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Properties of nylon 12 balloons after thermal and liquid carbon dioxide treatments

Andrew J. Ro [1], Vipul Davé *

Cordis Corporation, Bridgewater, NJ, United States

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ABSTRACT

Critical design attributes of angioplasty balloons include the following: tear resistance, high burst pressures, controlled compliance, and high fatigue. Balloons must have tear resistance and high burst pressures because a calcified stenosis can be hard and nominal pressures of up to 16 atm can be used to expand the balloon. The inflated balloon diameter must be a function of the inflation pressure, thus compliance is predictable and controlled. Reliable compliance is necessary to prevent damage to vessel walls, which may be caused by over-inflation. Balloons are often inflated multiple times in a clinical setting and they must be highly resistant to fatigue. These design attributes are dependent on the mechanical properties and polymer morphology of the balloon. The effects of residual stresses on shrinkage, crystallite orientation, balloon compliance, and mechanical properties were studied for angioplasty nylon 12 balloons. Residual stresses of these balloons were relieved by oven heat treatment and liquid CO_2 exposure. Residual stresses were measured by quantifying shrinkage at 80 °C of excised balloon samples using a dynamic mechanical analyzer. Shrinkage was lower after oven heat treatment and liquid CO_2 exposure compared to the as-received balloons, in the axial and radial directions. As-received, oven heat treated, and liquid CO_2-exposed balloon samples exhibited similar thermal properties (T_g, T_m, X_t). Crystallite orientation was not observed in the balloon cylindrical body using X-ray scattering and polarized light microscopy, which may be due to balloon fabrication conditions. Significant differences were not observed between the stress–strain curves, balloon compliance, and average burst pressures of the as-received, oven heat treated, and liquid CO_2-exposed balloons.

1. Introduction

A balloon catheter is used during an angioplasty procedure, where narrowed blood vessels that have been obstructed by cholesterol-laden plaque are widened to improve blood flow. The catheter is typically inserted into the femoral artery and guided through the vessel so that the balloon is placed in the clogged artery. The balloon is then inflated to clear the blockage. A glossary of technical terms used in the field of angioplasty and balloon design has been included in Table 1.

Specific design attributes for the balloon component of the catheter maximize the success of the angioplasty procedure [1]. Some design attributes include tear resistance and high burst pressures because a calcified stenosis can be difficult to open and nominal pressure of up to 16 atm can be used to expand the balloons. All balloons must have a rated burst pressure (RBP), the pressure at which 99.9% of balloons will not fail with 95% confidence [1], which provides assurance of balloon integrity up to a specified pressure. Balloons are often inflated multiple times in a clinical setting, thus another design attribute is high fatigue for up to 20 inflations to RBP. In an established range of nominal pressure, the balloon must have a reliable correlation of outer diameter (OD) and nominal pressure, also known as balloon compliance. Since balloon catheters must traverse through constricted passages, an important design attribute is a low crossing profile and so balloons must have very thin walls, typically in the order of 25 μm. However, very thin walls may lower its burst pressure and fatigue, thus this conflict must be resolved through the material properties of the balloon and other engineering solutions. In order to fulfill these complex design requirements, a significant understanding of the balloon manufacturing and material characterization is required [2]. Various polymers that have been used to prepare angioplasty balloons are the following: polyolefins, poly(vinyl chloride), polyurethanes, poly(ethylene terephthalate), polyamide, and polyether block amide.

The manufacturing process of the angioplasty balloons is a stretch blow molding process [2,3]. A localized area of extruded tubing is heated in a mold and then stretched at the proximal and distal ends in order to thin out the walls. The tubing is inflated and the heated, thinned out area of the tubing is expanded and deformed in the circumferential direction. During the stretch blow molding process, the polymer is maximally stretched to a point where stress is increased dramatically and the material is in a state of maximum strength [3]. On a molecular level, the polymer in this state is stretched to a point where translational movement of the polymer chains reduces the entanglements and the chains are aligned. Further stretching would result in chain breakage and material fracture. In-process control of extrusion and stretch blow molding parameters is crucial to

* Corresponding author. Tel.: +1 9082182710.
E-mail address: vdave1@its.jnj.com (V. Davé).
[1] Formerly with Cordis Corporation, Bridgewater, NJ.

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Table 1
Glossary of terms.

Term	Definition
Angioplasty	Procedure to open occluded and/or obstructed arteries
Balloon compliance	Change in balloon diameter as a function of inflation pressure
Balloon diameter	Nominal width of inflated balloon at a specified pressure
Crossing profile	Maximum cross section of the balloon when mounted on a catheter in its deflated and wrapped condition
Distal	Situated away from the point of attachment or origin or a central point
Flat width	The width of the balloon when it is flattened
Proximal	Situated next to or near the point of attachment or origin or a central point
Rated burst pressure	Maximum statistically guaranteed pressure to which a balloon can be inflated without failing
Stenosis	Abnormal narrowing in a blood vessel
Working length	The length of the cylindrical body of the balloon excluding the tapered ends

produce high quality balloons with reliable performance. Sauerteig and Giese [4] have demonstrated that the balloon flexural strength, compliance, and burst pressure have a dependence on the parison extrusion parameters, i.e. rotation speed of gear pump and cooling bath distance. Menary and Armstrong [5] have been developing a finite element simulation of the balloon blow molding process, using deformation data from a high-speed video capture of the balloon blowing process.

In this study, the effect of residual stresses on the balloon compliance, burst pressure, and mechanical properties was studied by measuring the shrinkage, morphological, and thermal properties of the balloons. Residual stresses were relieved in balloon samples by thermal heating and liquid carbon dioxide (CO_2) exposure, and the resultant compliance and burst pressure were measured in physiological conditions. Thermal heat at temperatures above the glass transition temperature allows segmental mobility of the polymer chains, thus decreasing the residual stresses in the amorphous phase. Liquid CO_2 plasticizes the polymer and also allows segmental mobility, thus decreasing residual stresses [6]. Nylon 12 was the polymer chosen for this study because it is a commonly used material for angioplasty balloons. Nylon 12 contains electron-donating functional groups (carbonyl functionality of amide groups) that have a Lewis acid–base type interaction with CO_2, which acts as an electron acceptor for the lone electron pairs on the carbonyl oxygen in the nylon [7]. CO_2 is in the liquid state at temperatures below 31.1 °C and at pressures greater than 5 atm. Liquid CO_2 was chosen to relieve residual stresses because temperatures were close to ambient conditions, which is beneficial due to the lack of negative thermal effects. Diffusivity of CO_2 was limited in order to prevent foaming, thus liquid CO_2 appeared to be an ideal state for CO_2 exposure.

2. Experimental

2.1. Balloon preparation

A schematic representation of the nylon 12 dilatation balloons is shown in Fig. 1. The dilatation balloons consist of a cylindrical body, two conical tapers, and two necks (proximal and distal). The working length of the balloon is defined as the length of the cylindrical body of the balloon excluding the tapered ends. The flat width is defined as the width of the balloon when it is flattened. A weighted digital drop gauge was used to measure the thickness of the balloon wall. The as-received dimensions of the balloon are summarized in Table 2. A stretch blow molding process, where extruded tubing was introduced into a heated, hollow mold and pressurized internally, was used to prepare the balloons.

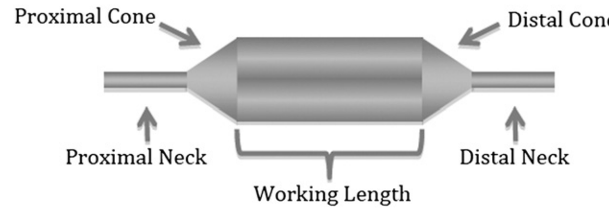

Fig. 1. Various sections of the dilatation balloon.

Two groups of as-received nylon 12 dilatation balloons were subjected to either oven heat or liquid CO_2 exposure. The balloons were oven heated by mounting the as-received balloons vertically and heating the samples at 60 °C for 1 h. The balloons were exposed to liquid CO_2 using a Thar SFE-1000 unit (Thar Technologies). The basic schematic of the extraction unit is shown in Fig. 2. The balloons were mounted vertically and placed in a 1 L cylindrical vessel, where temperature was regulated by a water bath circulator at 20 °C. The liquid CO_2 was allowed to reach the set pressure of 120 bar within 10 min and the duration of the exposure was carried out for 30 min at a continuous flow rate of 30 mL/min. The unit was depressurized in 5 min and the samples were immediately transferred to a nitrogen-filled oven for a residence time of 15 min at 25 °C in order to allow residual CO_2 to diffuse out. The resultant dimensions of the balloon samples prepared from oven heat and liquid CO_2 treatments are summarized in Table 2.

2.2. Characterization

Thermal properties of the balloon samples were analyzed using a TA Instruments Q-20 differential scanning calorimeter (DSC). Temperatures and enthalpies were calibrated using an indium standard. The samples (5–6 mg) were sealed in aluminum pans. The samples were heated from −20 °C to 200 °C at a rate of 10 °C/min (first heat), cooled to −20 °C at 10 °C/min, and then re-heated to 200 °C at a rate of 10 °C/min (second heat). Glass transition temperatures and enthalpies were quantified from the thermographs using the TA Universal Analysis 2000 software.

The tensile and relaxation properties of the balloon samples were analyzed using a TA Instruments Q800 dynamic mechanical analyzer (DMA). The samples were prepared by cutting 2 mm wide rectangular pieces from the axial (working length) and radial directions of the balloon samples (Fig. 3). The axial direction samples (2 mm × 8 mm) were cut out of the balloon portion excluding the taper regions. The radial direction samples were prepared by cutting 2 mm wide samples in the circumferential direction from the balloon portion excluding the taper regions. The resultant tubular piece was cut in the axial direction to yield a rectangular sample (2 mm × 8 mm). The gauge lengths of the samples were measured after mounting at 0.01 N preload force before each test. A preload force of 0.01 N was determined to be adequate for the sample to be stretched within the linear viscoelastic region (<1% strain) and well below the plastic deformation region. Stress–strain curves (axial and radial directions) were generated by keeping the mounted samples at 30 °C for 5 min and then subjected a tensile force at 1 N/min until 18 N. Relaxation curves (axial and radial directions) were generated by measuring the strain at 80 °C for 50 min at a constant force of 0.01 N.

Table 2
Dimensions of as-received, oven heated, and liquid CO_2 exposed dilatation balloons.

Balloon sample	Working length, mm (% change)	Flat width, mm
As-received	29.3 ± 0.3	3.74 ± 0.01
Liquid CO_2	28.7 ± 0.3 (2.0%)	3.63 ± 0.01
Heated	28.5 ± 0.0 (2.7%)	3.68 ± 0.01