Itaconate-based polyesters as potential inks for 3D printed biomaterials

Magdalena Miętus(1)*, Agnieszka Gadomska-Gajadhur(1)
(1) Faculty of Chemistry, Warsaw University of Technology, Warsaw, Poland
*magdalena.mietus.dokt@pw.edu.pl

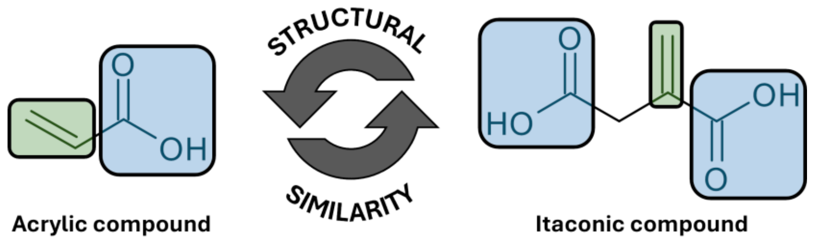
INTRODUCTION

To date, polyacrylate and PLA-based materials are most commonly used for 3D printing.[1,2] Those materials have significant advantages (biodegradability, biocompatibility for PLA, and good mechanical properties for acylate compounds). Nonetheless, they have some major disadvantages.[3] PLA is characterized by fragility and low cell adhesion (if we consider it for use in 3D bioprinting).[2] Furthermore, acrylate compounds are toxic and are usually obtained from non-renewable raw materials, which is against the trends of Green Chemistry. Thanks to the presence of multiple bonds in the structure of acrylate polymers, they can be subjected to UV light. It makes it possible to successfully print a high-quality model of the desired shape. 3D printing can also be used to obtain cellular scaffolds with applications in tissue engineering. For this, it is necessary to use non-toxic materials that have the potential to mimic the cellular matrix naturally found in the human body.

In this research, **poly(tetramethylene itaconate)** (**PBItc**) synthesis and UV-crosslinking will be investigated. Itaconic compounds are structurally similar to acrylate ones.[4] A C=C bond in the structure of the itaconic compound allows UV-enhanced crosslinking. This work reports the findings of a research study to determine how the photocrosslinking time primarily affects the mechanical, thermomechanical, thermal, and cytotoxicity properties of the received polymer films. The aim is to identify potential applications in any of the fields of tissue engineering.

[1] 10.1021/acssuschemeng.0c02168; [2] 10.3390/polym16081140; [3] 10.1007/s10856-010-4091-8; [4] 10.1039/c6gc00605a

BACKGROUND INFORMATION



Acrylic compound   Itaconic compound

Figure 1. Chemical structure of acrylic acid and itaconic acid.

Advantages of itaconic acid (IA):

- ☑ Biodegradable
- ☑ Produced by fermentation (*Aspergillus terreus* fungi)
- ☑ Antibacterial and anticancer properties
- ☑ Presence of double bond → post-polymerization reactions

Advantages of 1,4-butanediol (1,4-BD):

- ☑ Biodegradable
- ☑ Naturally occurs in the human body
- ☑ Produced by fermentation (*E. coli* bacteria)

PREPOLYMER SYNTHESIS

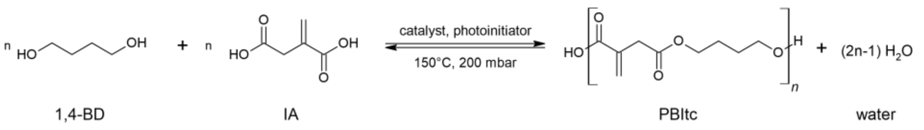
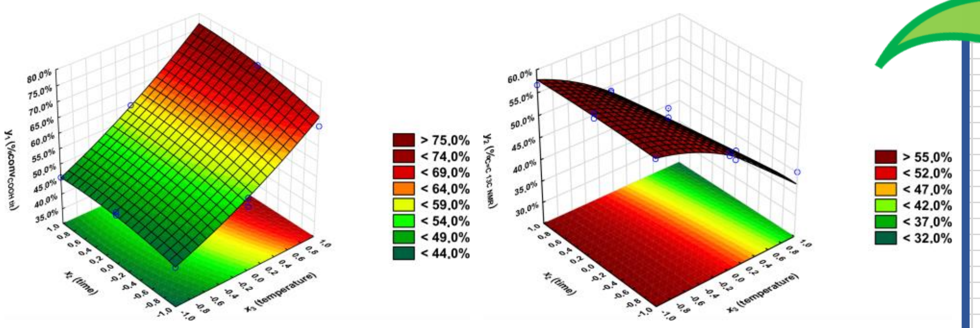
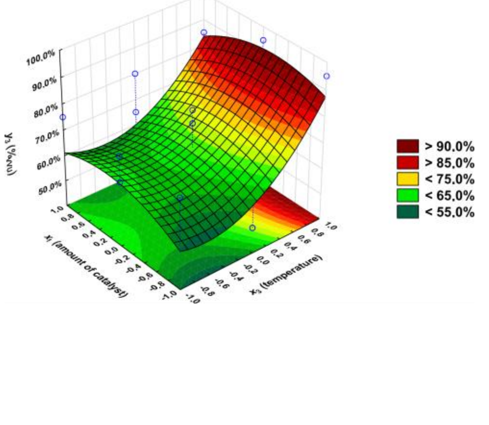


Figure 2. Synthesis of poly(tetramethylene itaconate) prepolymer.

Box-Behnken optimization



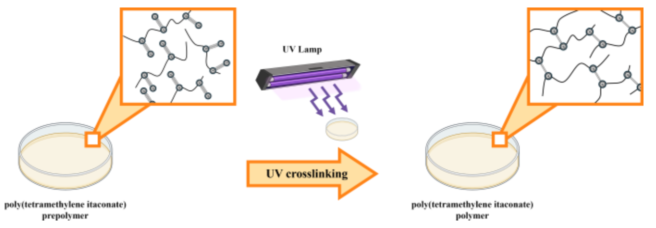


$conv_{COOH\ tit}$ → 66.1±3,9%
$\%C{=}C_{13C\ NMR}$ → 35.0%
$\%_{VVU}$ → 95.0%

Figure 3. Response surface plots of selected PBItc synthesis parameters.

Figure 4. Consistency of the PBItc optimal prepolymer.

PREPOLYMER CROSSLINKING



Modified parameter → Photocuring time 70 s - 15 min

Figure 5. Schematic representation of PBItc UV-crosslinking.

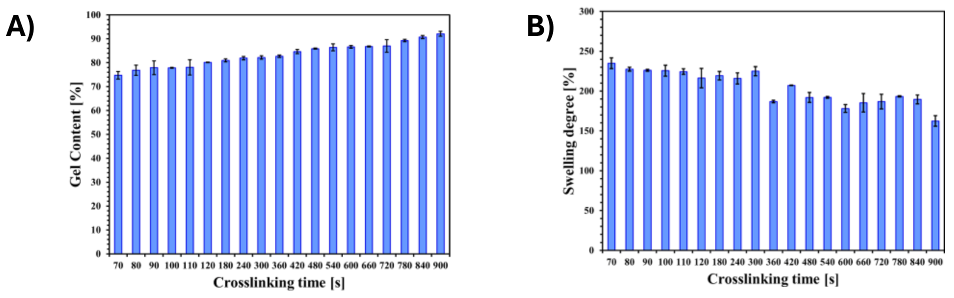


Figure 6. (A) Gel content; (B) Swelling degree of PBItc films.

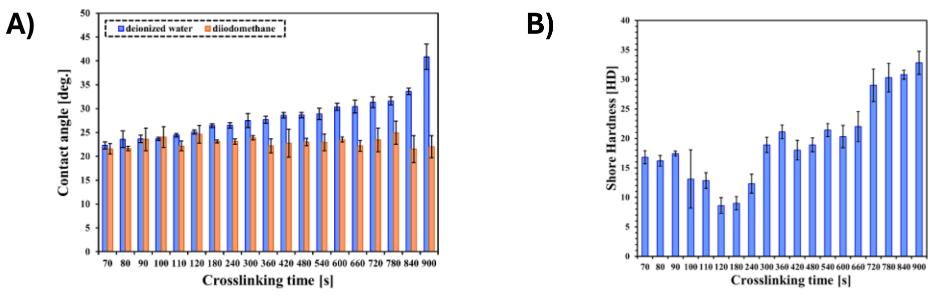


Figure 7. (A) Contact angle; (B) Shore hardness of PBItc films.

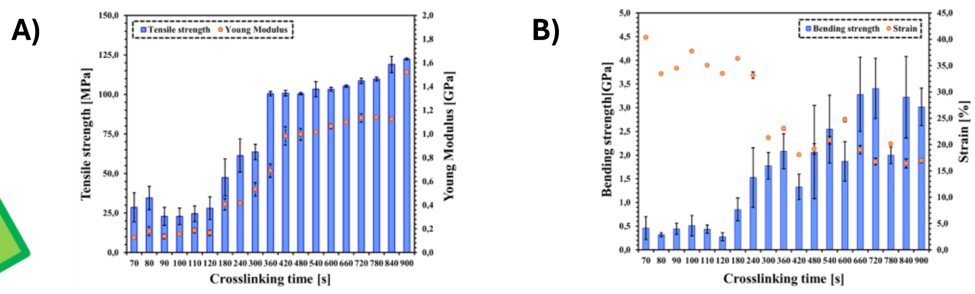


Figure 8. (A) Tensile strength; (B) Bending strength of PBItc films.

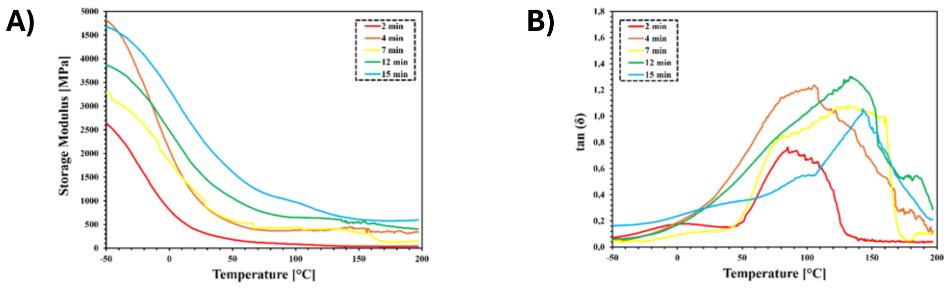


Figure 9. (A, B) DMTA curves for selected PBItc films.

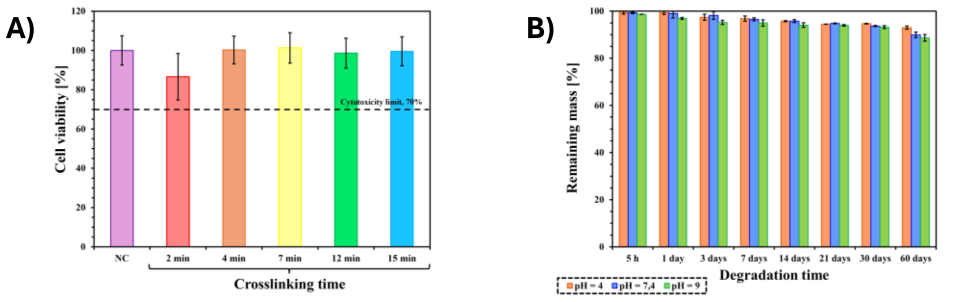


Figure 10. (A) Cytotoxicity effect of the 24 h extracts for selected PBItc films; (B) Degradation of PBItc (UV-cured for 4 min).

CONCLUSIONS

- ✓ PBItc was synthesized **without solvent** with the use of zinc acetate $Zn(OAc)_2$.
- ✓ The synthesis of PBItc was optimized and the applied statistical model **fits well** with the experimental results.
- ✓ UV-crosslinking time of **4 min** is sufficient to obtain a polymer film with suitable properties.
- ✓ PBItc polymer films show potential to be used as a 3D printed cellular scaffold for **soft tissue engineering (skin, ligament, muscle connective tissue)**.

Research was funded by the Warsaw University of Technology within the Excellence Initiative: Research University (IDUB) programme. This research was financed from the budgetary funds of the YOUNG PW II program - "Photo-crosslinked polyesters of itaconic acid and selected dihydroxyl diols enriched with magnetic microparticles for medical applications (MagnetItac)".

Faculty of Chemistry
WARSAW UNIVERSITY OF TECHNOLOGY