

Mechanism and Kinetics of Ultra-High Molecular Weight Polytetrafluoroethylene Sintering

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ABSTRACT: The effect of sintering time on the melt evolution of Ultra-High Molecular Weight Polytetrafluoroethylene was studied *in situ* by high temperature Wide Angle X-ray Scattering, and by cyclic thermal loading profiles within a Differential Scanning Calorimeter (DSC) and Thermo-Mechanical Analyzer (TMA). Results obtained from these techniques support the concept of molecular ordering in the melt state as a function of sintering time well above the melting temperature. TMA, which is not a conventional technique for monitoring thermal transitions, is shown to be sensitive enough for such purposes. Both DSC and TMA exhibit nonequilibrium melt behavior even 30°C above its equilibrium melting temperature for long time periods. A correlation between the DSC and TMA results is established. The cyclic thermal profile leads to a dramatic growth in enthalpy of crystallization/melting. The mechanism for this growth is associated with two independent processes; isothermal annealing at the sintering temperature and lamellar thickening in the solid state. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40967.

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INTRODUCTION

Polytetrafluoroethylene (PTFE) is a fluoropolymer with many outstanding properties including excellent thermal stability, chemical inertness and very low coefficient of friction, making it suitable for a wide range of applications.¹

Conventional melt processing techniques such as extrusion and injection molding cannot be applied to Ultra-High Molecular Weight PTFE resulting from its very high melt viscosity (10^{10} – 10^{11} poise).¹ Industrially, PTFE is processed by semi-continuous melt extrusion^{2,3} or compaction (pre-forming) of PTFE molding powder at room temperature followed by sintering.^{4–8} Sintering involves heating a preform above its melting temperature, dwelling at that temperature for a specified time followed by slow cooling to room temperature. This leads to the formation of a homogeneous part with improved mechanical integrity.¹

Although a significant amount of work has been devoted towards developing sintering models for polymers, Frenkel's expression for sintering of glasses still serves as the basis to illustrate what are conventional materials properties that affect the sintering process.⁹ It states that the thermodynamic driving force for sintering or particle coalescence is reduction in surface energy and the kinetics of this process is governed by the viscosity of the coalescing particles. Clearly, sintering of PTFE, a

polymer with very low surface energy and very high melt viscosity cannot be explained on the basis of such a model. This is not unexpected when one considers the distinctive features of PTFE melt. There is extensive literature that suggests the existence of partial order in PTFE melt. Neutron scattering studies on molten PTFE has shown existence of conformational order up to 400°C.¹⁰ Wide Angle X-ray Scattering (WAXS) results on molten PTFE suggest straight chain segments arranged parallel to one another packed in a disordered manner.¹¹ Microscopy studies have revealed the development of a folded chain structure in the melt state which increases in perfection with sintering time.¹²

Thus, the first step towards understanding the sintering process in PTFE involves an in depth study of the structure evolution of PTFE melt as a function of sintering time. In the present work, the time evolution of PTFE melt was investigated at different length scales by using an array of *in situ* experimental techniques. Thermo-Mechanical Analyzer (TMA) in the dynamic mode was used to probe the complex viscoelastic response of the melt by the application of an oscillatory loading of low amplitude. Further, the evolution of residual melt order was examined *in situ* by using high temperature X-ray scattering studies. The melt structure evolution was simultaneously characterized by employing a cyclic thermal loading profile within the Differential Scanning Calorimeter (DSC) and TMA. Herein,

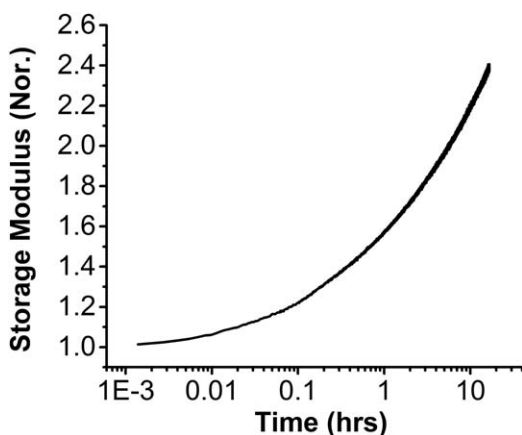


Figure 1. Storage modulus evolution of Ultra-High Molecular Weight PTFE as a function of annealing time at 370°C for 16 hours.

we propose a mechanism for the sintering process in PTFE based on a critical evaluation of our experimental results that probe different facets of this process.

EXPERIMENTAL

Material and Sample Preparation

M15X, a granular PTFE molding powder, supplied by Saint Gobain was used in the current work. Cylindrical green billets were compacted from the raw powder by following a controlled two-stage pre-forming strategy using Instron 5500R at room temperature. A 6 mm internal diameter compression mold was employed for this purpose allowing for plane strain compaction.

In the first stage, the powder was compacted at 1 mm/min strain rate to 4 MPa stress followed by a 5 min dwell time. In the second stage, it is again compacted at 1 mm/min strain rate to 20 MPa stress and held for 5 mins. The molding region was kept under vacuum during this process. This strategy was adopted after testing several other compaction methods on grounds of improved sample to sample reproducibility. After compaction, a resting time of 3 hrs or more was allowed for degassing and natural recovery. The resulting pre-forms had a density of approximately 2.15 g/c.c and an aspect ratio of approximately 5 : 6.

METHOD

Differential Scanning Calorimeter

DSC Q200 (TA Instruments, USA) was used to monitor the structure evolution of the PTFE melt by employing a cyclic thermal loading profile.

Thermo-Mechanical Analyzer

TMA Q400 (TA Instruments, USA) in the dynamic mode was used to probe the storage modulus evolution of PTFE melt as a function of sintering time by applying an oscillatory force of ± 0.002 N at 0.5 Hz frequency. A preload force of 0.01 N was applied to sustain contact between the probe and the specimen surface. The dimension changes associated with the melting/crystallization transitions was also measured using this technique. Further, the structure evolution of PTFE melt was

studied by using a cyclic thermal profile by harnessing this technique to monitor melting/crystallization transitions.

Wide Angle X-ray Scattering

WAXS was done using an in-house setup from Molecular Metrology Inc. (presently sold as Rigaku S-Max3000). It uses a 30 W microsource (Bede) with a $30 \times 30 \mu\text{m}^2$ spot size matched to a Maxflux[®] optical system (Osmic) leading to a low-divergence beam of monochromatic CuK_α radiation (wavelength $\lambda = 0.1542$ nm). After passing beam-defining and guard pinholes, the beam of about 0.4 mm diameter enters the sample chamber. A Fujifilm CR HR-V image plate at a distance of $L = 117$ mm was used to record the scattering. L was calibrated using the $q = 15.197 \text{ nm}^{-1}$, (110) peak from a tricosane standard. The image plate has a maximum resolution of 50 μm . The whole system is evacuated.

WAXS studies on molten PTFE at 370°C was performed inside an environmental chamber to study the evolution of melt state order as a function of sintering time.

RESULTS AND DISCUSSION

Figure 1 shows the storage modulus evolution of PTFE melt at 370°C as a function of sintering time. The specimen was equilibrated at 370°C for 10 minutes prior to data acquisition. This relatively long equilibration time was chosen keeping in mind the low thermal conductivity of the material. As shown in Figure 1, the modulus keeps increasing with annealing time and does not equilibrate within the experimental time frame.

Such a slow equilibration kinetics is not unlikely when one considers the ultra-high molecular weight and the inherent stiffness of the PTFE chains.¹³ However, the molecular mechanism responsible for this nonequilibrium melt evolution is one of the primary questions that this article aims to answer.

Recently published literature on UHMWPE has shown a similar increase in elastic modulus as a function of annealing time and this increase has been attributed to entanglement formation in a disentangled polymer melt. This work further showed that the kinetics of entanglement formation is a function of polymer

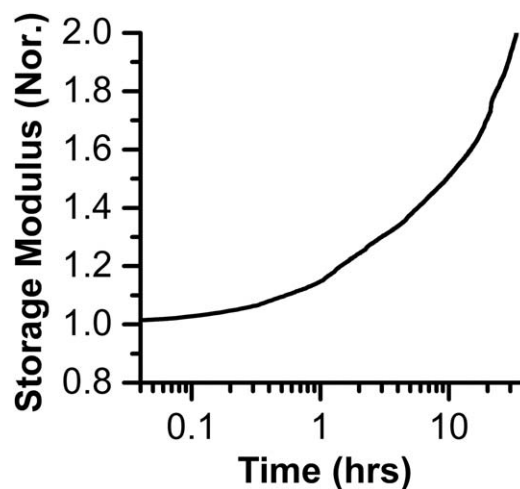


Figure 2. Storage modulus evolution for 280 hours (~ 12 days) of an industrially sintered Ultra-High Molecular Weight PTFE billet.

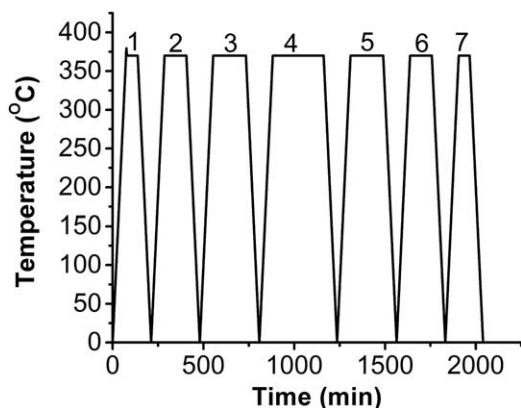


Figure 3. Cyclic DSC thermal loading profile.

molecular weight and significantly longer times are required for higher molecular polymers to reach an equilibrium entanglement density which corresponds to a plateau in storage modulus.¹⁴ This may be one of the potential mechanisms responsible for the nonequilibrium melt evolution observed in PTFE. In other words, entanglement formation might be the molecular mechanism that drives inter-particle sintering.

Next to investigate if melt equilibration is achieved in an industrial sintering process, the storage modulus evolution of a billet already sintered by St. Gobain was probed. The specimen was again annealed at 370°C but for significantly longer times (approximately 12 days). However, the melt did not equilibrate even in 12 days with the modulus continuing to increase with time (Figure 2).

This 12 day long nonequilibrium evolution might be a mere consequence of very slow entanglement kinetics. However, this increase in storage modulus can also come from some other molecular mechanism which is not entanglement formation and further investigation is necessary to confirm or refute this hypothesis.

Differential Scanning Calorimetry

A cyclic DSC profile, shown in Figure 3 was designed to interrogate the effect of thermal memory on PTFE (M15X) melting

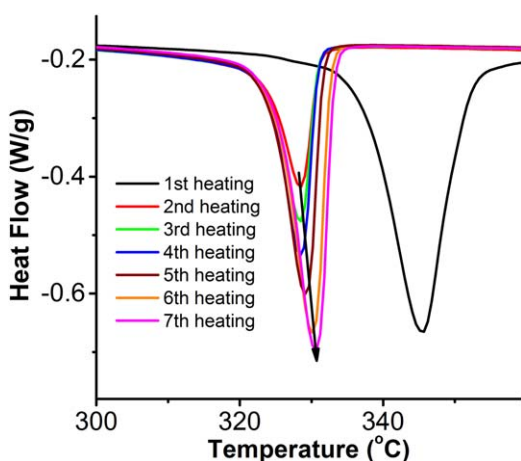


Figure 4. Effect of successive sintering steps on melting behavior of Ultra-High Molecular Weight PTFE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and crystallization. Cycling was done between 0°C and 370°C at a constant rate of 5°C/min. The thermal cycling was coupled with isothermal annealing for different durations at 370°C. Note that the isothermal times were chosen such that they sum up to 1000 min with the first and last having equal times, the second and next to last having the same times, and so on. The amount of time required to erase any memory in the PTFE melt would be identified by the pair of isotherms showing the same response. For example, if PTFE has no thermal memory then all the seven heating and cooling steps would yield identical values for melting/crystallization temperatures and enthalpies. Further, if PTFE crystallization was a function solely of the preceding annealing time, then the first and seventh cooling would be identical and the same would be true for second and sixth, third and fifth cooling.

Figure 4 shows the melting peaks for this profile. Note that both enthalpy of melting and melting temperature increases with successive sintering steps. An increase in melting temperature might correspond to lamellar thickening as a function of sintering time. The first melting is very different from the rest because of different morphologies of virgin (extended chain) and sintered PTFE (folded Chain).¹⁵ The enthalpy of crystallization increased whereas, the crystallization temperature decreased with successive sintering steps (Figure 5). This is counter intuitive and contradicts the initial entanglement hypothesis as these results indicate that sintering is associated with some other molecular process that leads to an increase in enthalpy of melting and crystallization.

Further, two exothermic peaks (Peaks 1 and 2) to the right of the main crystallization peak were reported, one of which grew at the expense of the other as a function of sintering time (Figure 6). Such, sintering time dependent disappearance and reappearance of molecular order is again indicative of the complex time evolution of the PTFE melt.

Thermo-Mechanical Analyzer

Another technique to characterize such a melt may be the TMA. Although TMA is not a conventional technique for monitoring crystallization and melting transitions, their results can complement the information received from a DSC. In order to

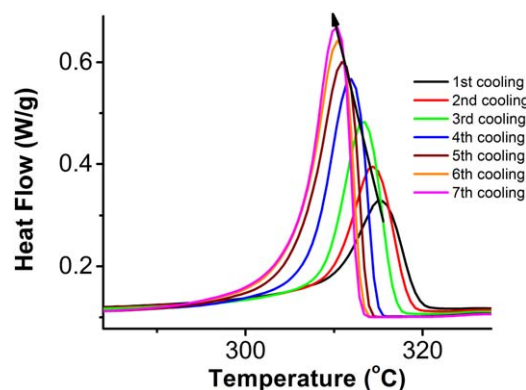


Figure 5. Effect of successive sintering steps on crystallization behavior of Ultra-High Molecular Weight PTFE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

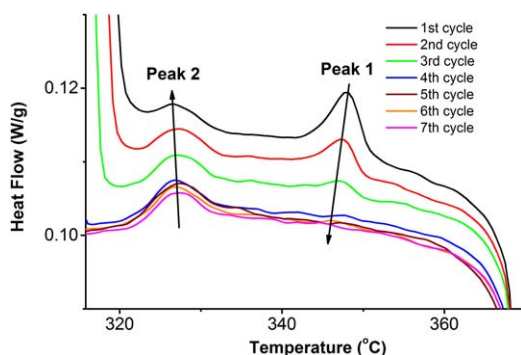


Figure 6. Peak 2 grows at the expense of Peak 1 as a function of sintering time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

do this the following cyclic TMA (Figure 7) was conducted and contrasted with the cyclic DSC. In these studies, the cycling was done between 150°C and 370°C owing to the lack of controlled cooling below 150°C in the air-cooled TMA. Nevertheless, such a variation was not expected to significantly alter the melting/crystallization behavior.

Figure 8 shows dimensional changes associated with the seven melting transitions. Again, the first melting is very different from the rest because of change in crystal structure from extended to folded chain. As can be seen, such a crystalline transition is very well captured even in the macroscopic dimension changes. Differentiation of the dimension changes yields Figure 9. Here the area under each melting peak corresponds to the dimension change associated with that melting transition. It shows that from second through seventh melting, both the melting temperature and the dimension change associated with the melting transitions increase. This is in agreement with our DSC results.

Figures 10 and 11 show the dimension changes associated with the crystallization transitions. Here, the dimension change associated with crystallization increases whereas the crystallization temperature decreases with successive sintering steps. Again, these results are in agreement with our DSC results.

Thus, TMA which measures macroscopic dimension changes, an extensive property of the system, is sensitive enough to capture

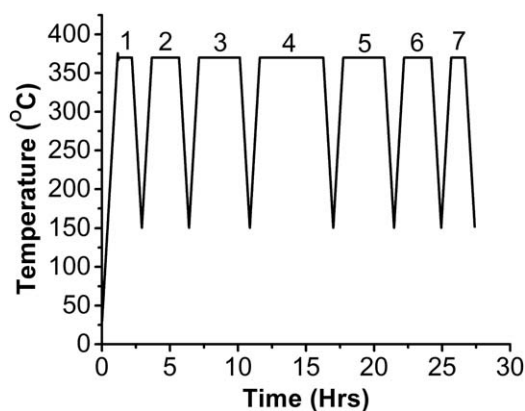


Figure 7. Cyclic TMA thermal loading profile.

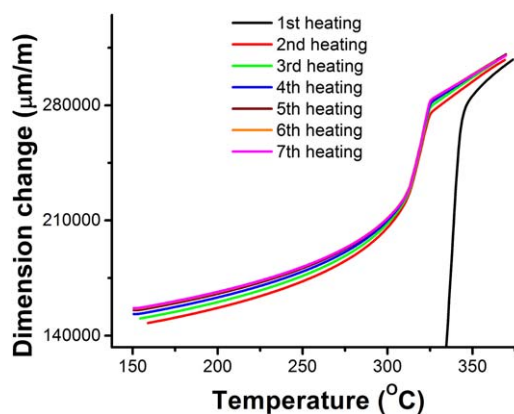


Figure 8. Dimension changes ($\mu\text{m/m}$) associated with seven melting transitions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

subtle variations in thermal transitions originating from microstructural rearrangement.

Figure 12 shows a correlation between the TMA and DSC crystallization data. The enthalpy of crystallization (ΔH_c) obtained from DSC correlates well with the dimension change associated with crystallization (Δh_c) obtained from TMA.

Therefore, TMA can be used not only independently but also in correlation with DSC to study melting/crystallization transitions and crystal structure. Further, both the cyclic DSC and TMA results indicate that sintering is associated with molecular ordering.

Closer Look at Cyclic DSC Crystallizations

As GPC cannot be performed on PTFE, an empirical way to determine its molecular weight was from its heat of crystallization measurements using the relation (1) based on data from Suwa¹⁶:

$$M_n = 2.1 \times 10^{10} \Delta H_c^{-5.16} \quad (1)$$

This might suggest that the ΔH_c increase (Figure 3) is a mere consequence of chain scission at 370°C and not a result of the

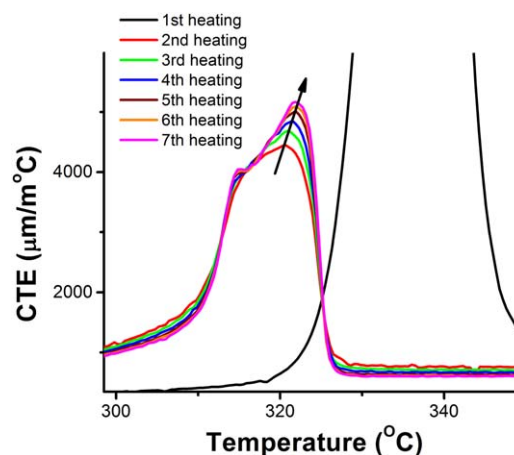


Figure 9. Derivative of the dimension changes associated with the seven melting transitions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

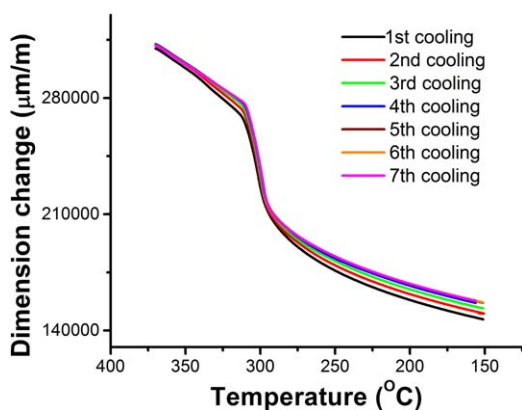


Figure 10. Dimension changes associated with seven crystallization transitions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cyclic thermal loading profile (Figure 1). Further, it has been shown that sintering (360–382°C) leads to slow thermal breakdown.¹⁷ To interrogate this, two independent continuous DSC experiments were conducted in which the sintering times were 1000 min (equal to the sum of the isothermal times of the cyclic DSC) and 2060 min (equal to the total time of the cyclic DSC). If chain scission was leading to the ΔH_c growth then ΔH_c corresponding to the seventh cooling in the discontinuous sintering should approximately equal that obtained after 1000 min continuous sintering. Further, the ΔH_c obtained after 2060 min continuous sintering should be significantly higher. A comparison of the experimental results is shown in Figure 13.

Isothermal sintering for 1000 and 2060 min (approximately equal to the total time for discontinuous sintering exp.) leads to much lower crystallization enthalpy than the 7th cooling cycle in discontinuous experiment. Thus, dramatic crystallinity growth was not a function of chain scission.

Figure 14 shows a different thermal history that leads to the same final enthalpy of crystallization 43 J/g, as that obtained from the seventh cooling step in cyclic DSC. In designing this thermal profile, it was assumed that the dramatic increase in

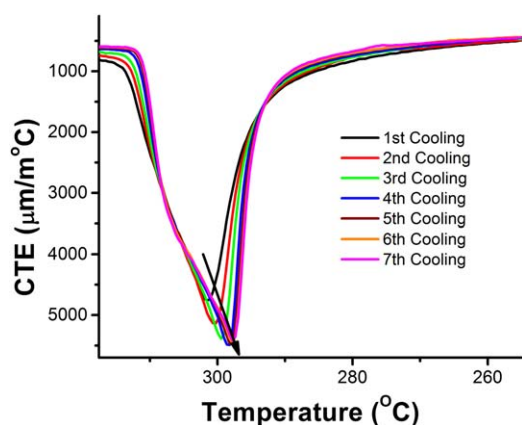


Figure 11. Derivative of the dimension changes associated with the seven crystallization transitions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

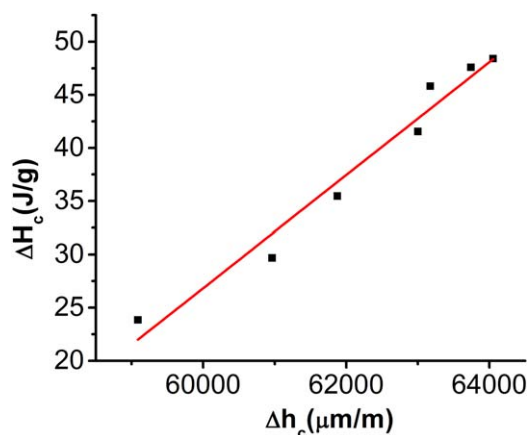


Figure 12. TMA-DSC correlation (Crystallization data). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

crystallinity in the cyclic DSC experiment was a result of two independent processes—Isothermal annealing at 370°C and Lamellar thickening in the solid state. For comparison sake, the isothermal annealing time at 370°C was kept equal to the sum total of the isothermal times in the cyclic DSC. Further, the solid state thickening time was chosen to be nearly equal to the total heating/cooling time in cyclic DSC. Previous work by Wunderlich has shown nearly 40% thickening of PTFE lamellae in 40 minutes on annealing at 316°C.¹⁸

Wide Angle X-ray scattering

In our quest to understand the molecular mechanism of PTFE sintering, the system was studied by a variety of experimental techniques. However, the results obtained were indicative of two distinct processes—Melt state molecular ordering as evidenced by an increase in crystallization/melting enthalpy with sintering time and entanglement formation as evidenced by increase in storage modulus with sintering time. A point to note here is that an increase in storage modulus can also come from molecular ordering. Further, there is evidence in literature of such molecular ordering in the melt state where Geil, based on

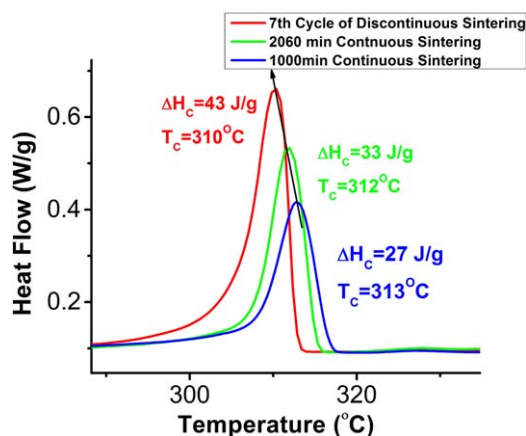


Figure 13. Comparison of final crystallinities resulting from different thermal treatments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

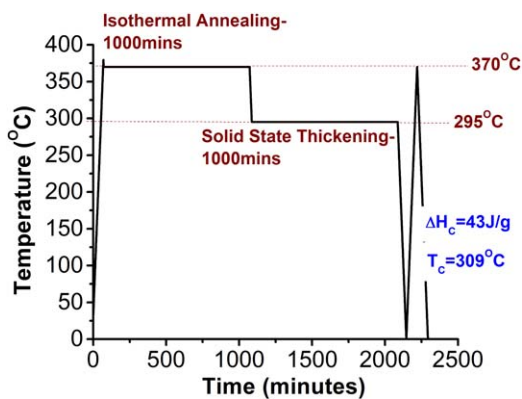


Figure 14. DSC temperature profile showing the independent effects of annealing and solid state thickening. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

microscopy studies, showed that increasing sintering times lead to the formation of striated bands on the cryogenically fractured surface of PTFE and it is well known in PTFE literature that such striated bands are a characteristic of PTFE crystalline structure.¹² However, this was not an *in situ* study as the samples were water quenched from the melt state and it was assumed that resulting structure will be identical to that prevailing in the melt. However, this might not be a good assumption for a material like PTFE which shows very fast crystallization kinetics. Therefore, in order to make any conclusive remark on this problem, one would need an *in situ* technique for monitoring the state of order or disorder in the melt.

One such technique might be X-ray scattering on molten PTFE. Although, it is highly unlikely for a material to show crystalline order in its melt state, WAXS studies on molten PTFE has revealed the existence of a distinct Bragg's peak well above its melting point, which is an *in situ* evidence of melt state order. This peak only disappears at 400°C but is present at conventional sintering temperatures.¹⁹ This is not surprising when one considers the extraordinary stiffness of the PTFE chains.¹³

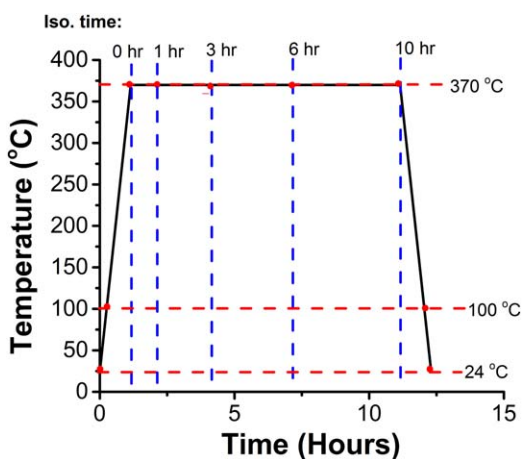


Figure 15. Temperature profile for high temperature WAXS studies. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

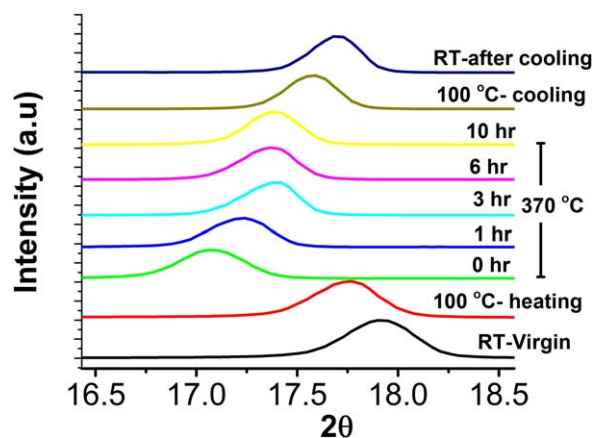


Figure 16. Evolution of 100 peak as a function of temperature and time (amorphous hump subtracted). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

However, we are interested in the time evolution of this peak. Therefore, in our high temperature X-ray scattering study, virgin PTFE was subjected to a temperature profile as indicated by Figure 15 and scattering studies were performed at locations indicated by the red dots.

Figure 16 shows the evolution of 100 peak as a function of temperature during heating and cooling and as a function of time at the sintering temperature of 370°C. In Figure 16, the broad amorphous scattering background has been subtracted. As can be clearly seen, increase in temperature from 24°C (Room temperature) to 370°C led to a significant decrease in scattering angle which is indicative of looser packing at higher temperatures. Further, following the 10 hour sintering step, subsequent cooling led to an increase in scattering angle which is indicative of better packing of the chains with decrease in temperature. There is existing literature on the comparison and contrasting of PTFE crystalline structure before and after sintering.¹⁹ The focus here, however is the evolution of melt state order at the sintering temperature. Figure 17 presents a closer look at the evolution of 100 peak at 370°C as a function of sintering time after subtraction of amorphous scattering background. As can be seen, increase in sintering time leads to a corresponding

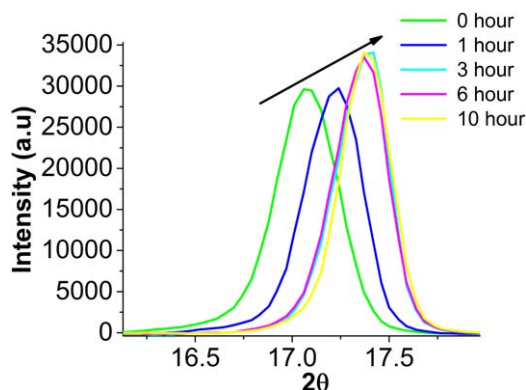


Figure 17. Evolution of 100 peak at 370°C as a function of sintering time (amorphous hump subtracted). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

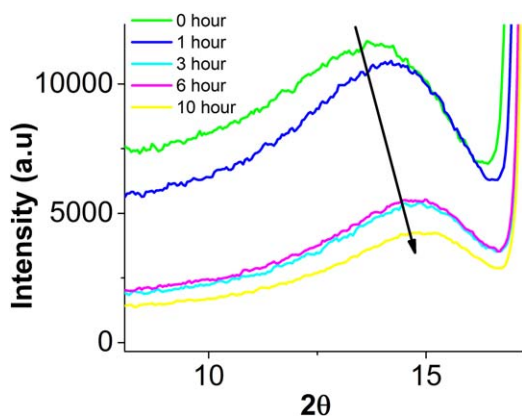


Figure 18. Evolution of amorphous hump at 370°C as a function of sintering time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increase in scattering angle which is indicative of better packing or more perfect crystals. This result shows that the residual order present in PTFE melt increases in perfection with sintering time. Moreover, the intensity of the 100 peak also increases with sintering time. Further, the associated amorphous hump which was subtracted from Figures 16 and 17, itself decreases with sintering time (Figure 18).

A simultaneous increase in the intensity of the crystalline peak (Figure 17) and a decrease in the associated amorphous hump (Figure 18) further shows that the crystalline content of PTFE melt increases with sintering.

CONCLUSIONS

This article elucidates the molecular mechanism of PTFE sintering. It was shown that PTFE not only exhibits the unique feature of melt state order but also the state of order achieves perfection with sintering time. This phenomenon was evidenced by our cyclic DSC, cyclic TMA, and high temperature X-ray scattering studies.

Further, TMA was established as a complimentary technique for monitoring melting/crystallization transitions. Both DSC and TMA exhibited a nonequilibrium evolution of PTFE melt. The enthalpy of crystallization and melting was found to increase with successive sintering steps. Further, the crystallization temperature decreased whereas the melting temperature increased with successive sintering. These results were endorsed by in-situ high temperature X-ray scattering studies on molten PTFE. Results obtained from the cyclic TMA experiment correlated well with the corresponding cyclic DSC. It was established that the dramatic growth in enthalpy of crystallization and melting

was not due to chain scissions at 370°C. Further, it was shown to be possibly resulting from two independent processes—Isothermal annealing at 370°C and lamellar thickening in the solid state.

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