Dynamic Mechanical Properties of Elastomers for Use in Circulatory Assist Devices

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Synopsis

The dynamic mechanical properties of several polyurethane and polyolefinic elastomers for use in circulatory assist devices have been studied. This work was a part of a project on the characterization of elastomers suitable for cardiovascular application. In this paper, changes in the dynamic modulus and internal friction of these elastomers (Avcothane-51®, Biomer®, butyl rubber, Pellethane®, and Hexsyn®) are described as a function of long-term static and dynamic exposure to whole human blood. The dynamic moduli of control of Pellethane and Hexsyn are higher than that of Avcothane, NBS butyl rubber, and Biomer at human body temperature (at 37°C). The dynamic moduli of Biomer specimen fatigued in whole human blood at 37°C are least affected in temperature range of 25°C to 140°C as compared with the control. The loss tangents are decreased slightly. It indicates small structural changes after fatigue in whole human blood. These five materials should be considered for use in most or some cardiovascular applications because their mechanical properties do not change appreciably. Biomer performs well under a variety of experimental conditions, long-term exposure to blood, uniaxial and biaxial fatigue test, and dynamic mechanical properties of specimen fatigued in whole human blood.

INTRODUCTION

The dynamic mechanical properties of several polyurethane and polyolefinic elastomers for use in circulatory assist devices have been studied. This work was a part of a project on the characterization of elastomers suitable for cardiovascular application.[1,2] Under contract to the National Institutes of Health, Monsanto Research Corporation has characterized several candidate materials for potential use in circulatory assist devices and evaluated the fatigue life of these materials under a variety of conditions. The development of a new fatigue tester, the characterization of candidate elastomers, and evaluation of the fatigue life of these elastomers has been reported elsewhere.[1,2] In this paper, changes in the dynamic modulus and internal friction of these elastomers are described as a function of long-term static and dynamic exposure to whole human blood.

EXPERIMENTAL

Dynamic mechanical properties were determined using a Rheovibron Viscoelastometer. This instrument applies a sinusoidal tensile strain to one end of the sample and measures the stress output at the other end. The instrument uses two transducers to read directly the absolute dynamic modulus $|E^*|$ (the ratio of maximum stress amplitude to maximum strain amplitude) and the phase

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angle δ between stress and strain. From these two quantities, the real part E' and imaginary part E'' of the complex dynamic tensile modulus $|E^*|$ can be calculated by the following relationships:

$$E' = |E^*| \cos \delta$$
$$E'' = |E^*| \sin \delta$$
$$E''/E' = \tan \delta$$

The principle of this direct reading method and the instruments are described in detail in previous papers.[3,4]

Dynamic measurements were made at 11 Hz. Samples were heated at 1°C/min in a nitrogen atmosphere under relaxed conditions. Measurements of the tensile modulus E and loss factor tan δ were made at 5°C or 10°C increments. Samples were allowed to equilibrate at temperature for 5–10 min before measurements were made. Five candidate materials were selected for analysis: (1) *Avcothane-51*®, a block copolymer of 90% poly(ether urethane) and 10% poly(dimethyl siloxane) film cast from an 11–15% by weight solution of a 2:1 mixture of tetrahydrofuran and dioxane, received from the AVCO Everett Co. Everett, Mass. (2) *Biomer*®, a poly(ether urethane) prepared from a 30% by weight solution in dimethylacetamide, dip-cast, and vacuum oven dried at 50°C, received from the Ethicon Co., Somerville, N.J. (3) *Butyl rubber*, a carbon-black-filled compound of isobutylene–isoprene (butyl) rubber designated as National Bureau of Standards Standard Reference Material 388J (NBS synthesized and vulcanized the material according to ASTM D 1388, formula 1A); NBS synthesizes, compounds, and vulcanizes the material and supplies it in sheet form to us. (4) Pellethane® CPR 2363-80A, an extruded thermoplastic polyether urethane elastomer, received from Upjohn Co. in North Haven, Conn. (5) *Hexsyn*®, a terpolymer of 95% poly(hexene-1) and 5% of a mixture of 4-methyl-1,4-hexadiene and 5-methyl-1,4-hexadiene in a 2:3 ratio. The polymer is vulcanized using a traditional accelerated, high crosslink efficiency mixture with carbon black, compounded by Goodyear Tire and Rubber Co., Akron, Ohio.

A number of the test specimens, 0.5 cm × 6 cm and about 0.05 cm thick were prepared from the received sheets and the treated sample. It was noted that in preliminary dynamic testing that samples were not required to successive conditioning before dynamic mechanical experiments were performed. Some of the test specimens were fatigued by a newly developed instrument,[1,2] either in air at 37°C or in whole human blood at 37°C (outdated citrate/phosphate/dextrose blood bank blood with heparin, antibiotics, and fungicides added and changed weekly). Nonfatigued specimens were tested as received or after static exposure to whole human blood for six months at 37° (changed monthly).

RESULTS AND DISCUSSION

Fatigued and control (unexposed and uncycled) specimens of five candidate materials were examined at 0% RH and 11 Hz by using Rheovibron viscoelastometer. Table I is a summary of dynamic moduli and loss tangent at 37°C on the representative specimens.

Overall, the precisions of dynamic modulus and loss tangent by this system

TABLE I
Dynamic Mechanical Properties of Elastomers

Sample	Dynamic modulus (dyne/cm^2)	Loss tangent (tan δ)	Comments
Avcothane	1.54×10^8	0.067	Virgin specimen, nonfatigued and unexposed
Avcothane	1.44×10^8	0.065	Cut specimen fatigued in air at 37°C, 2.0×10^6 cycles
Avcothane	1.48×10^8	0.068	Cut specimen fatigued in air at 37°C, 1.3×10^6 cycles
Biomer	1.10×10^8	0.086	Virgin specimen, nonfatigued and unexposed
Biomer	1.34×10^8	0.091	Trouser tear specimen aged in whole human blood for 6 months at 37°C, nonfatigued
Biomer	1.07×10^8	0.080	Cut specimen fatigued in air at 37°C, 3.3×10^6 cycles
Biomer	1.03×10^8	0.065	Cut specimen fatigued in whole human blood at 37°C, 2.6×10^6 cycles
NBS butyl rubber	1.85×10^8	0.155	Virgin specimen, nonfatigued and unexposed
NBS butyl rubber	1.60×10^8	0.195	Cut specimen fatigued in air at 37°C, 1.5×10^6 cycles
NBS butyl rubber	1.50×10^8	0.180	Cut specimen fatigued in air at 37°C, 2.0×10^6 cycles
Hexsyn	2.31×10^8	0.140	Virgin specimen, nonfatigued and unexposed
Hexsyn	2.03×10^8	0.150	Trouser tear specimen aged in whole human blood for 6 months at 37°C, nonfatigued
Hexsyn	1.05×10^8	0.190	Uncut specimen fatigued in whole human blood at 37°C, 3.9×10^6 cycles
Pellethane	2.52×10^8	0.075	Virgin specimen, nonfatigued and unexposed
Pellethane	2.20×10^8	0.063	Cut specimen fatigued in air at 37°C, 0.43×10^6 cycles
Pellethane	2.18×10^8	0.064	Cut specimen fatigued in air at 37°C, 0.78×10^6 cycles

are ±2% and ±0.002 respectively. The dynamic moduli of control of Pellethane and Hexsyn are higher than that of Avcothane, NBS butyl rubber, and Biomer at human body temperature (at 37°C).

Similar trends obtain the 100% modulus for these polymers.[2] Pellethan is a linear, segmented, thermoplastic polyurethane and shows high modulus. The internal friction or mechanical damping (tan δ) gives the amount of energy dissipated as heat during the deformation. It also relates the degree of mobility of polymer chain segments.[4] The loss tangents (tan δ) of controls of NBS butyl rubber and Hexsyn indicate higher values than those of Avcothane, Pellethane, and Biomer at 37°C. It indicates an isobutylene–isoprene and polyolefin rubber networks have higher energy dissipating mechanism than segmented polyurethane structure.

The dynamic moduli and loss tangent of the fatigued specimens in air and in whole human blood at 37°C are shown in Table I. The dynamic moduli and loss tangents of the fatigued Biomer and Avcothane in air show the least changes compared with the control. However, the dynamic modulus of the fatigued NBS butyl rubber in air is decreased about 20% at 37°C. The modulus of Pellethane is slightly decreased as compared with the control sample. Table I indicates the effect of human blood in aging for 6 months, and fatigued Biomer and Hexsyn. The dynamic modulus and loss tangent of the fatigued Biomer in whole human blood at 37°C are slightly decreased, but appear to be unaffected by fatiguing. However, the dynamic modulus of Hexsyn is decreased significantly.

The loss tangents (tan δ) of Biomer and Hexsyn specimens aged in whole human blood for 6 months were increased slightly. This may be due to adsorption of the blood components into the polymer structure, resulting in increasing energy loss during the cyclic deformation.

The dynamic moduli and loss tangents as a function of temperature (25–140°C or 220°C) of the five candidate materials were shown in Figures 1–5. The results of the specimens fatigued in air at 37°C of Avcothane, NBS butyl rubber, and Pellethane are shown in Figures 1, 3, and 4, respectively. The dynamic moduli and loss tangents of Biomer and Hexsyn specimens fatigued in whole human blood at 37°C were shown in Figures 2 and 5.

The glass transition temperatures by differential scanning calorimetry on these five materials were −52°C, Hexsyn; −72°C, Biomer; −57°C, Avcothane; −57°C, Pellethane; −70°C, NBS butyl rubber.[1] Therefore, the dynamic mechanical properties of these five materials indicate the mechanical properties changes beyond the glass transition temperature. The dynamic moduli in rubbery state (above T_g) of these viscoelastic materials gradually decrease when temperatures increase. The loss tangents of Biomer and Pellethane as a function of temperature indicate two transitions about 30°C and 180°C. These are related to the mobility of polymer network structure and increasing flexibility of polymer chain segments by induced heat. The Biomer is a linear-segmented, amine-terminated polyurethane which is "virtually crosslinked" by hydrogen bonding forces,

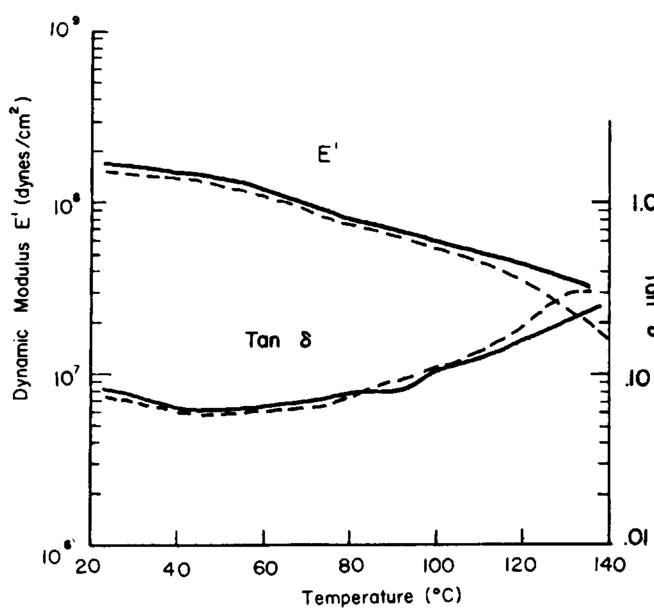

Fig. 1. The dynamic mechanical properties of Avcothane: (—) virgin specimen, nonfatigued and unexposed; (---) cut specimen fatigued in air at 37°C, 2.0 × 10^6 cycles.

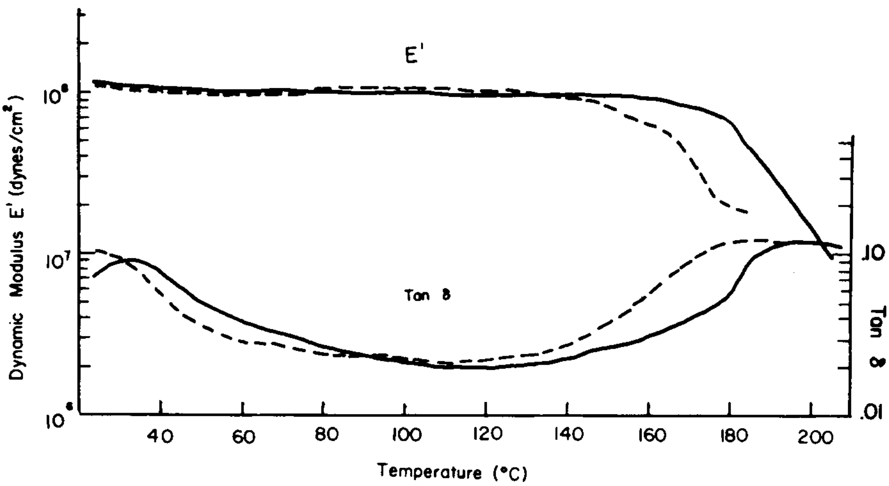

Fig. 2. The dynamic mechanical properties of Biomer: (——) virgin specimen, nonfatigued and unexposed; (- - -) cut specimen fatigued in whole human blood at 37°C, 2.6 × 10^6 cycles.

Pellethane is a linear, segmented, thermoplastic polyurethane. The segmented polymer chains show different transition temperature.

The dynamic moduli and loss tangents of Avcothane, NBS butyl rubber, and Pellethane fatigued in air at 37°C did not change greatly in a temperature range of 25–100°C. It appears to be the least affected by the cyclic extension of our uniaxial fatigue machine. Avcothane is a thermosetting silicone/urethane copolymer, this structure has good flexibility.

The dynamic moduli of Biomer specimen fatigued in whole human blood at 37°C are least affected in a temperature range of 25–140°C as compared with

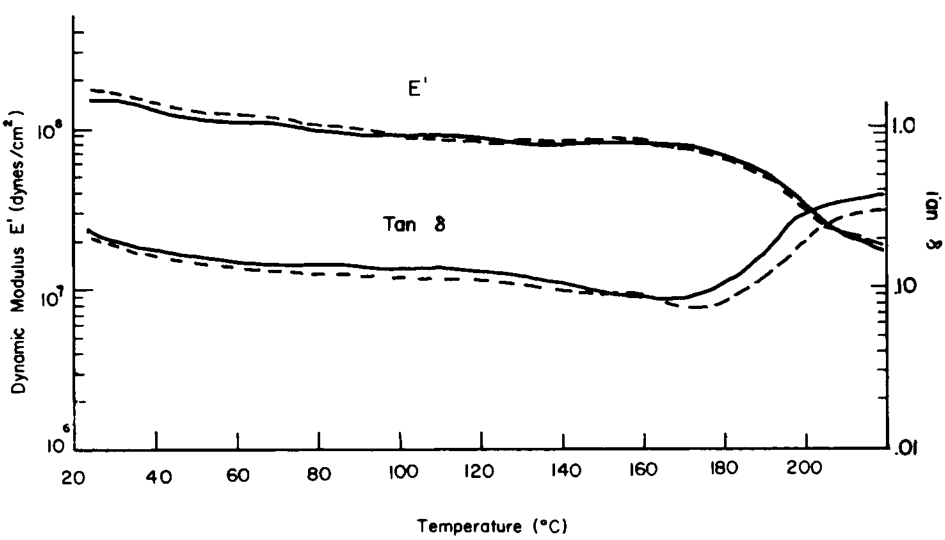

Fig. 3. The dynamic mechanical properties of NBS butyl rubber: (——) virgin specimen, nonfatigued and unexposed; (- - -) cut specimen fatigued in air at 37°C, 2.0 × 10^6 cycles.

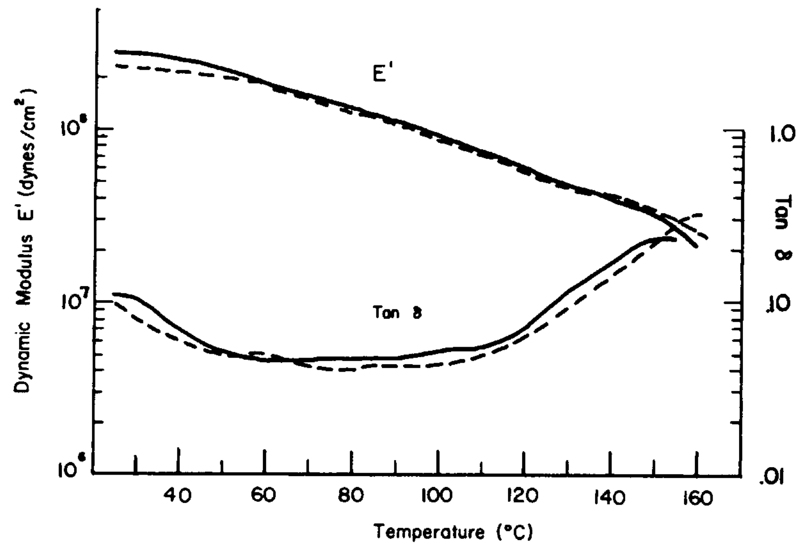

Fig. 4. The dynamic mechanical properties of pellethane: (—) virgin specimen, nonfatigued and unexposed; (- - -) cut specimen fatigued in air at 37°C, 0.78 × 10^6 cycles.

the control. The loss tangents are decreased slightly. It indicates small structural changes after fatigue in whole human blood. The dynamic moduli of Hexsyn specimen fatigued in whole human blood at 37°C are decreased in a temperature range of 25–100°C, while the values of loss tangents are increased

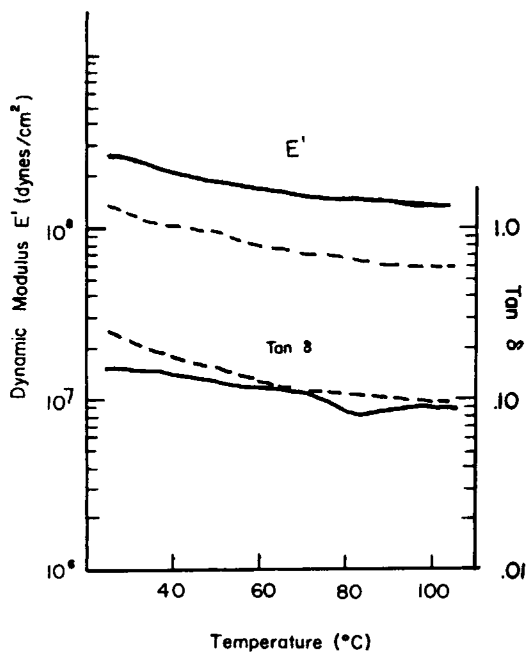

Fig. 5. The dynamic mechanical properties of Hexsyn: (—) virgin specimen, nonfatigued and unexposed; (- - -) cut specimen fatigued in whole human blood at 37°C, 3.9 × 10^6 cycles.

as compared with the control. Hexsyn appears to show the most change in modulus after fatigue testing, possibly due to the nature of the composite structure.

The phenomenological studies on dynamic mechanical properties of these five materials are reported and compared with conclusions of extensive studies of fatigue testing of the five candidate materials.[1] These five materials should be considered for use in most or some cardiovascular applications. Because their mechanical properties do not change appreciably. Biomer performs well under a variety of experimental conditions, long term exposure to blood, a uniaxial and biaxial fatigue test,[2] and dynamic mechanical properties of specimen fatigued in whole human blood. This material should be considered for use in most cardiovascular applications; particular advantages are the low permanent set, high resistance to creep, and generally good fatigue resistance.[5] More studies are required of the effect of blood on the fatigue life, in specific, an interaction between blood and polymer network in long time fatigue, and mechanical property structure relationships of elastomers.

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