European Polymer Journal 36 (2000) 1571–1577

EUROPEAN POLYMER JOURNAL

Influence of time and temperature on deformed films of poly ether-ether-ketone (PEEK)

C. D'Aniello[a], G. Romano[a], R. Russo[a,*], V. Vittoria[b]

[a]*Istituto di Ricerca e Tecnologia delle Materie Plastiche del C.N.R., Via Toiano, 6, 80072 Arco Felice (NA), Italy*
[b]*Dipartimento di Ingegneria Chimica ed Alimentare, Universitá di Salerno, Via Ponte Don Melillo, 84084 Salerno, Italy*

Received 5 May 1999; accepted 7 June 1999

Abstract

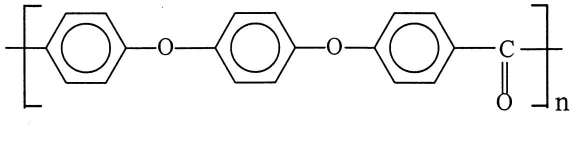
Amorphous films of poly ether-ether-ketone (PEEK) were drawn at 80 and 140°C up to 150% of the initial length, and analyzed immediately after the preparation, after 2 months at room temperature, and after 2 months at 120°C. X-rays, FTIR, differential scanning calorimetry were used to investigate the structural organization. Transport properties of dichloromethane vapor were used to determine the sorption in the different samples. It was found that the drawing at 80°C does not allow the crystallization, nevertheless producing an oriented sample in which a fraction of impermeable phase is present. This impermeable phase, already recognized in semicrystalline PEEK as "rigid amorphous phase", increases its fraction with the aging time. The drawing at 140°C produces a sample with a very high impermeable phase that does not increase further with the aging time. The dimensional stability of the samples with the temperature was also investigated. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: PEEK; DSC; Physical aging; Transport properties

1. Introduction

Glassy polymers, when stored at temperatures close but below their glass transition temperature (T_g), experience appreciable changes in their physical properties [1,2]. The changes of these properties, reported as "physical aging", are due to the fact that the system is not in the thermodynamic equilibrium, having an excess of free volume. The achievement of the equilibrium in the glassy state is hindered by kinetic phenomena. The free volume excess decreases with time, with a consequent decrease of chain mobility that produces a slowing down of the overall process, which is therefore defined as "self-retarding". The changes occurring in a material with aging can affect its application, performance, and lifetime: therefore a study of this effect is very important.

PEEK is a polymer which has attracted much interest as engineering polymer because of the good mechanical properties along with high temperature stability and resistance to chemical attack [3,4]. The repeat unit is:



Its T_g is at about 145°C and the melting temperature

---

* Corresponding author. Fax: +81-8663378.
E-mail address: russo@mail.irtemp.na.cnr.it (R. Russo).

PII: S0014-3057(99)00235-9

at 335°C. The crystalline form can be obtained by slowly cooling the melt (melt crystallization), or by crystallization at temperatures between T_g and the melting temperature (cold crystallization) [5–8]. Thermal analysis of crystalline PEEK have shown that poorly crystallized samples contain a fraction of amorphous phase of lower mobility, named the "rigid amorphous fraction" [6].

The transport properties, sorption and diffusion, are very useful in investigating the amorphous component of a polymer, even when a mesophase is present [9–13]. In many cases, the mesophase has proved to be impermeable to vapors at low activities, behaving like the crystalline phase. Also, in the case of semicrystalline PEEK, it has been found that the "rigid amorphous fraction" was impermeable to the low activity vapors [14].

Furthermore, it has been found that the aging of amorphous PEEK samples at temperatures slightly lower than T_g, produced a fraction of amorphous material impermeable to the vapors, presumably similar to the rigid amorphous fraction found in crystalline samples [15].

Orientation processes can also produce mesophases. For example a mesomorphic form of polyethylenetherephthalate (PET) can be obtained by drawing amorphous samples at temperatures below the glass transition. It shows a well defined X-ray pattern [16,17], and it is impermeable to the vapors [18].

In a previous paper, the effect of the drawing temperature was analyzed for PEEK, and it was found that the higher the drawing temperature, the more crystalline were the samples [19]. Moreover, several studies have dealt with the physical aging of PEEK, and its effects on the properties [20–24].

In this study we investigate the effect of the physical aging on oriented samples of PEEK obtained by drawing amorphous films at 80 and 140°C and aged for 2 months at room temperature and at 120°C, and thereafter analyzed with many techniques, in order to investigate the effect of different aging treatments.

The choice of two temperatures, is motivated by the fact that the amorphous PEEK we deform behaves differently depending on the drawing temperature. In fact, at 80°C we are far from T_g, and the deformation is carried out on a glassy system. At 140°C, the situation is different since we are close to the T_g and the chains mobility is greater than that at 80°C.

2. Experimental

Amorphous PEEK film (STABAR) 0.10 mm thick was kindly supplied by ICI. The film, as received, was drawn at two different temperatures (80 and 140°C) on an Instron tensile-testing machine at a crosshead speed of 10 mm/min. Tapes drawn at 150% of deformation were prepared. At both temperatures samples deform with neck propagation and, at this value of deformation, both samples are homogeneous since the neck is over [19]. The tapes were aged at room temperature and at 120°C for 2 months. Different samples are identified by a number, which indicates the temperature of drawing and a letter or a number like: "S", which refers to the tape analyzed immediately after the drawing, "A" which refers to the tape aged 2 months at room temperature, and "120" for the tape aged 2 months at 120°C. For example, the code 80-S refers to the sample drawn at 80°C tested immediately after the drawing, while the code 80-120 refers to the sample obtained at 80°C and aged 2 months at 120°C.

Density measurements were performed by means of the floating method, by mixing a solution of zinc chloride and pure water.

The wide angle X-ray diffractograms (WAXD) are obtained by using a PW 1050 Philips powder diffractometer (CuKα-Ni filtered radiation). The scan rate was 1°θ/min.

Infrared measurements were detected using a Perkin–Elmer FTIR Paragon 500 spectrophotometer with a resolution of 4 cm^{-1} (30 scans collected).

Differential scanning calorimetry (DSC) was carried out on the samples over the temperature range 0–400°C, using a Mettler TA3000 DSC, purged with nitrogen and chilled with liquid nitrogen. Runs were conducted on samples of about 12 mg at the heating rate of 20°C/min.

The sorption was measured by microgravimetric method, using a quartz spring balance having an extension of 15 mm/mg. The penetrant used was CH_2Cl_2 and the experiments were conducted at 25°C. Sorption was measured as a function of vapor activity $a=p/p_0$ where p is the actual pressure to which the sample was exposed and p_0 is the saturation pressure at the temperature of the experiment.

The dimensional changes of tapes immediately after the drawing and after the aging were followed in the Polymer Laboratories Dynamic Mechanical Thermal Analyzer interfaced with a Polymer Laboratories temperature controller. The apparatus was used in the creep mode in the interval of temperatures 50–250°C and with a constant applied stress of 17 MPa.

3. Results and discussion

3.1. Density

In Table 1, the densities of samples immediately after the drawing, aged for 2 months at room tempera-

Table 1
Density (g/mL) of drawn and aged samples

Temperature of drawing	Immediately after drawing	Aged 2 months at room temperature	Aged 2 months at 120°C
80	1.2693	1.2715	1.2719
140	1.2720	1.2719	1.2721

ture, and at 120°C are reported. From Table 1 we see that the density varies as effect of the drawing temperature, and as effect of the aging treatments. The increase due to the increased temperature of drawing is ascribed to the strain induced crystallization as already reported [19]. The density increases also as a consequence of the aging at room temperature and 120°C. The increase is appreciable in the sample drawn at lower temperature, while no real change is recordable in the sample drawn at 140°C. These data can be interpreted in terms of physical aging experienced by the sample drawn at 80°C, but not by the other sample. The drawing at 80°C produces a sample far from the thermodynamic equilibrium, while at 140°C, temperature close to the T_g of PEEK, the greater mobility produces samples closer to the thermodynamic equilibrium and therefore no changes of density after the annealing are recordable.

Since the density of the pure amorphous and pure crystalline phases are known [5], one can calculate the volume percent crystallinity X_c according to:

$$X_c = (d - d_a)/(d_c - d_a) \quad (1)$$

where d is the density of the sample under investigation, d_a is the density of the amorphous phase (1.2626 g/mL), and d_c is the density of the crystalline phase (1.4006 g/mL). The X_c values are in the range 5–7%. We do not speculate too much on the crystallinity for two reasons. The first deals with the use of Eq. (1) which holds true only for a biphasic model, and in deformed samples this assumption cannot be done. The second reason has origin on the different drawing temperature. Although the drawing ratio is the same, the different temperatures can produce two samples with different amounts of voids (shear bands, crazes, cracks).

3.2. X-ray analysis

The films drawn at 80°C show in the photographic pattern only polarized halos, indicating a certain degree of orientation, without clear evidence of a crystalline phase. These polarized halos could also be compatible with a sample containing small and/or defective crystals.

In the tape obtained at 140°C some oriented crystalline reflections appear, corresponding to the already reported crystalline structure of PEEK [4]. In any case, the crystallinity is low, although it is oriented.

The aging at room temperature and at 120°C does not produce any changes in the X-ray pattern.

3.3. Infrared analysis

The samples drawn at 80 and 140°C were analyzed in the mid-IR where there are some bands that appear and increase with the crystallization of PEEK. In particular, the bands are those appearing at 1305 and 970 cm^{-1}. In undeformed samples, a correlation has been found between WAXS crystallinity and the absorbance ratio 1305/1280 and 970/952 [25]. The crystalline bands are normalized with two bands not dependent on crystallinity. In our case, since we deal with deformed samples, it is uncertain if these ratios can be used for the determination of crystallinity. In any case, they can be associated to the population of chain segments in conformational order. For our drawn samples, the ratio 970/952 has been calculated and the values correspond to 25–30% of chain segments having conformational order. The aging does not have any effect on this ratio.

3.4. Differential Scanning Calorimetry (DSC)

The DSC traces of all investigated samples are reported in Figs. 1 and 2, and the calorimetric data are summarized in Table 2. In all the curves the glass transition, the exotherm of crystallization and the melting are shown. In the samples drawn at 80°C, the glass transition shows an endotherm, more pronounced in sample 80-120, due to the enthalpy relaxation [26].

The endothermic content at T_g is generally used to

Table 2
DSC data

Sample	$T_{\text{cryst.}}$ (°C)	$\Delta H_{\text{cryst.}}$ (J/g)	T_{fusion} (°C)	ΔH_{fusion} (J/g)
80-S	168.2	20.8	337.8	41.8
80-A	167.7	21.2	337.7	43.1
80-120	168.0	19.4	337.9	42.2
140-S	154.8	12.1	337.9	52.8
140-A	155.2	13.0	338.6	52.6
140-120	154.7	12.4	338.4	53.7

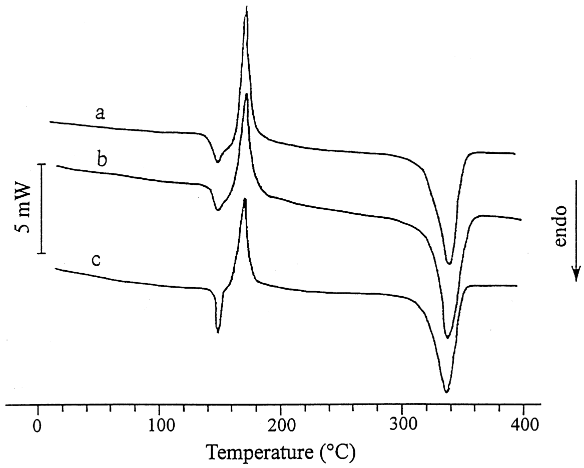


Fig. 1. DSC traces of samples drawn at 80°C: (a) immediately after the drawing; (b) aged 2 months at room temperature; (c) aged 2 months at 120°C.

evaluate the extent of the physical aging, and it has been proved that it increases logarithmically with aging time [27]. In the samples drawn at 80°C, the endotherm increases when the sample is aged at 120°C. At variance, in the samples drawn at 140°C, the endotherm is neither present after drawing nor increases with the aging time.

The presence of the exotherm indicates that the samples increase their crystallinity during the thermal scan.

According to the data of Table 2, we can say that on increasing the temperature of drawing, either the crystallization temperature or the enthalpy of crystallization decrease. This means that the drawing at higher temperature produces a sample with a better orientation which causes the crystallization to occur at a lower temperature. The reduced enthalpy of crystallization indicates that the samples obtained at higher temperature are more crystalline from the beginning, in agreement with X-ray results. This difference is noticed also in enthalpies of fusion. From Table 2, we also see that the physical aging does not produce any change in the crystallization temperatures and enthalpies as well as in the fusion temperatures and enthalpies.

3.5. Sorption

In Figs. 3 and 4, the equilibrium concentration of sorbed dichloromethane as a function of the vapor activity, respectively for samples drawn at 80 and 140°C, is reported. In each figure the curves related to the sample immediately after the drawing, the tapes aged 2 months at room temperature, and the tapes aged 2 months at 120°C are reported along with the curve of the undeformed amorphous PEEK. The two different drawing temperatures produce samples exhibiting different sorption behavior. First of all, on increasing

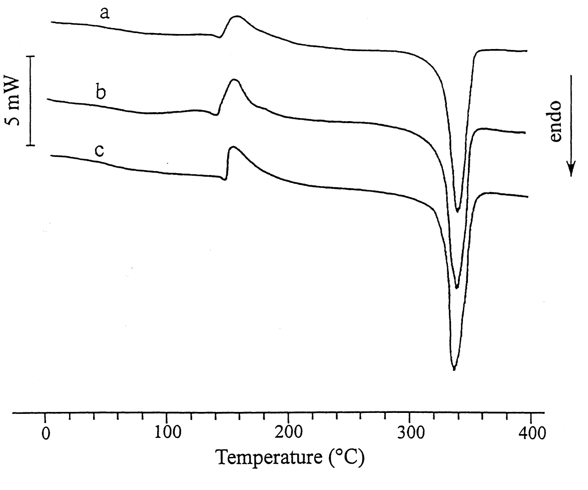


Fig. 2. DSC traces of samples drawn at 140°C: (a) immediately after the drawing; (b) aged 2 months at room temperature; (c) aged 2 months at 120°C.

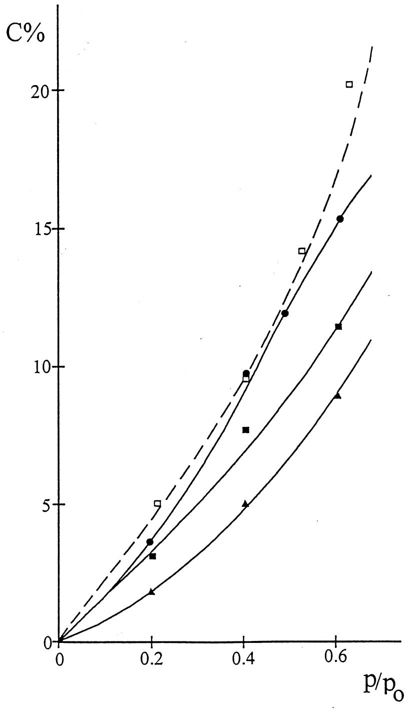


Fig. 3. The equilibrium concentration of CH_2Cl_2 (g of solvent/100 g of sample) as a function of vapor activity for samples: undeformed PEEK film (□); 80-S (●); 80-A (■); 80-120 (▲).

the temperature of drawing, the sorption decreases. Moreover for the tapes obtained at 80°C (Fig. 3) the curves of the tapes 80-S, 80-A and 80-120 are well separated. As for the drawing at 140°C (Fig. 4), the curves of samples 140-S, 140-A and 140-120 completely overlap.

The progressive reduction of sorption in the sample drawn at 80°C can be ascribed to the physical aging phenomenon. The decrease of sorption can be due to the reduction of free volume, but the increase of density cannot completely account for the large increase of the impermeable phase deducible from Fig. 3. This means, that we have to hypothesize that during the aging time some molecular rearrangements result in blocking the easy passage of sorbent molecules, and cause a reduction in the number of regions where the sorption primarily occurred. The reduction of the sorption is one of the effects of the physical aging. It can be interpreted in terms of reduction of free volume, but also in terms of formation of ordered regions, in which interchain packing occurs, in the glassy state. Terms like "ordered domains in the amorphous phase" or "rigid amorphous phase", are used in the literature to account for some properties exhibited by glassy polymers annealed at temperatures below their T_g. Recently, Qian has proposed the concept of interchain cohesional entanglements of neighbouring chain segments in the glassy state [28–31]. Cohesional entanglements can be considered as a sort of local nematic interaction between chain segments. This model is able to explain the sorption behavior of samples drawn at 80°C.

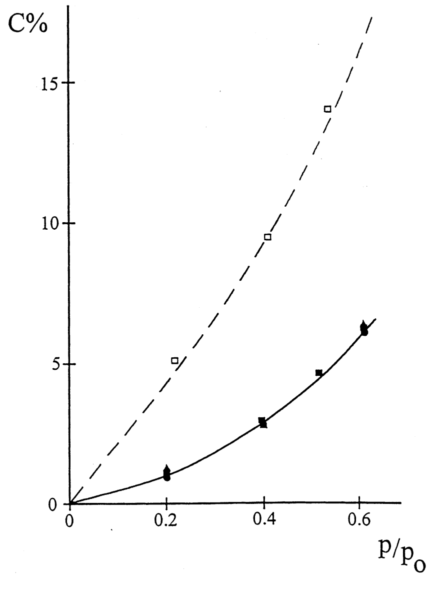


Fig. 4. The equilibrium concentration of CH_2Cl_2 (g of solvent/100 g of sample) as a function of vapor activity for samples: undeformed PEEK (□); 140-S (●); 140-A (■); 140-120 (▲).

On the other hand, we notice that the aging of samples drawn at 140°C does not produce any effect on the sorption behavior. As already discussed before, we again have to confirm that, since the drawing at 140°C is close to the T_g, the time scale required by the molecules to readjust themselves to their new equilibrium condition is comparable with the deformation time. In these conditions, the system is already in equilibrium and no changes in sorption properties are detectable, even if the aging is performed at 120°C.

3.6. Dimensional stability of fibers

The samples immediately after the drawing, and after the aging, have also been checked in terms of dimensional stability in the range 50–250°C with a constant applied stress of 17 MPa. In Fig. 5, the percent of the displacement is reported versus the temperature for the samples drawn at 80°C. In each curve we observe two regions. In the first region, below T_g, the fibers shrink and the shrinkage is more pronounced in tapes immediately after the drawing and annealed at room temperature. The shrinkage is related to the increased mobility of the tie molecules connecting different blocks that form during the deformation process [32]. The shrinkage is the consequence of the approaching of oriented blocks, caused by the conformational changes of tie molecules, with consequent decrease of their end to end distance, on increasing the temperature. Sample 80-120 does not shrink since the aging at 120°C already relaxed the tie molecules. Once the T_g is overcome, the chains are free to move and the viscous flow would elongate the sample till the failure, under the constant applied stress, if the crystallization did not occur. In fact, in Fig. 5 it is evident that the elongation occurs after the T_g, but after a while, the deformation stops as a consequence of the crystallization. The fiber analyzed immediately after the drawing is the first that crystallizes, while the fibers aged at room temperature and aged at 120°C have this process progressively delayed. This means, that the unaged sample crystallizes more rapidly than the aged samples. This also means that the changes occurring during the annealing represent a hindrance for the crystallization process. This behavior has already been observed in a previous study on syndiotactic polystyrene [33]. In that study, aged samples of sPS experienced a delay in the crystallization process with respect to the fresh melt pressed film. This was interpreted in terms of "ordered domains", formed during the aging time, hampering the crystallization at 120°C, probably because the crystallization had to pass through the destruction of the domains.

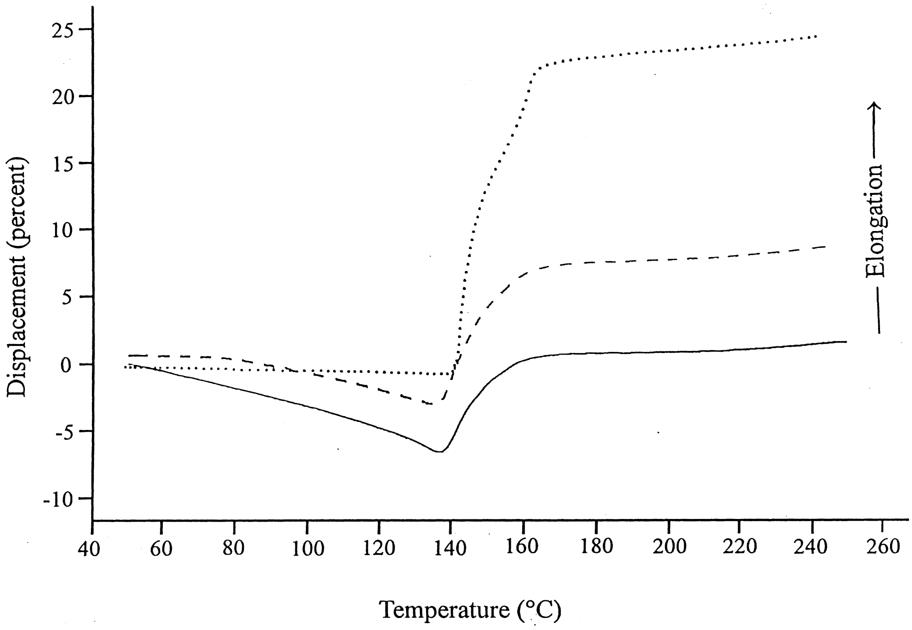


Fig. 5. Displacement vs temperature for samples drawn at 80°C. Immediately after the drawing (——); aged 2 months at room temperature (- - - - -); aged 2 months at 120°C (· · · · · ·).

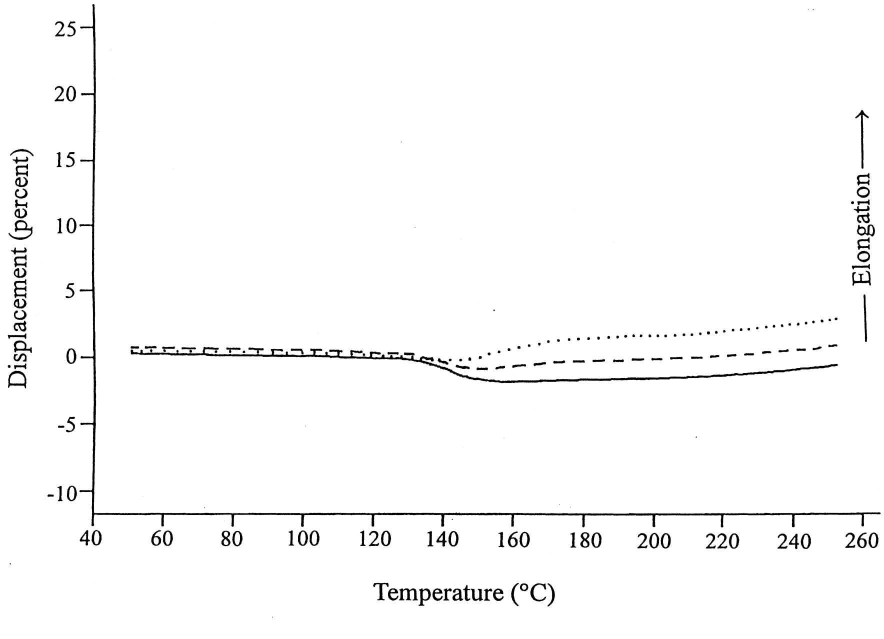


Fig. 6. Displacement vs temperature for samples drawn at 140°C. Immediately after the drawing (——); aged 2 months at room temperature (- - - - - -); aged 2 months at 120°C (· · · · · ·).

The sample drawn at 140°C (Fig. 6) with the two aged samples, does not exhibit any contraction in the region below T_g. Above the T_g, the elongation is very reduced and the length of the samples, both fresh and aged, is very stable, indicating that there is neither further crystallization, nor formation of ordered regions, as also shown by the transport properties.

4. Conclusion

We have analyzed samples of PEEK drawn 150% at 80 and 140°C and aged at different temperatures. The drawing at 80°C does not allow the crystallization, producing an oriented sample in which a fraction of impermeable phase is present from the beginning. This impermeable phase, already recognized as "rigid amorphous phase", in unoriented and semicrystalline samples, increases its fraction with the aging time. At variance, the drawing at 140°C produces a very high fraction of impermeable phase, in which a part is crystalline, and it remains stable with the aging time. This determines also a very high dimensional stability of the sample drawn at 140°C, either with the aging or with the temperature. In fact the length of the sample does not change up to 250°C.

The effects of physical aging, are therefore detectable only in the sample drawn at 80°C, while the sample drawn at 140°C does not show any change of the investigated properties as a consequence of the aging treatments. This is interpreted in terms of relaxed amorphous phase in the sample drawn at 140°C since the drawing temperature is very close to the T_g, and the time scale of the sample deformation is comparable with the time requested by the molecules to reach the new equilibrium condition.

References

[1] Struik LCE. Physical aging of amorphous polymers and other materials. Amsterdam: Elsevier, 1978.
[2] Hutchinson JM. Prog Polym Sci 1995;20:703.
[3] Attwood TE, Dawson PC, Freeman JL, Hoy LRJ, Rose JB, Staniland PA. Polymer 1981;22:1096.
[4] Ueda M, Sato M. Macromolecules 1987;20:2675.
[5] Blundell DJ, Osborn BN. Polymer 1983;24:953.
[6] Cheng SZD, Cao MY, Wunderlich B. Macromolecules 1986;19:1868.
[7] Cebe P, Hong SD. Polymer 1986;27:1183.
[8] Gupta H, Salovey R. Polym Eng Sci 1990;30:453.
[9] Vittoria V. J Polym Sci Phys Ed 1986;24:451.
[10] Vittoria V, Ruvolo A, de Candia F. J Macromol Sci Phys 1990;B29:411.
[11] de Candia F, Ruvolo A, Vittoria V. J Macromol Sci Phys 1992;B31:133.
[12] Vittoria V, Russo R, de Candia F, Magagnini PL, Bresci B. J Polym Sci Phys Ed 1991;29:1163.
[13] Vittoria V, Ruvolo A. J Appl Polym Sci 1992;44:2127.
[14] Michele A, Vittoria V. Polym Commun 1991;32:232.
[15] Michele A, Vittoria V. Polymer 1993;34:1898.
[16] Auriemma F, Corradini P, De Rosa C, Guerra G, Petraccone V, Bianchi R, Di Dino G. Macromolecules 1992;25:2490.
[17] Nicholson TM, Davies GR, Ward IM. Polymer 1994;35:4259.
[18] Bove L, D'Aniello C, Gorrasi G, Guadagno L, Vittoria V. Polymer 1996;37:5309.
[19] Russo R. J Appl Polym Sci 1992;46:2177.
[20] Capodanno V, Petrillo E, Romano G, Russo R, Vittoria V. J Appl Polym Sci 1997;65:2635.
[21] Kemmish DJ, Hay JN. Polymer 1985;26:905.
[22] Carfagna C, Amendola E, D'Amore A, Nicolais L. Polym Eng Sci 1988;28:1203.
[23] D'Amore A, Cecchini F, Pompo A, Apicella A, Nicolais L. J Appl Polym Sci 1990;39:1163.
[24] D'Amore A, Nicolais L. Comp Manufac 1992;3:25.
[25] Chalmers JM, Gaskin WF, MacKenzie MW. Polym Bull 1984;11:433.
[26] Hodge IM. J Non-Cryst Solids 1994;169:211.
[27] Aref-Azar A, Biddlestone F, Hay JN, Haward RN. Polymer 1983;24:1245.
[28] Qian R. Macromol Symp 1997;124:15.
[29] Qian R, Shen D, Sun F. Macromol Chem Phys 1996;197:1485.
[30] Wang Y, Shen D, Qian R. J Polym Sci Polym Phys 1998;36:783.
[31] Qian R, Wu L, Shen D, Napper DH, Mann RA, Sangster DF. Macromolecules 1993;26:2950.
[32] de Candia F, Russo R, Vittoria V, Peterlin A. J Polym Sci Polym Phys 1980;18:2083.
[33] de Candia F, Russo R, Vittoria V. Macromol Chem Phys 1994;195:735.