

Energy Losses in Ultrafiltration Hollow Fibers: Effect of Shape

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Received 26 June 1999; accepted 15 December 1999

ABSTRACT: Mechanical and dielectric relaxation of ultrafiltration hollow fibers were studied by thermally stimulated creep and current, and differential scanning calorimetry. The high sensitivity of thermally stimulated techniques shows 8 relaxations and/or transitions between -150 and 350°C (degradation). Not all are related to the intrinsic nature of the material—indeed, 4 of them can be directly related to the shape of the membrane (porosity, diameters, spinning conditions, etc.). Molecular mechanisms of these phenomena are discussed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 8–13, 2000

Key words: thermally stimulated current; thermally stimulated creep; hollow fibers; relaxations; transitions

INTRODUCTION

The filtration of water can be made by many types of membranes with various geometries. The hollow fiber geometry is usually chosen to increase the surface of filtration of the membranes. In our particular study, the edges of the fiber (inside and outside skins) are the separative layers of the membrane and they are mechanically supported by a porous volume (core). These hollow fibers are constituted of cellulose acetate, an hydrophilic material. Water always plays a crucial role in the performances of the membrane—in particular, in water filtration. It is well known that filtration properties are related to the interactions of the polymer with water.¹ For example, the size of the smaller particle stopped by the membrane is smaller than the physical diameter of the filtration pores because of the layers of bound water inside the pores.

The aim of this study is to list the relaxations and transitions that occur in the hollow fiber from

the frozen state (150°C) to the degradation (350°C). This preliminary study will be used for further studies to underline the structural changes induced by the spinning conditions and to study the effect of aging during the filtration processes.

EXPERIMENTAL

Techniques

The principle of the thermally stimulated techniques is described as follows:

A static shear stress in thermally stimulated creep (TSCr) or an constant electrical field in thermally stimulated current (TSC) is applied to a solid state sample at a given temperature. Then, the corresponding strain/polarization reaches an equilibrium value. This configuration is frozen by decreasing the temperature to T_0 , where the stress/field is cut off. Because of low molecular mobility, a large part of the strain/polarization remains frozen even if the stimulus disappears.

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Journal of Applied Polymer Science, Vol. 78, 8–13 (2000)
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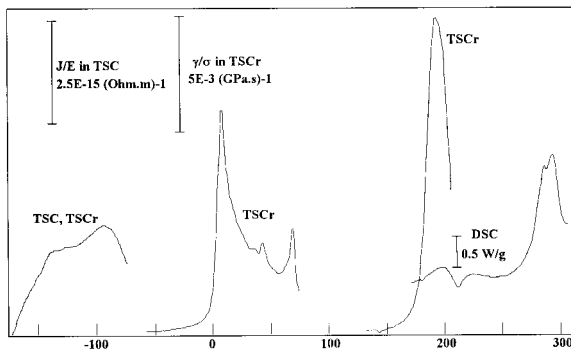


Figure 1 Relaxation and transitions of the standard fiber observed with the different methods.

The return to the initial state of the sample is induced by a controlled increase in temperature. The temperature T , the current I in TSC, the strain rate $\gamma' = d\gamma/dt$ in TSCr are simultaneously recorded vs time.

The peaks of the curves $\gamma'(T)/I(T)$ indicate mechanical or electrical energy losses due to molecular movements in the sample. Any modification of those movements, such as interaction with water, aging, or orientation, will induce a modification of TSCr/TSC spectra.

The TSC and TSCr spectra have been obtained using apparatus developed in the laboratory.^{2,3}

The differential scanning calorimetry (DSC) curves have been obtained using a Perkin Elmer DSC 7.

Materials

The ultrafiltration asymmetric hollow fibers have been provided by "Laboratoire membranes: Lyonnaise des Eaux—Dumez." They are constituted of cellulose acetate. The solidification of the fiber is obtained by coagulation after spinning.¹ Ultrafiltration properties and morphology are correlated to spinning and coagulation parameters.¹ These fibers are used to filter raw water and provide drinkable water. Filtration fibers with a 0.93 mm inner diameter fibers have been analyzed.

RESULTS AND DISCUSSION

Characterization of the Fiber

In TSCr and TSC, the retardation/relaxation mode were investigated between -150 – 200°C . Above 200°C , which is the glass transition determined by DSC, the porosity decreases, the sample

turns black on surface and begins to degrade. Therefore, to explore the part above 200°C , only DSC was used.

Figure 1 shows the total retardation modes and transitions of the fiber. The three techniques are involved to study the membrane.

These relaxations can be classified in three groups according to the size of the entities involved in the relaxation: from localized movements below 0°C , to delocalized motions above 200°C . The middle range will be the motion of molecules under the influence of water and the shape of the membrane.

Low Temperature Modes from -150 – 0°C (TSC, TSCr)

As shown in Figure 2, TSC spectra of the cellulose acetate are complex. The peaks are observed at -35 and -100 and $+20^\circ\text{C}$. These results are in agreement with literature concerning cellulose or cellulose derivatives.^{4–8} Relaxations in this temperature area, measured by dynamic mechanical or dielectric methods, are generally attributed to the movements of substituted groups and hydroxyl groups. The low equivalent frequency of the TSC spectrometry (10^{-3} to 10^{-4} Hz) is useful to separate each individual relaxation.

Peak at -135°C (Peak γ)

The first peak observed at -135°C is more intense in the first run than in the second run. Different authors have found a peak at -130°C on dehydrated cellulose. By analogy to their work,^{4,7} we also call this peak γ . It can be associated with the hydroxyl groups of the constitutive unit of cellulose. Since the OH groups of the crystalline phase are implicated in the hydrogen

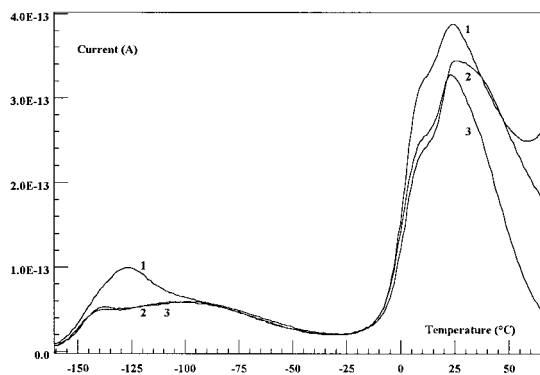


Figure 2 TSC. Spectra of cellulose acetate: effect of hydration. Numbers are the numbers of runs.

bounds, the OH groups mobile and accessible by the TSC technique are those present in the amorphous phase. Bertran and Dale⁹ have observed that water molecules are fixed on the OH groups of amorphous phase of cellulose. The evolution toward lower temperature of the peak at -135°C , upon hydration of the sample, has been already shown by Pissis⁴ when the amount of water is under 7% in weight. The water acts as a plasticizer of the polymer. In our study, the main difference between the first run and the second run is the water content (the first scan ends at 80°C in dry atmosphere). This relaxation mode can be associated with the hydroxyl groups motions under the influence of water.

Peak at -100°C (Peak β)

Unlike the peak at -135°C , this peak is not influenced by hydration. This peak appears sometimes on cellulose, it is usually called β . To keep the same nomenclature, we also call the peak β . Origin of the relaxation can be movements of bound water,^{5,7} or movements between two glucosic rings in the amorphous phase of cellulose.¹⁰ In cellulose derivatives, the nature of the substituted groups plays an important role on the properties of the material. Kim et al.⁵ observed, in cellulose derivatives, that the position and magnitude of this event is related to the nature of the substituted groups. Since our peak β is not influenced by hydration, it can be associated with the return to equilibrium of nonhydrophilic groups. In this study, the substituted groups are acetate groups; it is known that they are hydrophobic, so it is reasonable to think that the relaxation at -100°C is due to the motion of the acetate groups. Since acetate groups are more voluminous than OH groups, their relaxation have a higher activation energy; it is then expected that the relaxation peak of acetate groups appears higher in temperature than the peak of OH groups (-135°C).

At higher temperatures (0 – 25°C), the peaks can be related to the motion of free or bound water dipoles. The dielectric relaxation of water molecules will not be analyzed in this study.

Room Temperature Retardation Modes (TSCr)

In order to precise the origin of room temperature retardation modes, a particular procedure was used. A shear stress of 0.5 MPa was applied to the fiber at 27°C . The TSCr spectrum corresponding to the fiber is shown in Figure 3(a): three peaks

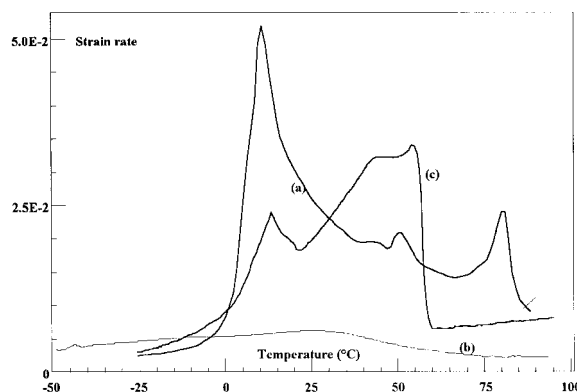


Figure 3 Effect of hydration on the retardation modes of the fiber (a) Standard test. (b) Same as (a) but annealed 2 min at 47°C . (c) DTA curve of the fiber pinched at its extremities.

are observed at 11, 53, and 70°C . After an annealing of 2 min at 47°C , a fresh sample displays only a broad peak at 25°C [Fig. 3(b)]. An identical spectrum may be obtained after dehydration for 20 min under secondary vacuum at room temperature.

The first conclusion is that the differences observed between the two spectra are due to water evaporation. DSC study and the previous works of Kim et al.⁵ have also permitted to associate an endothermic peak at 40°C with the evaporation of water. The second conclusion is that water leaves the fiber structure relatively quickly. The cryostat of the TSCr apparatus has walls at liquid nitrogen temperature; thus, any water molecules evaporated at the surface of the fiber condense on the walls. The sample chamber can be considered as a drying chamber.

If 2 min at 47°C are sufficient to dry the fiber, then the heating ramp at $7^{\circ}\text{C}/\text{min}$ will necessary dry the fiber during the test. As a result, curve (a) in Figure 3 is indeed the relaxation of the fiber when water leaves the fiber structure.

Peak at 11°C

This peak can be attributed to the melting of ice. Below 0°C , water is in solid state and blocks long-range motions of fiber. When water becomes liquid, the mobile polymeric sequences can release accumulated stress and give a mechanical retardation peak that starts at about 0°C . Relaxations at lower temperatures are blocked by the ice in the membrane and the peak at 11°C is a set of all these low temperature relaxations. To study them, the sample should be dehydrated first as

displayed in the low temperature part of Figure 1. Then, all the discussion on low temperature modes can also be verified with the TSCr experiment.

Peaks at 53 and 70°C

Water is a plasticizer of the membrane. The fiber is flexible and soft in presence of water, but when it dries the fiber becomes brittle and hard. A plasticizer is usually defined as a small molecule that interacts with some chemical groups present within the macromolecules. These groups, trapped by the plasticizer molecules, are not able anymore to develop interactions with the other macromolecules. The global cohesion can be affected because the mobility of the macromolecules is increased. During evaporation, water creates "voids" that momentary allow movements of polymeric chains. This increase of mobility allows the relaxation of a part of the stress applied at the beginning of the experiment as proven by the mechanical retardation modes in the TSCr spectrum. DMA curves in torsion on the same fibers, confirm this increase of mobility. A peak of $\tan \delta$ appears during the drying of the membrane.¹¹

The existence of the two peaks can be explained by a selective loss of water. Indeed, the evaporation of water is more difficult in the skin than in the porous zone. Thermal gravimetric analysis (TGA) results done by Staude and Passlack¹² on plane membranes during isothermal tests have shown two evaporation kinetics, one for the dense zone (skin), and one for the porous zone (core).

In the TSCr experiment, the fiber is clamped, so the water in the porous zone needs to pass through the skin to be evaporated. In order to replicate these conditions, a custom Differential Thermal Analysis (DTA) measurement was performed inside the TSCr cell.¹³ Two thermocouples were installed in the vicinity of the sample. One of the thermocouple is embedded inside a piece of fiber pinched at its edges, the other thermocouple is used as a reference in He. The superposition of the DTA curve over the TSCr curve is shown in Figure 3 (Curve c). One can see the peak of the melting of ice at around 10°C followed by the evaporation of the water. The two rates of evaporation are clearly visible. The position of the two evaporation modes do not coincide with the peaks at 53 and 70°C. The peak position depend on the sample mass, and the difference in position can be explain by the sample size difference between the

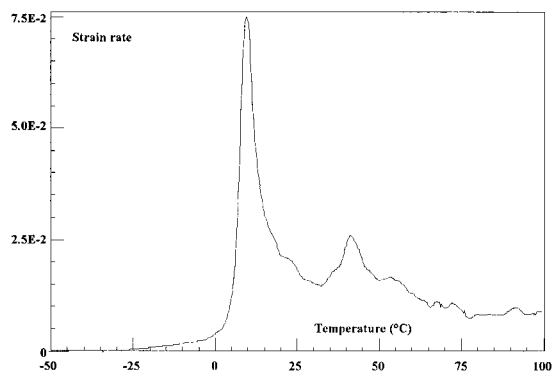


Figure 4 TSCr spectrum of a fiber without external skin.

DTA and TSCr experiments. The important result is the detection of the two rates of evaporation.

TGA results on the same fibers pinched at the extremities confirm the two evaporation rates.¹³ Thus, the following hypothesis is proposed: the peak at 53°C has been associated with a relaxation occurring during the evaporation of water in the porous zone and the peak at 70°C is associated with a relaxation occurring during the evaporation of water in the dense skin.

To prove this hypothesis, a special sample preparation was performed. The fiber was rotated along its axle, and the external skin was carefully removed from the fiber using a razor blade. Figure 4 represents the relaxation of the fiber without its external skin. The peak at 70°C disappears and the peak at 53°C is now centered around 43°C because the barrier effect of the skin has disappear so the porous zone can be quickly dried.

The three peaks in the room temperature range are related to the shape of the fibers. These modes are not intrinsic relaxation modes from the polymer and are due to interactions with water, water, porosity, and macroscopic shape of the membrane. This behavior seems to be "universal" because polysulfone hollow fibers shows also 3 peaks at 15, 60, and 80°C as seen in Figure 5. The position of the high temperature events are likely related to the interactions of the polymer with water.

High Temperature Transitions

In this area of temperature, macromolecules motions are large. In cellulose acetate, the glass transition occurs between 160 and 200°C, depending on the degree of acetylation and the molecular

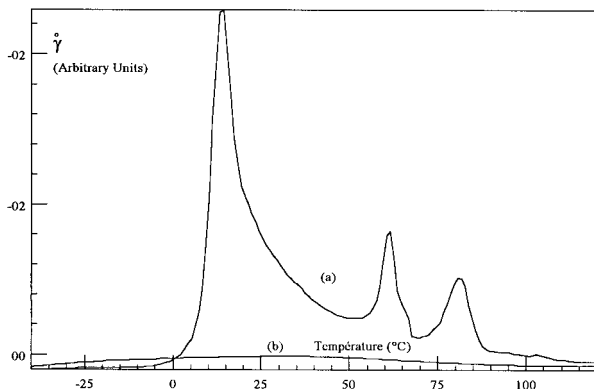


Figure 5 Effect of hydration on the retardation modes of a polysulfone fiber (a) wet fiber and (b) dried fiber.

mass. At higher temperatures, cellulose acetate crystals melts at 300°C. The melting is superimposed to the degradation, which starts above the glass transition.

Above the glass transition, the fiber can release the internal stresses accumulated during the spinning process. Then, the fiber shrinks¹⁴ and an irreversible compression of the porous zone occurs. Due to these sample size changes, DSC is the most suitable technique to study this temperature zone.

First, the standard polymer (in powder) has been analyzed from room temperature to 350°C at 20°C/min and compared with the spun polymer in the same operating conditions.

The comparison of the two samples is reported in Figure 6. The thermogram of the standard polymer shows the existence of three main events:

- a broad peak between 50 and 120°C. This endothermic transition disappears after an annealing at 120°C. It is associated with the water evaporation.
- a weak step near 200°C, characteristic of the glass transition of the polymer.
- several endothermic peaks near 300°C. These are associated with the melting of the crystalline zones before complete degradation.

Comparatively with the standard polymer, the spun fiber presents some differences. First, the glass transition appears at lower temperatures (190°C). Second, it presents a exothermic peak at 210°C characteristic of crystallization. During the spinning process, the polymeric chains are oriented. When their mobility are sufficient (at the

glass transition), the polymeric chains can move to a new equilibrium state (increase of local order). The same type of behavior has been already observed in polyethylene terephthalate¹⁵ and polyamids¹⁶ when the sample has been quenched from the equilibrium state to the non equilibrium state.

The melting appears between 280 and 290°C for the fibers. As the area of this peak is larger than that of the crystallization peak, we can conclude that, before the DSC experiment, there were some crystalline zones in the fiber. The melting peak is sharp and appears at lower temperature in fiber than in polymer. Crystallization probably modified the size and the purity of crystallites.

CONCLUSION

Thermal analysis techniques (TSC, DSC, TSCr) have been used to investigate the behavior of ultrafiltration hollow fibers in an extended range of temperature (−150–350°C). Four of the intrinsic relaxations or transitions of cellulose acetate have been retrieved. The originality of the study is the existence of four additional relaxations or transitions directly and only related to the shape of the fiber. By moving in the porous structure of the fiber, water acts as a tracer to characterize the morphology of the hollow fiber.

The three relaxations modes between 0 and 70°C are associated with the motion of water in the porous structure of the membrane. This behavior seems to be “universal” to the hollow fiber geometry and is related to the structural property of the membrane.

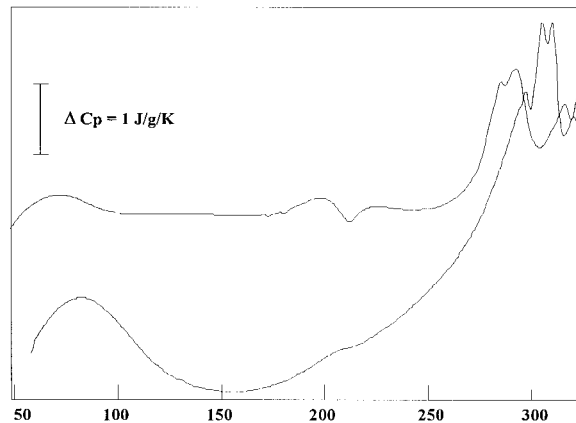


Figure 6 Standard polymer and fiber thermograms.

This work will be used to underline the effect of the spinning conditions and the damages created by the aging in normal filtration conditions.

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