The Effects of Glass Fiber Fillers on Epoxy Resin Performance

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Abstract

Premature failure of filtration members in biochemical processing is a costly issue for manufacturers. This research aims to determine whether or not the premature failure due to thermal fatigue in medical filtration devices can be mitigated by glass fiber addition. The study was conducted to identify the effects of e-glass fiber filler content in an epoxy matrix on the mechanical and thermal properties of the epoxy system. The epoxy was evaluated over a filler content of 0-50wt% in level increments of 12.5wt% and temperatures ranging from ambient to 160°C in increments of 15°C. Cylindrical and tensile bar specimens were prepared for each filler content level to evaluate the effect on thermal expansion, glass transition temperature and tensile properties. Caliper measurements of cylindrical specimens across the temperature range concluded that there is a significant inverse relationship between filler content and thermal expansion. Glass content did not present a significant effect on the glass transition temperatures which were measured though differential scanning calorimetry. Tensile testing of the samples found that the epoxy composite was stiffer at higher filler contents. These findings indicate that the addition of glass fibers may not serve as a viable method of increasing the filter production lifetime.

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1. Introduction and Motivation

1.1. Motivation

When producing goods meant for human consumption, it is key that the produced products contain only what is intended to be in them. This is especially true in the biochemical industries where drugs, vaccines, and other products intended for use in the human body are being manufactured. A critical step in these manufacturing processes is filtration and purification of the product. The chemical processes used to produce pharmaceutical and biomedical goods will result in some byproducts which need to be removed before the manufactured goods are fit for human consumption and will not produce preventable adverse side effects. There are many methods of filtration that can be employed in these manufacturing processes, including hollow fiber filtration. Hollow fiber filters consist primarily of semi-permeable hollow fibers, a filtration chamber, and end caps (Figure 1).
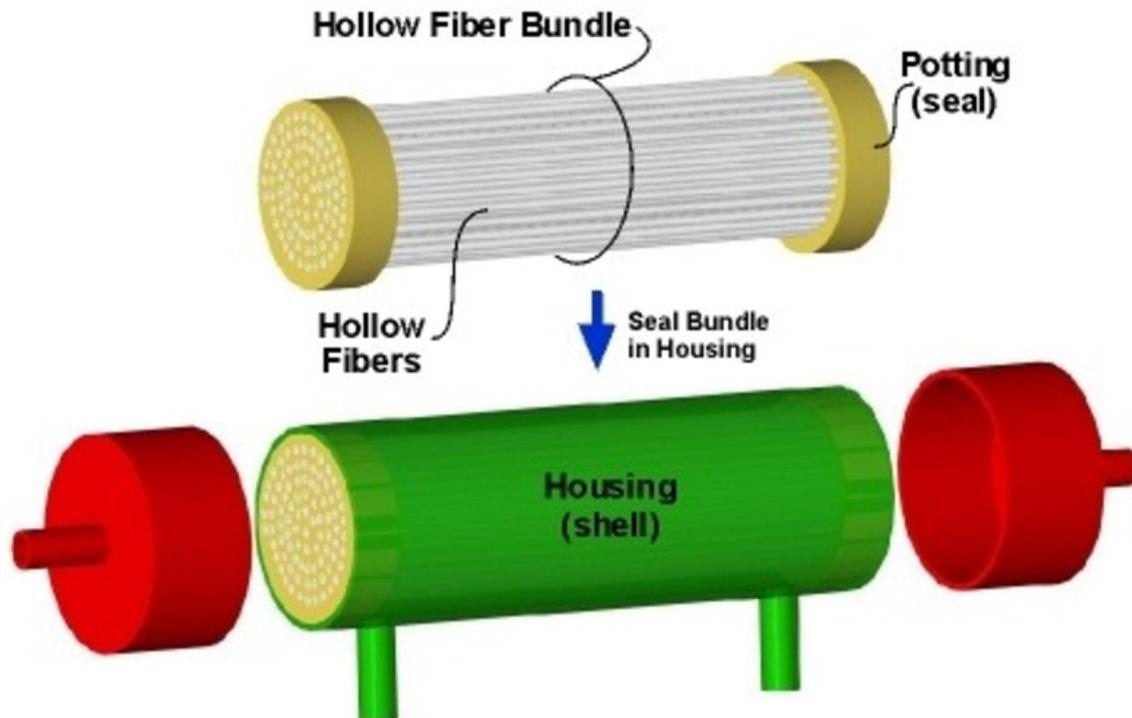
Figure 1. An exploded view of a hollow fiber filtration instrument [1].

A feed stream containing the desired compounds and impurities is introduced into the filtration instrument, where it then flows up to the end caps and into the hollow fibers. When passing through the hollow fibers, the feed stream is separated into the permeate and the retentate. Depending on the semi-permeable membrane and the contents of the feed stream, the desired compounds are filtered and

separated from impurities in either the permeate or the retentate. It is a requirement of these filtration devices that the materials they are composed of do not react with the compounds in the feed stream, as any reaction with the desired compounds may result in their alteration or destruction. One application of hollow fiber filters that illustrates the importance of this unreactive requirement is the use of hollow fiber filters as artificial kidneys (Figure 2) [2].
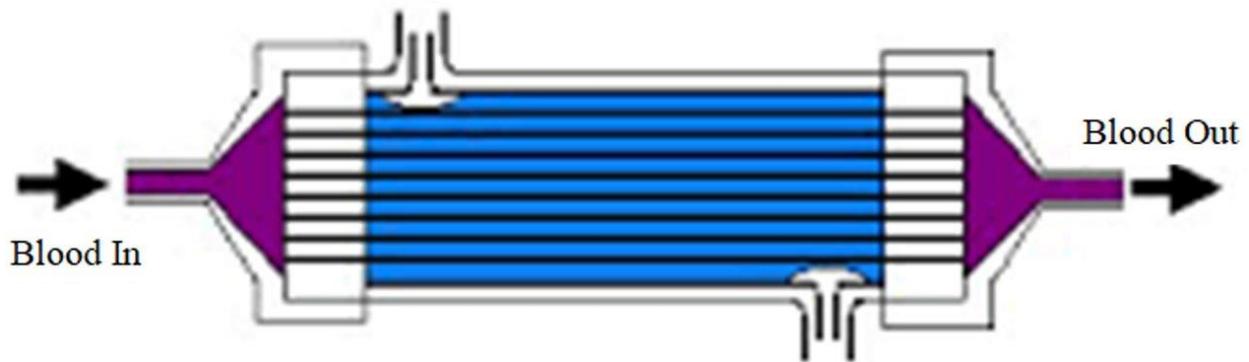
Figure 2. A schematic representation of a hollow fiber filter in the application of an artificial kidney [2]

In this schematic, the blood of a dialysis patient is the feed stream, and flows up to the end caps before following into the hollow fibers where toxins are removed. As the end caps interface with the blood, it is critical that they are not conducive to a harmful reaction such as hemolysis, as that would kill the dialysis patient. For this reason it is necessary that the end caps are made of a material which is rated class VI by the United States Pharmacopeia (USP), meaning the material is essentially biologically inert. It is also a requirement of the end caps that the hollow fibers are able to be potted, or inserted through, the end caps. Finally, the end caps fulfill a structural role in the filter assembly, keeping the permeate in the filtration chamber. The sum of these specifications requires a material that is USP class VI, potable, and has appreciable structural properties.

1.2. Thermoset Polymers

Cured epoxy systems are a type of thermoset polymer which exhibit strong, stiff mechanical behavior as well as strong chemical stability and a potable period [3, 4]. Thermoset polymers are plastics that are composed of polymer chains which are cross-linked by covalent bonds. Many thermosets, including epoxies, are step-growth polymers, which means that the covalent bonds formed between monomers are a result of a chemical reaction of two functional groups. In the case of epoxies, this reaction is called curing and occurs between a resin and a hardener. An epoxy resin is an organic molecule containing multiple epoxide groups; a hardener is an organic molecule which contains functional groups that will react with

the epoxide group to form a covalent bond, such as an amine (Figure 3) [5]. For the purposes of clarity, the term epoxy will refer to the cured system for the remainder of this paper.

$$\overset{O}{\overset{/\ \backslash}{\sim CH-CH_2}} + H-N-H \quad \rightarrow \quad \overset{OH}{\underset{|}{\sim CH-CH_2-N-H}}$$

Figure 3. A general curing reaction between an epoxide group and an amine curing agent [5].

Epoxy resins mixed with amine hardeners are typically capable of curing at room temperature, although elevated temperatures will increase the rate of curing and the final monomer conversion [5]. As soon as the resin and hardener are mixed, the monomers will begin to react and form short chain oligomers. As the curing reaction proceeds the residual functional groups in the oligomers will continue to react with other monomers and oligomers, forming a cross-linked network (Figure 4) [6].

Figure 4. A schematic representation of the curing reaction of a thermoset polymer [6].

As the degree of curing, or monomer conversion, increases, the viscosity, strength, and stiffness of the polymer will increase as well [5, 6]. This provides a window early in the curing process in which the viscosity of the epoxy is low enough to be penetrated by, or potted by, hollow fibers. At high degrees of conversion, the epoxy system will be too solid to be penetrated by these fibers as a result of the covalently bound network structure. The formation of covalent bonds between epoxide groups and hardeners during curing results in a decrease in the distance between the two reacting groups. The curing reaction will therefore result in chemical contraction of the bulk epoxy as the resin and hardener react. A high conversion of monomer components to polymer will result in a cross-linked 3-dimensional network structure (Figure 5).

Figure 5. A schematic representation of a highly cross-linked network polymer. Consider each gold sphere to be a trifunctional hardener, enlarged for clarity purposes [7].

During the formation of the network structure, chains may become adsorbed, stretched, or otherwise stressed as a result of uneven chemical contraction. Residual stresses from curing can be resolved by annealing the thermoset, which provides thermal energy for polymer chains to shift to a lower energy state [8]. As a result of the cross-linked network structure, epoxies are typically strong, stiff materials that undergo brittle fracture [3]. Epoxies also typically exhibit strong chemical resistance and relatively large thermal expansion [4]. The strong chemical resistance that is characteristic of epoxies is a result of the bonds formed during curing. The reaction between amines and epoxides forms a very stable bond that is highly resistant to most chemical action. The relatively large thermal expansion of thermosets like epoxies is due to the covalent bonds in the polymer structure. The length of covalent bonds between atoms in the polymer chain increases as the temperature increases due to the increased Brownian motion of the constituent atoms. The large number of connected bonds in the 3-dimensional network of thermosets results in a large characteristic thermal expansion.

Materials that have a cross-linked network structure are amorphous materials that do not exhibit long range order or crystallization. As a result thermoset polymers do not melt, but rather undergo a glass transition where the material shifts from a rigid, glassy solid to a viscoelastic rubbery material [6, 9]. The glass transition temperature is the temperature at which the intermolecular forces that hold polymer chains in place are overcome by thermal energy, and there is some long range mobility of polymer chains. However, the network is still covalently bound and so thermosets tend to exhibit strong dimensional stability at high degrees of cross-linking. Due to the potability, appreciable structural properties, and strong chemical resistance, epoxies are commonly used to construct the end caps of hollow fiber filters.

1.3. Delamination and Thermal Fatigue

Hollow fiber filters, like all instruments used in biochemical manufacturing, must be regularly sterilized. Sterilization of equipment can be performed in a number of ways, although one of the most common methods of sterilization is autoclaving. An autoclave immerses the instrument in 120°C steam at elevated

pressure [10]. The high temperature steam results in efficient heat transfer to surfaces of the instrument and kills pathogens and other undesirable organisms that may be present. However, as a result of the autoclave process the entire instrument is typically raised to these elevated temperatures, which can result in some issues such as the premature failure of these filters. The premature failure of the filters occurs primarily by one of two mechanisms: delamination or cracking from thermal fatigue. The rigid housing material of some hollow fiber filters expands at a greater rate than the epoxy end caps do. As there is appreciable adhesion between the epoxy and rigid housing, this uneven thermal expansion results in the development of interfacial stresses between the housing and epoxy as well as internal stresses in the epoxy (Figure 6).
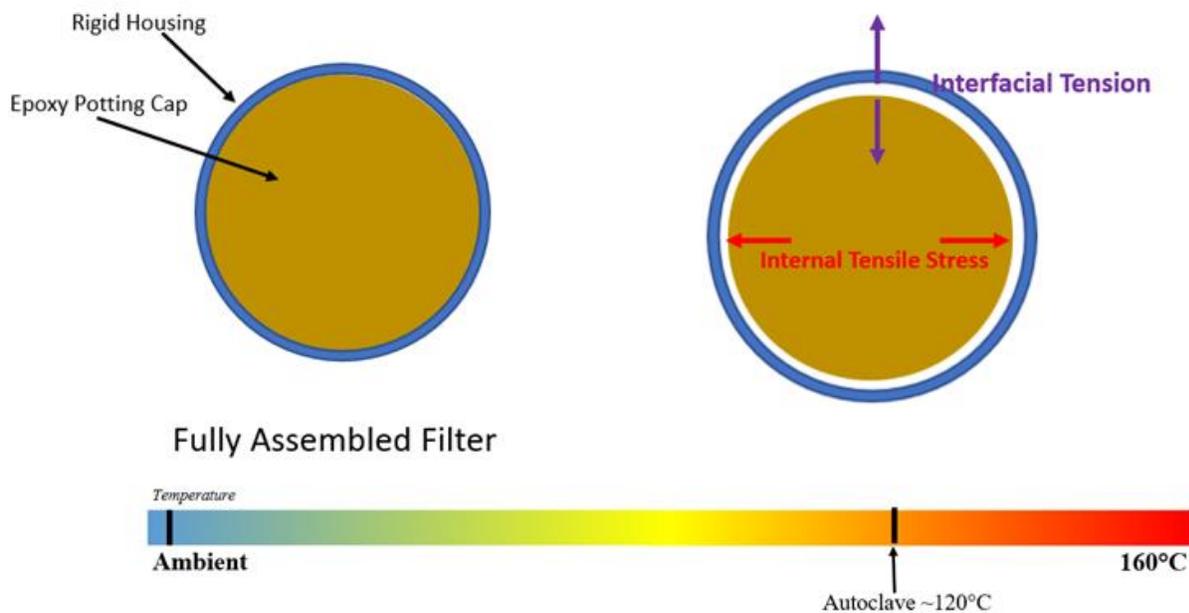
Figure 6. A schematic representation of a fully assembled filter at (left) ambient temperatures and (right) elevated temperatures.

The interfacial and internal stresses that are developed on heating are not fully resolved on cooling, resulting in some residual stresses in the assembly. More unresolved stresses are developed in the material each time autoclave sterilization occurs as the material is thermally cycled. Eventually, the unresolved interfacial stresses overcome the adhesive interaction between the rigid housing and epoxy which results in delamination of the end cap. The thermal cycling can also result in thermal fatigue and failure by cracking of the epoxy end cap [11]. To minimize the premature failure of hollow fiber filters sterilized by autoclave, the unresolved stresses imparted by cyclic uneven thermal expansion must be mitigated. Mitigation can occur either through the strengthening of the epoxy end caps or by matching the thermal expansion of the rigid housing and the end cap.

1.4. Fillers

The thermomechanical properties of epoxies need to be altered to prevent premature failure of the epoxy end caps, however, the chemical and surface behavior of the epoxy need to remain unchanged. Fillers are inorganic materials, typically fibers or particles, that are commonly added to epoxy formulations to modify the thermomechanical properties of the material [12, 13]. Fillers do not participate in the curing reaction or network formation, but act as the reinforcing phase in the composite material. There are hundreds of different filler types that can be used to modify dozens of properties [12, 14]. Fibrous fillers are typically added to enhance the strength of a material, whereas particulate fillers generally reduce the strength of the material [12, 15]. The addition of fillers will typically decrease the thermal expansion of the material, proportional to the amount and kind of filler present [16]. Fillers will only alter the glass transition behavior of polymers on the nanoscale, and microscale fillers do not have an appreciable effect on the bulk glass transition behavior [17]. It is also important to note that the addition of fillers will increase the viscosity of the uncured thermoset formulation, which is an important consideration in the processing of the material.

Fillers incorporated into epoxy end caps are subject to the same USP class VI material requirement as the epoxy. Although fillers do not modify the bulk chemical behavior of the polymer matrix that they are incorporated in, the chance of interaction with the feed stream must not pose a risk to the integrity of the product. E-glass fibers are an inert filler material that generally increase the strength of the polymer that they are incorporated into.

To determine if premature failure of epoxy end caps can be mitigated through the incorporation of fillers, this investigation will explore the effect of adding E-glass fibers, in the content range of 0 to 50wt%, on the coefficient of thermal expansion, glass transition temperature, elastic modulus and yield strength of a two-part amine cured epoxy at ambient temperatures and up to 160°C.

2. Methodology

To evaluate the effects of filler content on the cured epoxy, specimens of each sample were formed and subject to mechanical and thermal testing. During mechanical testing, specimens were fixed at the ends and subject to extension until fracture. Thermal testing specimens were heated from ambient temperature to 160°C to observe expansion and glass transition behavior. Tests were performed 5 times per sample, with each test being conducted on a separate specimen.

2.1. Sample Preparation

Mechanical testing specimens were formed via casting into tensile bar molds. Specimens for the evaluation of thermal expansion behavior were formed via casting into cylindrical molds so that radial and longitudinal expansion could be compared. The glass transition behavior of the epoxy was determined using differential scanning calorimetry (DSC); 5-20mg samples were cut from a thin film for DSC evaluation.

2.1.1. Mold Formation

To form specimens of tensile bar geometry, it was necessary to form a mold to cast the epoxy into. The molds were produced by securing polystyrene tensile bars to the bottom of a glass dish. ProSil 1025 mold-making silicone rubber was prepared per the manufacturer recommendations and poured over the secured polystyrene tensile bars, where it was left for 72 hours to cure fully. After 72 hours, the cured silicone mold was removed from the glass dish and trimmed to remove excess silicone so that two molds could fit in a single tray (Figure 7).

Figure 7. Silicone molds for casting tensile samples.

To produce cylindrical specimens for thermal expansion measurements, a mold was formed using ProSil 1025 mold-making silicone rubber. Delrin rods with a 1 inch diameter were used as mold positives to produce straight, smooth negatives in the mold. To ensure the straightness of the mold negatives, the Delrin rods were evaluated for straightness over 12-inch sections by use of a dial indicator and v-blocks at the ends of the rod per the total indicator readout test (Table I) [18].

Table I: Straightness of Delrin Rods			
Sample	Total Indicator Travel (1/1000 inch)	Bow (1/1000 inch)	Radial Deviation from Ideal
Rod 1	18.5	9.25	1.850%
Rod 2	12	6	1.200%
Rod 3	16	8	1.600%

After finding the Delrin to be satisfactorily straight, the rods were cut into 6-inch sections and mounted in a wooden collar to ensure that the rods were seated vertically. The collar was seated on top of a bowl filled with the mold-making silicone rubber and left for 5 days to cure fully. The resultant silicone mold had 5 negatives of vertical, straight cylinders (Figure 8).

Figure 8. Silicone mold for casting cylindrical samples.

The epoxy formulation is cured in this mold to form the epoxy specimens of the desired geometry.

2.1.2. Epoxy Formulation

The epoxy system evaluated in this report is proprietary; the resin, a diglycidal ether of bisphenol A, is referred to as "Part A," and the aromatic amine curing agent is referred to as "Part B." The filler in these formulations is e-glass fibers. The epoxy formulations evaluated in this experiment have a constant mix ratio; the formulation varies only in the amount of glass filler added (Table II).

Table II: Epoxy Formulations				
Formula	Part A (g)	Part B (g)	E-Glass Fibers (wt%)	E-Glass Fibers (g)
Neat	67	50	0.00%	0
Glass Fiber A	67	50	12.50%	16.7
Glass Fiber B	67	50	25.00%	39
Glass Fiber C	67	50	37.50%	70.2
Glass Fiber D	67	50	50.00%	117

The epoxy was prepared in a WhipMix bowl under a fume hood by adding Part A, the glass fibers, then Part B. Before handling the glass fibers, all instruments were treated with a Zerostat 3 Anti-Static gun to prevent the static cling of glass fibers to regularly handled surfaces. The glass fibers were carefully deposited on the surface of Part A before being covered with Part B. As air was entrained in the polymer fluids during pouring, the unmixed formulation was degassed in a vacuum chamber for 5 minutes, prior to mixing. Mixing was performed using a WhipMix VMP2 Vacuum Mixer. The mixer was set to perform a premix vacuum for 30 seconds, followed by 4 minutes of mixing at 100rpm and 30 more seconds of vacuum at the end of the mixing cycle.

2.1.3. Curing and Heat Treatment

The mixed epoxy was loaded into the silicone molds with 50mL resin syringes to prevent air inclusion in the molds. The loaded molds were loaded into an oven which was preheated to 80°C. After 30 minutes, the oven temperature was raised to 100°C for an additional 30 minutes before the temperature was raised to 120°C for a final hour. After curing, the samples are removed from the mold and annealed at 120°C for two hours to simulate the polymer microstructure expected after sterilization by autoclave.

2.2. Mechanical Testing

Samples were evaluated for mechanical properties by employment of the tensile test. Tensile specimens were loaded into the Instron tensile testing instrument such that the long axis of the specimen was aligned with the motion of the jaws. The extension rate was set to 5 mm/min, and an extensometer was used to evaluate the modulus in the first 0.001mm of extension [19]. Specimens were tested until failure, with 5 specimens being tested per sample.

2.3. Thermal Expansion Testing

Samples were evaluated for the coefficient of thermal expansion (CTE) through an iterative process of heating and recording of dimensions. Groups of 5 specimens were loaded onto baking trays by sample and heated in an oven to a predetermined temperature. The dimensions of the specimens were recorded at

15°C increments from 55°C to 160°C. Specimens were removed one at a time and the radial and longitudinal dimensions were measured and recorded with mechanically geared calipers in triplicate. Once all of the samples were measured, the oven was raised to the next temperature and the following iteration began.

2.4. Thermal Response Testing

Material samples were evaluated to determine glass transition temperatures by heating the sample from 25°C to 160°C at a scanning rate of 10°C/min [20]. 10mg specimens were loaded into the aluminum pans, and the mass of the specimen was recorded. Specimens and reference pans were then loaded into the DSC instrument. Samples were heated, cooled, then heated again to ensure the polymer structure was not altered by the thermal history of processing so that the data most accurately reflects a construct that has been annealed. The midpoint temperature is reported as the glass transition temperature.

3. Experimental Results and Discussion

3.1. Thermal Expansion

Thermal expansion behavior was evaluated via mechanical caliper measurements about the radius and longitudinal axis to determine a coefficient of thermal expansion across fiber contents and temperature (Figure 9). Testing yielded two primary trends: decreased expansion as filler content increases and increased expansion as temperature increases. Multivariate linear regression analysis concluded that the negative correlation between thermal expansion and fiber content and the positive correlation between thermal expansion and temperature were both statistically significant. The statistical analysis did not yield any significant interaction between filler content and temperature with respect to thermal expansion behavior.
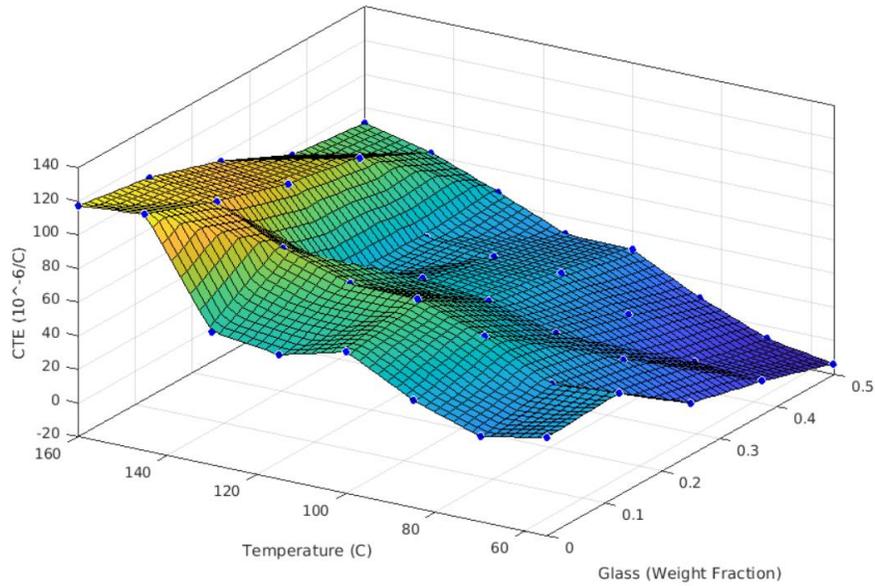
Figure 9. A 3D surface of the values the coefficient of thermal expansion plotted against glass content and temperature.

The findings on thermal expansion behavior were consistent with the literature consensus. Work done by Hadipeykani and coworkers yielded similar trends between increasing filler content and decreasing thermal expansion of epoxy composites [16]. Evaluation of the thermal expansion behavior of filled and unfilled epoxy mortars done by Ribiero and coworkers found similar parabolic expansion on the epoxy-based material, where the coefficient of thermal expansion increases with increasing temperature [21]. Inclusion of glass fibers into the epoxy matrix decreases the rate of thermal expansion of the material, which increases the difference in expansion between the epoxy end caps and the rigid housing of the filters. Increasing the difference in expansion behavior would increase the magnitude of internal and interfacial stresses experienced by the epoxy and epoxy-housing interface, increasing the chances of premature failure by both mechanisms.

3.2. Thermal Response

The glass transition temperatures of epoxy samples evaluated by differential scanning calorimetry did not exhibit any significant differences across the levels of filler content (Figure 10). The glass transition temperatures ranged between 336K and 343K, with consistent variance across samples.
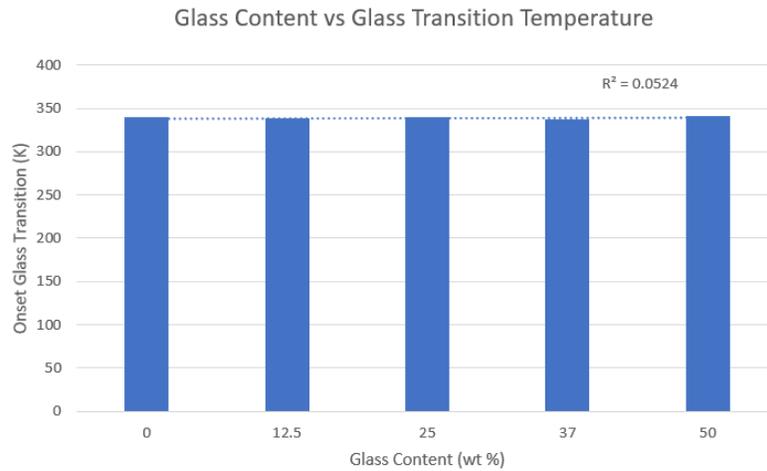
Figure 10. A bar graph of the average onset glass transition temperatures across glass content.

Linear regression analysis of the relationship between filler content and glass transition revealed that the glass content of the composite did not have a statistically significant effect on the glass transition temperature. The glass transition temperature of polymeric materials is altered by surface and interfacial interactions with other phases, such as inorganic fillers [17]. As a result, glass transition modification is typically only observed with the addition of nanoscale materials. The addition of glass micro-fibers has no significant effect on glass transition temperature or therefore long-range molecular mobility. The inclusion of these fibers will therefore not prevent or mitigate premature failure of epoxy endcaps via this mechanism.

3.3. Mechanical Performance

Tensile testing of the prepared tensile samples yielded a positive trend between glass content and stiffness negative trend between glass content and ductility (Figure 11).

The positive trend between glass content and stiffness can be explained by load transfer from the continuous polymer matrix to the stiffer reinforcing fibers. The glass reinforcing fibers experience brittle fracture at higher loads than the epoxy matrix, and failure of the glass fibers will therefore result in the brittle fracture of the composite. The observed trends are in agreement with Mallick's publication on fiber-reinforced composites [13].

Evaluation of the tensile strength of the prepared epoxy samples was inconclusive due to frequent occurrences of anomalous fracture behavior during testing. Tensile samples formulated with glass inclusion exhibited uneven contraction on curing, resulting in slightly bowed specimens (Figure 12).

Figure 12. Tensile specimens formulated with 25wt% glass exhibit a bowed shape as a result of even chemical contraction during curing.

Tensile specimens that were loaded into the Instron for tensile testing experienced a bending moment as the bowed specimens were extended and straightened. The development of a bending moment result in fracture that occurred outside the gauge length of the specimens, regardless of the presence of stress concentrators (Figure 13).
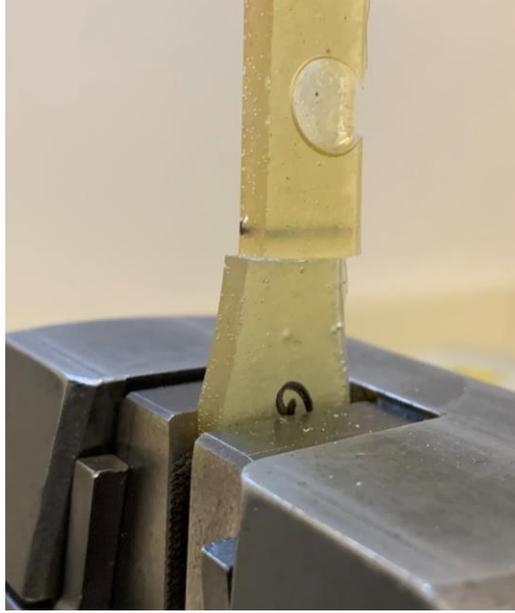
Figure 13. A tensile specimen with a large, stress concentrating void that fractured outside the gauge length due to a bending moment.

Although the literature consensus expects an increase of tensile strength with the addition of reinforcing fibers, strong conclusions about the tensile strength of the material cannot be drawn from the gathered data as the specimens failed by a different modality than specified in the ASTM standard. Without conclusive data on the effect of glass content on the tensile strength of the composite material, a conclusion as to whether or not the premature failure of epoxy end caps can be mitigated through this mechanism cannot be reached.

4. Conclusions

Epoxy end caps of medical hollow fiber filtration devices fail prematurely due to uneven thermal expansion and thermal fatigue from heating cycles during sterilization. The thermomechanical properties of epoxy formulations can be modified via the addition of filler material to the epoxy matrix to mitigate this premature failure. The addition of filler fibers decreases the thermal expansion of the epoxy, which further increases the difference in thermal expansion behavior between the epoxy and rigid housing. The addition of filler material exacerbates the premature failure of the epoxy members instead of mitigating it through this mechanism. There is no relationship between filler content and glass transition temperature, and the addition of filler material has no effect on the premature failure of epoxy members by this mechanism. Increasing filler content results in a stiffer, less ductile material. As tensile strength testing was inconclusive due to anomalous fracture behavior, conclusions cannot be drawn on whether or not

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premature failure will be mitigated through this reinforcing mechanism. Overall, the addition of e-glass fibers to the epoxy formulation is not a promising method of reducing premature failure of the epoxy members.

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Appendix

Multivariate Linear Regression of CTE Values on Temperature and Glass Content

	Estimate	Standard Error	t-value	Pr (> | t |)
(Intercept)	-10.99562	6.50617	-1.690	0.0994
***Glass	-87.71994	10.29396	-8.521	2.97e-10
***Temperature	0.78112	0.05295	14.753	< 2e-16

***Highly Significant

CTE vs Glass Content (85°C)

$y = -83.911x + 54.756$
$R^2 = 0.7733$

CTE vs Glass Content (115°C)

$y = -63.765x + 65.553$
$R^2 = 0.6356$

CTE vs Glass Content (145°C)

$y = -112.32x + 120.04$
$R^2 = 0.9844$