Polymer Testing 65 (2018) 420–428

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Statistical design of sustainable thermoplastic blends of poly(glycerol succinate-co-maleate) (PGSMA), poly(lactic acid) (PLA) and poly(butylene succinate) (PBS)

Oscar Valerio[a,b], Manjusri Misra[a,b], Amar K. Mohanty[a,b,*]

[a] School of Engineering, Thornbrough Building, University of Guelph, Guelph, N1G 2W1, Ontario, Canada
[b] Bioproducts Discovery and Development Centre, Department of Plant Agriculture, Crop Science Building, University of Guelph, Guelph, N1G 2W1, Ontario, Canada

ARTICLE INFO

Keywords:
Glycerol
Polyglycerol
Thermoplastic
Polymer blend
Mixture design

ABSTRACT

The feasibility of designing novel sustainable thermoplastic materials containing poly(glycerol succinate-co-maleate) (PGSMA) as a way for upgrading glycerol utilization was explored. The target of the design was to fabricate sustainable blends of PGSMA, poly(lactic acid) (PLA) and poly(butylene succinate) (PBS) with mechanical performance comparable to petroleum based polypropylene and its copolymers. A feasibility region for PGSMA blend compositions was found using statistical mixture design of experiments (DOE) where tensile and impact properties were comparable to commercial polypropylene materials. The mechanical performance of new formulations in this feasibility region was modeled through linear regression and accurately predicted, with a prediction error of 5 and 13.5% for tensile and impact properties, respectively. A blend of 35/40/25 PGSMA/PLA/PBS displayed a tensile strength of 33.8 MPa, tensile modulus of 1.47 GPa and notched Izod impact of 159 J/m, being comparable to some commercially available polypropylene products.

1. Introduction

In an effort for decreasing petroleum dependence and thus alleviating environmental concerns on its effects, the usage of biobased plastics has been industrially adopted in many countries as a strategy for increasing sustainability of plastic consumption. The engineering design and synthesis of biobased thermoplastics that can match some key properties of petroleum based plastics is thus an important research challenge in current development. In particular, designing biobased thermoplastics that could match the mechanical performance of common polyolefins such as polypropylene at a similar production cost could help in promoting a gradual transition towards biobased thermoplastics for certain applications where durability of the parts is not an issue. Melt blending technologies are of particular interest in the engineering design of thermoplastic materials, given that they can be easily scaled up for adoption at industrial level [1,2]. Thus, a common technique in the design of biobased thermoplastics is the melt blending of biobased polymers displaying poor mechanical behavior but relatively low cost, with synthetic high performance biobased polymers in order to produce a final material with a balanced cost to performance ratio. The development of biobased thermoplastic starch blends [3–5] and plasticized proteinaceous blends [6–10] are good examples of this method.

Poly(glycerol-co-diacid)s are an emerging family of biobased polyesters which can be synthesized in simple polycondensation procedures using glycerol and diacids as co-monomers. Poly(glycerol sebacate) synthesized using glycerol and sebacic acid is by far the most widely studied polyester from this family since its first description as a biocompatible biodegradable elastomeric material [11]. Given the attractiveness of biomedical applications, the vast majority of research on poly(glycerol-co-diacids) is oriented to biomedical usages of poly(glycerol sebacate) [12]. Nevertheless, novel applications for different poly(glycerol-co-diacids) are emerging as this is required in order to strengthen the biorefinery concept around the oleaginous biomass, where glycerol is a major co-product of biodiesel production [13,14]. Interestingly, the total cost of production at industrial level of these poly(glycerol-co-diacids) using glycerol from biodiesel biorefineries has been estimated as ~0.9 USD/lb using process simulation tools [15], which makes them attractive candidates for the development of commercially viable applications. In particular, poly(glycerol succinate) (PGS) and poly(glycerol succinate-co-maleate) have been described as elastomeric materials which can be synthesized using glycerol from biodiesel production and biobased succinic acid [16,17]. These biobased materials have been used in earlier literature as toughness

* Corresponding author. Bioproducts Discovery and Development Centre, Department of Plant Agriculture, Crop Science Building, University of Guelph, Guelph, N1G 2W1, Ontario, Canada.
E-mail address: mohanty@uoguelph.ca (A.K. Mohanty).

https://doi.org/10.1016/j.polymertesting.2017.12.018
Received 3 November 2017; Received in revised form 8 December 2017; Accepted 16 December 2017
Available online 24 December 2017
0142-9418/

enhancers in thermoplastic blends due to their elastomeric properties [18–20]. In spite of the simplicity of their production route and an estimated low production cost at industrial level, these amorphous elastomers present poor mechanical performance for being used as thermoplastic materials in replacement of common polyolefins due to a low achievable molecular weight before crosslinking [21]. Therefore, the strategy of blending PGSMA with secondary thermoplastics to improve the mechanical performance of the final material appears as a logical choice.

Among synthetic biobased and biodegradable polymers, poly(lactic acid) or polylactide (PLA) and poly(butylene succinate) (PBS) are currently the materials with highest industrial production capacity, jointly reaching nearly 328 kton/year in 2016 [22]. This includes PBS synthesized both from petroleum and renewable sources. PLA is a well-known thermoplastic material, with a high tensile strength (~65 MPa) and modulus (~3.2 GPa) which is produced industrially from biomass fermentation to lactic acid followed by polymerization of lactide. This fully biobased semi-crystalline thermoplastic has been used in applications such as biomedical devices and rigid and flexible packaging [23,24]. Its wider adoption in commercial applications has been often limited by its brittleness, evidenced as a low elongation at break (~3%) and notched Izod impact resistance (~20 J/m) [25]. PBS is also a semi-crystalline thermoplastic material displaying a lower tensile strength (30–35 MPa) and modulus (0.3–0.5 GPa) compared to PLA [26]. This ductile material displays a much higher elongation at break than PLA (> 200%) but still its impact resistance remains low (40–70 J/m) [27]. Partially biobased PBS is currently produced at industrial level from biobased succinic acid and petroleum based 1,4-butanediol, yielding PBS of around 60% biobased content [28]. It is projected that by 2017 the industrial production of biobased 1,4-butanediol will be fully operational, enabling the production of 100% biobased PBS [29]. PBS has been commercially adopted mainly in flexible packaging and agricultural applications [22]. Being PLA and PBS the most widely produced biodegradable synthetic polymers and with a prosperous market forecast, their usage as blending partners for PGSMA seems in line with current trends in biobased sector development.

Due to the complementary mechanical properties displayed by PLA and PBS, melt blending of these two polymers has been researched aiming to produce a final material achieving a balance between stiffness (tensile modulus) and toughness (elongation at break and impact resistance). Blends of PLA and PBS have been reported as immiscible, and thus the mechanical behavior of simple blends of PLA/PBS is unsatisfactory [30–32]. Reactive compatibilization has been used to increase the mechanical performance on the PLA/PBS system. The usage of free radical initiators has been shown effective on increasing both tensile and impact toughness of the blends in samples fabricated using compression molding [33,34]. Reactive blending with isocyanate resulted on an effective way for improving impact toughness of the system, achieving a non-break behavior on notched Izod impact testing [35]. Similarly, the addition of PBS grafted nanocellulose (PBS-CNC) in PLA/PBS blends resulted in a significant improvement of notched Izod impact on the final composite [36]. Although these strategies were proved successful, the fabrication of a PLA/PBS blend displaying high notched Izod resistance without the usage of non biobased additives like isocyanides and using a fast and simple, one step blending and injection molding strategy remains a challenge to present date. In this context, the usage of PGSMA as a component in a ternary blend PGSMA/PLA/PBS could help in improving impact resistance on the PLA/PBS blend while they contribute with strength and stiffness, to achieve a final PGSMA/PLA/PBS blend material with balanced mechanical performance.

Statistical design of experiments (DOE) is a technique commonly used in the engineering design of polymeric materials [37–41]. The value of DOE is the possibility of analyzing multiple and simultaneous effects of selected parameters on experimental responses with a minimal set of experiments. Mixture design is a special type of DOE methodology that specially suits the design of polymer blends and composites, given that it allows for analyzing the effect of variating the proportion of the components in the blend on the responses of interest. Using this approach, the mechanical performance of biobased polymeric materials has been tailored in earlier literature [42,43]. Thus, in the present paper the design of a ternary polymeric blend of PGSMA, PLA and PBS using a mixture design of experiments is described, with the aim of achieving a final blend displaying balanced tensile (strength and modulus) and impact (notched Izod) properties in a range comparable to a reference petroleum based thermoplastic such as polypropylene.

2. Experimental section

2.1. Materials

Technical glycerol was obtained from a local biodiesel producer (BIOX corporation, Canada) containing 95 wt% glycerol [17]. Succinic acid (99 + wt%, KIC chemicals, UK), maleic anhydride (99 wt%, Sigma Aldrich, Canada) and 2,5-Bis(tert-butyl-peroxy)-2,5-dimethylhexane (Luperox 101, technical grade 90%, Sigma Aldrich, Canada) were used as received. Injection grade poly(lactic acid) (Ingeo 3251D, Natureworks, USA) with an MFI of 35 g/10 min (190 °C, 2.16 kg) [44] was purchased in the form of pellets. Partially biobased film grade poly (butylene succinate) (FZ91PM, PTT MCC Biochem, Thailand) with an MFI of 5 g/10 min (190 °C, 2.16 kg) [45] was kindly donated by CG-Tech (Canada).

2.2. Synthesis of poly(glycerol succinate-co-maleate) (PGSMA)

PGSMA was synthesized using a simple one pot polycondensation procedure as reported before [19,20]. Glycerol (143 g, 1.5 mol), succinic acid (130 g, 1.1 mol) and maleic anhydride (36 g, 0.4 mol) were placed on a 1L four mouth glass reactor equipped with a dean stark apparatus, heating mantle and mechanical stirrer. The mixture was heated up to 150 °C and stirred at 250 rpm under an inert nitrogen atmosphere. Viscosity of the PGSMA product was monitored in a cone plate viscometer at 100 °C and 100 s^{-1} (CAP 2000+, Brookfield, USA). The reaction was carried until a viscosity on the range of 250–350 P was obtained to reach the highest molecular weight possible before gelation [21]. The PGSMA product obtained displayed a viscosity of 340 P (100 °C and 100 s^{-1}), a molecular weight of 1251 ± 31 g/mol and a polydispersity of 4.6 ± 0.3 as determined by gel permeation chromatography.

2.3. Design of experiments and model fitting

A mixture design was selected to analyze the effect of the blend composition on mechanical properties. The goal was to fabricate PGSMA/PLA/PBS blends using a minimal amount of PBS. The control factors for the design were the weight percentage of PGSMA, PLA and PBS on the blends. For coding the design into the statistical software, weight fractions of PGSMA, PLA and PBS adding a total of one were used. The design was built using Minitab software with the following inputs: $0.3 < PGSMA < 0.5$, $0.3 < PLA < 0.5$, $0.1 < PBS < 0.3$. These limits were chosen based in our previous research and in a preliminary experimental design (data not shown). The experimental design obtained consisted of 26 runs considering two replicates for each point (13 different blend formulations with a duplicate each) (Fig. 1f and Table S1). Stepwise regression method was employed on Minitab for fitting the regression model to the experimental data. In this method, a full cubic model was used as the reference regression model. This methodology starts by estimating the response variable Y with a linear model in the form $Y = \beta_1 * X_1 + \beta_2 * X_2 + \beta_3 * X_3$, where β are the predictors and X_1, X_2 and X_3 are the weight fractions of PGSMA, PLA and PBS respectively in the blend formulation. Through successive