, Y.; Xiong, C. Investigation of the Nano-Hydroxyapatite with Different Surface Modifications on the Properties of Poly(Lactide-Co-Glycolide Acid)/Poly(Trimethylene Carbonate)/Nano-Hydroxyapatite Composites. *Colloid Polym. Sci.* **2020**, *299*, 623–635.
25. Zhang, J.; Luo, L.; Lyu, S.; Pudil, B.; Schley, J.; Benz, M.; Buckalew, A.; Chaffin, K.; Hobot, C.; Sparer, R. Unique Microstructure and Mechanical Properties from Melt Processing Poly(Lactide-Co-Glycolide)/Poly(Trimethylene Carbonate). *Mater. Res. Soc. Symp. Proc.* **2010**, *1239*.
26. Han, J.; Branford-White, C.J.; Zhu, L.M. Preparation of Poly(ε-Caprolactone)/Poly(Trimethylene Carbonate) Blend Nanofibers by Electrospinning. *Carbohydr. Polym.* **2010**, *79*, 214–218.
27. Jiang, T.; Zhang, G.; Li, H.; Jina, X. Preparation of Electrospun Poly (ε-Caprolactone)/Poly (Trimethylene-Carbonate) Blend Scaffold for in Situ Vascular Tissue Engineering. *Adv. Mat. Res.* **2013**, *629*, 60–63.

 doi:10.20944/preprints202408.1521.v1

28. Wu, J.; Zhang, Z.; Gu, J.; Zhou, W.; Liang, X.; Zhou, G.; Han, C.C.; Xu, S.; Liu, Y. Mechanism of a Long-Term Controlled Drug Release System Based on Simple Blended Electrospun Fibers. *J. Controlled Release* **2020**, *320*, 337–346.
29. Jiang, T.; Zhang, G.; He, W.; Li, H.; Jin, X. The Tissue Response and Degradation of Electrospun Poly(ε -Caprolactone)/Poly(Trimethylene-Carbonate) Scaffold in Subcutaneous Space of Mice. *J. Nanomater.* **2014**, *2014*, 837695.
30. Bat, E.; Kothman, B.H.M.; Higuera, G.A.; van Blitterswijk, C.A.; Feijen, J.; Grijpma, D.W. Ultraviolet Light Crosslinking of Poly(Trimethylene Carbonate) for Elastomeric Tissue Engineering Scaffolds. *Biomaterials* **2010**, *31*, 8696–8705.
31. Liang, J.; Grijpma, D.W.; Poot, A.A. Tough and biocompatible hybrid networks prepared from methacrylated poly(trimethylene carbonate) (PTMC) and methacrylated gelatin. *Eur. Polym. J.* **2020**, *123*, 109420.
32. Eriksson, T.; Mace, A.; Mindemark, J.; Brandell, D. The Role of Coordination Strength in Solid Polymer Electrolytes: Compositional Dependence of Transference Numbers in the Poly(ϵ-Caprolactone)-Poly(Trimethylene Carbonate) System. *Phys. Chem. Chem. Phys.* **2021**, *23*, 25550–25557.
33. Derewenda, Z.S. C-H Groups as Donors in Hydrogen Bonds: A Historical Overview and Occurrence in Proteins and Nucleic Acids. *Int. J. Mol. Sci.* **2023**, *24*, 1–23.
34. Wan, Q.; Thompson, B.C. Control of Properties through Hydrogen Bonding Interactions in Conjugated Polymers. *Adv. Sci.* **2024**, *11*, 1–26.
35. Ma, Y.; Song, F.; Yu, J.; Wang, N.; Jia, P.; Zhou, Y. Combining Renewable Eleostearic Acid and Eugenol to Fabricate Sustainable Plasticizer and its Effect of Plasticizing on PVC. *J. Polym. Environ.* **2022**, *30*, 2099-2108.
36. Surendren A.; Mohanty A.K.; Liu, Q.; Misra, M. A Review of Biodegradable Thermoplastic Starches, Their Blends and Composites: Recent Developments and Opportunities for Single-use Plastic Packaging Alternatives. *Green Chem.* **2022**, *24*, 8606-8636.
37. Goswami, S.R.; Nair S.S.; Wang, S. Yan, N. Recent Progress on Starch Maleate/Polylactic Acid Blends for Compostable Food Packaging Applications. *ACS Sustain. Chem. Eng.* **2022**, *10*, 3-15.
38. Vieira, M.G.A.; Da Silva, M.A.; Dos Santos, L.O.; Beppu, M.M. Natural-Based Plasticizers and Biopolymer Films: A Review. *Eur. Polym. J.* **2011**, *47*, 254–263.
39. Choi, J.S.; Park, W.H. Effect of Biodegradable Plasticizers on Thermal and Mechanical Properties of Poly(3-Hydroxybutyrate). *Polym. Test.* **2004**, *23*, 455–460.
40. Matveev, Y.; Grinberg, Vy.; Tolstoguzov, V. The Plasticizing Effect of Water on Proteins, Polysaccharides and Their Mixtures. Glassy State of Biopolymers, Food and Seeds. *Food Hydrocoll* **2000**, *14*, 425–437.
41. Dharmalingam, K.; Ramachandran, K.; Sivagurunathan, P.; Kalamse, G.M. Molecular Interactions in Alcohol-Ethyl Methacrylate Mixtures. *Spectrochim Acta A* **2008**, *69*, 467–470.
42. Mathis, C.H.; Divandari, M.; Simic, R.; Naik, V. V.; Benetti, E.M.; Isa, L.; Spencer, N.D. ATR-IR Investigation of Solvent Interactions with Surface-Bound Polymers. *Langmuir* **2016**, *32*, 7588–7595.
43. Omar, A.A.; Hanafi, M.H.M.; Razak, N.H.; Ibrahim, A.; Razak, N.A.A. A Best-Evidence Review of Bio-Based Plasticizer and the Effects on the Mechanical Properties of PLA. *Chem. Eng. Trans.* **2021**, *89*, 241–246.
44. Hess, F.; Kipping, T.; Weitschies, W.; Krause, J. Understanding the Interaction of Thermal, Rheological, and Mechanical Parameters Critical for the Processability of Polyvinyl Alcohol-Based Systems during Hot Melt Extrusion. *Pharmaceutics* **2024**, *16*, 472.
45. Eslami, Z.; Elkoun, S.; Robert, M.; Adjallé, K. A Review of the Effect of Plasticizers on the Physical and Mechanical Properties of Alginate-Based Films. *Molecules* **2023**, *28*, 6637.
46. Alee, M.; Fu, J.; Duan, Q.; Yang, M.; Liu, H.; Zhu, J.; Xianyang, B.; Chen, L.; Yu, L. Plasticizing Effectiveness and Characteristics of Different Mono-Alcohols, Di-Alcohols, and Polyols for Starch-Based Materials. *Starch/Staerke* **2023**, *75*, 2300059.
47. Galdeano, M.C.; Grossmann, M.V.E.; Mali, S.; Bello-Perez, L.A.; Garcia, M.A.; Zamudio-Flores, P.B. Effects of Production Process and Plasticizers on Stability of Films and Sheets of Oat Starch. *Mater. Sci. Eng. C* **2009**, *29*, 492–498.
48. Dickey, A.N.; Faller, R. Investigating Interactions of Biomembranes and Alcohols: A Multiscale Approach. *J. Polym. Sci. Part B: Polym. Phys.* **2005**, *43*, 1025–1032.
49. Dai, F.; Zhuang, Q.; Huang, G.; Deng, H.; Zhang, X. Infrared Spectrum Characteristics and Quantification of OH Groups in Coal. *ACS Omega* **2023**, *8*, 17064–17076.
50. Feller, S.E.; Brown, C.A.; Nizza, D.T.; Gawrisch, K. Nuclear Overhauser Enhancement Spectroscopy Cross-Relaxation Rates and Ethanol Distribution across Membranes. *Biophys. J.* **2002**, *82*, 1396–1404.
51. Magoń, A.; Pyda, M. Melting, Glass Transition, and Apparent Heat Capacity of α-d-Glucose by Thermal Analysis. *Carbohydr. Res.* **2011**, *346*, 2558–2566.
52. Lee, J.W.; Thomas, L.C.; Schmidt, S.J. Investigation of the Heating Rate Dependency Associated with the Loss of Crystalline Structure in Sucrose, Glucose, and Fructose Using a Thermal Analysis Approach (Part I). *J. Agric. Food Chem.* **2011**, *59*, 684–701.

 doi:10.20944/preprints202408.1521.v1

53. Hurtta, M.; Pitkänen, I.; Knuutinen, J. Melting Behaviour of D-Sucrose, D-Glucose and D-Fructose. *Carbohydr. Res.* **2004**, *339*, 2267–2273.