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Improving tensile strength of an injection-molded biocompatible thermoplastic elastomer

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ABSTRACT

Poly(styrene-block-isobutylene-block-styrene) (SIBS) is a thermoplastic elastomer often used in implantable structures due to its exceptional biocompatibility. However, because overall performance is extremely sensitive to fabrication conditions, optimal processing of the raw material remains a challenge. In this study, the Taguchi method is proposed for characterization of the effect of injection molding parameters on the ultimate tensile strength of a SIBS block copolymer. An L_9 orthogonal array is used with three factor levels for nozzle temperature, mold temperature, packing time and injection speed. Analysis indicates that mold temperature has the least effect on tensile strength, and injection speed the greatest effect. A response surface methodology (RSM) design and an artificial neural network (ANN) were used to model tensile strength based on processing parameters. Both methods proved successful in predicting tensile strength with errors of 3% and 2.55% for RSM and ANN, respectively. Optimized validation samples showed ultimate tensile strengths of 17.7 MPa, which is an improvement of almost 40% over reported strengths for the same material. The results presented here are expected to expand the use of SIBS into new applications requiring improved mechanical properties, without sacrificing biocompatibility via the addition of fiber or particle reinforcement.

1. Introduction

Poly(styrene-block-isobutylene-block-styrene) (SIBS) copolymer is a thermoplastic elastomer (TPE) that possesses outstanding biocompatibility and generates close to no foreign body reaction when implanted in the human body [1–6]. SIBS has a triblock linear structure formed by a block of polyisobutylene between blocks of polystyrene (PS). The composition of SIBS can be tailored by changing the degree of polymerization and the weight percentage of the block components in order to achieve desired material properties. The PS provides the copolymer with a glassy microstructure that enhances its mechanical strength, while the polyisobutylene has an amorphous soft structure with increased chain mobility. Different formulations of SIBS have distinctive characteristics that are driven by the polystyrene content. SIBS with higher weight percentage of PS has a mechanical performance closer to that of a toughened plastic, whereas SIBS with lower polystyrene content behaves like a softer elastomeric plastic [1,2,7–9]. The range of possible mechanical properties that are achievable with this type of thermoplastic elastomer, together with the high degree of biocompatibility, make it an ideal material for bio-implantable structures and devices such as stents, artificial heart valves, grafts, drug eluting carriers and many others [10]. Traditional in vivo structural materials are known to produce foreign body reactions ranging from mild to severe [11], hence the need for new implantable materials which cause no adverse reactions. Although the possibilities that SIBS offers are extensive due to its biocompatibility, any potential structural application will be limited by the mechanical properties of the material. For example, Wang et al. [12] performed an in vivo assessment of SIBS heart valves implanted into sheep. The valves suffered material cracking and failure, leading to the death of the animals testing the implants [12]. Hence, in order to fully exploit the biocompatibility of SIBS, it is essential that the mechanical properties be optimized for the specific application.

Block copolymers have an inherent range of material properties due to their composite nature. Any change in block ratio and/or molecular weight may lead to different overall properties. Consequently, any variation in the polymerization process could lead to different mechanical properties. Further, altering the relative amount of polystyrene and polyisobutylene results in a wide range of morphologies for the PS phase. This can be attributed to the chemical incompatibility of the different blocks, which drives micro phase separations and different morphologies in the block copolymer TPE [5]. St. Lawrence et al. [9] performed a microstructure characterization of SIBS and found that at lower mass fractions of styrene, the PS forms spherical structures throughout the polymer. At higher PS contents, the spherical domains become double gyroid structures, and at even higher weight percentages of PS these structures become lamellar. Furthermore, the fabrication techniques might change the overall properties of SIBS not only during the polymerization process but also during thermoforming or solvent forming. Due to the composite nature of the material, the

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interface between the different systems is a key factor in maximizing material properties. Among other consequences, a weakened interface may lead to premature crack propagation and failure of the material. The quality of this interface is heavily influenced by the fabrication technique employed. KANEKA Corporation manufactures a 30% PS by weight SIBS (denominated SIBSTAR 103T) with a published ultimate tensile strength of 18 MPa. Lim et al. [13], however, performed a study and reported an ultimate tensile strength of 12.7 MPa for the same material. It is not unlikely that the discrepancy in reported properties originated from the fabrication technique and the solidification characteristics of the plastic.

Plastic injection molding (PIM) is one of the most common manufacturing techniques for thermoplastics. Its main advantages are fast production of parts, material and color flexibility, little to no waste and low labor costs. There are a few disadvantages to this process that make it unsuitable for certain applications, such as the high initial tooling cost, design restrictions and complex process parameters that affect the performance of the product. Among these process parameters are nozzle temperature, mold temperature, injection speed, holding time, holding pressure and cooling time [14,15]. The complexity of the PIM process is exacerbated not only by the sheer number of variables affecting material properties, but also by the relationships among these variables. In order to deal with this complexity, many studies have employed design of experiment and engineering optimization techniques to better understand PIM, to minimize defects during production, or to maximize desired product characteristics [16–24]. For example, Altan investigated the effect of PIM parameters on shrinkage utilizing the Taguchi method, analysis of variance and artificial neural networks (ANNs). Polypropylene and polystyrene were measured experimentally and the process parameters for minimum shrinkage were found [25]. Using both techniques it was possible to minimize shrinkage to 0.937% and 1.224% for polypropylene and polystyrene respectively. Mamaghani et al. also employed the Taguchi method design of experiment in order to maximize tensile strength and hardness of an Acrylonitrile Butadiene Styrene (ABS) organoclay composite. Optimal Taguchi parameters produced a nanocomposite with an improvement of 11.5% in ultimate tensile strength and 8.5% in Rockwell hardness compared to that of the base material [24]. In another example of PIM optimization, Farshi et al. simulated warpage and shrinkage defects of a polyethylene automobile ventiduct grid. Using a sequential simplex algorithm, process parameters were optimized to minimize shrinkage and warpage [26]. Further insight into PIM optimization was provided by Tzeng et al., who proposed response surface methodology (RSM) and genetic algorithms coupled with ANN to optimize injection molding parameters for maximum strength and impact resistance of a polycarbonate composite [27]. Both methods proved to be effective predictors and optimizers of injection molding parameters. Parameter optimization methods have also been divided into stages. Chen et al., for example, proposed a two-stage method for optimizing multi-input multi-output PIM processes. In the first stage, Taguchi methods were coupled together with ANN and genetic algorithms in order to reduce process variance. The second stage of the method integrated particle swarm optimization in order to find final optimal process parameters [28]. Experimental results not only showed that the process satisfied quality requirements but also improved process stability. In a separate study, Chen et al. made use of Taguchi methodology for parameter selection and neural networks coupled with genetic algorithms in order to search for optimized responses [29]. It was proposed that this approach was able to solve multiple-input multiple-output optimization problems. Using the coupled procedure it was possible to maximize quality based on weight and length of the injection molded parts.

The knowledge base regarding injection molding optimization of thermoplastics is well-developed, as evidenced by the studies available in the open literature. However, there is a general lack of such studies for thermoplastic elastomeric block copolymers, which present unique challenges. In this study, a Taguchi orthogonal array design of experiment was utilized to determine the effect of different injection molding parameters on the ultimate tensile strength of a 30 wt.% PS SIBS block copolymer (SIBSTAR 103T). Selected PIM parameters were melt temperature (T), mold temperature (T_m), injection rate (Sp) and packing time (t). RSM and ANN techniques were applied in order to model and predict tensile strength. Predictions from both methods were compared to experimental results in order to validate the performance of these methods.

2. Experimental

KANEKA Corporation generously provided pellets of a 30% styrene content SIBS with a molecular weight of 132,000 g/mol (commercial name of SIBSTAR 103T). Pellets were processed with a specialized bench top injection molding setup. Dumbbell specimens were fabricated using a mold compliant with ASTM Standard D638 Type V. The injection molder was equipped with a linear actuator and speed controller in order to precisely control the injection speed. For each of the different parameter settings, the first SIBS specimens injected were discarded in order to ensure process stability. Subsequently, a group of eight samples were fabricated and tested in order to reduce measurement variation. All process parameters outside those being optimized remained fixed throughout the experiment. Cooling time was held constant at 2 min at room temperature prior to demolding. The custom injection molding system was designed specifically for precise control of injection rate in lieu of active control or passive measurement of packing pressure. As such, packing pressure was excluded from the optimization process. For commercial systems capable of precise control of packing pressure, this additional variable (or any other) can easily be incorporated into the method outlined here, with the potential for even greater improvement in tensile strength. Dumbbell specimens were tested using an Instron 5966 Tensile Testing Machine at a constant rate of 500 mm/min until failure of the sample.

2.1. Taguchi method

The Taguchi method is a widely used engineering technique to analyze and optimize processes. This method utilizes orthogonal arrays in order to quantify individual effects of parameters and predict experimental outcomes without running full-factorial experimental domains. To accomplish this, it utilizes a specific Signal to Noise ratio (S/N) to characterize product quality. The S/N ratio is determined based on the goal of the experiment. It can be divided into three different types: larger is better, nominal is best, and smaller is better. The relevant equations are as follows:

$$\frac{\mathrm{S}}{\mathrm{N}} = -10\log_{10}\left[\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right] \text{ Larger is better} \quad (1)$$

$$\frac{\mathrm{S}}{\mathrm{N}} = 10\log_{10}\left[\frac{\overline{y_i^2}}{\sigma^2}\right] \text{ Nominal is best} \quad (2)$$

$$\frac{\mathrm{S}}{\mathrm{N}} = -10\log_{10}\left[\frac{1}{n}\sum_{i=1}^{n}y_i^2\right] \text{ Smaller is better} \quad (3)$$

where y_i is the observed response of the ith measurement, n is the number of measurements, σ is the standard deviation of the observed response and $\bar{y}$ is the mean of the response. One drawback of this method is that it does not work with continuous factors, so it is used in experimental setups where factors are categorical or to reduce experimental complexity. In this study, the selected S/N ratio was Larger is Better based on the goal of maximizing tensile strength, and an L_9 orthogonal array was used to analyze the four variables at three distinct levels. All of the analysis was performed with Minitab statistical software.