# Supercritical $CO_2$ processing and annealing of polytetrafluoroethylene (PTFE) and modified PTFE for enhancement of crystallinity and creep resistance

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## Abstract

A method is reported to improve creep resistance in tension for polytetrafluoroethylene (PTFE) and modified PTFE (M-PTFE). PTFE and M-PTFE from different sources were annealed in air, $N_2$ or supercritical $CO_2$ (sc$CO_2$) at a range of temperatures, pressures and time intervals. Annealing PTFE in sc$CO_2$ increases crystallinity from 9 to 53%, depending on the material and annealing conditions. No corresponding increase occurs for samples annealed in air or $N_2$. In comparison to as-received PTFE, significant improvements in tensile creep resistance (18–60%) are observed also dependent upon the material and annealing conditions. For a given temperature and duration, the increase in PTFE tensile creep resistance after annealing in air or $N_2$ is greater than after annealing in sc$CO_2$ despite the higher crystallinity for post-sc$CO_2$ processed PTFE. Density measurements indicate that the effect of increased crystallinity is counterbalanced by sc$CO_2$-generated microvoids, particularly at higher pressures, leading to smaller creep resistance. In contrast, thermal annealing in air or $N_2$, which does not significantly change the density or enhance the crystallinity of PTFE or M-PTFE, yields better tensile creep resistance. The detailed morphological origin of improved resistance to tensile creep is unknown, but stress relief by thermal annealing is evident.
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*Keywords:* Polytetrafluoroethylene; Creep resistance; Supercritical $CO_2$

## 1. Introduction

Polytetrafluoroethylene (PTFE) has a unique combination of heat resistance, low friction, chemical resistance, and electrical properties [1]. It is widely used in electrical, mechanical and chemical applications, such as wire insulation, seals, and tapes [2]. Because of extremely high molecular weight ($M_w \sim 10^7–10^8$ g/mol) and viscosity (10 GPa s at 380 °C), conventional PTFE resins are not melt processable. Commercially, PTFE is processed by ram and paste extrusion due to this high molecular weight and insolubility in common solvents. PTFE molding powder is compressed into billets and sintered at high temperature (340–380 °C) prior to skiving sheets or machining parts

[1,3]. On a laboratory scale, PTFE can be extruded using a capillary rheometer [4], while special PTFE bimodal molecular weight blends can be melt processed [5].

Solution processing is an alternative for some polymers that cannot be melt processed. However, no processing solvent exists for PTFE due to high molecular weight and crystallinity. Using solubility data for related polymers, Tuminello predicted that PTFE should be soluble in supercritical $CO_2$ (sc$CO_2$) at very high temperatures and pressures [6]. In earlier studies, we found that sc$CO_2$ plasticized perfluorinated polymers and acted as a processing aid [7–9]. Building on that work, we report here on post-processing properties, particularly creep, of PTFE treated with sc$CO_2$ and compare these properties with those of PTFE annealed at ambient pressure.

A well-known material deficiency for PTFE is high cold-flow or creep under load. PTFE creep resistance is improved by adding a co-monomer such as perfluoropropylvinylether (<0.1%) during polymerization [10]. This modified PTFE (M-PTFE) has better creep resistance and lower melt

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viscosity, but typical co-monomers are costly. Howard, et al. [11] developed a method for preparing PTFE compositions with improved creep resistance. Unsintered PTFE powder was mixed with one or more low molecular weight polyfluorinated substances followed by special processing (at least 0.7 MPa and 327 °C). The resulting PTFE compositions had up to 60% improved creep resistance compared with untreated PTFE.

In general, a composite approach is most commonly used for creep reduction. Fillers such as minerals, carbon black, bronze powder, and glass fibers are utilized. PTFE composites have improved creep resistance, but the presence of filler changes properties such as dielectric constant, conductivity, impact strength and toughness. In addition, composites are not suitable for applications that require high purity PTFE. Alternatively, crosslinking by irradiation in the molten state can significantly decrease PTFE creep [12–15]. However, PTFE is sensitive to radiation resulting in chain scission and degradation accompanying radiation even at low doses. Depending on conditions, deterioration of mechanical properties occurs [16].

The objective of the present study was to investigate whether $CO_2$ plasticization would effect a change in solid-state structure that might improve creep resistance. PTFE and M-PTFE skived tapes from various sources were annealed in air, $N_2$ or $scCO_2$ over a range of time intervals and temperature conditions. The annealed samples were evaluated by differential scanning calorimetry (DSC), changes in density, and by measuring creep in tension. Under optimum processing conditions, creep was substantially reduced but not in the manner we anticipated.

## 2. Experimental

### 2.1. Materials

PTFE (M-15) and modified PTFE (M-111 and M-112) skived tapes were generously provided by Daikin America (Orangeburg, NY). Other PTFE skived tapes were purchased from PTFE Industries (New Britain, CT) and McMaster-Carr (Atlanta, GA) and designated as PTFE-2 and PTFE-3, respectively. The thickness is 0.5 mm for all these tapes. High purity $CO_2$ (99.9%) was purchased from Roberts Oxygen Company (Rockville, MD).

### 2.2. Annealing procedures

#### 2.2.1. In scCO₂
M-15 skived tapes were placed in a high-pressure vessel (GC-5 Series, High Pressure Equipment Company, Erie, PA) connected to a $CO_2$ tank through a high-pressure pump (P-50 Series, Thar Designs, Pittsburgh, PA). The vessel was first purged with $N_2$ or $CO_2$ twice and then filled to tank pressure (~6 MPa) at room temperature. The temperature

was increased to 290 or 330 °C, and then the pressure was increased to 34.5 or 64.8 MPa employing the Thar $CO_2$ pump. Samples were treated at the designated temperature and $CO_2$ pressure for specified durations (2 or 4 h). Time intervals were chosen based on earlier studies [17]. For 330 °C annealing, the temperature was decreased to 290 °C prior to venting. At 290 °C, $CO_2$ was slowly vented at a rate of 34.5 MPa/h through a needle valve. Following venting, the vessel was allowed to cool to ambient temperature.

#### 2.2.2. In N₂ or air at ambient pressure
Samples were placed in the same pressure vessel used for $CO_2$ annealing and purged with $N_2$ twice. Annealing in air was done in a programmable oven under ambient pressure. In both cases, heating was at 290 or 330 °C for 2 or 4 h followed by slow cooling to room temperature.

### 2.3. Density measurements

The density of as received and post-processed PTFE was determined on both rectangular (~0.5 mm thick) and disc-shaped samples (~3–5 mm thick). For each rectangular film, five measurements of each dimension were made using calipers, and four samples were measured for each processing condition. For geometric measurements, the maximum standard deviation for density was $\pm 0.057$ g/cm$^3$ (2.7% error). For the disc-shaped samples, an electronic densimeter (ED 120T, A&D Co. Ltd, Japan) calibrated at 22 °C using 0.9978 as the specific gravity for water was employed. For each sample, at least four measurements were made. In addition, samples from two different processing runs were used. The maximum standard deviation in the density measurement was determined to be $\pm 0.032$ g/cm$^3$ (1.5% error). However, most samples exhibited more uniform densities between sample runs with typical deviations less than $\pm 0.010$ g/cm$^3$ ($<0.5\%$ error).

### 2.4. DSC analyses

Test pieces were cut from as received and processed samples and were analyzed, at least in duplicate, on a TA Instruments Q1000 DSC (20 °C/min, 0–400 °C). The enthalpy of fusion ($\Delta H_f$) was estimated by integration of the melting endotherm at 330 °C employing a linear baseline drawn from 200 to 360 °C.

### 2.5. Factorial data analysis

A factorial data analysis with PTFE heat of fusion ($\Delta H_f$) as the dependent variable was performed using MINITAB release 13 software (Minitab Inc., State College, PA). In coded form, where the two levels of each of the independent variables are given values of $+1$ and $-1$, Eq. (1) describes the quantitative relationship among pressure ($P$), temperature ($T$), and time ($t$) in the annealing experiments with an

adjusted $R^2 = 0.838$:

$$\Delta H_f = 45.2 + 4.5T + 3.3P + 1.3TP - 1.0TPt \qquad (1)$$

Code forms are: $T$, $+1 = 330\ °C$ and $-1 = 290\ °C$; $P$, $+1 = 64.8$ MPa and $-1 = 34.5$ MPa; $t$, $+1 = 4$ h and $-1 = 2$ h.

## 2.6. Creep measurement procedures

### 2.6.1. At room temperature

Tensile creep experiments were performed with an MTS 2/G machine in tension using a 4.45 kN load cell. Rectangular samples 0.5 mm thick × 12.7 mm wide were mounted in the grips to give a gauge length of about 50.8 mm. Pre-loading (0.015 MPa) was employed to straighten the sample which was then subjected to constant stress for 24 h. All creep data are reproducible within ±4% experimental error.

### 2.6.2. At elevated temperatures

In high temperature creep experiments, the test samples were placed in the MTS grips as described above and the built-in oven was used to control the temperature at which the creep tests were performed. Rectangular PTFE skived tape was mounted on the grips to give a gauge length of ca. 50.8 mm. The temperature of the oven was increased to 150 °C over about 1 h. During this process, the sample between the two grips relaxed and the crosshead was adjusted slightly to keep the sample straight. As a result, the gauge length increased to ca. 55.9 mm. Thirty minutes after the oven reached 150 °C, the creep in tension experiment was initiated. The sample was first pre-loaded to 0.015 MPa, loaded to constant stress (1.03 MPa), and kept at this stress and temperature for 24 h.

## 3. Results and discussion

### 3.1. Thermal annealing

Annealing polymeric materials relieves internal stresses produced during processing and leads to better mechanical properties [18]. Annealing can change polymer microstructure, including crystallinity, lamellar and amorphous layer thickness, and density [19–21]. As a direct consequence of structure changes, melting behavior [22,23] and mechanical properties [24,25] are altered by thermal annealing. The term 'annealing' is typically reserved for sub-$T_m$ heat treatment. Despite NMR evidence of molecular motion at 300 °C [26], PTFE is resistant to flow, even above $T_m$ (327 °C). In our experience a sheet of PTFE may be heated to 330 °C for 2–4 h with retention of original shape on cooling. In the discussion below the term annealing is used even though the 330 °C heat treatment exceeds $T_m$.

The data for PTFE (M-15) and modified PTFE (M-112) are discussed together below with appropriate comparisons. According to ISO 12086, the 'PTFE' designation is permitted for resins that contain up to 0.1 mol% perfluoro(alkyl vinyl ethers) [1].

### 3.2. Crystallinity of PTFE annealed under various conditions

Heats of fusion ($\Delta H_f$) were estimated by DSC. The melting point of PTFE (327 °C) and M-PTFE (322.1 °C for M-111 and 320.4 °C for M-112) was unchanged after processing. Table 1 provides a summary of $\Delta H_f$ for PTFE (M-15) and M-PTFE (M-112), as received and after annealing. Heats of fusion for as received PTFE M-15 and modified PTFE M-112 are similar (37 J/g). The degree of crystallinity is 43%, assuming $\Delta H_f = 85.4$ J/g for 100%

Table 1
Heat of fusion ($\Delta H_f$) and crystallinity for PTFE (M-15) and modified PTFE (M-112) measured from DSC traces for samples annealed under different conditions

| Sample treatment (*T/P* atmosphere/duration) | PTFE (M-15) | | M-PTFE (M-112) | |
|---|---|---|---|---|
| | $\Delta H_f$ (J/g)[a] | % Crystallinity[b] | $\Delta H_f$ (J/g)[a] | % Crystallinity[b] |
| As received | 37.2 (0.7) | 43.6 | 36.7 (0.8) | 43.0 |
| 290 °C/1.0 MPa $N_2$/4 h | 38.5 (0.8) | 45.1 | 37.6 (0.6) | 44.0 |
| 330 °C/1.0 MPa $N_2$/4 h | 37.7 (1.5) | 44.1 | | |
| 290 °C/34.5 MPa $CO_2$/2 h | 39.1 (1.7) | 45.8 | 38.4 (1.1) | 44.9 |
| 290 °C/34.5 MPa $CO_2$/4 h | 38.5 (1.2) | 45.1 | | |
| 290 °C/64.8 MPa $CO_2$/2 h | 42.8 (1.7) | 50.1 | 40.1 (1.1) | 47.0 |
| 290 °C/64.8 MPa $CO_2$/4 h | 42.8 (2.1) | 50.1 | | |
| 330 °C/34.5 MPa $CO_2$/2 h | 44.9 (2.2) | 52.6 | 42.7 (0.4) | 50.0 |
| 330 °C/34.5 MPa $CO_2$/4 h | 45.4 (1.9) | 53.2 | | |
| 330 °C/64.8 MPa $CO_2$/2 h | 57.1 (3.2) | 66.9 | 50.2 (0.8) | 58.7 |
| 330 °C/64.8 MPa $CO_2$/4 h | 52.3 (3.6) | 61.2 | | |

[a] Estimated by integrating DSC melt endotherms from 260 to 340 °C. Standard deviation shown in parenthesis, a minimum of three samples from at least two different processing runs.
[b] Calculated from $\Delta H_f$ based on 100% crystalline PTFE having a $\Delta H_f = 85.4$ J/g [25].

crystalline PTFE [27]. After annealing at ambient pressure in $N_2$ either at 290 or 330 °C, $\Delta H_f$ was not distinguishable from as received samples within experimental error. Evidently, thermal annealing is insufficient to increase the degree of crystallinity perhaps due to extremely rapid crystallization [28].

Depending on temperature and pressure, $\Delta H_f$ (DSC) for post-$scCO_2$ annealed PTFE clearly increased (Table 1). The increase in crystallinity was moderate after 290 °C treatment. At the higher $CO_2$ pressure (64.8 MPa), crystallinity increased 15% for PTFE (M-15) and 9.3% for M-PTFE (M-112) compared to as received samples. Annealing at 330 °C, which is above the $T_m$ of PTFE, resulted in marked increases in crystallinity. A maximum $\Delta H_f$ of 57.1 J/g was found after annealing PTFE at 330 °C and 64.8 MPa (2 h) for M-15. This maximum value corresponds to a degree of crystallinity of 67%, a 53% increase over as received PTFE. Contemporaneous results show linear dilation for PTFE in $scCO_2$ increases up to 53% (320 °C, 67 MPa) [17]. The high degree of swelling clearly favors increased crystallization at high temperatures and pressures. Few comparisons can be made, but sub-$T_m$ $CO_2$ induced-crystallization has been observed for poly(ether-etherketone) [22,29].

A factorial data analysis with PTFE heat of fusion as the dependent variable was performed. The independent variables of temperature and pressure were found to be highly significant main effects ($+4.5T$, $+3.3P$, from Eq. (1)). An interaction of temperature and pressure ($+1.3T \times P$) is also evident. The time of treatment is not an important variable within the limited range studied. The observed versus predicted $\Delta H_f$ from Eq. (1) for PTFE M-15 is shown in Fig. 1. These data suggest that if higher pressures and
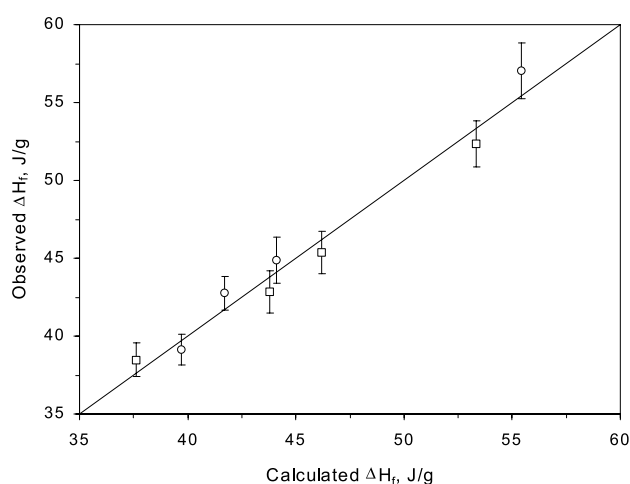
temperatures were accessible, even larger values for $\Delta H_f$ could be obtained.

The increase in crystallinity derived from the DSC data prompted an evaluation of mechanical properties for $scCO_2$ processed PTFE. Mechanical properties were also determined for PTFE annealed in air (or $N_2$) as control experiments.

### 3.3. Density measurements

Previous research using $scCO_2$ to facilitate processing resulted in foams [30,31]. In the present work, a slow vent rate was used to minimize pore generation. Although PTFE foaming was not observed visually, microporosity was a concern. Density of as-received and processed PTFE was measured by two methods (Table 2). Because post-$CO_2$ processed PTFE maintained the original rectangular shape, geometric measurements were first used to determine density (Table 2, column 2). Secondly, density was measured using a commercial densimeter. The results show that density decreases with increasing $CO_2$ pressure at both 290 and 330 °C. After 330 °C/64.8 MPa $CO_2$ processing, which gave the highest crystallinity, PTFE density drops to 2.03 g/cm$^3$, which is 6.0% below as received (2.16 g/cm$^3$). The decreased densities for post-$CO_2$ processed PTFE listed in Table 2 indicate the presence of microvoids. The change in appearance for $scCO_2$ treated PTFE (white/opaque) in comparison to as received PTFE (translucent) is consistent with an increase in crystallinity in combination with microvoids.

Densities of thermally annealed PTFE are also reported in Table 2. Measurements using the densimeter show no statistical differences between as received and annealed ($N_2$) densities. In contrast, densities determined geometrically indicate a slight increase in density (3.7%). Given the inherent uncertainty in quantifying small density changes via measurements of sample geometry, the data in Table 2 confirm that no change, or at best, a slight densification of annealed PTFE occurs. Visually, annealed samples remained similar to as received samples, and were translucent.

Subsequent sections report mechanical properties of post-annealed PTFE. Tensile stress–strain measurements are followed by creep measurements at ambient temperature, creep above the α-transition temperature, and creep recovery. These measurements were directed at discovering the relative contributions of density and crystallinity to mechanical properties.

### 3.4. Mechanical properties in tension

Tensile stress–strain data for as received and post-processed PTFE are presented in Fig. 2 and Table 3. Yield behavior is not clearly observed for any sample. Super-critical $CO_2$ and thermal annealing did not change significantly the shape of the stress–strain curve except for



Fig. 1. Effects of independent processing variables on $\Delta H_f$ of M-15 (PTFE) processed at 290/330 °C and 34.5/64.8 MPa $CO_2$: (○) 2 h and (□) 4 h duration. Factorial analysis was employed to determine the most relevant processing variables yielding Eq. (1) (see text) suggesting temperature is slightly more significant than pressure and that duration is not a significant factor.

Table 2
Densities of PTFE (M-15) samples annealed under different conditions

| Sample conditions (T/P atmosphere/duration) | Density (g/cm$^3$) | |
| --- | --- | --- |
| | Films[a] | Discs[b] |
| As received | 2.18 (0.013) | 2.160 (0.003) |
| 290 °C/1.01 MPa N$_2$/4 h | 2.26 (0.015) | 2.159 (0.003) |
| 330 °C/1.01 MPa N$_2$/4 h | – | 2.160 (0.004) |
| 290 °C/34.5 MPa CO$_2$/2 h | 2.14 (0.012) | 2.091 (0.004) |
| 290 °C/34.5 MPa CO$_2$/4 h | 2.17 (0.015) | 2.105 (0.004) |
| 290 °C/64.8 MPa CO$_2$/2 h | 2.11 (0.034) | 2.104 (0.014) |
| 290 °C/64.8 MPa CO$_2$/4 h | 2.10 (0.021) | 2.075 (0.008) |
| 330 °C/34.5 MPa CO$_2$/2 h | 2.09 (0.027) | 2.064 (0.006) |
| 330 °C/34.5 MPa CO$_2$/4 h | 2.02 (0.011) | 2.034 (0.032) |
| 330 °C/64.8 MPa CO$_2$/2 h | 1.98 (0.057) | 2.047 (0.020) |
| 330 °C/64.8 MPa CO$_2$/4 h | 2.00 (0.041) | 2.028 (0.005) |

Standard deviation shown in parenthesis, a minimum of two samples from at least two different processing runs.
[a] Measured geometrically.
[b] Measured on electronic densimeter.
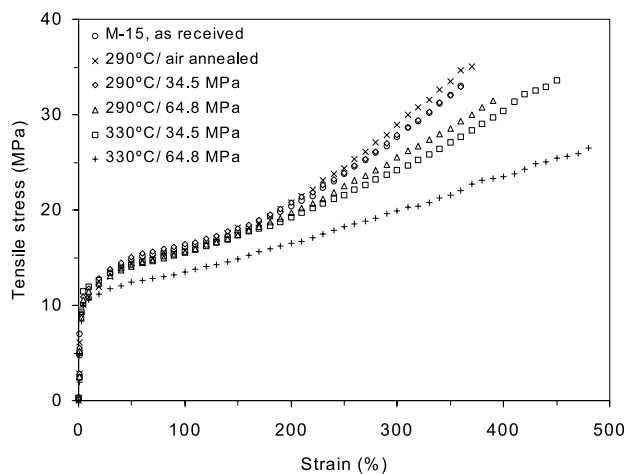


Fig. 2. Tensile stress–strain curves for M-15 (PTFE) annealed under different conditions.
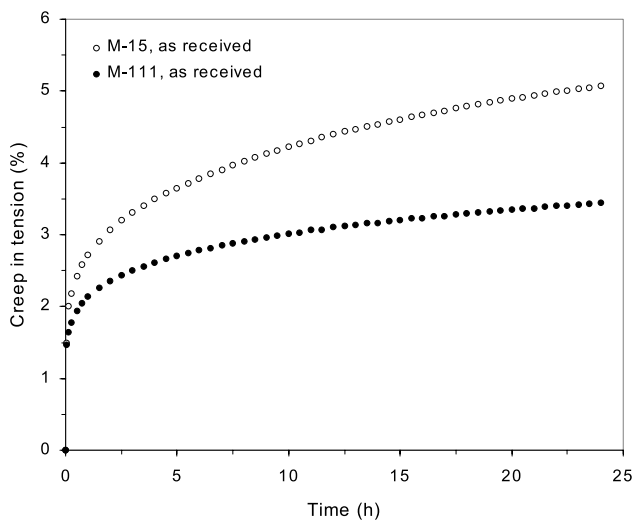


Fig. 3. Tensile creep results (4.83 MPa stress, 23 °C) for as received M-15 (PTFE) and M-111 (M-PTFE) samples.

330 °C/64.8 MPa CO$_2$ treatments. An 8% increase in modulus after thermal annealing is observed compared to as received PTFE (Fig. 2, Table 3) serving as a reference for thermal/scCO$_2$ annealing.

Although the crystallinity of scCO$_2$ treated PTFE increased with temperature and CO$_2$ pressure (vida supra), within experimental error an increase in modulus for CO$_2$ treated samples over that for thermal annealing is not observed. At both temperatures, the modulus after 34.5 MPa scCO$_2$ annealing is consistently higher than that for post 64.8 MPa scCO$_2$ PTFE. The stress at break decreased and elongation at break increased after CO$_2$ treatment, particularly for higher pressures. Evidently, despite slow pressure release, decreased density resulting from the presence of microvoids for post-CO$_2$ annealed PTFE is more significant in determining tensile properties rather than increased crystallinity.

### 3.5. Creep behavior of as received PTFE

Fig. 3 presents the tensile creep curves of as received PTFE M-15 and modified PTFE M-111 at room temperature

Table 3
Mechanical properties of PTFE (M-15) samples annealed under different conditions

| Sample conditions (T/P atmosphere/duration) | Modulus (MPa) | Stress at break (MPa) | % Elongation |
| --- | --- | --- | --- |
| As received | 446 (18) | 33 7 (1.1) | 369 (16) |
| 290 °C/1.01 MPa N$_2$/4 h | 480 (6) | 39.8 (3.5) | 398 (29) |
| 290 °C/34.5 MPa CO$_2$/2 h | 489 (13) | 32.3 (1.5) | 361 (7) |
| 290 °C/64.8 MPa CO$_2$/2 h | 458 (20) | 34.1 (3.7) | 387 (6) |
| 330 °C/34.5 MPa CO$_2$/2 h | 472 (17) | 32.2 (2.2) | 440 (16) |
| 330 °C/64.8 MPa CO$_2$/2 h | 415 (18) | 26.3 (1.4) | 483 (23) |

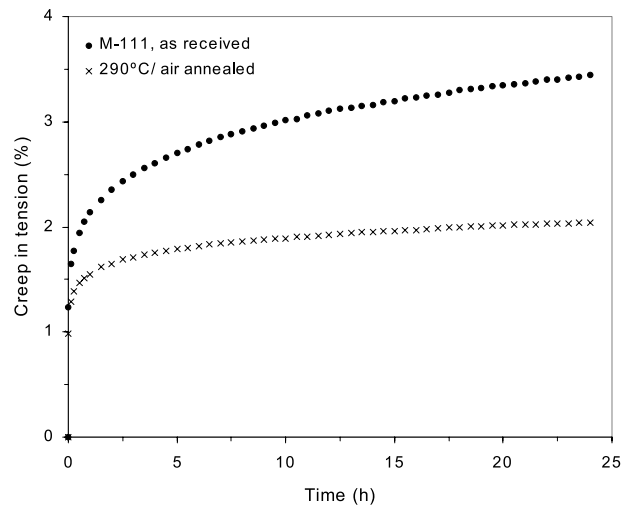Standard deviation shown in parenthesis, a minimum of three samples.

(a)
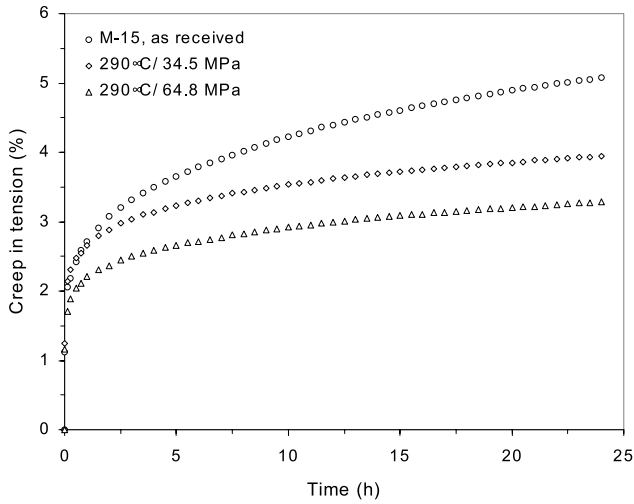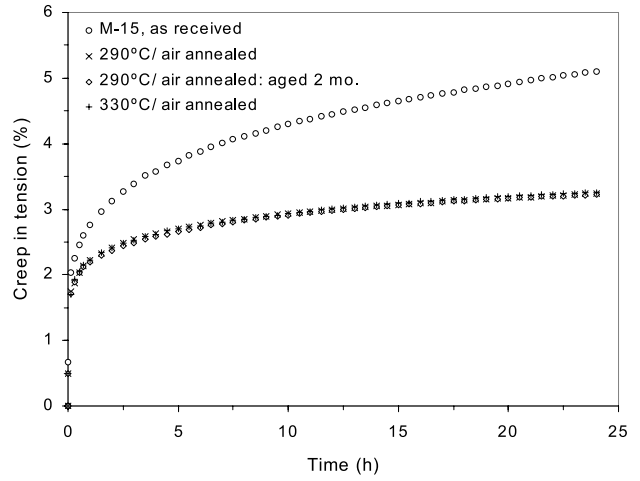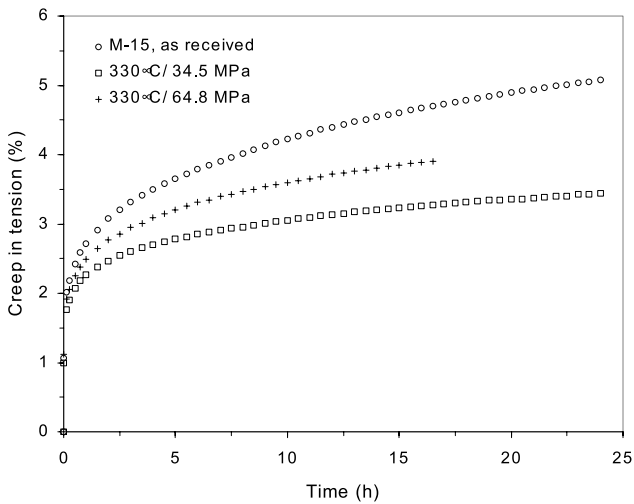


(b)

Fig. 4. Tensile creep results (4.83 MPa stress, 23 °C) for M-15 (PTFE) before and after 34.5/64.8 MPa $CO_2$ treatment for 2 h at 290 °C (a) and 330 °C (b).

under 4.83 MPa tensile stress. The curves shown in Fig. 3 are typical for creep behavior for semi-crystalline materials subjected to constant stress [32]. The response falls into three parts: (i) instantaneous elastic response, (ii) retarded viscoelastic response and (iii) permanent flow response [32]. The creep behavior may be modeled with a four-parameter model obtained with Maxwell and Voigt models in series [32,33]. From Fig. 3, it is evident that at the same stress M-111 exhibits lower creep than M-15 PTFE. Modified PTFE is made by introducing



(a)



(b)
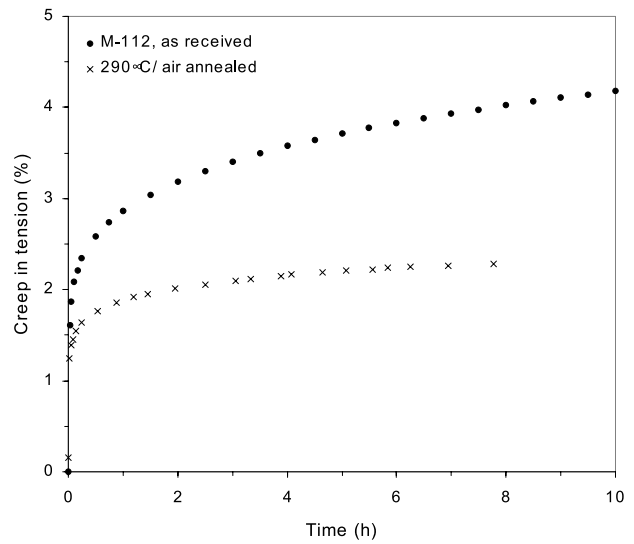


(c)

Fig. 5. Tensile creep results (4.83 MPa stress, 23 °C) for (a) M-15 (PTFE), (b) M-111 (M-PTFE) and (c) M-112 (M-PTFE) before and after annealing in air for 4 h. For M-15, a 2-month old sample that was annealed at 290 °C overlays with samples annealed at 290 and 330 °C.
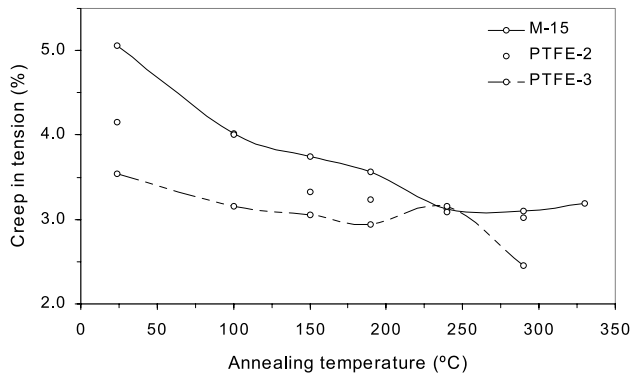
Fig. 6. Effect of annealing temperature on the creep behavior (4.83 MPa stress, 23 °C, 24 h) of PTFE (samples from different sources: M-15, PTFE-2 and PTFE-3). Lines do not represent curve fits but are provided as a guide.

perfluoropropylvinylether (PPVE) as a co-monomer during polymerization. PPVE incorporation in M-111 (less than 0.1 wt%) results in branching and decreased molecular weight, which leads to a reduction in creep [10].

### 3.6. Creep behavior of $CO_2$ annealed PTFE

Fig. 4(a) presents the room temperature tensile creep curves (at 4.83 MPa stress) for PTFE M-15 annealed in scCO$_2$ at 290 °C at 34.5 and 64.8 MPa CO$_2$ for 2 h. PTFE creep decreased with increasing scCO$_2$ pressure. In contrast to tensile measurements, the results indicate a correlation of decreased creep with increased crystallinity. Thus, tensile creep decreased ∼30% with a 290 °C/64.8 MPa CO$_2$ treatment, which corresponds to a 15% increase in crystallinity. Creep also decreased after a 330 °C/34.5 MPa CO$_2$ treatment (Fig. 4(b)). However, creep resistance is sharply reduced for post-64.8 MPa PTFE (relative to post-34.5 MPa) at 330 °C while still decreased relative to as received PTFE.

Interestingly, increased crystallinity plays a more prominent role in reducing tensile creep compared to improving stress–strain behavior. Despite decreased density, resistance to creep improves except after processing at the highest pressure and temperature (330 °C/64.8 MPa CO$_2$), which results in the lowest density (2.028 g/cm$^3$) and highest microporosity. As noted above, in trying to minimize microvoids, the CO$_2$ vent rate was very slow, no greater than 34.5 MPa/h, but even at these slow vent rates, microvoid formation occurred.

### 3.7. Creep behavior after annealing in $N_2$ or air

In 'control' experiments, tensile creep for samples annealed at ambient pressure (N$_2$ or air) decreased ∼35%. Fig. 5(a) shows results for as received M-15, M-15 annealed at 290 and 330 °C for 4 h, and 290 °C annealed M-15 tested 2 months after annealing. Again, creep tests were performed at room temperature and at 4.83 MPa stress. All the annealed samples show ∼35%
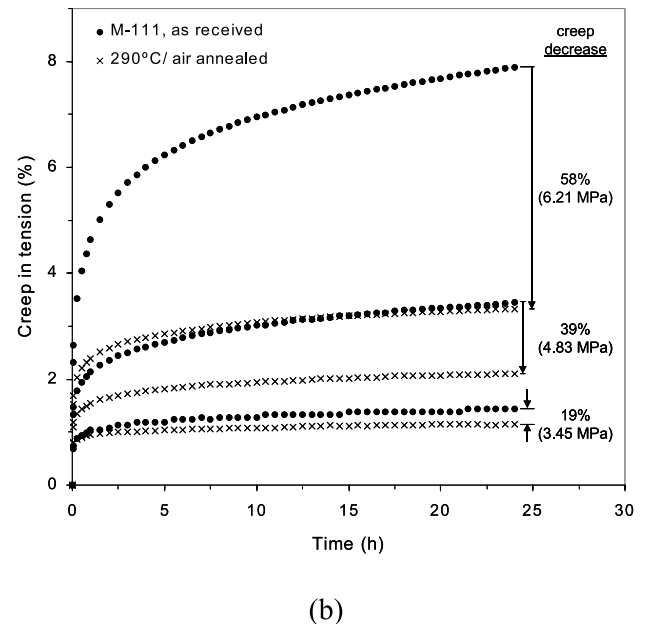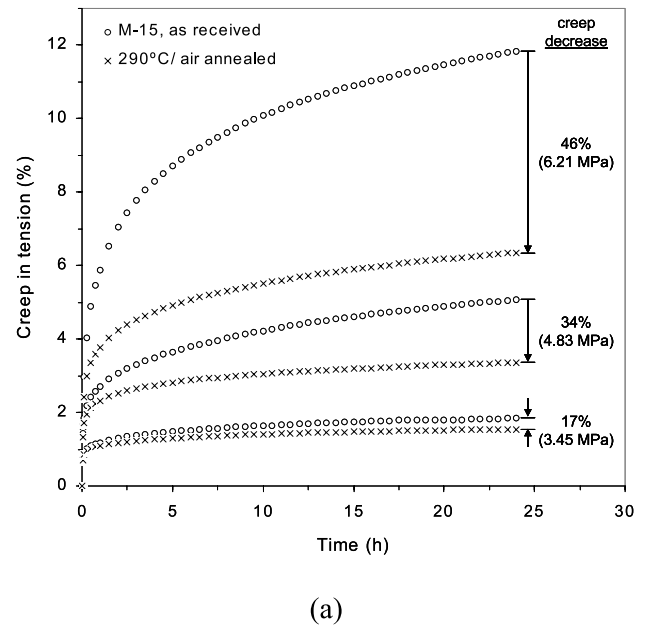


(a)



(b)

Fig. 7. Comparison of tensile creep between as received and annealed samples under different applied stresses: (a) M-15 (PTFE) and (b) M-111 (M-PTFE). The % creep decrease at 24 h is shown for pairs of as received (○) and annealed (×) curves.

decrease in creep compared to the as received samples and have indistinguishable creep response. The annealed samples are very stable. Creep behavior does not change after 2 months implying a long-term effect for thermal annealing. Analogous results are obtained with modified PTFE M-111 (Fig. 5(b)) and PTFE M-112 (Fig. 5(c)), except creep was reduced even more (∼40%) compared to as received. Comparing Fig. 5(a) and (b), one can see that creep behavior of annealed PTFE M-15 is quite similar to as received modified PTFE M-111. This result suggests
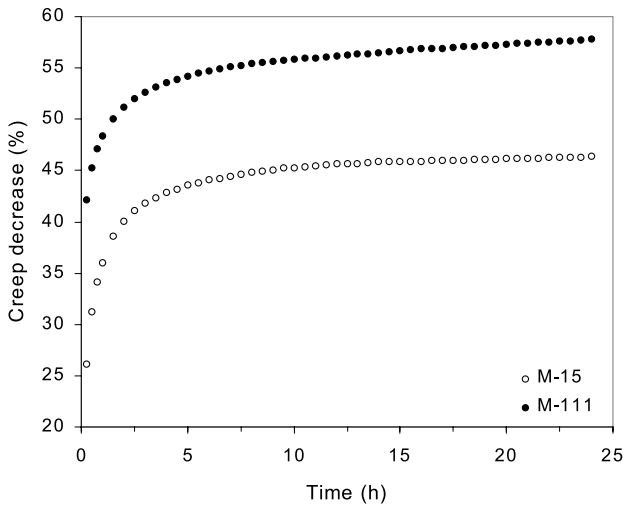
Fig. 8. Creep decrease as a function of creep time for M-15 and M-111.

feasibility for PTFE M-15 replacing modified PTFE M-111 in some applications. This prospect might be economically attractive.

### 3.8. Effect of annealing temperature

In order to study systematically the effects of annealing on creep behavior, a broad range of temperatures and PTFE skive tapes from two other sources were employed. Creep tests were carried out at room temperature and constant stress (4.83 MPa). The tensile creep curves for PTFE tapes annealed at different temperature are presented in Fig. 6. The creep of as received PTFE samples from various sources is different no doubt due to varying processing and thermal history. Compared with the M-15, as received PTFE-2 and PTFE-3 samples have lower creep. Annealing M-15 at low temperature (100 °C) leads to ∼18% decrease in tensile creep at 24 h, but provides only a slight decrease in creep for PTFE-2 and PTFE-3. With increased annealing temperature, creep decreases and levels off at 240 °C, where there are 35% (M-15) and 25% (PTFE-2) decreases in creep. Creep decreases modestly (10–18%) for PTFE-3 annealed at 100–240 °C, while creep decreases by 30% after 290 °C annealing. In summary, creep decreases with increased annealing temperature and annealing at or above 240 °C results in creep values that are nearly the same for PTFE from different sources.

### 3.9. Effect of stress

Creep tests were carried out at several different stress levels. Creep curves of as received and annealed PTFE M-15 and modified PTFE M-111 samples are shown in Fig. 7. For M-15 (Fig. 7(a)), when stress was increased from 3.45 to 6.21 MPa, the creep difference between as received and annealed sample increased from 17 to 46%. Thus, annealed samples displayed improved creep resistance at
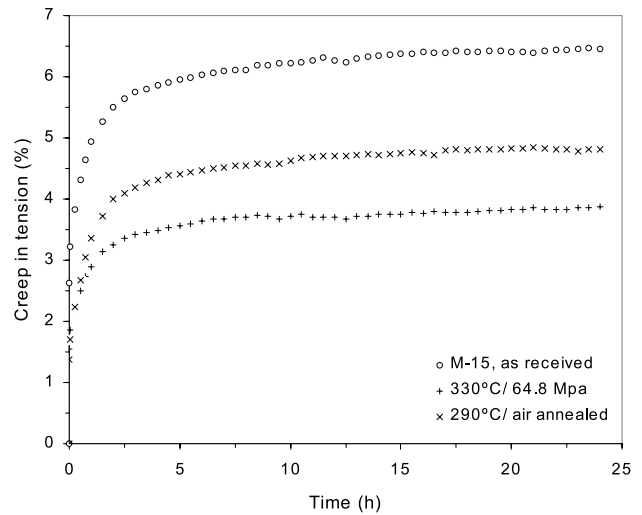


(a)
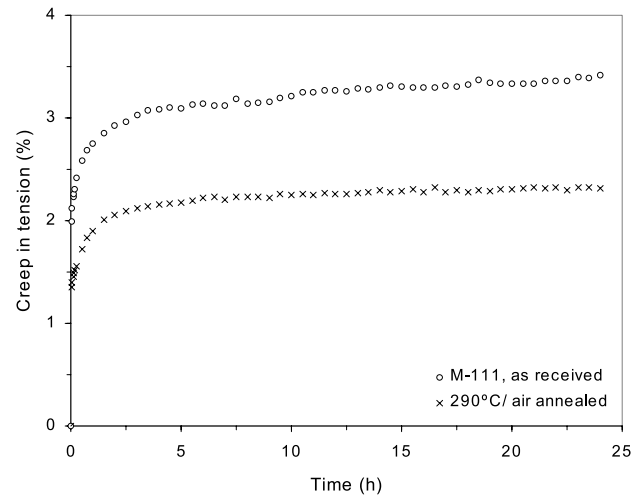


(b)

Fig. 9. Elevated temperature tensile creep results (1.03 MPa, 150 °C) for (a) M-15 (PTFE) and (b) M-111 (M-PTFE) before and after annealing in air for 4 h. For M-15, a $CO_2$ processed sample is also shown (330 °C/64.8 MPa $CO_2$/2 h).

higher stress levels. Similar behavior was observed for modified PTFE (M-111), except the creep decreases were even greater, as shown in Fig. 7(b). For example, at 6.21 MPa, creep decreased 58%. This large improvement in creep resistance is noteworthy and may favorably affect the lifetime of PTFE in some applications. The results provide impetus for annealing as an effective method to improve PTFE creep resistance, at least for skive tapes. To our knowledge, there are no reports that disclose PTFE creep reduction to such a great extent by thermal annealing.

Another interesting phenomenon is observed from creep curves. In the cold flow region, the plateau creep rate due to permanent flow, which may be obtained from the slope of creep curves in this region, was much higher for as received
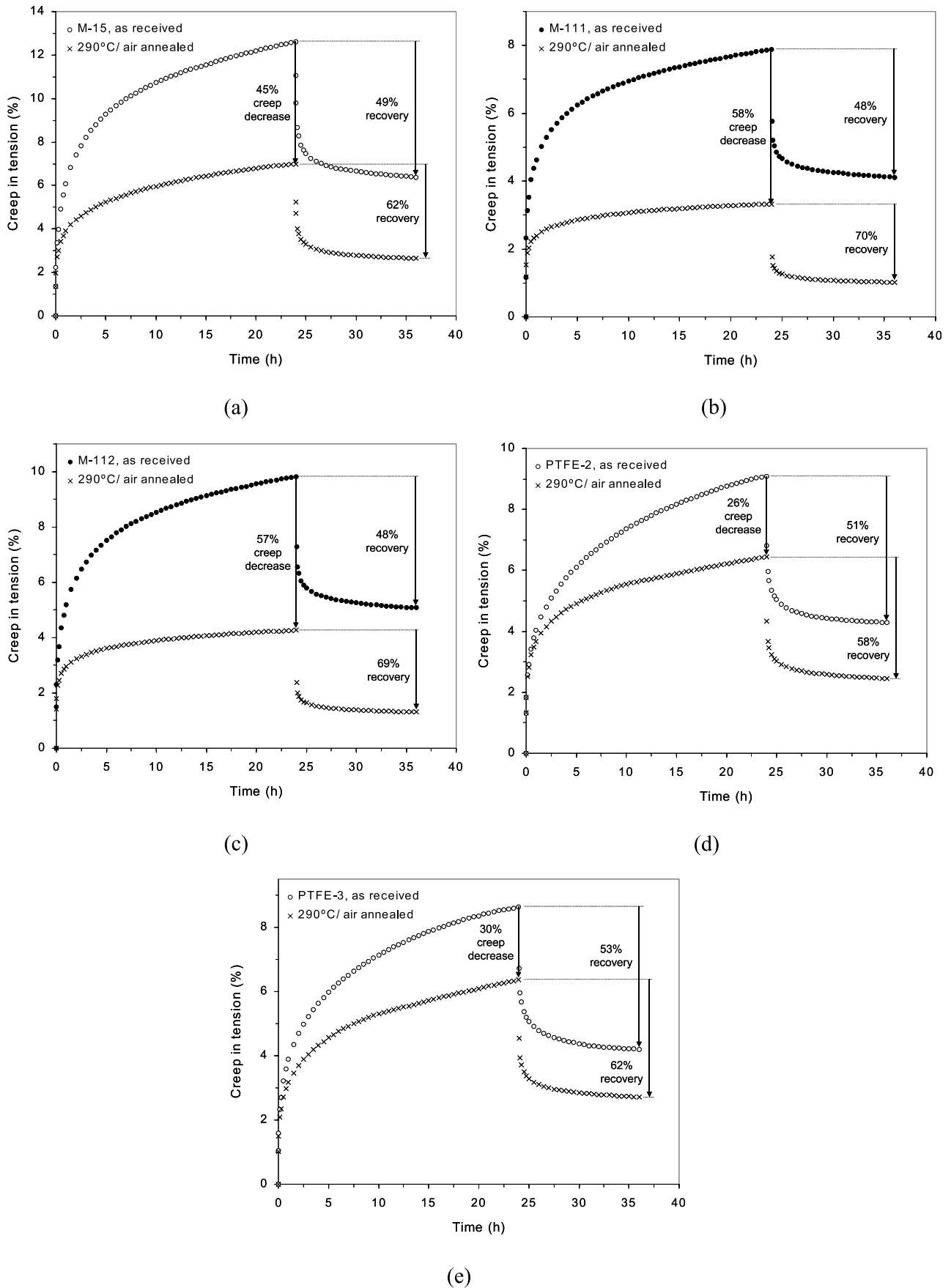
Fig. 10. Creep and recovery results for different PTFE samples (as received and annealed at 290 °C in air for 4 h): (a) M-15, (b) M-111, (c) M-112, (d) PTFE-2 and (e) PTFE-3. The % creep decrease at 24 h is shown for pairs of as received and annealed curves, and % recovery at 12 h is shown for each sample.

samples compared to annealed samples. Consequently, the difference in creep between as received and annealed samples increases over time (Fig. 8). Since, the difference in creep decrease gradually grows with time, PTFE annealing may provide improvements for long-term applications. Current work is directed at generating master curves for PTFE creep using time-stress superposition principle in order to better predict the long-term creep response of annealed PTFE.

### 3.10. Creep at elevated temperature

It is well known that PTFE has a second order $\alpha$-transition at $\sim 130\,^{\circ}$C, but the exact assignment of this transition is still controversial [12]. In any case, this $\alpha$-relaxation is most likely associated with motion of large segments in the PTFE amorphous phase. If this is the case, the mechanical properties should be dominated by the crystalline phase above 130 °C. As noted above, the PTFE crystallinity was increased after heat treatment in $scCO_2$. Measurements at 150 °C on thermally annealed and $scCO_2$-treated PTFE were carried out to assess the effect of increased crystallinity (Fig. 9(a)). At 24 h, thermally annealed PTFE showed the lowest creep reduction (40%). Creep for $scCO_2$-treated PTFE, though having higher crystallinity, was not improved compared to either the air or $N_2$ annealed samples. Once again, this result is consistent with the presence of microporosity created during $scCO_2$ processing, which offsets the effects of increased crystallinity, with a net result of higher creep. In the room temperature tests, the creep strain of as received samples steadily increases with time, while at 150 °C, the creep strain reaches a plateau after about 6 h for both as received and annealed samples. The same results were also obtained for modified PTFE M-111 (Fig. 9(b)).

### 3.11. Creep and recovery

Creep and recovery tests were carried out for PTFE from several sources. In this experiment, the sample was stretched under a constant stress (6.21 MPa) at room temperature for 24 h, at which time the stress was immediately released back to zero and the sample was allowed to recover for 12 h. Typical creep-recovery curves are shown in Fig. 10. For M-15 (Fig. 10(a)), the 24 h creep decrease at 6.21 MPa stress is about 45%, which is much higher than the creep decrease at lower stresses (e.g. 4.83 MPa and 34%, Fig. 7(a)). The creep recovery at 12 h for annealed samples (62%) is higher than that of as received samples (49%). For modified PTFE M-111 and M-112 (Fig. 10(b) and (c)), similar results were obtained, except the creep reduction was higher ($\sim 57\%$) and creep recovery was better (70%). This result provides further evidence that annealing PTFE enhances creep performance at high stress. Thermal annealing is more effective for modified PTFE than PTFE for reducing creep. For PTFE-2

and PTFE-3, the results show that thermal annealing increases the creep resistance to 26–30%, and that annealed samples have greater creep recovery (58–62%) than as received samples. However, the creep stress dependence observed for M-15 (PTFE) is not apparent for PTFE-2 and PTFE-3. This is ascribed to differences in processing and thermal history.

## 4. Conclusions

Thermal annealing effects on creep for PTFE and M-PTFE were investigated at different conditions. Annealing in $scCO_2$ increases the degree of crystallinity. Increased $scCO_2$ swelling at higher pressures and concomitant favorable kinetics of crystallization favors enhances crystallinity. Increased physical crosslinking as a result of higher crystallinity, which is expected to decrease creep, is counterbalanced by the formation of microvoids and lower density generated during $CO_2$ processing. Interestingly, thermal annealing at high temperatures and ambient pressure improves the tensile creep resistance for PTFE and modified PTFE, but there was only a slight change in density and no measurable increase in crystallinity. The detailed morphological origin of improved resistance to tensile creep is unknown, but stress relief by thermal annealing is evident. This suggests that thermal annealing imparts stress relief to PTFE after fabrication. The fact that different PTFE sources yielded a range of initial creep resistance followed by convergence after thermal annealing is consistent with fabrication procedures incorporating varying amounts stress. Finally, results show that thermal annealing can reduce creep by 18–60% depending on the material and test conditions and that creep recovery for annealed PTFE is also better in comparison to as received samples.

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