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Research paper

Investigation of structure–property relationships of polyisobutylene-based biomaterials: Morphology, thermal, quasi-static tensile and long-term dynamic fatigue behavior

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ABSTRACT

This study examines the morphology, thermal, quasi-static and long-term dynamic creep properties of one linear and three arborescent polyisobutylene-based block copolymers (L_SIBS31, D_IBS16, D_IBS27 and D_IBS33). Silicone rubber, a common biopolymer, was considered as a benchmark material for comparison. A unique hysteretic testing methodology of Stepwise Increasing Load Test (SILT) and Single Load Test (SLT) was used in this study to evaluate the long-term dynamic fatigue performance of these materials. Our experimental findings revealed that the molecular weight of polyisobutylene (PIB) and polystyrene (PS) arms [$M_n^{PIB(arm)}$ and $M_n^{PS(arm)}$], respectively had a profound influence on the nano-scaled phase separation, quasi-static tensile, thermal transition, and dynamic creep resistance behaviors of these PIB-based block copolymers. However, silicone rubber outperformed the PIB-based block copolymers in terms of dynamic creep properties due to its chemically crosslinked structure. This indicates a need for a material strategy to improve the dynamic fatigue and creep of this class of biopolymers to be considered as alternative to silicone rubber for biomedical devices.

1. Introduction

Polyisobutylene-based block copolymers are a relatively new class of thermoplastic elastomers (TPEs) with outstanding biocompatibility, biostability and mechanical properties. (El Fray and Altstädt, 2003; El Fray et al., 2006; Puskas and Chen, 2004; Puskas et al., 2004a). Synthesized by living carbocationic polymerization (Puskas and Kaszas, 2003), the first generation of this class of materials has a linear triblock architecture (L_SIBS), as shown in Fig. 1(a). A version of L_SIBS has been in clinical practice as the drug-eluting coating on the Taxus coronary stent, FDA-approved in 2004 (Ranade et al., 2004; US FDA, 2004). A review by Pinchuk and co-workers (Pinchuk et al., 2008) pointed out that L_SIBS has a relatively low

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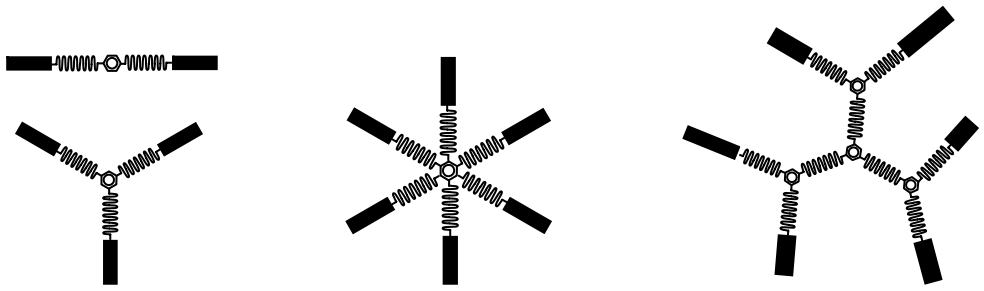

(a) First generation. (b) Second generation. (c) Third generation.

Fig. 1 – The three generations of PIB-based block copolymers by carbocationic polymerization (≡ PIB; ≡ PS or other derivatives).

creep resistance and cannot be steam-sterilized, which can limit the application of L_SIBS on biomedical devices. Newer generations of this material have since evolved with various architectures given in Fig. 1(b) and (c), such as the second generation of multi-arm star polymers (Jacob and Kennedy, 1999), and the third generation (D_IBS) with dendritic or tree-like branched core structure of polyisobutylene (PIB) with end blocks of polystyrene (PS) or its derivatives (Puskas and Grasmüller, 1998; Puskas et al., 2004b).

Not only static mechanical properties, but the long-term dynamic fatigue behavior of polymers has great importance in biomedical devices. When applied over a long period of time, even a small amount of dynamic loading can induce creep and fatigue damage (e.g. micro-cracks) in the polymers. El Fray et al. first introduced the stepwise increasing load (SILT) and single load (SLT) tests to examine the dynamic creep and fatigue behavior of L_SIBS using S-2 dumbbell samples and showed that the fatigue resistance was superior over medical grade silicone (El Fray, 2003; El Fray et al., 2006). An additional advantage of the various PIB-based thermoplastic elastomeric block copolymers (TPEs) compared to medical grade silicone is the possibility to tailor material properties by variation of the hard/soft phase composition, the molecular weight and the overall architecture, coupled with ease of processing, e.g. compression molding (Puskas and Grasmüller, 1998; Puskas et al., 2004b). Puskas et al. investigated the fatigue properties (including long-term stress relaxation) of PIB-based TPEs with a branched (dendritic) core (D_IBS) (Puskas et al., 2009a) using smaller micro-dumbbells in accordance to ASTM D1708 (2006). Their work employed a strain-controlled method to evaluate the dynamic stress relaxation response of implantable micro-dumbbells. To study dynamic creep behavior, the implementation of stress-controlled SILT and SLT for soft materials like D_IBS and using micro-dumbbells requires a precise control of the load sensitivity and noise suppression to maintain a reasonable load signal to noise ratio for data acquisition and analysis.

This work extends our studies to investigate the effect of network structure on the phase morphology, and static and dynamic mechanical properties of linear and branched PIB-based TPEs. This work will also demonstrate the successful implementation of our dynamic fatigue testing methodology to evaluate the dynamic creep performance of soft TPEs and their suitability as alternatives to silicone rubber in biomedical devices.

Table 1 – Materials used in the current study.

Material designation	Hard (PS) phase (wt%)	M_n	M_w/M_n	N[a]
L_SIBS31	31	67,000	1.2	2
D_IBS33[b]	33	70,000	4.5	4
D_IBS27	27	178,000	2.7	4
D_IBS16[b]	16	119,000	2.4	3

[a] Number of arms; rounded numbers.
[b] Puskas et al. (2009a).

2. Experimental work

2.1. Materials

Three different D_IBS polymers were investigated. L_SIBS (SIBSTAR 073T) was provided by the Kaneka Corporation. Table 1 lists the materials. L_SIBS31 refers to the L_SIBS sample with 31 wt% PS, while D_IBS27 stands for the branched polymer that contains 27 wt% PS. The average number of end blocks or "arms" (N) in the branched samples is calculated as B+2 where B is the average number of branches per chain obtained from polymerization kinetics as reported (Puskas et al., 2009a). A medical-grade silica-reinforced crosslinked silicone rubber (MED 4050-Nusil Technology) was used as a control, because this is the only material approved for breast implant shells by the US Food and Drug Administration and our research is focusing on this topic.

2.2. Sample preparation

All block copolymer samples were compression molded using a hydraulic hot press (Webber PW10) into 1 mm thick flat sheets, while silicone rubber was used as supplied (1.5 mm thick sheets). Micro-dumbbells were cut from the flat sheets with a cutting tool and the hydraulic press to the dimensions following the specifications defined by ASTM D1708 (2006). The micro-dumbbells were annealed for 24 h in water at 37 °C, followed by drying in a vacuum oven at 23 °C for 48 h and stored in a desiccator before characterization.

2.3. Dynamic Mechanical Thermal Analysis (DMTA)

DMTA of the materials was conducted using a Rheometrics RSA 2 instrument in tension mode controlled by the RHIOS