TWO-STAGES OF THERMAL AND PHOTO CURING REACTIVE POLYMER NETWORK FROM BIO-BASED PRECURSORS

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DEDICATION

This thesis is dedicated to my grandparent, who taught me that the best kind of knowledge to have is that which is learned for its own sake. It is also dedicated to my family memebers, who taught me that even the largest task can be accomplished if it is done one step at a time.

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ABSTRACT

Shape memory polymers (SMP) are a class of smart materials that can be fixed in a temporary shape and regain its permanent shape upon stimulus. Bio-based polymer with shape memory effect can overcome environmental and economic issues. It can be used as actuator, sensor and for drug delivery system in medical area. Two stages curing reactive bio-based polyester network namely, poly(octanediol-*co*-dodecanedioate-*co*-citrate-*co*-itaconate) were synthesized. The produced samples were formulated as $PC_xI_yt_z$, where x represented molar ratio of citric acid, y represented molar ratio of itaconic acid, and z represented photo-curing duration which varies from 0 to 60 min. In the first curing stage, prepolymer of PC_xI_y was thermally crosslinked. At later time, a second curing was completed through photo initiated free-radical polymerization. From Fourier-transform infrared spectra of $PC_xI_yt_z$, the intensity of the absorption bands at 660 cm^{-1} and 700 cm^{-1} were found decreased with increasing photocuring time. Swelling ratio of bio-based polyester was decreased from 2750 % to 250 % after exposed under UV light for 60 min. All of the synthesized bio-based polymers existed as a semi-crystalline polymer with melting-transition temperature and crystallization-transition temperature vary with photocuring time. Based on X-ray diffraction analysis, the polymer crystallinity of the bio-based polymer decreased with time of photocuring. The Young's modulus of $PC_xI_yt_z$ decreased with increasing photocuring time which may be due to increase in elasticity and softness upon second curing. Shape-recovery temperature of all of the $PC_xI_yt_z$ was found around 37 °C. Two formulations of $PC_xI_yt_z$ were successfully synthesized with excellent shape memory effect (SME). Therefore, this bio-based polymer with shape memory property can be potentially explored in bio-3D printing and medical industry as a printing and an adhesive material respectively.

ABSTRAK

Polimer memori bentuk adalah kelas bahan pintar yang mampu dibentuk kepada bentuk sementara dan kembali kepada bentuk kekal apabila diberi rangsangan. Polimer berasaskan bio dengan kesan memori bentuk dapat mengatasi isu alam sekitar dan ekonomi. Ia boleh digunakan sebagai aktuator, penderia dan untuk sistem penghantaran ubat dalam bidang perubatan. Pempolimeran dwi peringkat rangkaian poliester reaktif berasaskan bahan- bio iaitu poli (oktandiol-ko-dodekandioat-ko-sitrat-ko-itakonat) telah berjaya disintesis. Sampel yang dihasilkan telah dinamakan sebagai $PC_xI_yt_z$, di mana *x* mewakili nisbah molar asid sitrik, *y* mewakili nisbah molar asid itakonik, dan *z* mewakili masa pempolimeran foto yang berubah daripada 0 ke 60 min. Pada peringkat pempolimeran pertama, pre-polimer daripada PC_xI_y disilangkan secara haba. Seterusnya, proses pempolimeran kedua telah dilengkapkan melalui pempolimeran radikal bebas dengan pemula foto. Dari spektrum Fourier pengubahan inframerah $PC_xI_yt_z$, keamatan band penyerapan pada 660 cm^{-1} dan 700 cm^{-1} didapati menurun seiring dengan peningkatan waktu pengikatan silang. Nisbah pembengkakan poliester berasaskan bio telah menurun daripada 2750 % kepada 250 % selepas didedahkan kepada cahaya UV selama 60 min. Semua polimer berasaskan bio yang disintesis wujud sebagai polimer semi-kristal dengan suhu peralihan lebur dan suhu peralihan penghabluran yang berubah seiring tempoh pempolimeran foto. Berdasarkan analisis pembelauan sinar X, penghabluran polimer berasaskan bio menurun dengan masa foto pempolimeran. Modulus Young $PC_xI_yt_z$ menurun dengan peningkatan masa pempolimeran foto yang mungkin disebabkan oleh peningkatan dalam keanjalan dan kelembutan bedasarkan proses pempolimeran kedua. Suhu bentuk-pemulihan bagi semua $PC_xI_yt_z$ ditemui sekitar 37 °C. Dua formulasi $PC_xI_yt_z$ telah berjaya disintesis dengan sifat memori bentuk yang sangat baik. Oleh itu, polimer berasaskan bio dengan sifat memori bentuk ini boleh diterokai dalam percetakan-bio 3D sebagai bahan percetakan serta sebagai bahan pelekat dalam industri perubatan.

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LIST OF ABBREVIATIONS

CA	Citric acid
CNC	Cellulose nanocrystal
CNT	Carbon nanotube
DMPA	2,2-dimethoxy-2-phenylacetophenone
DSC	Differential scanning calorimetry
FTIR	Fourier transform Infrared spectroscope
GO	Graphene oxide
HBPU	Hyperbranched polyurethane
IA	Itaconic acid
PLA	Polylactic acid
PSSe	Poly(propylene sebacate)
SMP	Shape memory polymer
TGA	Thermogravimetric analyzer
THF	Tetrahydrofuran
TPU	Thermoplastics polyurethane
UV	Ultraviolet and visible
XRD	X-ray diffraction
ZDA	Zinc diacrylate

CHAPTER 1

INTRODUCTION

1.1 Background of study

In this recent, there is a paradigm shift in replacing the petroleum-based polymers with those derived from bio-masses. Development of bio-based polymer seems to be a cost effective and sustainable approach. The unstable price of crude oil is undeniably stated as the main reason for the fluctuation in manufacturing cost of petroleum based material. Ultimately, bio-based polymers sound sustainable, eco-efficient, and environment friendly whereas petroleum-based materials are the major composition of landfill due to non-biodegradability.

Biomass, including crops, aquatic plants, wood, and animal waste is one of the most important renewable resource. In the past decade, a huge number of bio-based polymers were successfully utilizing these renewable resources. Almost all of the bio-based polymers have no disposal issue at its end-of -life. The predicted market value of evaluation of worldwide bio-based polymer production capacity will increase from 6.6 million tons (€13 billion) from 2017 to 8.5 million tons in the next following five years (Figure 1.1) (Carus 2017). This is a great anticipation for the research and development of bio-based polymers.

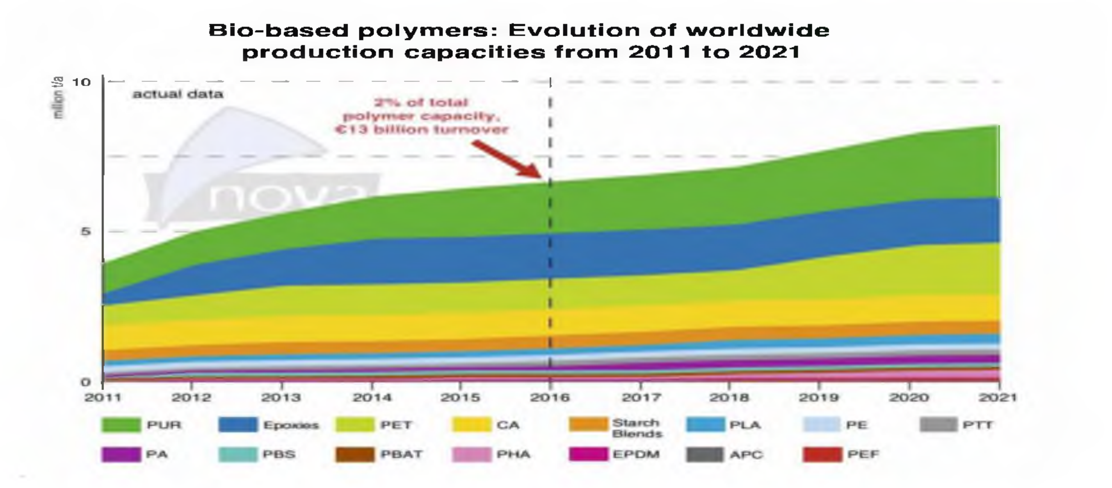

Figure 1.1 Bio-based polymer: Evolution of worldwide production capacities from 2011 to 2021. (Carus 2017).

Interestingly, shape-memory properties of these bio-based polymers also have been revealed. Shape-memory polymers (SMP) are a class of smart materials that can be fixed in a temporary shape and regain its permanent shape upon heating (Xie 2011). SMP were found in number of application ranged from aerospace, automotive, and most promisingly, in medical field. Typically, shape-memory properties of the thermosetting polymers (shape recovery percentage of thermoset polyurethane is 98 %) are better than that of thermoplastic (shape recovery percentage of thermoplastics polyurethane ≈ 92.2 %) which may due to the presence of crosslinking network (Park, *et al*. 2014, Xie, *et al.* 2016).

By the using renewable resources, Guo and co-workers (2011) successfully synthesized a series of bio-based SMP namely, poly(propylene sebacate) (PPSe). In subsequent years, they also published works related to the characterization of PPS/inorganic filler composites (zinc diacrylate & boehmite nanoplatelets) (Guo, *et al.* 2014, Guo, *et al.* 2012). Besides, stimuli responsive drug releasing system based on bio-based polymer has been revealed (Serrano, *et al.* 2011). Although crosslinking network play important role in the shape-memory performance, reshape/remold of the permanent shape may still remain as significant limitation.

In this project, a series of two-stages curing reactive polymer networks were synthesized using 1,8-octanediol, citric acid, itaconic acid, and 1,12-dodecanedioic acid. We hypothesize that the mechanical, thermal, chemical, structural, and shape-memory properties of the bio-based polymer can be simply tailored thru manipulating photo-curing duration as well as stoichiometric of citric acid to itaconic acid. Here, it is expected that two stages curing method may serve as an alternative to fabricate a bio-based shape-memory polymer in a complex structure. We believe that the outcome of this work may certainly attract as much attention as it perhaps deserved from the researchers, industry, and end-users.

1.2 Problem statement

Currently, replacing petroleum-based polymeric materials with those derived from bio-based feedstock may seem to be a more viable alternative (Carus 2017). In market, all petroleum-based materials are non-renewable. As compared to counterparts, bio-based materials are sustainable, eco-friendly, eco-efficient, and less harmful to environment. Furthermore, most of the landfills contains materials manufactured from non-renewable resources that are still increasing consistent with the growth of population. In such circumstances, there is quite a significant demand to promote exploration of a new generation of bio-based materials with degradability, leaving no disposal issue at its end-of-life.

Due to the presence of crosslinking network, bio-based thermosets have a better shape-memory effect as compare to the bio-based thermoplastics (Yang, *et al.* 2004). In contrast, bio-based thermosets are less processable than its counterpart. Traditional polymer processing methods such as injection moulding as well as liquid moulding are limited to thermoplastics and relatively simple 3D shapes due to the requirement for demolding. Whereas much effort has been made on ever more complex SMP along with remouldability, processes for creating 3D complex shapes have remained challenging.

Generally, thermal curing is the most common method to synthesize bio-based crosslinked polymer. Synthesis of bio-based crosslinked polymer by using one cuing method (mostly are thermal curing) have been done by many research groups (Guo, *et al*. 2014, Miao, *et al*. 2012, Tsujimoto, *et al*. 2015, Gyawali, *et al*. 2010b). However, some of the researcher discovered that double polymer network enables altered crystallinity and mechanical properties of crosslinked polymer (Yacakci, *et al*. 2015, Meng, *et al*. 2015, Nair, *et al*. 2012). By cooperating with photo curing method, two-stage crosslinkable polymer network could be remould or reconfigure a new permanent shape from first stage- thermal curing.

In this project, a novel bio-based shape-memory polymer was synthesized. Two curing stages were conducted. 1,8-octanediol, citric acid, itaconic acid, and 1,12-dodecanedioic acid were reacted to obtain prepolymer. Two different curing stages were conducted in the prepolymer. Following are some of the questions behind the effort in producing two stages reactive curing polymer network from bio-based precursors:-

a) What is the effect of stoichiometric ratio of citric acid to itaconic acid on properties of bio-based polymers?

b) What is the effect different photo-curing time on the properties of bio-based polymers?

c) How are the shape-memory properties of the bio-based polymers?

1.3 Objective of study

The objectives for this project have been embark as,

a. To analyze the effect of stoichiometric ratio of citric acid to itaconic acid on properties of bio-based polymers.

b. To study the effect of photocuring time on properties of bio-based polymers.

c. To evaluate shape memory properties of the bio-based polymers.

1.4 Scopes of study

The scopes of the project were cover synthesis, characterization as well as testing on the bio-based polymers produced. All monomers were melted and reacted to obtain prepolymers which was be cured under two different stages. Stoichiometric ratio of citric acid to itaconic acid and photo-curing duration were manipulated. The first curing stage is thermally crosslinked process and the second stage is photo-induced free radical crosslink process. Samples produced were characterized by Fourier Transform Infrared Spectroscopy (FTIR). Polymer crystallinity were evaluated by using X-ray diffraction (XRD) method. Also, the transparency of polyester with different photo-curing time was studied by using ultraviolet-visible light spectrometer.

The photocuring time of curable polyester sample was manipulated between 0 to 60 minutes. Gel content and swelling ratio of the polyester were determined by measuring the mass of insoluble portion in tetrahydrofuran (THF). Thermal properties of the polyester can be studied by differential scanning calorimetric (DSC). Besides, tensile testing was conducted to determine the elongation at break, tensile strength, and Young’s modulus of all samples.

The performance of shape-memory effect was quantified through angle banding upon heating and thermomechanical cycle from dynamic mechanical analysis (DMA).

1.5 Significant of study

This study contributed to the improvement and innovation on synthesis of polymer process. I believe that this research encouraged the related researchers to be drawn to this novelty and innovated method of synthesis of bio-based polyester *via* thermal and photo curing process. Combination of two different curing method to lead the shape reconfiguration of thermoset polymer and to replace to traditional injection moulding method. This study could consider of the outcomes of the manufacturing industry demand and global environmental issues.

REFERENCES

Ainara, S., Foster, E. J., Christoph, W., Arantxa, E., and Maria Angeles, C. (2014). Thermoplastic shape-memory polyurethanes based on natural oils. *Smart Materials and Structures*, 23(2): 025033.

Ainara, S., Maria, L.G., Angel, V., Arantxa, E., and Maria, A.C. (2013). The role of cellulose nanocrystals in the improvement of the shape-memory properties of castor oil-based segmented thermoplastic polyurethanes. *Composites Science and Technology*, 92: 27-33.

Akinro, A.O., Ikumawoyi, O. B. Yahaya, O., and Ologunagba, M. M. (2012). Environmental impacts of polyethylene generation and disposl in Akure City, Nigeria. *Global Journal of Science Frontier Research Agriculture & Biology*, 12(3): 1-9.

Behl, M. and Lendlein, A. (2007). Shape-memory Polymers. *Materialstoday,* 10: 20 -28.

Barrett, D. G., Lup, W., and Yousaf, M. N. (2009). Aliphatic polyester elastomers derived from erythritol and α,ω-diacids. *Polymer Chemistry*, 2010(1): 296-302.

Bitencourt, C. M., Favaro-Trindade, C. S., Sobral, P. J. A., and Carvalho, R. A. (2014). Gelatin-based films additivated with curcuma ethanol extract: antioxidant activity and physical properties of films. *Food Hydrocolloids*, 2014 (40): 145-152.

Bioplastics Opportunities. (n.d.). *Bio-based polymers*. [Brochure]. Ljubljana, SI:Plastice

Bruggeman, J. P., Bruin, B., Bettinger, C. J., Langer, R. (2008). Biodegradable poly(polyol sebacate) polymers. *Biomaterials*, 29(2008): 4726-4735.

Calvo-Correas, T., Gabilondo, N., Alonso-Varona, A., Palomares, T., Corcuera M. A. and Eceiza, A. (2016). Shape-memory properties of crosslinked biobased polyurethanes. *European Polymer Journal*. 78: 253-263.

Cardoso, E. C. L., Seagllust, S. R., Moraes, G. F., Ono, L. S., Parra, D. F., & Lugao, A. B. (2011, October 24-28). *Density crosslink study of gamma irradiated LDPE predicted by gel-fraction, swelling and glass transition temperature* *characterization.* Paper presented at International Nuclear Atlantic conference, Brazil.

Carus, M. (2017, February 20). Bio-based polymer worldwide: ongoing growth despite difficult market environment. *Nova-Institute GmbH*. P. 1-4.

Chen, Y. K., Chen, K. L., Wang, Y. H., and Xu, C. H. (2015). Biobased heat triggered shape-memory polymers based on polylactide/epoxidized natural rubber bland system fabricated via peroxide-induced dynamic vulcanization: Co-continuous phase structure, shape memory behavior, and interfacial compatibilization. *Industrial & Engineering Chemistry Research*, 2015(54): 8723- 8731.

Coulson, M. (2013, May 1). TECH SPOTLIGHT: PVC alternatives for the medical industry. *Medical Design*. Retrieved from http://medicaldesign.com/materials/tech-spotlight-pvc-alternatives-medical-industry

Goerz, O. and Ritter, H. (2013). Polymers with shape memory effect from renewable resources: crosslinking of polyesters based on isosorbide, itaconic acid an succinic acid. *Polymer International*, 62(5): 709-712

Guo, B., Chen, Y., Lei, Y., Zhang, L., Zhou, W. Y., Rabie, A. B. M., and Z, J. (2011). Bio-based poly(propylene sebacate) as shape memory polymer with tunable switching temperatire for potential biomedical applications. *Biomacromolecules*, 2011(12): 1312-1321.

Guo, W., Kang, H., Chen, Y., Guo, B., and Zhang, L. (2012). Stronger and faster degradable biobased poly(propylene sebacate) as shape memory polymer by incorporating boehmite nanoplatelets. *ACS Applied Materials & Interfaces*, 4: 4006-4014.

Guo, W., Shen, Z., Guo, B., Zhang, L., and Jia, D. (2014) Synthesis of bio-based copolyester and its reinforcement zinc diacrylate for shape memory application. *Polymer*, 55: 4324-4331.

Gyawali, D., Tran, R. T., Guleserian, K. J., Tang, L. P., and Yang, J. (2010a). Citric acid-derived photo-cross-linked biodegradable elastomers. *Journal of Biomaterial Science Polymer Edition 2010*, 21(13): 1761-1782.

Gyawali, D., Nair, P., Zhang, Y., Tran, R. T., Zhang, C., Samchukow, M., Makarov, M., Kim, H. K. W., and Yang, J. (2010b). Citri acid- derived *in situ* crosslinkable biodegradable polymer for cell delivery. *Biomaterials*, 31 (2010): 9092-9105.

Kalita, H. and Karak N. (2013a). Bio-based hyperbranched polyurethanes/Fe_3O_4 nanocomposites as shape memory materials . *Polymer Advanced Technologies*, 2013(24): 819-823.

Kalita, H. and Karak, N.. (2013b). Biobased hyperbranched shape-memory polyurethanes: Effect of different vegetable oils. *Journal of Applied Polymer Science*, 2014(39579): 1-8.

Kang, H., Li, M., Tang, Z., Xue, J., Hu, X., Zhang L.,and Guo, B. (2014). Synthesis and characterization of biobased isosorbide-containing copolyesters as shape memory polymers for biomedical applications. *Journal of Materials Chemistry B*, 2(45): 7877-7886.

Lai, S.M., and Lan, Y.C. (2013). Shape memory properties of melt blended polylactic acid (PLA)/thermoplastic polyurethane (TPU) bio-based blends. *Journal of Polymer Research*,20:140.

Lee, T.S., Rahmat, A.R., and Rahman, W.A. (2013). Polylactic acid. *PDL Handbook Series*.USA: Chadds Ford, PA.

Li, H., Sivasankarapillai, G., McDonald, A. G. (2015). Highly biobased thermally stimulated shape memory copolymeric elastomers derived from lignin and glycerol-adipic acid based hyperbranced prepolymer. *Industrial Crops and Products*, 67(2015): 143-154.

Liu, C., Qin, H., and Mather, P.T. (2007). Review of progress in shape-memory polymers. *Journal of Materials Chemistry*, 2007(16): 1543-1558.

Mbeh, D. A., and Nascimento, R. O. (2015). Biocompatibility of shape-memory polymers for biomedical applications. In Yahia, L. (Ed.) *Shape Memory Polymers for Biomedical Applications*. Cambridge, UK: Elsevier.

McKeen, L. W. (2014). Introduction of plastics, polymers, and their properties. *The Effect of Temperature and other Factors on Plastics and Elastomers (3rd Ed.)*, 2014: 1-45.

Meng, Y., Jiang, J., and Anthamatten, M. (2015). Shape actuation via internal stress induced crystallization of dual cure networks. *American Chemical Society Macro Letters*, 2015(4): 115-118.

Miao, S., Nicholas, C., Wang, Pi., Liu, Y., Su, Z., and Zhang, S. (2013). Soybean oil based polyurethane networks: Shape-memory effects and surface morphologies. *Journal of the American Oil Chemists' Society*, 90: 1415-1421.

Miao, S., Wang, P., Su, Z., Liu, Y., and Zhang, S. (2012). Soybean oil-based shape-memory polyurethanes: Synthesis and characterization. *European Journal of Lipid Science and Technology*. 114(12): 1345-1351.

Migneco, F., Huang, Y. C., Birla, R. K., Hollister, S. J. (2009). Poly)glycerol dodecanoate), a biodegradable polyester for medical devices and tissue engineering scaffolds. *Biomaterials*, 30(33): 6479-6484.

Nair, D. P., Cramer, N. B., Gaipa, J. C., McBride, M. K., Matherly, E. M., McLeod, R. R., Shandas, R., and Bowman, C. N. (2012). Two-stage reactive polymer network forming systems. *Advanced Functional Materials*, 2012(22): 1502-1510.

Nijst, C. L. E., Bruggemen, J. P., Karp, J. M., Ferreira, L., Zumbuehl, A., Bettinger, C. J. and Langer, R. (2007). Synthesis and characterization of photocurable elastomers from poly(glycerol-co-sebacate). *Biomacromolecules*, 2007(8): 3067-3073.

Park, J. H., Dao, T. D., Lee, H., Jeong, H. M., and Kim, B. K. (2014). Properties of graphene/shape memory thermoplastics polyurethane composites actuating by various methods. Materials, 2014 (7): 1520-1538.

Qi, X., Yang, G., Jing, M., Fu, Q., and Chiu, F. (2014) Microfibrillated cellulose reinforced bio-based poly(propylene carbonate) with dual shape memory and self-healing properties. *Journal of Materials Chemistry A*, 2: 20393-20401.

Serrano, M. C., Carbajal, L., Ameer, G. A. (2011). Novel biodegradable shape memory elastomers with drug-releasing capabilities. *Advanced Materials*, 2011(23): 2211-2215.

Suman, T., and Niranjan K. (2013). Bio-based tough hyperbranched polyurethane-graphene oxide nanocomposites as advanced shape memory materials. *Royal Society of Chemistry Advances*, 3:9476-9482.

Tamara, C., Nagore, G., Ana, A., Teodoro, P., M.Angeles, C., and Arantxa, E. (2016). Shape-memory properties of crosslinked biobased polyurethanes. *Europea Polymer Journal*, 78: 253-263.

Tsujimoto, T., Ohta, E., and Uyama, H. (2015). Plant oil-based shape memory polymer using acrylic monolith. *Express Polymer Letters*, 9(2015): 757-763.

Wong, T. W., M. U. Wahit, M. R. Abdul Kadir, M. Soheilmoghaddam and H. Balakrishnan (2014). Anovel poly(xylitol-co-dodecanedioate)/hydroxyapatite composite with shape-memory behavior. *Materials Letters*, 126(0): 105-108.

Xie, T. (2011). Recent advances in polymer shape memory. *Polymer*,52(2011): 4985-5000.

Xie, F., Huang, L. N., Leng, J. S., and Liu, Y. J. (2014). Thermoset shape memory polymers and their composites. *Journal of Intelligent Material Systems and Structures,* 27(18): 2433-2455.

Yakacki, C. M., Saed, M., Nair, D. P., Gong, T., Reed, S. M., and Bowman, C. N. (2015). Tailorable and programmable liquid-crystalline elastomers using a two-stage thiol-acrylate reaction. *The Royal Society of Chemistry Advances*, 2015(5): 18997-19001.

Yang, J., A. R. Webb, S. J. Pickerill, G. Hageman and G. A. Ameer (2006). Synthesis and evaluation of poly(diol citrate) biodegradable elastomers. *Biomaterials*, 27 (9): 1889-1898.

Yang, J., and Webb, A. R. (2004). Novel citric acid-based biodegradable elastomers for tissue engineering. *Advanced Material*, 16(6): 511-516.

Yuan, D., Chen, Z., Xu, C., Chen, K., and Chen, Y. (2015). Fully bio-based shape memory material based on novel co-continuous structure in poly(lactic acid)/natural rubber. TPVs fabricated via peroxide-induced dynamic vulcanization and in situ interfacial compatibilization. Sustainable Chemistry & Engineering, 3(11):2856-2865.