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Thermal treatment of expanded polytetrafluoroethylene (ePTFE) membranes for reconstruction of a valved conduit[1]

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Abstract. The unique micro porous structure of expanded polytetrafluoroethylene (ePTFE) that allows bio-integration for fixation, as well as overall mechanical integrity make it used successfully in a number of biomedical and clinical applications, which include the reconstruction of the pulmonary valve in in right ventricular outflow tract reconstruction (RVOT) operations. The objective of this study was to determine the effects of the thermal treatment on physical and mechanical properties of ePTFE membranes. ePTFE sheets were cut into 16 rectangle strips (10 mm by 60 mm) and evenly separated into 4 groups. One group was the blank control (group A), while the rest of the three groups (group B to D) were heated to 350°C and cooled to 24°C at different cooling rates (10°C/min, 20°C/min and rapid ambient air cooling) in a temperature controlled atmosphere. The mechanical and morphological characteristics of all the samples were tested using a tensile test machine and a scanning electron microscopy (SEM). The results show that the elastic modulus of group B to D was 24.95%, 33.45% and 72.76% higher than group A. The percentage elongation of groups B to D was found to be between 2.3% and 40.45 % lower than group A. The proportion of pores in the ePTFE membrane was reduced following the thermal treatment. There were no morphology differences observed between groups B to D. In summary, the selection of cooling rate was important for preserving the mechanical properties of ePTFE membranes under thermal treatment. These findings may provide useful information for the preparation of molded ePTFE valve in RVOT operations.

Keywords: Expanded polytetrafluoroethylene (ePTFE), mechanical properties, thermal treatment

1. Introduction

In recent years, implants of artificial organs have become increasingly important in modern medicine [1]. The use of polymer to produce flexible leaflet valve has long been a focus of research since 1950s [2]. As a polymer, the ePTFE membranes were firstly reported as a valve material in an animal trail [3], and thereafter have been applied as pulmonary valve for pediatric patients [4], chordae tendineae for mitral valve repair [5, 6] and heart valves in right ventricular outflow tract reconstruction

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(RVOT) operations [7, 8]. The benefit of using ePTFE is that it provides a better modulus match than most continuous polymers for many soft biological tissue application [9], easier availability, higher biocompatible and resistance to degeneration or calcification [4]. Recently, ePTFE valved conduits with bulging sinuses of Valsava for RVOT reconstruction has been reported and showed excellent early to mid-term results in patients [10].

The leaflet geometry of the valve leaflets plays an important role in the valve performance [11]. Many prosthetic valve designs have attempted to mimic the three-dimensional geometry characters of native valve to reduce stresses and improve function and durability [2]. To create the complex 3D geometry, heating is a selection to process the polymer materials. However, in our experiment on the thermal forming of ePTFE single point attached commissures (SPAC) valve leaflet with 3D geometry profile, it was found that the ePTFE membranes became more rigid after thermal treatment. This phenomenon indicated that the thermal treatment procedure might change the mechanical properties of the material and cause it to become rigid. A rigid valve leaflet will influence the opening and closing of the valve, narrowing the flow tunnel and lead to thrombus caused by high shear stress in this area [12].

Knowledge of the physical and mechanical properties of ePTFE under various thermal treatments is necessary for an understanding of hemodynamics and tissue response after implantation. In literature, many studies have been conducted to identify the mechanical and physical properties of ePTFE at room temperature [13, 14] and at high temperature [15, 16]. However, there is a general lack of information on the impact of the cooling procedure on the physical and mechanical properties of ePTFE membranes.

In this study, the mechanical and morphological changes of ePTFE membranes under various cooling rate regimes were examined by using tensile testing and field emission Scanning Electron Microscopy (SEM).

2. Materials and methods

2.1. Preparation of samples

The materials used in this study were thin-walled (0.1mm) ePTFE pericardial membranes (GORE PRECLUDE Pericardial Membrane, Gore-Tex, W. L. Gore & Associates, Inc., Flagstaff, Arizona, U.S.A.). Sixteen ePTFE rectangle strips of 16 mm×60 mm in size were cut from the pericardial membranes. Sample strips were evenly divided into four groups.

(a) (b) (c)

(a) Gradual cooling 10 °C/min, (b) Gradual cooling 20 °C/min, (c) Rapid cooling)

Fig. 1. Thermal treated ePTFE membranes.

The first group (group A) was a blank control group, which didn't undergo any thermal treatment. Group B to D were heated to 350°C, the operating temperature of thermal molding of ePTFE valve leaflet, for 3 minutes. Then these groups were cooled to room temperature in a temperature controlled atmosphere at cooling rates of 10°C/min, 20°C/min and rapid cooling, respectively. Samples of thermal treated ePTFE membranes are shown in Figure 1.

2.2. Test methods

Tensile testing of the ePTFE materials was performed using an Instron material testing machine (Instron Static Tester Series 5569, Instron Corp., Canton, MA). The machine was used to obtain the mechanical characteristics of the specimens.

The samples were fixed by claws. To prevent slippage between sample and claws and to avoid damage to the surface of ePTFE membrane, the inner sides of the claws were lined with self-adhesive coarse grit tape and a layer of silicon film. The length of tensile section was 25 mm.

Care was taken to keep a consistent directional orientation for the samples: parallel to the long axis of the sample for longitudinal measurements. Indelible ink marks were made on the sample and extension measurements were taken from this baseline to avoid edge-clamping errors. The samples were loaded under tensile speed controlled at a rate of 0.25 mm/s. The tensile load was measured by a load cell (Instron static loading cell, Model 2580-105) with a range of 500 N. The accuracy of the load cell was 0.5 % of the load range. The load and displacement data were digitally recorded at 4Hz using a computer and the manufacturer's software (Instron Merlin, Instron Corp., Canton, MA) until specimen failure. Subsequently, the elastic modulus was calculated from Eq. (1):

$$E = \frac{\delta}{\varepsilon} \qquad (1)$$

Where E is the elastic modulus, δ is the stress and ε is the strain.

Detailed morphological examinations of the test samples were carried out by using a SEM (JSM 7600 F, JEOL Ltd., Akishima, Tokyo, Japan). Strips from the four groups were cut into 0.5 x 0.5 cm square specimens. Because ePTFE is a good insulating material, the samples required an electrically conducting layer (e.g. gold or carbon) to enable use of the SEM. In this study, a sputter coater (Polaron Emitech SC7640, Quorum Technologies Ltd, UK) was used to deposit a thin film of gold on to the surface of specimens. After applying the coating, the specimens from each group were observed using the SEM. The scanning voltage was set to 5 kV, and magnification factor was set to 5000.

3. Results

Load and displacement recorded by the tensile test machine were converted to engineering stress and strain. From the stress-strain curve, a huge disparity between sample groups can be observed. Figure 2 shows the stress-strain behavior of the ePTFE membrane samples under different thermal treatment conditions along the tensile direction.

The slope of curves rises with the increase of cooling rate, corresponding to an increase of tensile stiffness. The strain ratio at break decreases with the increase of cooling speed. Specific date see Table 1.

Figure 3 shows the averaged elastic modulus and percentage elongation of each sample group.

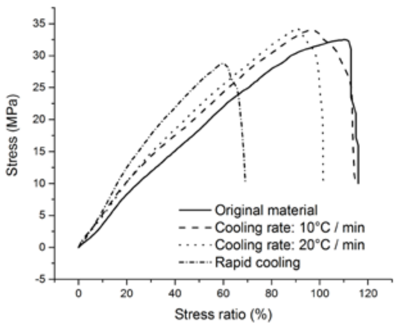


Fig. 2. Stress-strain curve of ePTFE membrane under different thermal treatments.

Compared with control group, the elastic modulus was 24.95%, 33.45% and 72.76% higher for the test samples at cooling rates of 10°C/min, 20°C/min and the rapid cooling condition, and the percentage elongation was 2.3%, 12.88% and 40.45% lower at the cooling rate of 10°C/min, 20°C/min and rapid cooling, respectively. The results show the effect of cooling rate on the ePTFE membrane. Rapid cooling noticeably changed the mechanical property of the film, while slow and controlled cooling preserved the original mechanical property.

Table 1

Specific data of elastic modulus (E) and extension at break (L)

Sample Number	Original material		10°C/min Gradual Cooling		20°C/min Gradual Cooling		Rapid cooling	
	E (MPa)	L (mm)	E (MPa)	L (mm)	E (MPa)	L (mm)	E (MPa)	L (mm)
1	34.75	28.07	42.16	28.76	48.22	25.29	56.64	18.35
2	33.50	27.45	42.54	27.68	43.54	23.48	62.15	17.25
3	34.39	30.19	43.32	29.18	43.46	27.25	57.11	17.06
4	34.03	30.62	42.74	28.00	47.16	25.33	60.20	16.61
Mean	34.17	29.08	42.69	28.41	45.59	25.34	59.03	17.32
S.D.*	0.54	1.56	0.49	0.69	2.46	1.54	2.61	0.74
C.V. (%)**	1.57	5.36	1.14	2.42	5.39	6.08	4.43	4.27

Note: *S.D.: Standard Deviation
**C.V.: Coefficient of Variation

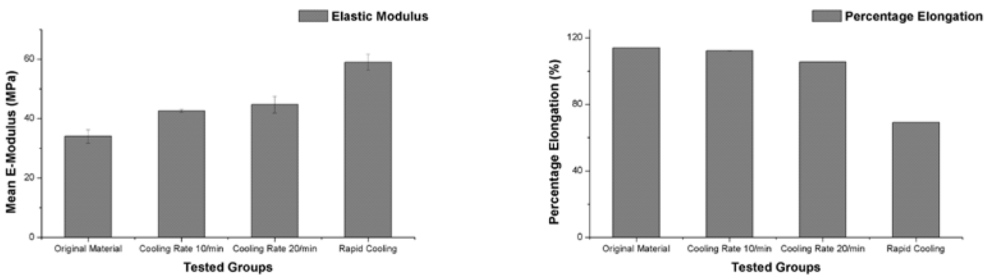
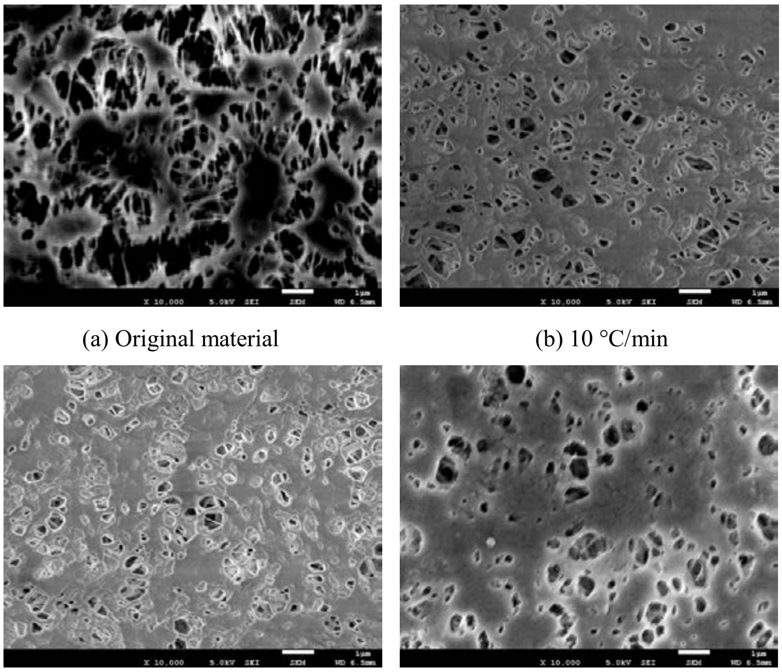


Fig. 3. (a) Elastic modulus and (b) Percentage elongation of sample groups.



(a) Original material (b) 10 °C/min

(c) 20 °C/min (d) Rapid cooling

Fig. 4. SEM images of ePTFE under different cooling rates.

Figure 4 shows the scanning electron microscopy (SEM) micrographs of the ePTFE surfaces of samples. It can be seen that the microstructure of original material is characterized by island-like fractions called nodes that are interconnected by fibrils, Figure 4(a). In original material, the size of nodes range from 0.5μm to 2μm, and size of pores between nodes and fibrils range from 1μm to 2μm. This micro porous characteristic made ePTFE a good biocompatible material which incorporated into the surrounding tissue, the cells can penetrate into the porous instead of been encapsulated [17].

The spatial porous structure still existing after thermal treatment. However, the structure re-organized and resulted in a coarser structure with a larger proportion of nodes and fewer, smaller pores, as showed in Figure 4(b) to 4(d). No obvious morphological differences were observed between groups that underwent different cooling rates.

4. Discussion

In this study, an experimental investigation was carried out to investigate the changes of physical and mechanical properties of ePTFE membrane subjected to various different cooling rates after heating.

To form the 3D geometry profile of SPAC valve, a process temperature higher than the melting point of ePTFE material is required. It is generally accepted that the melting process of PTFE material starts at 320°C [14, 18]. However, there is a controversy concerning the actual melting point of PTFE. In some studies, 327°C was regarded as the melting point of PTFE [14, 15], while other studies suggested that the melting point of PTFE is around 345°C [16, 18]. Based on our future application, 350°C was chosen as the thermal treatment temperature in this reported study.

Table 2

Geometric parameters of ePTFE tested in the study of Catanese et al. [9]

Internodal Distance (μm)	Outer Diameter (mm)	Wall Thickness (mm)	n	Elastic Modulus (MPa)
23	3.93	0.99	12	55.2
31	2.31	0.57	12	47.1
32	3.96	0.99	11	57.1
32.7	3.22	1.01	14	59.3

In investigating the impact of thermal treatment on the ePTFE membrane, validation is of the utmost importance if the results are to be trusted. The material used in our study is ePTFE membranes of 0.1mm thickness. Due to the lack of direct comparison of results, a benchmark work based on the same material (same thickness) and the same test condition is hard to achieve. However, according to the literature, some results come from tests on thicker material are available [9, 19].

In the experiment of Catanese et al. [9], the effect of microstructure features (internodal distance, linear density and reduction ratio) on the mechanical properties of ePTFE (International Polymer Engineering, Inc., Tempe, AZ) was investigated. The material they chose were ePTFE tubes of 1mm and 0.5 mm thickness. Specific results of tested ePTFE membranes were listed in Table 2.

In the *in-vitro* measurement done by Fujimoto et al. [19], they chose ePTFE of 400 μm thick (Impra-Bard, Tempe, Arizona) as the test material. And the test result of elastic modulus of ePFTE is 51.5 MPa.

Compare with the previous studies, the elastic modulus of the original ePTFE measured in this paper is slightly lower. However, the results from our test are still within a reasonable range. The differences may be caused by the differences of the materials chose between studies.

The results of the tensile test showed that thermal treatment changed the mechanical properties of ePTFE membrane, which increased the elastic modulus and decreased the percentage elongation. The elastic modulus was increased as cooling rate of the ePTFE was increased. Simultaneously, the percentage elongation of the ePTFE membrane decreased with increasing cooling rate. These results run counter to a previous study that suggest the thermal treatment has no effect on mechanical properties of the ePTFE material [18]. This conflict can be explained by the different temperature used for thermal treatment in this study. According to Rahl et al. [20], a PTFE particle is composed of a ribbon-like crystalline structure folded into a spherical shape. The ribbon-like structure is easy to pull out from the sphere, because it is connected by a weak attractive interaction force [15].

After the PTFE material was stretched into an ePTFE sheet, some ribbon-like crystalline structures were pulled out, interconnected and subsequently formed a fibril structure. The rest of the structures folded and formed the node (Figure 4(a)). Subjecting the ePTFE to a thermal treatment below the melting point causes the crystal structure to remain stable and maintain its connection by the weak attractive interaction force. Once the applied temperature is higher than melting point of PTFE, the crystal in the nodes will transform in to a polymeric structure, resulting in resistance to pull the ribbon-like structure out of the node and an increase of the mechanical strength of the membrane [15]. This theory helps to explain the increase of elastic modulus after the thermal treatment in the current study and resolve the conflict concerning mentioned before. The thermal treatment temperature applied in reference is 300°C [18], which is far below the melting point of ePTFE.

With regard to the morphology, the microstructure of the original ePTFE observed in this study agrees well with previous observations [14, 16]. Our results also showed the change of microstructure of the ePTFE sheets after thermal treatment. Instead of thin fibrils between nodes, the union of nodes and consequent reduction of the node proportion were observed after thermal treatment. This phenomenon is mainly due to the adhesion of the neighboring particles in a node that takes place at the melting point [15].

5. Conclusions

The thermal treatment created a drastic change in both mechanical properties and morphological characteristics of ePTFE films. The following conclusions can be drawn from this study:

1. For a rapid cooling, there is a significant change in the elastic modulus and percentage elongation. With gradual cooling rate, the elastic modulus and percentage elongation can be controlled and improved. Current results suggested that adequate cooling procedure should be considered when apply thermal treatment on ePTFE membrane, especially in applications of which the mechanical properties to be the most outstanding property we should focus on. Gradual cooling should be considered under such situations. This finding provided an important reference for clinical surgeons who may prepare the molded ePTFE valve leaflet before operation.
2. Thermal treatment considerably affects the morphology characteristics of ePTFE membrane. The fibril structures relaxed at the node joints and consequently reduced the porous proportion of the film due to the melting and union of the nodes. Current study expanded the understanding of mechanical properties of ePTFE membrane under different thermal treatment procedures.
3. For ePTFE that was subjected to thermal treatment, the morphological characteristics of the ePTFE membranes have no obvious differences under different cooling speed.

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References

[1] Y. Liu, S. Cui, C. He, J. Li and Q. Wang, High cycle fatigue behavior of implant Ti-6Al-4V in air and simulated body fluid, Bio-Medical Materials and Engineering **24** (2014), 263–269.

[2] D. Bezuidenhout, D.F. Williams and P. Zilla, Polymeric heart valves for surgical implantation, catheter-based technologies and heart assist devices, Biomaterials **36** (2015), 6–25.

[3] F. Nistal, V. García-Martínez, E. Arbe, D. Fernández, E. Artiñano, F. Mazorra, et al., In vivo experimental assessment of polytetrafluoroethylene trileaflet heart valve prosthesis, The Journal of Thoracic and Cardiovascular Surgery **99** (1990), 1074–1081.

[4] M. Ando and Y. Takahashi, Ten-year experience with handmade trileaflet polytetrafluoroethylene valved conduit used for pulmonary reconstruction, The Journal of Thoracic and Cardiovascular Surgery **137** (2009), 124–131.

[5] Y. Tomita, H. Yasui, T. Iwai, T. Nishida, H. Tatewaki, S. Morita, et al., Surgical application for a prolapse of the anterior mitral leaflet by replacing artificial chordae with polytetrafluoroethylene grafts, Surgery Today **35** (2005), 812–818.

[6] F. Bizzarri, A. Tudisco, M. Ricci, D. Rose and G. Frati, Different ways to repair the mitral valve with artificial chordae: a systematic review, Journal of Cardiothoracic Surgery **5** (2010), 22.

[7] M.J. Gillespie and D.B. McElhinney, Transcatheter pulmonary valve replacement: A current review, Current Pediatrics Reports **1** (2013), 83–91.

[8] W. Mazur, M. Siegel, T. Miszalski-Jamka, R. Pelberg, Ross Procedure, in: CT Atlas of Adult Congenital Heart Disease, 2nd ed., Springer, London, 2013, pp. 319–321.
[9] J. Catanese, D. Cooke, C. Maas and L. Pruitt, Mechanical properties of medical grade expanded polytetrafluoroethylene: the effects of internodal distance, density, and displacement rate, Journal of Biomedical Materials Research **48** (1999), 187–192.
[10] T. Miyazaki, M. Yamagishi, Y. Maeda, Y. Yamamoto, S. Taniguchi, Y. Sasaki, et al., Expanded polytetrafluoroethylene conduits and patches with bulging sinuses and fan-shaped valves in right ventricular outflow tract reconstruction: Multicenter study in Japan, The Journal of Thoracic and Cardiovascular Surgery **142** (2011), 1122–1129.
[11] F.L. Xiong, W.A. Goetz, C.K. Chong, Y.L. Chua, S. Pfeifer, E. Wintermantel, et al., Finite element investigation of stentless pericardial aortic valves: relevance of leaflet geometry, Annals of Biomedical Engineering **38** (2010), 1908–1918.
[12] S.I. Bernad, A. Bosioc, E.S. Bernad and M.L. Craina, Comparison between experimentally measured flow patterns for straight and helical type graft, Bio-Medical Materials and Engineering **24** (2014), 853–860.
[13] C.S. Jørgensen and W.P. Paaske, Physical and mechanical properties of ePTFE stretch vascular grafts determined by time-resolved scanning acoustic microscopy, European Journal of Vascular and Endovascular Surgery **15** (1998), 416–422.
[14] R.R. Kowligi, H.H. Taylor and S.A. Wollner, Physical properties and testing methods for PTFE cardiovascular patches, Journal of Biomaterials Applications **7** (1993), 353–361.
[15] T. Kitamura, S. Okabe, M. Tanigaki, K.I. Kurumada, M. Ohshima and S.I. Kanazawa, Morphology change in polytetrafluoroethylene (PTFE) porous membrane caused by heat treatment, Polymer Engineering & Science **40** (2000), 809–817.
[16] H. Wang, S. Ding, H. Zhu, F. Wang, Y. Guo, H. Zhang, et al., Effect of stretching ratio and heating temperature on structure and performance of PTFE hollow fiber membrane in VMD for RO brine, Separation and Purification Technology **126** (2014), 82–94.
[17] N. Purinton and S. Filter, Gore-tex: An introduction to the material and treatments, The Book & Paper Group Annual **11** (1992), 141–155.
[18] C.W. Lou, C.W. Lin, C.H. Lei, H.C. Chen, Y.M. Li and J.H. Lin, Weaving technology and mechanical properties of extended-PTFE fabrics, Journal of Materials Processing Technology **192-193** (2007), 319–322.
[19] K.L. Fujimoto, K. Tobita, J. Guan, R. Hashizume, K. Takanari, C.M. Alfieri, et al., Basic science and experimental study placement of an elastic biodegradable cardiac patch on a subacute infarcted heart leads to cellularization with early developmental cardiomyocyte characteristics, Journal of Cardiac Failure **18** (2012), 585–595.
[20] F.J. Rahl, M.A. Evanco, R.J. Fredericks and A.C. Reimschuessel, Studies of the morphology of emulsion-grade polytetrafluoroethylene, Journal of Polymer Science Part A-2: Polymer Physic **10** (1972), 1337–1349.