Journal of Thermal Analysis, Vol. 49 (1997) 107-114

CHARACTERIZATION OF POLYMERS USING THE THERMALLY STIMULATED CURRENT TECHNIQUE

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Abstract

Thermally Stimulated Current (TSC) technique is a relaxation technique, such as DMA, but works at very low equivalent frequency (10^{-3}–10^{-4} Hz) and thus clearly resolves the peaks related to the molecular mobility. The effect of orientation on Polypropylene fibers, the relaxation of internal stresses on Polycarbonate disks, and the effect of aging on acrylic airplane windows have been investigated using the TSC method.

Keywords: aging, internal stresses, orientation, TSC

Introduction

Usually when a plastic part is manufactured, it passes from the molten state to the solid state during the shaping process. Processing and cycle time is very important for the manufacturers; rapid cooling to shorten cycle time is not unusual. The orientation of the macromolecules in the rubbery state (equilibrium), are trapped in by the quenching to the glassy state (non equilibrium). Aging time or an elevation of the temperature can provoke the return to equilibrium of these macromolecules. The relaxation of these internal stresses with time changes the dimensions of the plastic and sometimes causes the plastic piece to fail its end use.

Stretching semicrystalline polymers at a temperature between the melting and the glass transition temperature area induces structural changes in the amorphous phase. The amorphous phase is being oriented and the resulting thermomechanical behavior of the polymer will change from the non-oriented state.

Aircraft cabin windows are naturally under stresses due to residual stresses from molding, and other added stresses from temperature and pressure gradients. It is exposed to potential aggressive conditions (chemical, thermal, mechanical, UV exposure) during its utilization. Aging, under the conditions noted above, may be seen as crazing on the exterior side of the window (whitening or spider web like appearance).

The Thermally Stimulated Current Technique was applied to study the molecular mobility in those materials.

0368–4466/97/ $ 5.00

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Experimental

Method

Thermally Stimulated Current (TSC) was first introduced by Bucci and Flieshi [1], and was applied in various fields as recently reviewed by Lavergne and Lacabanne [2].

In this method, an electrical field is applied at a temperature (T_p) during a time t_p longer than the relaxation time τ (T_p) of the dipoles. By cooling the material to the temperature $T_o << T_p$, the polarization of the dipoles is frozen because the relaxation time τ (T_o) of the dipoles is larger than τ (T_p). The polarization remains in the sample even when the electrical field is cut off.

By heating the dielectric, the relaxation time τ (T) of each relaxing entity decreases, when it reaches the experiment time (around one second) the entity relaxes and induces a current of depolarization if the dielectric is connected to an electrometer. The current I(t) as a function of temperature is the TSC spectrum of the sample. This method allows, in a single measurement, the collection of data relative to the global spectrum characteristic of the material. The high resolution (10^{-3}–10^{-4} Hz) allows separation of the different components of the polarization better than the other methods such as AC (dielectric loss) or D.C. (isothermal discharge) for measuring molecular mobility. The apparatus used was a TSC/RMA spectrometer TSC 9000 (TherMold, Stamford, CT, USA).

Materials

The study of the internal stresses was made on research polycarbonate compact disks. Three different locations were chosen (Inside, Center, Outside) to visualize the internal stresses.

The crimped fibers are constituted of polypropylene. The fibers were tested both as received and after being subjected to a strain under a constant load during several days. They were analyzed "Unstretched" and "Stretched".

The aircraft cabin windows were acrylic crosslinked-oriented polymers. The crosslinking is applied only on the surfaces of the windows. The samples have been presented on two different states, aged and not aged.

The origin of these samples was confidential.

Results and discussion

Internal stresses

When the macromolecules relax the internal stresses, there is a motion of the chains and necessarily a motion of the dipoles along these chains. If the sample is connected to an electrometer, this motion of dipoles creates a displacement current. This current is generated below the glass transition temperature, because the orientation in molding process is frozen by rapidly cooling the sample to temperatures below the glass transition.

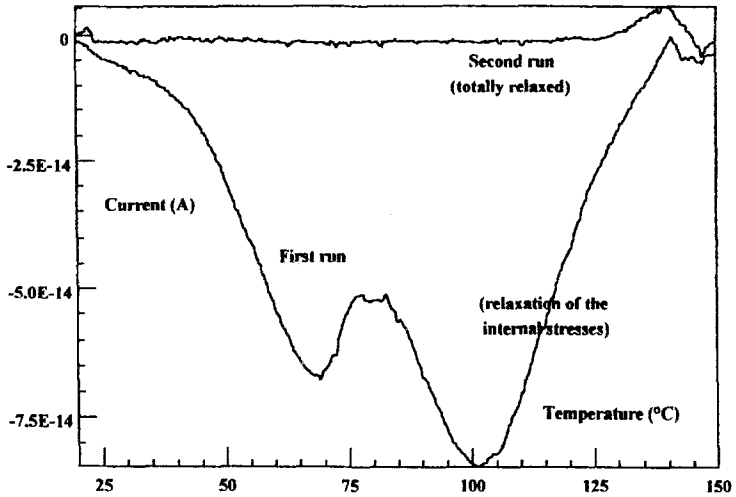

Fig. 1 Relaxation of internal stresses (two consecutive runs on the same sample)

Monitoring the internal stresses with the TSC apparatus, one places the sample between the electrodes and records the current during a heating ramp from room temperature to T_g.

A polycarbonate compact disk sample was cut in 30 mm^2 small squares and placed between the electrodes (stainless steel electrode, 7 mm diameter) of the TSC apparatus. The current spontaneously generated by the sample is recorded *vs.* temperature during a heating ramp of 7 °C min^{-1} from 20 to 150 °C. Figure 1 shows two consecutive runs on the same piece of sample. During the first run, one observes the relaxation of the internal stresses as the temperature increases. The sign of the

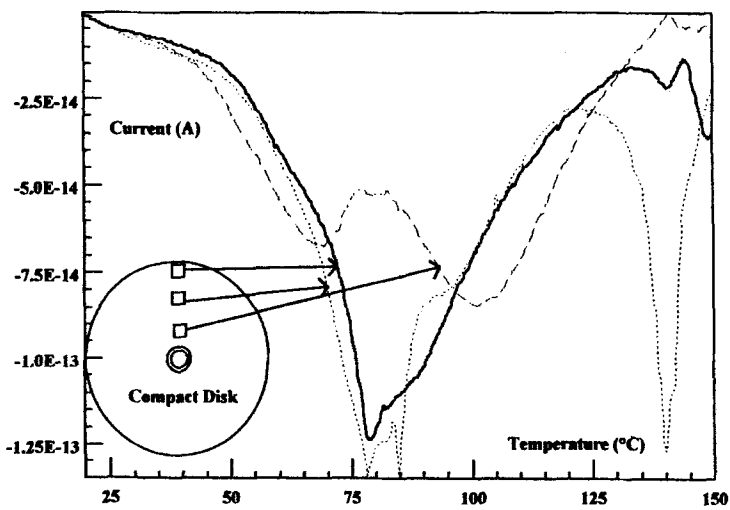

Fig. 2 Internal stresses across the radius for a given molding process

current depends on the orientation of the sample. Tests have shown that placing the sample upside down gives a positive curve. The second run is a flat curve showing the sample with the internal stresses already relaxed.

The peaks, appearing at around 70 and 100°C, were also observed as a relaxation by Yianakopoulos *et al.* [3] in cold drawn polycarbonate. For high drawing ratio, the peak can be split into two components. This peak can be due to the relaxation of residual stresses, or an increase of free volume induced by the drawing process [3]. The samples are not oriented in the glassy state, actually the orientation is frozen in the solid as for a plastic deformation induced by drawing the sample.

Figure 2 shows the level of internal stresses across the radius of a compact disk. The outside and the center of the disk have the same level of internal stresses. There is a gradient of internal stresses on the inside of the disk. The amount of internal stresses is almost the same (area under the curve before the glass transition) for each location. The cooling pattern of the mold is different on the inside in comparison of the rest of the disk.

Polypropylene fibers

To study the structural changes in the amorphous phase induced by the stretching, the TSC was applied in temperatures below 100°C. Unstretched and stretched fibers were layed between the electrodes (stainless steel electrode, 7 mm diameter) in a perpendicular direction of the axis of the fibers. Samples were heated to 70°C where a DC voltage of 1000V/mm was applied for 5 min. The samples were then cooled to –150°C and short circuited for 5 min. Once frozen for 5 min the samples were heated on a ramp of 7°C min^{-1} from –150 to 100°C. The resultant spectra are presented as Figs 3 and 4.

Figure 3 shows the response of the unstretched fibers. There are three distinct events visible in this figure: one at –47°C, one near –20°C and one near 0°C.

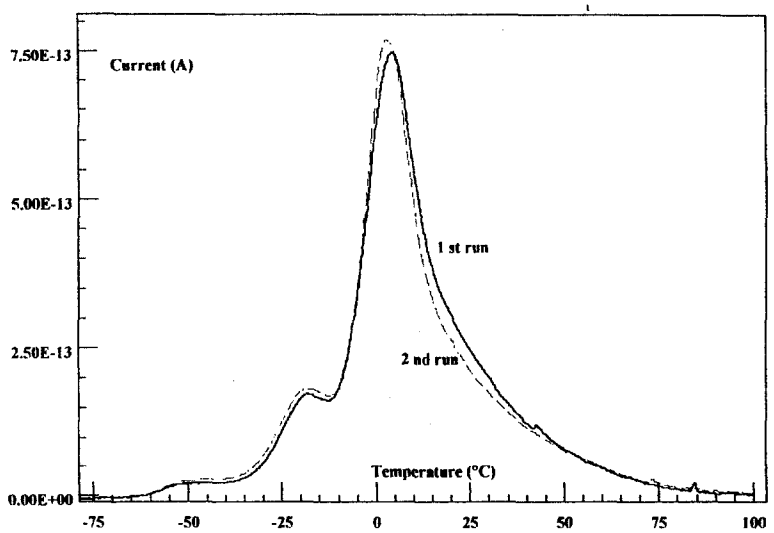

Fig. 3 TSC Spectra of the Unstretched polypropylene fiber

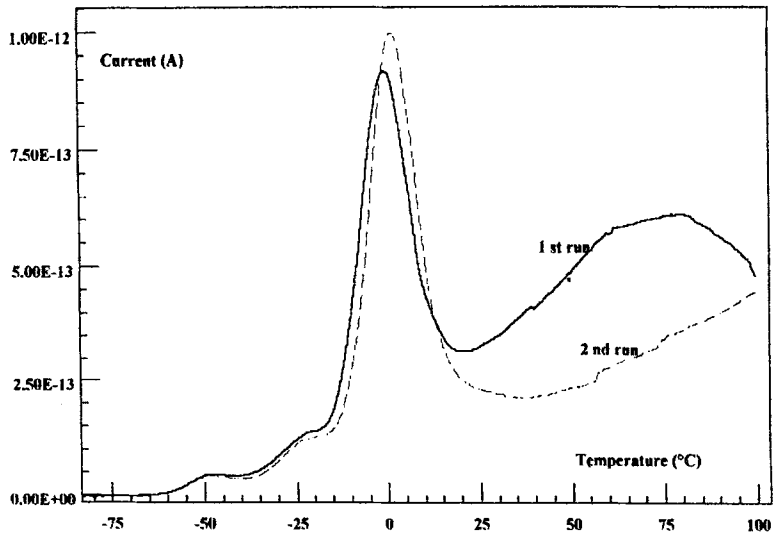

Fig. 4 TSC Spectra of the Stretched polypropylene fiber

It is well established that the β relaxation in polypropylene corresponds to the motions liberated at the glass transition which is seen at about –10°C [4, 5]. This peak at about 0°C is therefore the dielectric manifestation of the glass transition of this sample.

The peaks seen at –47°C and –20°C are most likely due to the relaxation of lateral groups or other related localized molecular motion. The spectra shown on this figure are of two consecutive runs with a sample which was not removed between tests. The unstretched sample is relatively stable below 100°C. The ramp to 100°C does not change the mobility behavior of electrets in the sample.

Figure 4 illustrates a very different behavior. There are 2 more peaks or shoulders evident in these data. The peak at 80°C is related to the polarization of the sample. This peak is the low temperature contribution of an upper temperature relaxation/transition. This type of peak is called a polarization peak and is therefore not analyzed in this experiment.

The shoulder at 60°C is of interest in this study as this has been reported in literature specific to oriented isotactic polypropylene [5]. As reported for a semicrystalline polymer, when the amorphous phase is not at equilibrium, the glass transition relaxation event can be related to two (2) peaks, T_{gl} and T_{gu} (lower and upper T_g). T_g lower (T_{gl}) corresponds to the "true" amorphous state of the polymer. T_g upper (T_{gu}) corresponds to the "constrained" amorphous state. The macromolecules in the constrained amorphous state have developed a degree of order. The thermal energy required to activate the molecules in the constrained state is higher and the resultant T_g peak appears at a higher temperature. The non-equilibrium state is induced by either drawing the polymer [5] or by changing the crystallinity of the polymer [6].

The differences seen between the first and the second run are due to the fact that the sample is not in an equilibrium state. The decrease in the intensity of the second run is related to the recovery of creep that has been imparted on the sample. This recovery is induced by heating the sample during the test. Since the curve does not return to 0 it is noted that this recovery is only partial. After recovery is induced, the "constrained" amorphous phase becomes a "true" amorphous phase. This is the reason why the peak around 0°C increases from the first to the second run.

The relative intensities of the peaks at –50°C and at 0°C are almost the same for both samples. There is a difference seen in this data at temperatures of –20°C and above 25°C. If the peak at –20°C is due to the movement of lateral groups, perhaps these groups can be involved in interactions during the orientation process. In this view, once involved in interactions, these groups become inaccessible during polarization. The result of this is that the peak intensity for this event decreases.

Aging on airplane windows

A study of aging starts usually by the study of the non-aged material. Samples were taken from an acrylic window (stretched and crosslinked on the surface). Two 1 mm thick samples were cut from each side of the window and a 1 mm thick sample was taken from the middle of the window.

Figure 5 shows the relaxation spectra of the cabin window across the thickness of the window. The arrows visualize the polarization temperature. Three events can be seen on each curve; at –40°C, between 30 to 75°C, and around 125°C.

In TSC spectra of this acrylic polymer, which is analogous to PMMA, the first peak at –40°C is associated to the β relaxation [7, 8] of the polymer which is due to localized movements. At the higher temperature, the α relaxation corresponding to the glass transition which can be the peak at around 120°C.

The peak at 50°C is influenced by the amount of water in the polymer which platicizes the chains. In this figure, the samples were dried under vacuum before the test.

In Fig. 5, the effect of the crosslinking in the surface is obvious. The mobility is lower for the macromolecules on the surfaces because of the crosslinking, one

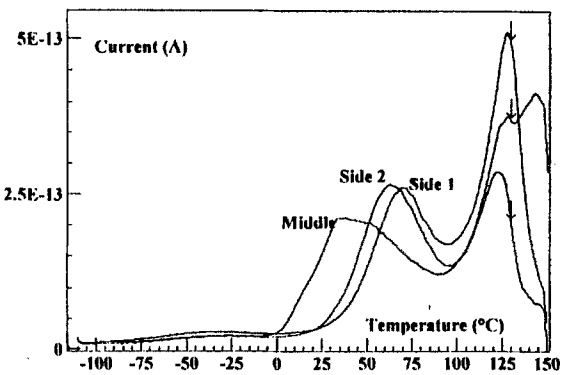

Fig. 5 TSC spectra of a crosslinked, stretched non-aged window. Comparison of the position of the sample across the thickness of the window

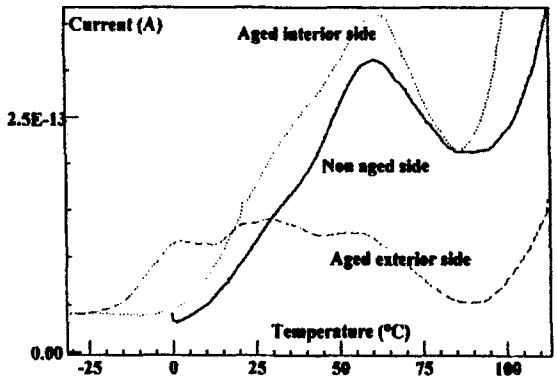

Fig. 6 Comparison of TSC spectra of an aged and non-aged window

needs more energy to activate the motions, therefore the peaks appear at a higher temperature. The effect on the glass transition peak (120°C) is less important, the α peak of the middle sample appears 5°C below the peak of the side samples.

In Fig. 6, the behavior of two sides of an aged crazed aircraft window are compared to a side of a non aged window. The peak at 30°C is more pronounced for the crazed window. There is also a peak at lower temperature. The peak is usually centered at 65°C and is also shifted to a lower temperature.

This behavior is typically an effect of some plasticizer. In terms of in use behavior, the molecular mobility (at room temperature) is high on the surface of the window. The window is submitted to stresses such as mounting, temperature gradient, pressure gradient, internal stresses...

The mode of deformation by crazing is common with acrylics. If the mobility of the polymer is suddenly increased by an external agent, a non-damageable stress in normal conditions can induce crazing. Bending a 5 mm piece of non-aged window between the fingers is not damageable for the plastic, but doing the same after spreading some acetone creates lines of crazing in a perpendicular direction to the stress. Crazing also appears in a random direction upon thermal shocks when there is a plasticizer on the surface.

The apparition of crazing is probably due to an increase of the molecular mobility on the exterior surface of the aircraft window. One of the possible causes could be a sulfuric acid attack of the surface. These windows are very sensitive to sulfuric acid. The airplane companies have problems after any big volcano eruption (Mont. Pinatubo and Mont. El chicon). It can also be a combination of several aggressions (UV and acid). The continuity of this work is to study the effect of individual treatments to mimic the natural aging.

Conclusion

The TSC technique was used to study real problems such as internal stresses, effects of plastic deformation, aging. The low equivalent frequency of the technique

(10^{-3}–10^{-4} Hz) gives an excellent resolution power in a short experimental time (30 min) in particular to study phenomena in the glassy state or related to the glass transition.

The level of internal stresses can be measured as a spontaneously generated current increase. This method can be applied on non-flat pieces by metal deposit and on opaque pieces where the birefringence cannot be applied. The glass transition in plastically oriented polypropylene fibers has been investigated. The TSC technique has shown an increase of the mobility on the surface of a crosslinked acrylate airplane window during aging. This mobility is one of the two ingredients (stress and mobility) that cause the crazing of the aircraft windows.

References

1 C. Bucci and R. Fieschi, Phys. Rev. Lett., 12 (1964) 16.
2 C. Lavergne and C. Lacabanne, IEEE Elec. Insu. Mag., 9 (1993) 5.
3 G. Yianakopoulos, J. Vanderschueren and J. Niezette, IEEE Trans. Elect. Insul. 24, 3 June 1989.
4 Ph. D. Thesis, Daniel Ronarc'h (1983) Toulouse, France.
5 M. Jarrigeon, B. Chabert, D. Chatain, C. Lacabanne and G. Nemoz, Molecular Sci.-Phys., B17 (1980) 1.
6 M. Mourges-Martin, A. Bernes and C. Lacabanne, J. Thermal Anal., 40 (1993) 697.
7 A. Gouramy, M. Bendaoud, C. Lacabanne and R. F. Boyer, J. Poly. Sci., Poly. Phys. Ed., 23 (1985) 889.
8 J. Vanderschueren, M. Ladang and J. M. Heushen, Macromolecules, 13 (1980) 977.