

Morphological Evolution of Polytetrafluoroethylene in Extreme Temperature Conditions for Aerospace Applications

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ABSTRACT: The organic electrical insulator polytetrafluoroethylene (PTFE) is used in aerospace industry under extreme conditions of temperature and electric field. The melting temperature of PTFE is about 327°C and nowadays operating temperature of this kind of insulators can reach about 300°C and up to 350°C for new generations of machines. All thermal, electrical and mechanical operating stresses, especially high temperature and voltage can be factors of ageing acceleration and/or degradation of the insulators that could cause premature failures. Our present work is focused on the organic insulator behavior at high temperature in order to understand the mechanisms of thermal ageing and degradation. The change of morphology of PTFE during the thermal ageing has been studied. Thin films in PTFE were aged by accelerated method under oxidizing environment (air) and severe thermal constraints between 340 and 450°C. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39841.

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INTRODUCTION

Nowadays the knowledge of mechanisms associated with thermo-electrical ageing is essential to the development of a new generation of electrical insulators.¹

Polytetrafluoroethylene (PTFE) is a semicrystalline thermoplastic polymer, usually opaque and white. It exhibits good thermal and dielectric properties as well as an excellent chemical resistance. Its operating temperature can go up to 260°C,^{2,3} the dielectric strength varies between 50 and 170 kV mm⁻¹. PTFE contains two types of chemical bonds: apolar C—C bonds (energy = 348 kJ mol⁻¹) and highly polarized C—F bonds (energy = 507 kJ mol⁻¹).⁴ Because of its unbranched chain architecture and helical conformation, this polymer is globally apolar although it contains very polar bonds. Its relative permittivity is stable and low (2.2) for a wide frequency range (1–10⁷ Hz).⁵ Resulting from the helical conformation, the fluorine atoms cover the molecular chains, which protect the polymer against thermal and chemical attacks.⁶ Consequently PTFE is chemically inert to acids, bases, ketones, alcohols, and hydrocarbons.

In general, when a polymer is exposed to an important thermal constraint, chemical degradation reactions may take place, such as the macromolecular chain scissions and the formation of new molecules. This may affect significantly the molecular

weight, the chains arrangement as well as the size distribution of macromolecules. Hence, all these processes may cause modifications of their physico-chemical properties. Lewis and Naylor have reported the first results on the thermal decomposition of PTFE in 1947.⁷ They heated PTFE at 600°C at pressures of 5 mm (6 × 10² Pa) to 760 mm (1 × 10⁵ Pa) as well as at 700°C at a pressure of 41 mm (5 × 10³ Pa). They explained that the main products of pyrolysis are TFE (tetrafluoroethylene) monomers by depolymerization reactions. HFP (hexafluoropropene) and *c*-C₄F₈ (cyclo-perfluorobutane) can be formed in secondary reactions depending on the reaction temperature, the pressure and the atmosphere.

PTFE is a material widely used in aerospace applications; mainly as electrical insulator, which operates at high temperature under high electric field. The PTFE insulators we have studied work in air and the operating temperature varies between -55 and 250°C (300°C peak). In theory, these PTFE insulators remain in solid state in this temperature range. However, for new generations of machines, the peak temperature may reach 350°C, which is higher than its melting temperature (about 327°C). Additionally thermo-oxidative ageing in the fluid state may accelerate deterioration of electrical insulating performance.

Above 327°C, PTFE becomes transparent due to the melting of the crystalline part. Its mechanical properties in molten state are very different from most of thermoplastics. It possesses a

high viscosity (10^{10} Pa s⁻¹ at 380°C) because of its very high molecular weight. PTFE looks more like a gel than a liquid. Its molten shape stays stable, which is an advantage of this type of polymer for high temperature insulator application.

There are some additional constraints undergone by PTFE insulators, such as operating voltage (7 kV mm⁻¹), pressure (between 37 and 102 kPa), moisture, salt, oil and kerosene present in the atmosphere. Currently, there are very few specifications on the insulators for high temperature and/or high voltage applications, furthermore their ageing and degradation patterns are not well known.

The aim of the present work is to study the effect of high temperature (especially above melting temperature) in oxidizing atmosphere on the ageing and degradation process, and eventually the mechanisms of thermal ageing and degradation. PTFE thin films were aged by accelerated method with exposure time varied from 2 to 300 h under oxidizing environment and severe thermal constraints up to 450°C. Samples were characterized by TGA which allows us to describe the thermal behavior and stability of the polymer; sample weight evolution and DSC characterization were used in order to follow the ageing process as well as the morphology evolution of PTFE.

EXPERIMENTAL

Materials

The PTFE samples are commercially available (Goodfellow) in form of thin film with a thickness of about 50 μm.

Thermal Ageing in Air

The samples were cut in pieces of 5 × 5 cm², placed in Pyrex containers, and then underwent accelerated ageing cycles. They were heated at a heating rate of about 10°C min⁻¹ from room temperature to a constant ageing temperature (between 340 and 450°C) during 2–300 h. This thermal ageing was carried out in an oven CARBOLITE LHT6/120, whose temperature homogenization is realized by forced air convection. After each cycle of ageing, samples were slowly cooled ($\approx 2^\circ\text{C min}^{-1}$) until room temperature, as in actual cooling conditions of PTFE insulators. Before and after each ageing cycle, weight loss measurement, and DSC were used for the characterization of aged samples.

Thermogravimetry Analysis (TGA)

TGA experiments were performed using a thermo balance SETARAM 92-16.18 with a heating rate of 10°C min⁻¹ and a flow rate of 100 mL min⁻¹. The as-received samples were prepared in pieces of about 5 mg and then heated from room temperature until 630°C under two atmospheres (air or nitrogen). Weight loss of samples was recorded versus temperature.

Weight Loss Measurement

This method allows us to record the samples weight evolution during accelerated ageing cycles in air under various ageing parameters (time and temperature). Our 5 × 5 cm² samples were directly weighted before and after each ageing cycle by a microbalance, which accuracy is 10⁻⁵ g. Measurable mass of samples can be more important (10⁻³ to 220 g) than that of TGA.

For the study of the ageing time effect, ageing temperature was maintained constant; three temperatures higher than the melt-

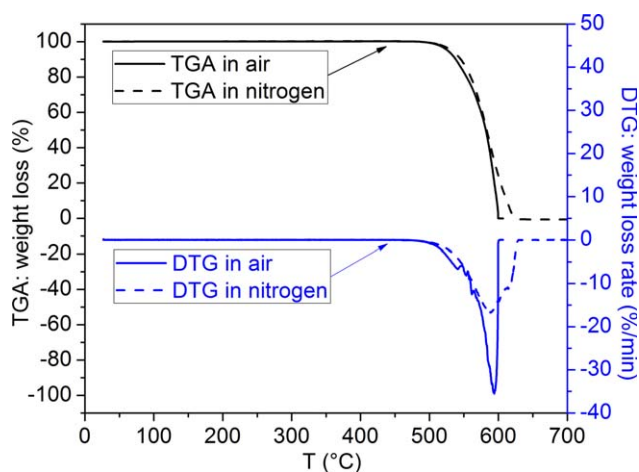


Figure 1. TGA and DTG curves of as-received PTFE under different atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ing point ($\sim 327^\circ\text{C}$) of PTFE were chosen: 340, 400, and 450°C. Ageing time varied from 2 to 300 h.

Differential Scanning Calorimetry (DSC)

DSC measurements were performed using a TA DSC 2010 CE calorimeter. Measurements on samples of around 10 mg were performed in nitrogen from -55 up to 400°C with a heating and cooling rate of 10°C min⁻¹. As TGA results show no significant weight loss until about 500°C, we supposed that there was no remarkable thermal decomposition of samples during DSC measurements. Hence, two scans were carried out for each sample: the first one erases the thermal history of the samples. The comparison between samples was done only using the second scan.

The effect of temperature and ageing time on the morphological evolution of samples was studied with the same protocol as the one used for weight loss measurement, in order to correlate the morphological evolution and the weight loss behavior.

RESULTS AND DISCUSSION

Thermogravimetry Analysis (TGA)

The TGA thermogram (Figure 1) of as-received PTFE shows that there is no weight loss until about 483°C. Above this temperature, PTFE loses its weight very fast in a single stage. This temperature can then be considered as the degradation temperature. For the decomposition in air, PTFE loses completely its weight at 600°C. Its decomposition in nitrogen is slower as the temperature of complete decomposition is about 626°C. The 5% weight loss temperature is 525°C for decomposition in air and 532°C for that in nitrogen.

Differential thermogravimetric (DTG) thermogram (Figure 1) describes the weight loss rate of PTFE versus time. The minimum of curves around 600°C corresponds to the maximal decomposition rate: the maximal rate in air is about twice as fast as that in nitrogen. This result shows that the oxygen in air accelerate the degradation process. This conclusion is similar to the TGA results reported by Conesa and Font⁴ under different atmospheres (air, nitrogen) on PTFE.

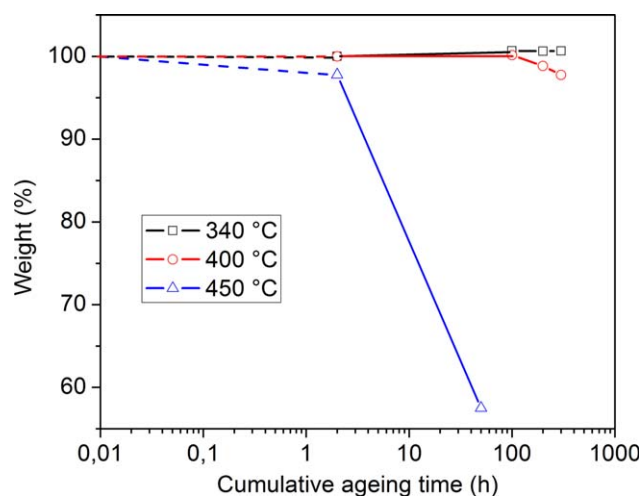


Figure 2. Weight loss of PTFE samples versus cumulative ageing time at different ageing temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Weight Loss Measurements

As previously mentioned, the C—F bonds energy (507 kJ mol^{-1}) is higher than the C—C bonds (348 kJ mol^{-1}), so when the temperature is high enough, the weaker bonds will break first. The most likely mechanisms for the PTFE pyrolysis are the end-chain scissions of C—C bonds,³ which produce radicals and form TFE monomers by an “unzip reaction”. Thus small molecules evaporate in gas phase during the heating, which consequently decrease samples weight.

In Figure 2 we show the ageing time effect on the weight loss at 340 and 400 °C after 2, 100, 200, and 300 h of ageing, and at 450 °C after 2 and 50 h of ageing. We can observe that there is no weight loss at 340 °C after 300 h, the PTFE remains stable at these chosen parameters; at 400 °C, a small weight loss is observed from 200 till 300 h of ageing. This thermal behavior is consistent with the results reported by Simon and Kaminsky.³ At 450 °C, the weight loss becomes fast; this can be described as a very severe degradation stage of the polymer. PTFE quickly decomposes and it loses almost half of its initial weight after 50 h of ageing. We stopped the ageing measurements at this temperature after 50 h because of very important degradation of samples.

Differential Scanning Calorimetry (DSC)

Figure 3 correspond to the first and second scan DSC thermograms of an as-received PTFE sample. During heating at a rate of $10^\circ\text{C min}^{-1}$, two peaks at 19 and 30 °C can be observed, which correspond to the crystalline phase transitions.

PTFE exhibits four different allotropic forms of crystalline structures depending on the temperature and the pressure⁸: below 19 °C under atmospheric pressure, the PTFE has a crystalline structure with a triclinic elementary cell (phase II); between 19 and 30 °C, phase II transforms into phase IV, its elementary cell belongs to the hexagonal crystallographic system; above 30 °C, phase IV transforms into phase I, the elementary cell becomes pseudohexagonal which is described as a randomly packed hexagonal structure.⁹

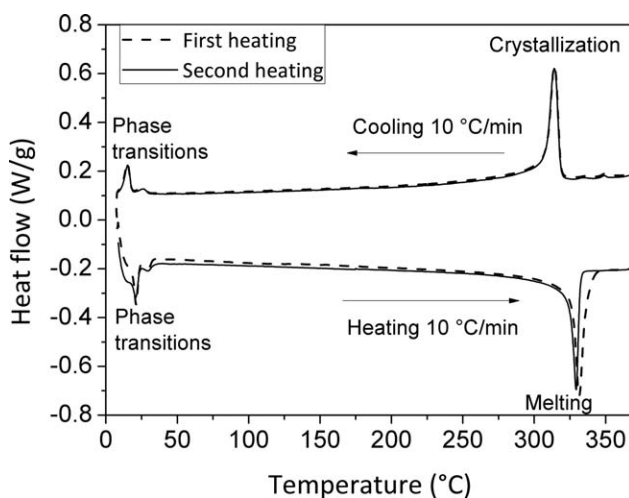


Figure 3. DSC curves of as-received PTFE (first and second heating).

In theory the glass transition occurs at about 120 °C,¹⁰ however it is not observed for DSC measurements. This is probably due to the high degree of crystallinity of the samples. The as-received PTFE crystallizes in the form of extended chains with high degree of crystallinity (92–98%) because of an increase of chain mobility and less chain entanglement during the polymerization. The melting temperature of as-received PTFE occurs at $\sim 342^\circ\text{C}$. This temperature is much higher than that of melted PTFE which occurs at about 327 °C because of formation of folded chains and lamellas with a lower degree of crystallinity.¹¹ Our samples have an intense endothermic peak at 332 °C during heating at first scan which correspond to the melting of never-melted PTFE. This melting curve is much larger, more intense and occurs at higher temperature than that of second scan (328 °C). During cooling from molten state, PTFE crystallizes at 315 °C (first and second scans) and other crystalline phase transitions take place at 25 and 13 °C (phase I transforms into phase IV and then phase IV transforms into phase II).

The effect of temperature and ageing time on the morphological evolution of samples has been studied, focusing on the melting and crystallization phenomena. The evolution of DSC melting peak after 2 h of thermal ageing for 340, 400, and 450 °C is shown in Figure 4. The melting peak of aged samples moves to higher temperature while increasing the ageing temperature. This can be attributed to the enhanced crystal perfection or formation of thicker lamellae. The melting peaks area (fusion enthalpy), which is proportional to the degree of crystallinity, increases with the ageing temperature treatment. This can be explained by the formation of smaller molecules resulting from the end-chain scissions of macromolecules during the ageing then the chain rearrangement after slow cooling from the melting point. These scissions may enhance the chain mobility and/or increase crystallization in the amorphous regions. At ageing temperature of 450 °C, the melting peak is much larger than that of as-received sample. It may be due to the larger molecular weight distribution resulting from the end-chain scissions of backbone at high temperature. Many smaller molecules of different sizes increase the molecular size dispersion.

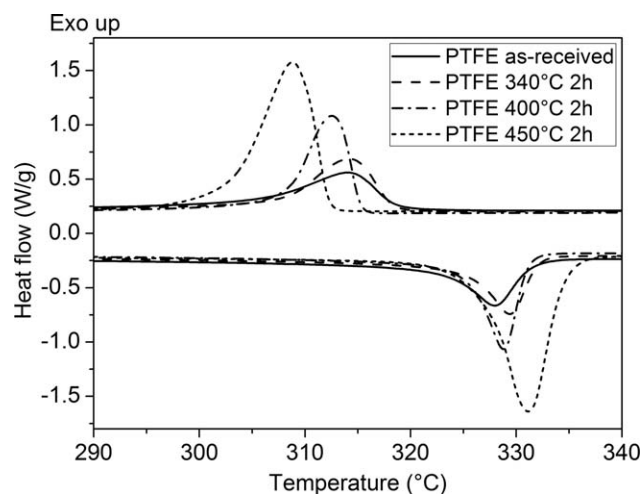


Figure 4. Melting and crystallization curves of PTFE after 2 h of ageing at various temperatures.

The effect of ageing time is studied by maintaining the ageing temperature constant. For an ageing temperature of 340°C (Figure 5), the width of melting curves is similar and the melting peaks move very slightly toward higher temperatures from 2 h of ageing [Figure 6(a)]. The peak area and hence the degree of crystallinity increases progressively for ageing durations from 2 h until 300 h. This can be explained by the end-chains scission at the beginning of the thermal ageing. Molecular weight decreases very slowly at first and only the end-chains are concerned, there is not a significantly influence in the melting temperature and in the shape of the melting curves.

A more noticeable evolution is shown at 400°C (Figure 7). At the beginning the degree of crystallinity increases progressively until 100 h of ageing, then PTFE becomes less crystallized for 200 and 300 h. The decrease of crystallinity may be a symptom of the advanced degradation stage of crystalline regions. The melting temperature evolution is similar to that at 340°C, the

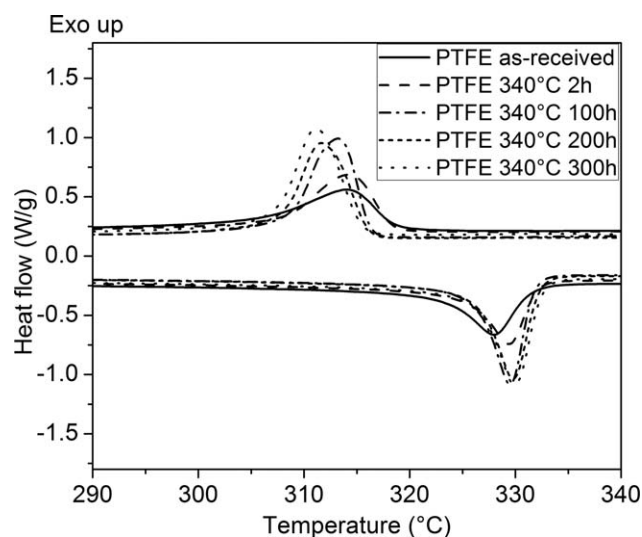


Figure 5. Melting and crystallization curves of PTFE aged at 340°C for various ageing times.

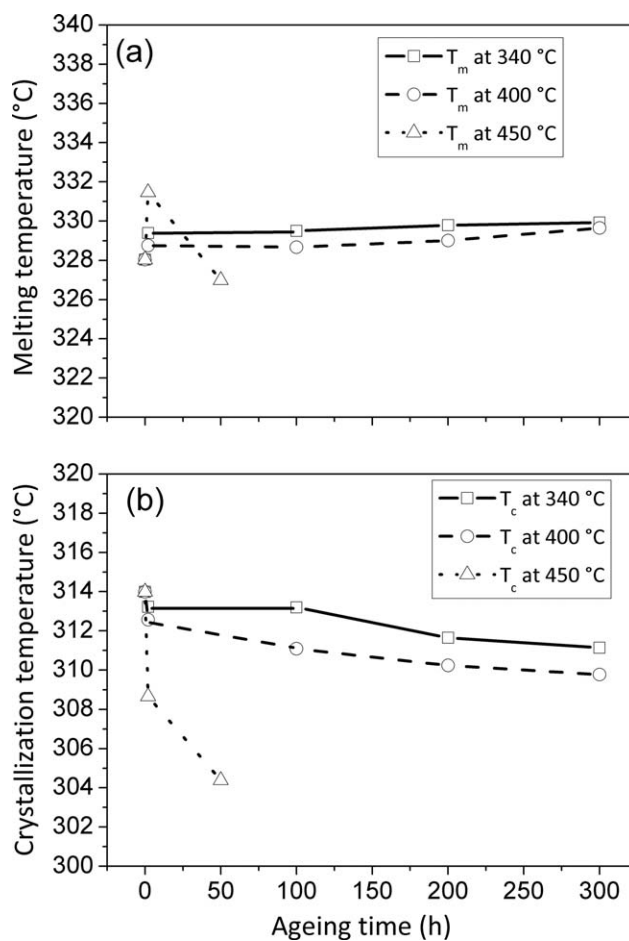


Figure 6. (a) Melting temperature of PTFE versus ageing time; (b) Crystallization temperature of PTFE versus ageing time.

melting peaks move very slightly toward higher temperatures from 2 h of ageing [Figure 6(a)].

At 450°C (Figure 8), this evolution becomes more significant with a faster degradation rate. A large and intense melting peak

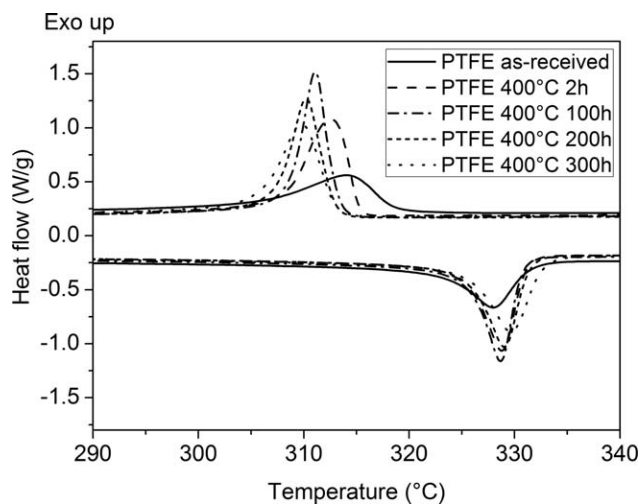


Figure 7. Melting and crystallization curves of PTFE aged at 400°C for various ageing times.

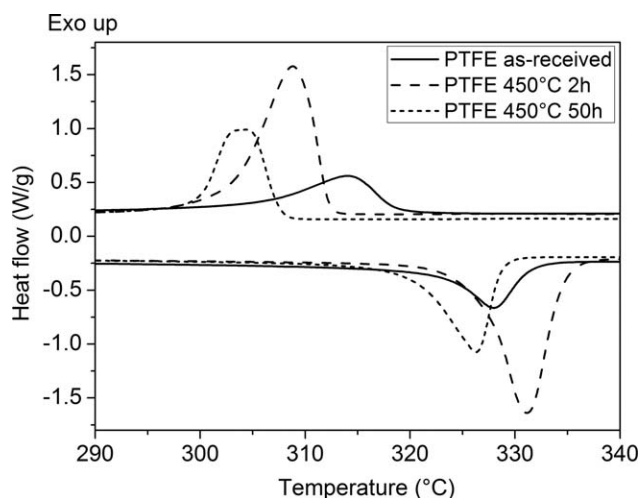


Figure 8. Melting and crystallization curves of PTFE aged at 450°C for various ageing times.

at higher temperature [Figure 6(a)] than for the as-received is observed after 2 h of ageing. For the sample aged during a longer time (50 h), an important decrease of melting point and crystallinity is observed. This may be due to the fast decrease of molecular weight.

The crystallization exothermic peaks of aged samples presented in Figures 4, 5, 7, and 8 show that the thermal ageing affects the crystallization kinetics in the same way: aged PTFE crystallizes at lower temperature than that of as-received [Figure 6(b)]. And crystallization peaks moves towards lower temperatures in terms of ageing time and temperature.

The degree of sample crystallinity was evaluated following eq. (1):

$$X(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \quad (1)$$

where ΔH_m is the enthalpy of fusion measured by DSC and ΔH_m^0 is the enthalpy of fusion of 100% crystallized PTFE (82 J g^{-1}).¹²

According to the Figure 9 which indicates the crystallinity evolution of samples as a function of the cumulated ageing time, we can distinguish three ageing stages according to the temperature: the ageing at 340°C is an earlier stage, the degree of crystallinity increases slowly and monotonically, and then it reaches the maxima after 300 h of ageing. The crystallinity evolution at 400°C is nonmonotonic; it increases rapidly until 100 h of ageing. Then it decreases slightly, this can be an intermediate stage; finally, ageing at 450°C is an advanced stage, the degree of crystallinity increases very rapidly at 2 h of ageing then followed by a sharp decrease after 50 h.

CONCLUSION

The experimental results show no noticeable weight loss for ageing at 340°C till 300 h of ageing. A weight loss was observed from 200 h of ageing at 400°C. These phenomena can be accel-

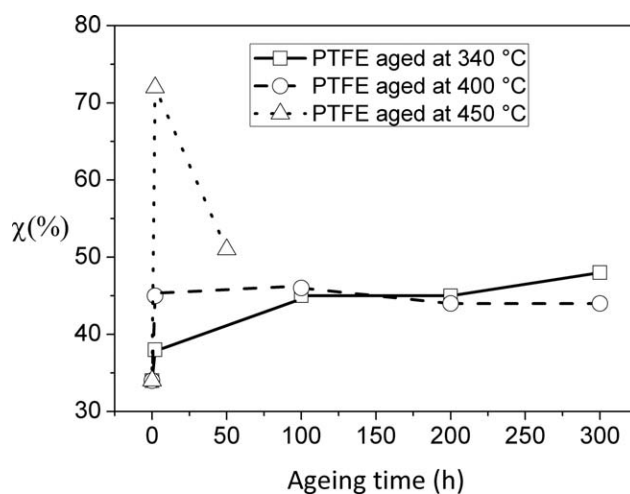


Figure 9. Crystallinity of PTFE versus ageing time at different temperatures.

erated by temperature elevation: at 450°C, a noticeable weight loss was observed.

The environment can affect the thermal degradation of the PTFE. The decomposition rate is faster in air than that in nitrogen because of the presence of oxygen in the atmosphere.

From DSC measurements, irreversible changes of morphology were observed for the samples aged at 340, 400, and 450°C for different durations. The results have shown that the thermal ageing affected the crystallinity, the melting and crystallization temperature of samples, which can be explained as a consequence of the chain rearrangement and the main chain scissions during the thermal ageing. The ageing process is a temperature and time dependent phenomena. For a short ageing duration (2 h), increasing ageing temperature induced higher melting temperature and the degree of crystallinity. For a longer duration and ageing at high temperatures (200 h at 400°C and 50 h at 450°C), samples became less crystallized and a strong decrease of melting temperature was observed for ageing at 450°C for 50 h.

Our further work will be focused in the effect of thermal-oxidative ageing and in the synergies with the mechanisms of thermo-electrical ageing of classical PTFE samples and PTFE cable insulators.

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REFERENCES

- Martinez-Vega, J. *Dielectric Materials for Electrical Engineering*; Wiley: Great Britain and United States, **2010**.
- Kutz, M. *Applied Plastics Engineering Handbook*; Elsevier, Myer Kutz Associates. Inc.: Delmar, NY, **2011**; p 55.
- Simon, C. M.; Kaminsky, W. *Polym. Degrad. Stab.* **1998**, *62*, 1.

4. Conesa, J. A.; Font, R. *Polym. Eng. Sci.* **2001**, *41*, 2137.
5. Li, L.; Bowler, N.; Kessler, M. R. *IEEE Trans Dielectrics Electrical Insul* **2010**, *17*, 1237.
6. Sperati, C. A.; Starkweather, H. W. *Fortschr* **1961**, *2*, 487.
7. Lewis, E. E.; Naylor, M. A. *J. Am. Chem. Soc.* **1947**, *69*, 1968.
8. Clark, E. S. *Polymer*. **1999**, *40*, 4659.
9. Fu, T.; Mo, Z.; Han, P.; Qi, Y.; Wu, S.; Chen, D. *Chin. J. Polym. Sci.* **1986**, *2*, 170.
10. Sussi, M. A.; Govinda Raju, G. R. Conference on Electrical Insulation and Dielectric Phenomena, **1990**, Annual Report pp. 196–201, 28–31 October 1990, Pocono Manor, PA.
11. Khanna, Y. P. *J. Mater. Sci. Lett.* **1988**, *7*, 817.
12. Lau, S. F.; Suzuki, H.; Wunderlich, B. *J. Polym. Sci. Polym. Phys. Ed.* **1984**, *22*, 379.