Molding of Biomedical Segmented Polyurethane Delamination Events and Stretching Behavior

G. A. ABRAHAM, P. M. FRONTINI, T. R. CUADRADO

Institute of Materials Science and Technology (INTEMA), National University of Mar del Plata–National Research Council (CONICET), J. B. Justo 4302 (7600), Mar del Plata, Argentina

Received 22 October 1997; accepted 16 January 1998

ABSTRACT: Segmented polyurethane devices for medical applications are generally processed by the solution-casting technique. The processing parameters in the molding and demolding stages strongly affect the physicochemical properties of the finished articles. Thus, the solution concentration, immersion cycle and drying temperature, type of mold (material and geometry), additives, and the drying time between the casting of successive layers define the surface and bulk properties of the manufactured articles. In this work, new commercially available medical-grade segmented polyurethanes were processed by two techniques to obtain multilayer films. Processing parameters were chosen to ensure the generation of a coating with the desired structural and surface characteristics. In the solution-casting technique, multiple dipping of the preshaped former into the polymer solution were used to obtain proper film thickness. Thin and uniform plaques were produced by the spin-casting technique. The two materials selected have different chemical compositions: one is an aromatic poly(ether urethane urea) (Biospan™) and the other an aromatic ether-free polyurethane (Chronoflex™). An analysis of the possibility of delamination events, considering the influence of surface-modifying additives and drying times, is presented. The freeze–fracture surface appearance is qualitatively described by SEM. In addition, tensile properties are determined and their influence on demolding and assembling procedures are also discussed. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2159–2167, 1998

Key words: segmented polyurethane devices; solution-casting technique; delamination; demolding technique; tensile properties

INTRODUCTION

Polyurethane (PU) elastomers have found useful biomedical applications due to their excellent combination of physical and mechanical properties (toughness, flexibility), coupled with their relatively good biocompatibility and biostability.

Due to their outstanding blood-contacting performance and their excellent mechanical properties, these materials became the choice for a wide variety of biomedical devices such as catheters, ventricular assist bladders, vascular grafts, leaflet heart valves, pacemaker leads, mammary prostheses, and a number of other current biomedical applications.

The most common route of synthesis for all PUs is the two-stage method. Initially, the diisocyanate and polyol are reacted together to form an intermediate prepolymer. This oligomer diisocyanate end-capped macroglycol is then converted into the final high molecular weight polymer by reaction with a low molecular weight diol or diamine as the chain extender.

Segmented PUs (SPUs) are elastomeric multi-

Correspondence to: G. A. Abraham.

Contract grant sponsor: National Research Council, Argentina (CONICET).

Journal of Applied Polymer Science, Vol. 69, 2159–2167 (1998)

 CCC 0021-8995/98/112159-09

block copolymers composed of alternating blocks of soft and hard segments. The soft segment is typically a polyester-, polyether-, or polyalkyl-diol with a molecular weight between 500 and 5000. The hard segment is normally a chain-extended aromatic or aliphatic diisocyanate. Depending on the chemical composition, the hard and soft phases tend to mix or segregate due to their immiscibility and produce a phase-mixed or phase-separated morphology of hard segment rich and soft segment rich phases, which are connected through urethane linkages. At operating temperature the hard segment rich phase, generally less than 30%, provides physical crosslinks and dimensional stability and acts as a reinforced filler within the rubbery (partially crystallizable or noncrystallizable) soft segment matrix.

Biomer™, a poly(ether urethane urea) developed by Ethicon, Inc., was extensively studied in the literature, and was the first SPU evaluated as a biomedical material by Pierce et al.[1] in 1967.

Wang and Cooper[2] investigated the morphology and properties of segmented polyether polyurethane ureas and the effect of the urea linkage, hard segment content, and block length on the extent of phase separation and domain structure. Physicochemical characterization of SPUs have been reported[3] and several studies dealing with *in vitro* surface degradation[4–6] and *in vivo* degradation[7] are available.

The processing parameters can strongly affect the physicochemical properties of the finished articles. Solution concentration, choice of solvent and evaporation rate, immersion cycle, temperature, mold design (molding of the surface to be in contact with blood), release agent quality, and drying time between casting of successive layers define the thickness of the final coating and the surface and bulk properties of the manufactured articles.[8,9]

SPU devices are generally processed by the solution-casting technique. Multiple dipping of the preshaped former into the polymer solution is performed to obtain the desired film thickness.

The presence of surface-active polymeric additives also affects the coating structure[10] and the physical and chemical properties of the surface.[11]

The influence of stretching in demolding procedures and delamination events has been barely considered in the literature.[9] Orang et al.[9] analyzed the influence of processing conditions on interlayer adhesion of Biomer membranes during cast molding of cardiovascular devices from SPU solutions. No delamination was reported for samples cast from 12% Biomer solution when drying times of 1 h between layers were applied, but Orang et al.[9] reported that relatively poor interlayer adhesion was shown as extensive delamination in samples fractured in liquid nitrogen for an 8-h drying time. They also investigated[9] tensile properties and reported different behaviors regarding final elongation and load break at different solution concentrations. Therefore, it appears that delamination and tensile properties may be important aspects to be considered when an optimal performance for the final device is required.

Much of the research on biomedical PUs focuses on a relatively few commercial elastomers. However, since 1992, the commodity materials that constitute over 95% of implantable devices are slowly being withdrawn from the medical market. This has occurred because several suppliers have been joined in expensive lawsuits related to allegedly defective products.[12] Therefore, numerous companies have decided to discontinue the manufacture and sale of some medical-grade PUs to try to avoid the potential liability costs such as those confronted by silicone raw materials producers.[13]

After the withdrawal of some traditional SPUs, new medical-grade formulations were approved by the Food and Drug Administration for the future manufacture of blood contacting devices, which also have to be extensively evaluated.

In this work two new commercially available medical-grade SPUs of appreciably different chemical compositions were processed by two techniques, solution casting and spin casting, to obtain multilayer films. The processing parameters were chosen to ensure the generation of a coating with the desired structural and surface characteristics.

This article analyzes the possibility of delamination events. A suitable mechanical test was designed to induce delamination at temperatures below the soft segment glass transition temperature. The influence of surface-modifying additives, drying time between casting of successive layers, and film structure is considered. The freeze–fracture surface appearance was qualitatively described by SEM.

The stretching demolding technique may induce permanent deformation in final devices. So the tensile response of both materials was established and compared. To simulate the changes induced by the demolding technique, proper samples were submitted to different elongation levels and hysteresis cycles were carried out in tension.

Residual strain, strain recovery, and hysteresis cycles were determined. Results were interpreted in terms of molecular and supermolecular structure.

EXPERIMENTAL

Materials

Two solution-grade PUs in *N,N*-dimethylacetamide (DMAc) were selected, consisting of 25% solids by weight. Biospan™ (The Polymer Technology Group) is a segmented poly(ether urethane urea) derived from a linear block copolymer of 4,4′-diphenylmethane diisocyanate (MDI) extended with a mixture of ethylene diamine (ED) and 1,3-cyclohexanediamine, and poly(tetramethylene oxide) glycol (PTMO). The composition of Biospan was reported to be similar to Biomer (Ethicon, Inc.).[14] The chain-extended MDI is referred to as the aromatic hard segment and PTMO is referred to as the soft segment; this polymer contained as additive a linear copolymer of diisopropylaminoethyl methacrylate and decyl methacrylate 5% (w/w) based on dry polymer.

Chronoflex AR™ (Cardio Tech Int.) is a PU-polycarbonate of 4,4′-diphenylmethane diisocyanate (MDI) chain extended with 1,4-butane-diol (BD) and polycarbonate-diol. It has an aromatic hard segment of chain extended MDI and a soft segment of polycarbonate oxide.[15]

PU PROCESSING

Device Molding by Solution Casting

Different processing routes were reported for the fabrication of SPU devices.[8,16] We selected the following solution-casting molding process and established the processing parameters suitable to produce a broad variety of biomedical devices.

Former Preparation and Surface Conditioning. The selection and conditioning of the substrate (former) is an important step in the molding process by solution casting. The device surface chemistry is influenced by the substrate quality (metallic or polymeric),[11] and the selected former design and material determine the demolding technique.

In this work, a nonmetallic former of low melting temperature wax (Ancowax MF 3820/7, Anco S.A., T_m = 70–74°C), having excellent surface reproducibility and minimal shrinkage, and a gypsum die were used.

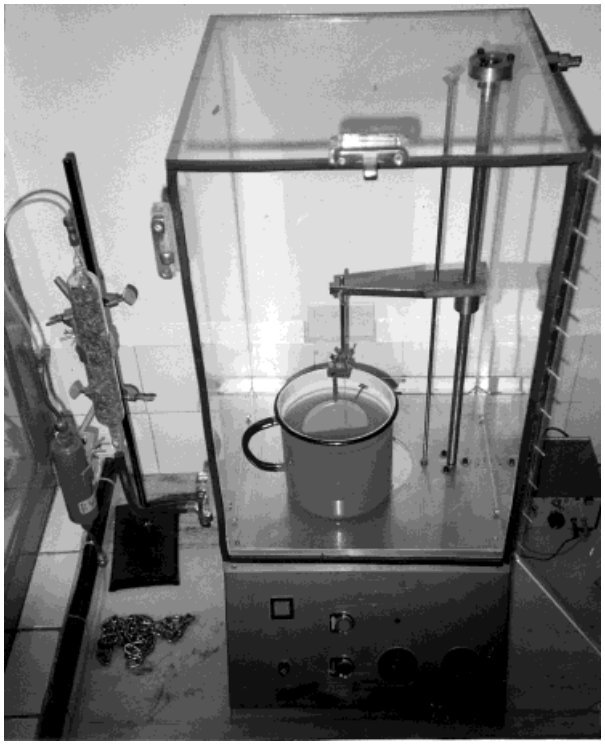


Figure 1 Dipping chamber.

The former was sprayed with a tetrafluoroethylene release agent dry lubricant (Miller–Stephenson) prior to dip casting in an RTV silicone rubber, one component solution (Nusil Technology). The latter treatment was applied to produce a homogeneous, clean and smooth former surface required when the blood-contacting device surface has to be obtained from the former side.

PU Multilayer Films. To mold the PU part, the surface-treated former was several times dipped at a variable angle into 25% (w/w) polymer solutions held at 45°C in a nitrogen atmosphere. For the formulations tested, the optimal dipping rate in the forward and the backward motion was 1.5 cm min^{-1}, so the former could be steadily coated and the PU layer thickness obtained could be kept uniform under rotation in the oven along the drying process. Figure 1 shows the dipping process.

To allow the immersion at different angles and upside down positions, as well as to obtain a homogeneous multilayer film thickness by rotation at variable positions within the oven, a connection set was designed. For each layer drying process the former was fixed to a support rotating at 15 rpm for approximately 3 h in air laminar flow at 50°C.

After the last coating, the coated former was dried for 8 h. The wax was removed, increasing the temperature above its melting point (lost-wax technique), and then the silicone whole film was easily released from the PU part. In these conditions a four-layer PU film of 0.8-mm thickness was obtained.

Cleaning and Assembling. The final piece was dried under a vacuum at 60°C for 24 h to eliminate the last traces of solvent, cleaned in an ultrasonic bath with a Sparkleen detergent in bidistilled water, and then dried under a vacuum at 60°C for 12 h.

To carry out the assembling of different device parts, it was necessary to shape coupling sections by thermal treatment for 2 h at 140°C. This temperature must be higher than the glass transition temperature of hard segments. (Biospan™ and Chronoflex™ have $T_{g,h}$ at 130°C.) In this way stressed areas were avoided that could be degraded faster than relaxed ones in the presence of biological fluids.

Subsequently, the final piece was newly cleaned, dried, and stored in a dry atmosphere at room temperature until sterilization procedures were applied.

Compensatory chambers, blood sacs for left ventricular assist devices (LVAD), and diaphragms for pneumatic assist devices were fabricated following this procedure. These cardiovascular devices were successfully applied in clinical trials.[18]

Samples Molding for Testing by Spin Casting

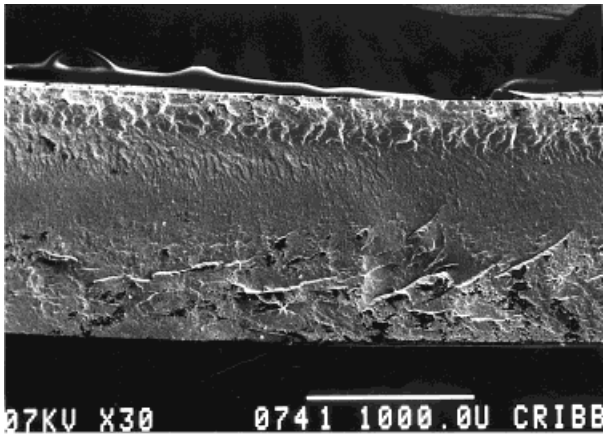
To prepare appropriate samples to perform mechanical testing, a spin-casting device was designed. This device consists of a 10-cm i.d. grillon cup that is spun at 12 rpm and held at 60°C in air to obtain thin and uniform films. In addition, to eliminate the last traces of solvent, films were dried under a vacuum for 24 h in a convection oven at the same temperature.

In the same way, multilayer plaques were prepared with 8-h drying times between deposition of successive layers. In these conditions, homogeneous (four Biospan layers or four Chronoflex layers) and heterogeneous samples (two Biospan layers and two Chronoflex layers) were performed.

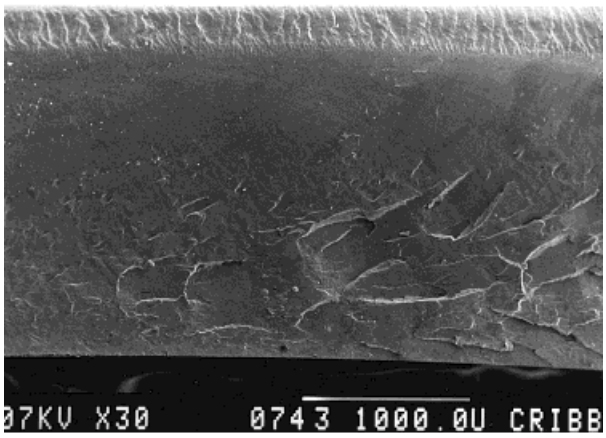
PU Characterization

Delamination

To visualize the presence of delamination events, a preliminary test was carried out. One side razor blade notched samples ($10 \times 5 \times 3$ mm) held with forceps were immersed in liquid air for several minutes and then fractured transversely from the notched side to reveal the bulk material. Scanning electron micrographs of the freeze–fracture surfaces were acquired with a Jeol-JSM-35CF microscope. All samples were vacuum dried at room temperature and coated with 60 Å of gold prior to scanning.



(a)



(b)

Figure 2 SEM micrographs of freeze-fractured (a) Biospan sample and (b) Chronoflex sample.

The analysis of the homogeneous Biospan micrographs [Fig. 2(a)] revealed brittle fracture behavior with stress whitening typical of a material under its glass transition temperature. The Chronoflex fracture surfaces also exhibited brittle fracture [Fig. 2(b)] with less stress whitening. From this preliminary test, no clear signs of delamination were found in both materials.

We designed a test to induce delamination between layers inspired in a short-beam test usually

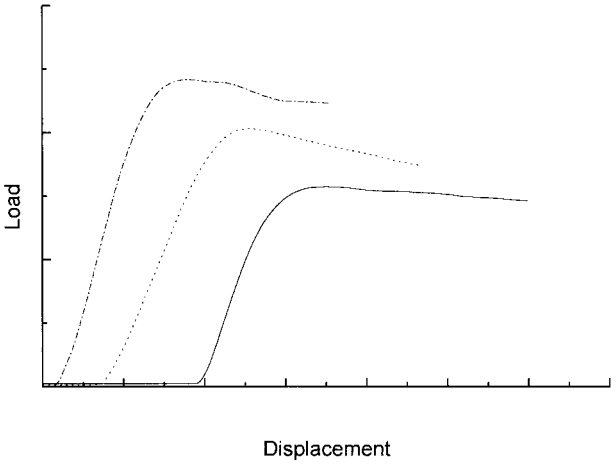


Figure 3 Short-beam test: load–displacement curves for (—) Biospan, (---) Chronoflex, and (– · – · –) heterogeneous samples.

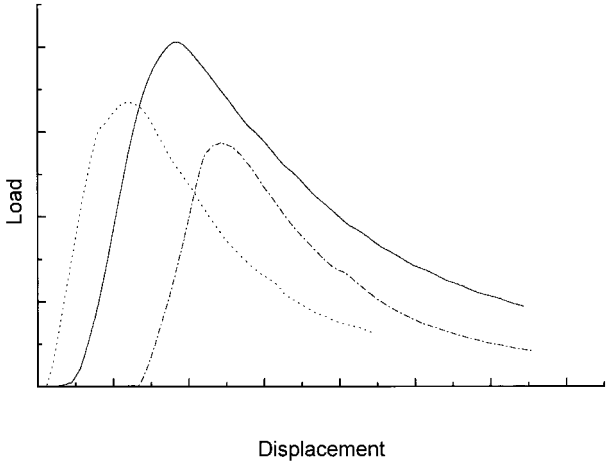


Figure 4 Three point bending test: load–displacement curves for (—) Biospan, (---) Chronoflex, and (– · – · –) heterogeneous samples.

applied to determine interlaminar adhesion in laminated composites. This test was carried out on rectangular samples (20 × 10 × 3 mm, cut from spin-cast plaques) in an Instron 1125 machine with a thermostatic cabinet capable of controlling a temperature of −100°C at a crosshead speed of 5 mm/min.

Under short-beam test conditions, the homogeneous and heterogeneous samples did not show delamination between layers. Samples evidenced stress yielding and extensive stress whitening, which was completely recovered by annealing at room temperature.

Short-beam test load-displacement traces are shown in Figure 3. Fracture was not reached during the tests, so they were stopped from outside at a high level of deformation.

Three point bending fracture, using 60 × 10 × 3 mm single-edge notched bend specimens (SENB), were also performed under the same test conditions. Controlled precracked experiments (SENB) displayed the stable crack propagation mode as shown in the load-displacement curves (Fig. 4) that are consistent with the stress whitened appearance of samples revealed by the naked eye.

Figure 5 shows an SEM micrograph of a Biospan sample. On the right side (smooth razor blade notched region) we can observe small pits associated with the acrylic additive. On the left side pits appear enlarged and oriented in the crack propagation direction and exhibit stress whitening around them, confirming deformation.

Wu et al.[10] found that the amphiphilic additive Methacrol 2138F (similar to the additive reported for Biospan)[14] is phase separated as discrete domain structures approximately 0.5 μm in diameter. This additive decreases the interfacial free energy by introducing long alkyl chains of low polarity in the interface. The formation of small pits about 5 μm in diameter on the device surface after implantation was previously assigned to the leaching out of the additive.[7,19]

In the case of Chronoflex, optical macrophotos and SEM micrographs (not shown here) showed a new smooth fracture surface without evidence of delamination.

The typical surface of each material was found for heterogeneous samples [Fig. 6(a,b)], with a complete integration between both materials.

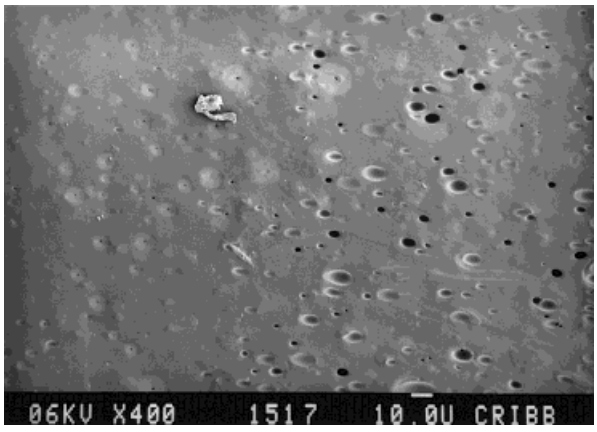
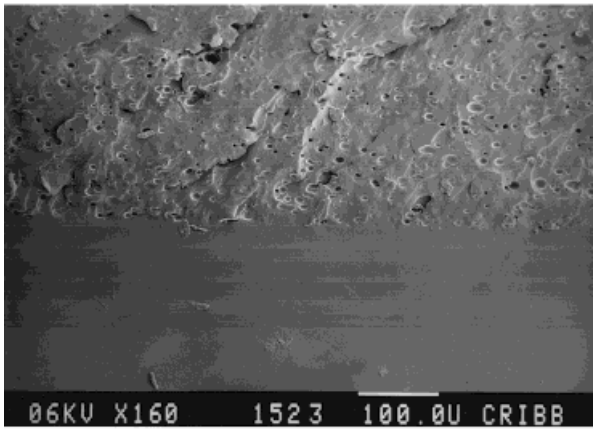


Figure 5 SEM micrograph of precracked Biospan sample after crack propagation. On the right side is a notched area, and on the left side is a notch propagation area.

(a)



(b)

Figure 6 Heterogeneous samples: (a) optical macrophoto and (b) SEM micrograph.

Each material fractured independently but with total adhesion. Therefore, we can conclude that neither homogeneous nor heterogeneous samples exhibited signs of delamination.

It appears that the solvent present in each new layer improved the interlayer continuity, making possible the perfect adhesion through strong intermolecular interactions and interphase mixing. The presence of hydrogen bonds between different groups, depending on the chemical formulation, also improves the interlayer adhesion.

Due to the low solubility of the acrylic copolymer in the SPU base polymer and the possibility of SPU microgel formation, the uniformity of the surface can be compromised. The defects introduced by microgels can be overcome by performing an appropriate solution filtration before the solution-casting step.

Even if we were not able to observe delamination under the conditions tested in this study, we believe that the generation of interlayer defects such as bubbles, dust, residual microgels, and additive segregation may contribute to delamination of the final pieces and must also be minimized.

Tensile Experiments

When PU parts are produced using metallic former, stretching is the only way to demold the devices. High percents of residual strain can be produced, depending on the level of elongation applied in the demolding stage. Therefore, to employ demolding techniques based on PU stretching, the tensile properties of each particular SPU composition, as well as device geometry, must be examined.

The tensile properties of thermoplastic elastomers depend on the size, shape and concentration of hard domains, intermolecular bonding within hard domains, and the ability of soft segments to crystallize under strain.

Uniaxial stress–strain data at room temperature were obtained at a crosshead speed of 50 mm/min from an 1122 Instron Tensile Machine with an extensometer for elastomers. The samples were prepared following ASTM D638 standard recommendations.

Stress hysteresis analysis was performed in a 4476 Instron Tensile Machine at room temperature and the same type of samples and speed as for the stress–strain test. Each sample was submitted to increasing amounts of strain. This test provides data from 100 to 400% of elongation without and with a 72-h relaxation at zero load before starting each loop. All data reported are averages of at least three tests on different samples.

Figure 7 shows the stress–strain curves for Biospan and Chronoflex samples. Departures from simple rubber elastic behavior are particularly marked in Biospan, probably as a result of strain-induced crystallization and reorganization of hard domains. The elongation at failure depended on the particular SPU chemical composition. The high tensile strength and elongation at failure of Biospan samples compared with Chronoflex samples is consistent with their higher urea content, which results in more cohesive hard domains.[20]

The strain level applied to remove the PU part will depend on the device geometry. From size measurements, a strain range between 250 and 400% was calculated to obtain the PU part of the three different models of blood sacs for LVAD shown in Figure 8.

To evaluate the residual strain (ε_r), Biospan

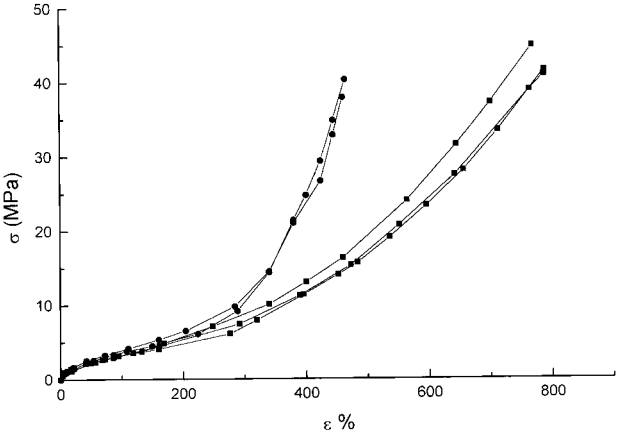


Figure 7 Stress–strain curves. (■) Biospan and (●) Chronoflex.

and Chronoflex samples were deformed to different elongations between 100 and 400% and then relaxed during 72 h at room temperature before starting a second stretching until the same level and subsequent relaxation.

Figure 9 shows the residual strain values versus initial elongation without and with a 72-h relaxation. Residual strains comprising between 3.5 and 8.5% after 72 h were observed for the strain levels applied to remove the above devices. Chronoflex samples showed higher residual strain than Biospan for elongations higher than 300%.

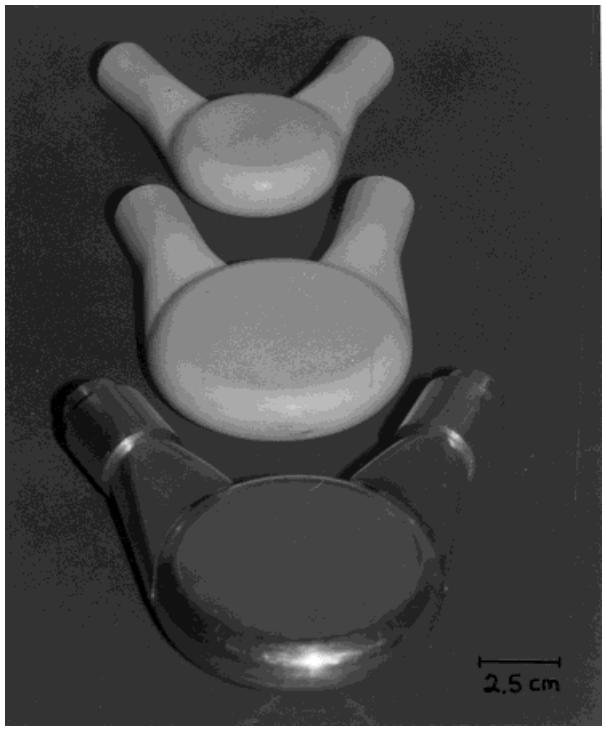


Figure 8 Different designs of blood sacs for LVAD.

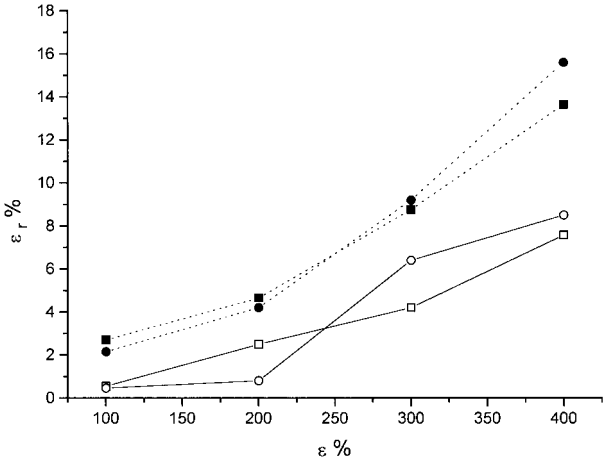


Figure 9 Residual strain percent as a function of elongation after the first cycle for (■) Biospan and (●) Chronoflex at 0 h. The hollow symbols indicate values at 72 h.

The strain recovery between 0 and 72 h (shown in Fig. 10) was calculated from that of the corresponding residual strains by using the residual strain at 0 h as a reference value. Both materials had the same recovery percent when 100 and 400% strains were applied, but they followed opposite trends within this interval. The 250% strain value seems to define two strain ranges where different samples showed higher strain recovery percents; Chronoflex was below 250%, and Biospan was above this value. Above 200% strain Chronoflex appears to exhibit an important structural change associated with hard domain disruption between 200 and 300% strain, which produces a lower strain recovery. Biospan showed a

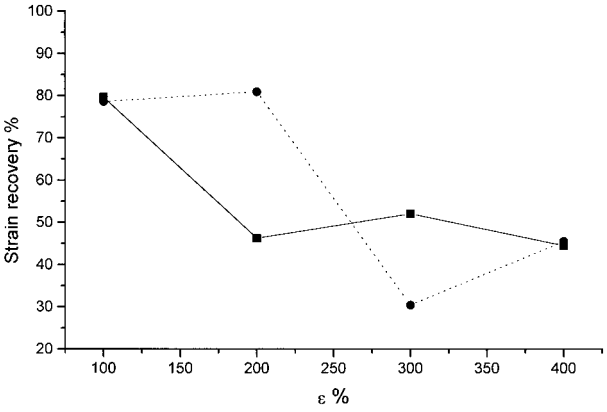


Figure 10 Strain recovery percent between 0 and 72 h for the first cycle. (■) Biospan and (●) Chronoflex.

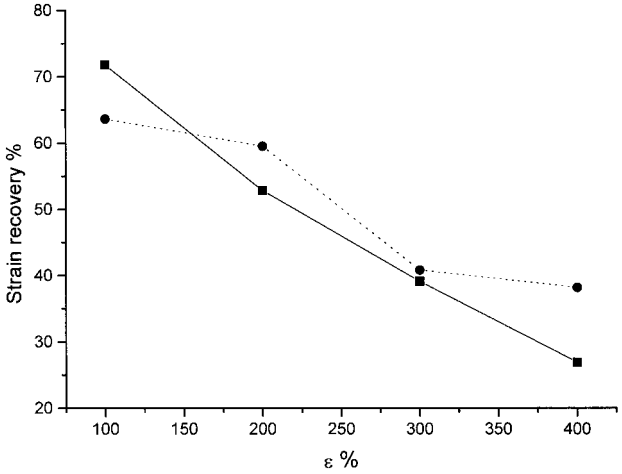


Figure 11 Strain recovery percent between 0 and 72 h for the second cycle. (■) Biospan and (●) Chronoflex.

constant strain recovery value (average of 47.5%) after a pronounced decrease in this value at 100% strain.

Figure 11 shows that strain recovery between 0 and 72 h for the second cycle decreased, and it follows a different pattern compared to the first cycle. Figure 12 shows stress hysteresis cycles without and with a 72-h relaxation for a Biospan sample deformed to 400%. The residual strain increased after the second cycle [Fig. 12(a,b)]. Hence, the number of cycles affects the final dimensions of the sample.

Hysteresis cycles caused by repeated loading and unloading at different elongations were performed in unrelaxed samples. Figure 13 shows the cycles obtained when a 400% strain was applied and the same cycle sequence after 72 h. The residual strain of unrelaxed samples also increased on increasing the number of deformation cycles, while the stress decreased for the same strain level (stress softening). The main reason for this plastic deformation was reported to be the disruption of the ordering in the hard domains more than hydrogen bonding disruption.[21]

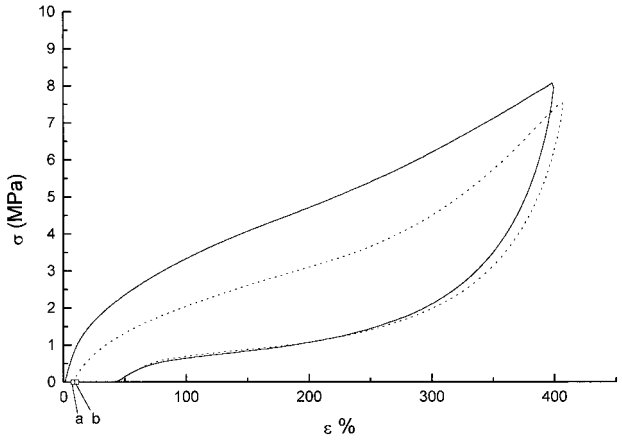


Figure 12 Stress hysteresis versus elongation for Biospan sample deformed to (—) 400% and (---) after 72-h relaxation. (a) Residual strain after 72 h of the first cycle and (b) residual strain after 72 h of the second cycle.

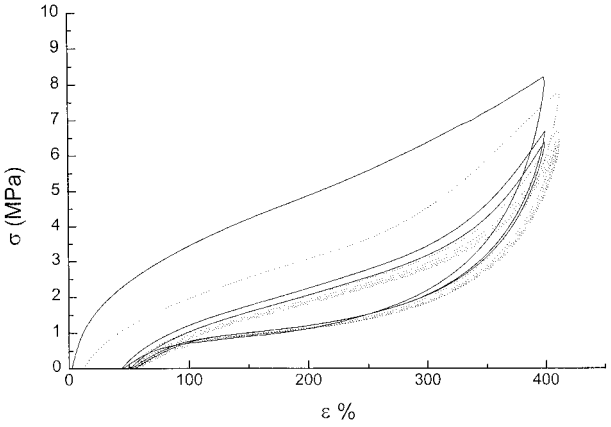


Figure 13 Repeated stress hysteresis cycles versus 400% elongation. (—) Unrelaxed original Biospan sample and (---) after 72-h relaxation.

In a previous work[22] we reported the stress hysteresis behavior with increasing strain levels for sterilized and nonsterilized samples. We found that hysteresis percent and the residual strain percent increased after sterilization.

Therefore, it is clear that the chemical composition of each material will determine the tensile behavior and, in this sense, the device geometry will define the distribution of residual strain percent present in the PU part molded. The typical stress softening phenomena of these elastomeric materials, the high residual strain percent after the demolding stage, and the shape recovery previous to the PU part assembling procedures are important aspects to be considered in the production protocol design.

CONCLUSIONS

The fabrication of biomedical devices by the solution-casting technique is a labor-intensive process that depends on many parameters. A complete analysis based on the selected SPU formulation

should be performed before establishing the production protocol.

No delamination between layers was observed under the conditions used in this study (8-h drying time, −100°C short-beam test, and −100°C SENB fracture test). Both homogeneous and heterogeneous multilayer sample freeze–fracture surfaces exhibited good interlayer adhesion.

The stress–strain behavior of each processed SPU depended on the chemical composition and the sterilization method, as well as on any other sample treatment applied.

Residual strains comprising between 3.5 and 8.5% after 72 h were observed for applied strain levels typical of blood sac device removing procedures.

Chronoflex samples showed higher residual strain than Biospan for elongations higher than 300%.

When the assembling procedures involve strain operations, the residual strain percent associated with each step in the production protocol must be evaluated to define tolerances in the final device design.

A predictive model of the SPU solvent-cast film drying that is capable of estimating the concentration profile and the residual solvent as a function of drying time between successive layers is matter for our next publication.

This work was supported by the National Research Council, Argentina (CONICET). G.A. thanks CONICET for the fellowship awarded to him. We wish to thank J. Asarou and H. Asencio of INTEMA for the technical assistance for the equipment design. We also wish to thank Prof. Marta Rink of the Chemical Industry and Chemical Engineering Department, Polytechnic of Milan (Italy), for useful discussions and for allowing us to conduct short-beam and three-point bending experiments in her laboratory.

REFERENCES

1. W. S. Pierce, M. C. Turner, J. W. Boretos, H. D. Metz, S. P. Nolan, and A. G. Morrow, *Trans. ASAIO,* **13,** 299 (1967).
2. C. B. Wang and S. L. Cooper, *Macromolecules,* **16,** 775 (1983).
3. M. D. Lelah, L. K. Lambrecht, B. R. Young, and S. L. Cooper, *J. Biomed. Mater. Res.,* **17,** 1 (1983).
4. R. E. Marchant, Q. Zhao, J. M. Anderson, and A. Hiltner, *Polymer,* **28,** 2032 (1987).
5. R. E. Marchant, Q. Zhao, J. M. Anderson, A. Hiltner, and R. S. Ward, in *Surface Characterization of Biomaterials,* B. D. Ratner, Ed., Elsevier, Amsterdam, 1988, p. 297.
6. G. F. Meijs, S. J. McCarthy, E. Rizzardo, Y. Chen, R. C. Chatelier, A. Brandwood, and K. Schindhelm, *J. Biomed. Mater. Res.,* **27,** 345 (1993).
7. Y. Wu, C. Sellitti, J. M. Anderson, A. Hiltner, G. A. Lodoen, and C. R. Payet, *J. Appl. Polym. Sci.,* **46,** 201 (1992).
8. M. D. Lelah and S. L. Cooper, *Polyurethanes in Medicine,* CRC Press, Boca Raton, FL, 1989, p. 73.
9. F. Orang, C. J. G. Plummer, and H.-H. Kausch, *Biomaterials,* **17,** 485 (1996).
10. Y. Wu, Q. Zhao, J. M. Anderson, A. Hiltner, G. A. Lodoen, and C. R. Payet, *J. Biomed. Mater. Res.,* **25,** 725 (1991).
11. R. S. Ward, *Medical Plastics & Biomaterials,* Canon Communications, Inc. Netherlands, 1995.
12. P. M. Galletti, *J. Biomed. Mater. Res.,* **32,** 289 (1996).
13. M. Szycher, A. Siciliano, and A. M. Red, in *Polymeric Biomaterials,* S. Dumitriu, Ed., Marcel Dekker, New York, 1994, p. 233.
14. *Products Information,* The Polymer Technology Group, Inc., Emeryville, CA.
15. *Products Information,* Cardio Tech Int., Woburn, MA.
16. W. M. Phillips, W. S. Pierce, G. Rosenberg, and J. H. Donachy, in *Synthetic Biomedical Polymers, Concepts and Applications,* M. Szycher and W. J. Robinson, Eds., Technomic, Lancaster, PA, 1985.
17. M. Cable, D. S. Finch, B. Ralph, and K. Gilding, Paper presented at the Fifth World Biomaterials Congress, Toronto, Canada, 1996.
18. D. Liotta and C. B. Alvarez, in *Assisted Circulation IV,* F. Unger, Ed., Springer-Verlag, New York, 1994.
19. C. Freij–Larsson, M. Kober, B. Wesllén, E. Willquist, and P. Tengvall, *J. Appl. Polym. Sci.,* **49,** 815 (1993).
20. T. O. Ahn, S. Jung, H. M. Jeong, and S. W. Lee, *J. Appl. Polym. Sci.,* **51,** 43 (1994).
21. T. D. Wang and D. J. Lyman, *J. Polym. Sci., Polym. Chem.,* **31,** 1983 (1993).
22. G. A. Abraham, P. M. Frontini, and T. R. Cuadrado, *J. Appl. Polym. Sci.,* **65,** 1193 (1997).