

Retraction of Injection-Molded Polypropylene

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Synopsis

The retraction of injection-molded polypropylene at temperatures close to its melting point has been studied. At a given temperature above 150°C., retraction reaches a limit within a few minutes. Upon increasing the temperature, this equilibrium retraction changes to a higher characteristic value. The previous heating history strongly affects the equilibrium retraction. In fact, specimens can be prepared which exhibit negligible retraction up to the melting point where complete shrinkage occurs. Equilibrium retraction at a given temperature is ascribed to a melting of crystallites smaller than the specific size associated with that temperature. The remaining larger crystallites prevent further shrinkage.

INTRODUCTION

Annealing of molded polymer specimens has been used extensively to relieve "molded-in" stresses.¹ With amorphous polymers particularly, heat-distortion temperatures can be improved by appropriate annealing. However, there are limitations in choosing annealing temperatures, since at temperatures too close to the second-order transition temperature, severe shrinkage or retraction of oriented specimens takes place. In the case of polyolefins, annealing at moderate temperatures has been a part of the fabrication procedure, and some authors have reported the effect of such heat treatment on polymer properties.¹

When heat-treating polyolefins at temperatures approaching the melting point, particularly with heating in a liquid, several authors have observed the increase of lamellae thickness.^{2,3} In a recent paper, Farrow³ showed that long-term annealing of polypropylene at 160°C. gives rise to large crystallites rather than increased crystallinity, and the melting point is increased correspondingly. Neither the practical aspects of high temperature annealing nor some of the theoretical points have been considered with respect to annealing close to the melting point.

This paper is concerned with the dimensional changes of oriented polypropylene moldings annealed near the melting point. The concept of equilibrium retraction is introduced, and a tentative explanation is proposed along with possible uses of the data. This information can also be used to predict conditions for annealing specimens close to the melting point, without significant shrinkage or distortion, for mechanical property studies.

EXPERIMENTAL

Material

A commercial polypropylene, Pro-fax 6511E, manufactured by Hercules Powder Company, was used in these studies.

Specimen Preparation

A 1-oz. Watson-Stillman molding machine was used to mold the $6\frac{1}{2} \times \frac{1}{2} \times \frac{1}{8}$ in. dumbbell-shaped specimens. From the center section of these moldings, $2\frac{1}{2}$ -in. rectangular specimens were cut with a modified Atlas milling machine.

Shrinkage Measurements

The shrinkage of the molded specimens was measured in a cell immersed in a constant temperature bath ($\pm 0.1^\circ\text{C}$.) containing either glycerine or Dow Corning Silicone Fluid 710. The observation of dimensional changes of the specimen in the cell is based on the principle of following the deformation via a linear variable differential transformer. The time-deformation relationship is continuously recorded. The differential transformer is connected to the specimen with a rod, which is counter-

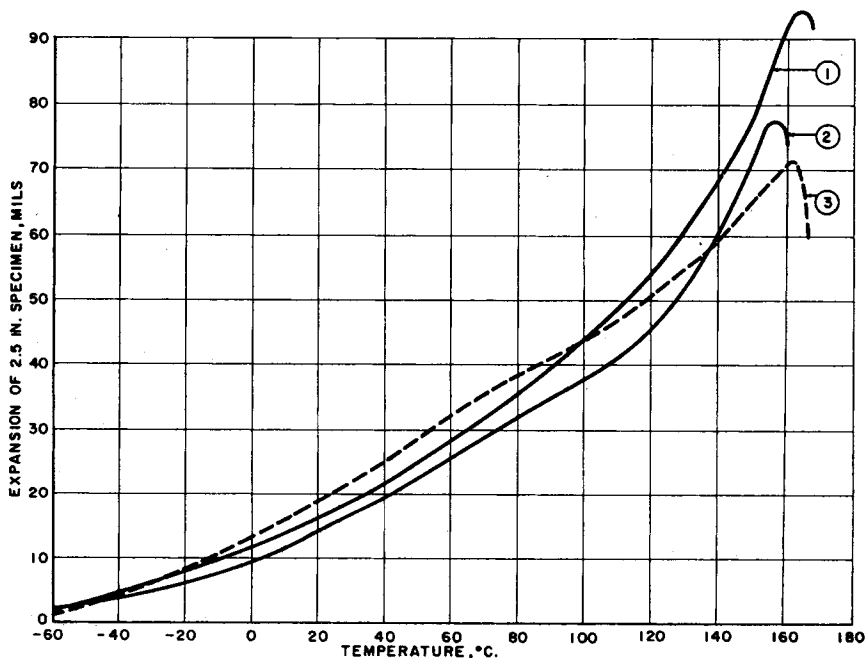


Fig. 1. Linear expansion of polypropylene specimens: (1) compression-molded; (2) injection-molded with flow; (3) injection-molded across flow.

balanced with a weight and a pulley system. With this method, only the small force necessary to counterbalance the effect of buoyancy acts on the specimen.

The 2¹/₂-in. specimen is placed in the measuring cell while it is out of the constant temperature bath. The transformer rod is first placed in contact with the specimen, zero adjustment is made, and the cell assembly is lowered into the bath. In all cases the expected linear thermal expansion (Fig. 1) occurs, followed by shrinkage if sufficiently high temperatures are used. The data are reported as per cent shrinkage, based on the original estimated expanded length of the specimen at the experimental temperature.

Retraction measurements were also carried out with the specimens held in a wire cage to prevent the action of any external forces. This method was particularly useful when high-temperature annealing studies were carried out.

RESULTS AND DISCUSSION

All molded and extruded polymers are known to have some degree of molecular orientation depending on the specific fabrication conditions. This orientation is reflected in shrinkage of the formed shape near the second-order transition temperature of the amorphous polymer, and near the melting point with crystalline polymers. Retraction measurements have allowed the estimation of molecular orientation and internal stress of polystyrene. Also, a simultaneous change in birefringence has been measured.⁴

In the case of polyolefins, similar studies have been missing. It was observed by Price⁵ that an injection-molded linear polyethylene sample showed little retraction at temperatures below 125°C., but at 127°C. up to 55% shrinkage occurred and remained constant for varying exposure times.

In the present studies it was observed that, within only about 2 min. from the beginning of the experiment, the extent of shrinkage in injection-molded polypropylene becomes constant and does not change further even during a prolonged (ca. 6 hr.) period at a constant temperature. Upon increasing the temperature, this "equilibrium retraction" may increase, but always becomes constant in a few minutes. It is the main observation upon which this study is based.

It should be pointed out that this behavior is different from that of amorphous polymers, such as polystyrene, where at an appropriate constant temperature a sigmoidal shrinkage curve is observed. In experiments having practical time limits, no equilibrium retraction is attained with amorphous polymers such as polystyrene.

Equilibrium retraction values are not entirely quantitative, as there may be some error in estimating the expanded dimension of the specimen at the

experimental temperature. The difficulty in estimation is primarily due to the orientation of the specimen. Further, reporting of the per cent shrinkage based on the room temperature dimensions would not be entirely satisfactory. Injection-molded specimens show what might be called secondary shrinkage when they are annealed at a temperature where retraction does not appear to occur. After cooling to room temperature, shrinkage up to 4–5% has been observed, but generally shrinkage of 0.5–2% is to be expected. In one case, where a series of measurements were made, an injection-molded sample showed 1.9, 1.3, and 0.6% secondary shrinkage at 140.4, 133.6, and 125.1°C., respectively. The extent of secondary shrinkage appears to be independent of the duration of the experiment, as is shown for injection-molded Pro-fax 6511E in Table I.

TABLE I

Exposure time, min.	Shrinkage, %	
	149.9°C., Banbury- degraded	146.0°C., virgin
0.5	0.44	1.37
1.0	0.65	2.02
4.0	0.61	2.18
12.0	0.73	2.22
30.0	0.69	2.18
60.0	0.77	2.18

Reproducibility and the Effect of Molding Conditions on Equilibrium Retraction

In order to have an idea of the confidence limits in our studies, a series of ten experiments was run at two shrinkage levels of about 11 and 22%, corresponding to 162.1 and 164.1°C. The standard deviations were 0.49 and 0.40%, respectively. Accordingly, the 95% confidence limits were found to be less than 1% in both cases. Experiments were further carried out both in glycerine and Dow Corning Silicone Fluid 710. No significant difference in retraction data was obtained.

It is of importance to have an idea of the extent of molecular orientation in the retraction specimens. In fact, the major criticism of measuring retraction of amorphous thermoplastic materials is their strong dependence upon molecular orientation resulting from differences in molding.

For this reason specimens were molded at eight different conditions, starting with the most oriented ones and going up to 30°F. above the short shot conditions at 13,000 and 9000 psi of ram pressure. The equilibrium retractions for this series are summarized in Table II. These data indicate that, above 6% equilibrium retraction, all values, except the least oriented (9000 psi at 440°F.), fall within the 95% confidence limit.

Compression-molded specimens, presumably having only some random molecular orientation, exhibit no measurable equilibrium retraction. In

TABLE II

Molding conditions		Equilibrium retraction, %					
Temperature, °F.	Pressure, psi	152°C.	154°C.	158°C.	160°C.	163°C.	165°C.
		380	13,000	1.42	3.11	6.77	9.84
390	13,000	1.74	2.18	7.00	9.06	15.65	38.75
400	13,000	1.23	2.36	6.30	9.65	15.07	38.13
410	13,000	0.61	1.83	7.34	8.61	14.90	37.57
410	9,000	0.61	3.31	7.14	9.50	16.17	39.14
420	9,000	0.61	1.12	6.05	10.26	16.04	39.03
430	9,000	0.20	0.92	6.26	8.32	14.70	39.53
440	9,000	0.00	0.62	3.36	7.31	14.24	37.68

fact, even on complete melting the specimen will show only general deformation but no significant major retraction in any specific dimension.

Effect of Annealing

In studying the effect of subsequent heat treatment of injection-molded specimens, bars were placed, directly from the mold, between two pieces of plate glass and then into an air-circulating oven at 125 and 135°C. for the two series. These specimens were annealed for 4 hr.; two controls were run. One series was cooled at room temperature, while the specimens from the other were immediately dropped into a Dry Ice bath and kept there for 24 hr. The retraction data are depicted in Figure 2.

At this point it may be appropriate to discuss the phenomenon of equilibrium retraction in more detail and attempt to evaluate it in light of published work. The fact that the retraction reaches a certain value in a very short time when kept at a constant temperature may be related to a melting of crystallites smaller than the specific size associated with that temperature,^{6,7} while the larger crystallites appear effectively to control the maintenance of molecular orientation.

With respect to the data in Figure 2, we suggest that annealing polypropylene at 125 and 135°C., as contrasted to ambient cooling from the melt or Dry Ice quenching, provided conditions for melting of small crystallites with growth to larger ones. This heat treatment was not sufficient to melt the larger crystallites, so that the equilibrium retraction above 164°C. was equivalent for all four samples. One can further suggest that by plotting the equilibrium retraction temperature curves (separate specimen for each temperature, Fig. 2), it is possible to obtain a qualitative idea of the distribution of crystallite sizes by differentiation.

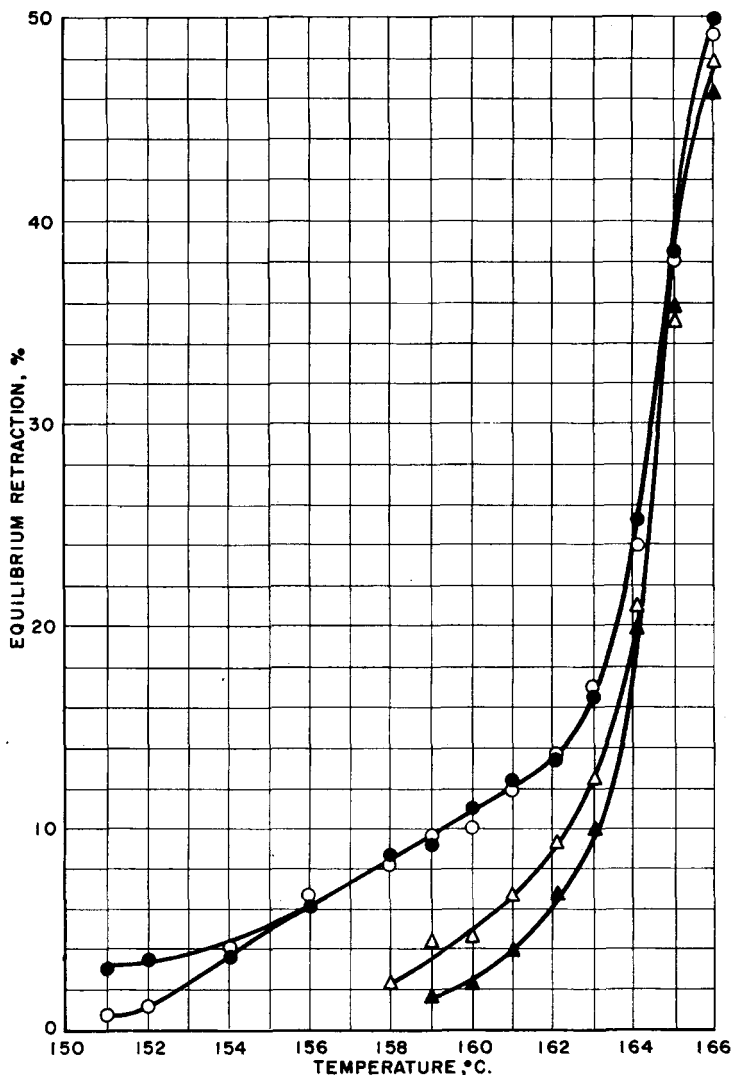


Fig. 2. Effect of annealing on equilibrium retraction of polypropylene: (O) control; (●) Dry Ice-quenched; (Δ) annealed at 125°C.; (▲) annealed at 135°C.

Effect of Melt Index on Equilibrium Retraction

Because of the lack of a wide range of different melt index polypropylenes of the same isotacticity, we investigated thermally degraded polypropylene samples with regard to their equilibrium retractions at a specified temperature. All but two samples were degraded by devolatilizing from a xylene solution, and by using different conditions of temperature and time polymers with varied melt index were obtained. The other two samples were

degraded in a size B Banbury mixer under a nitrogen atmosphere. The equilibrium retraction at 162°C. is depicted in Figure 3. It is of interest to note that even though no appreciable change was experienced in the

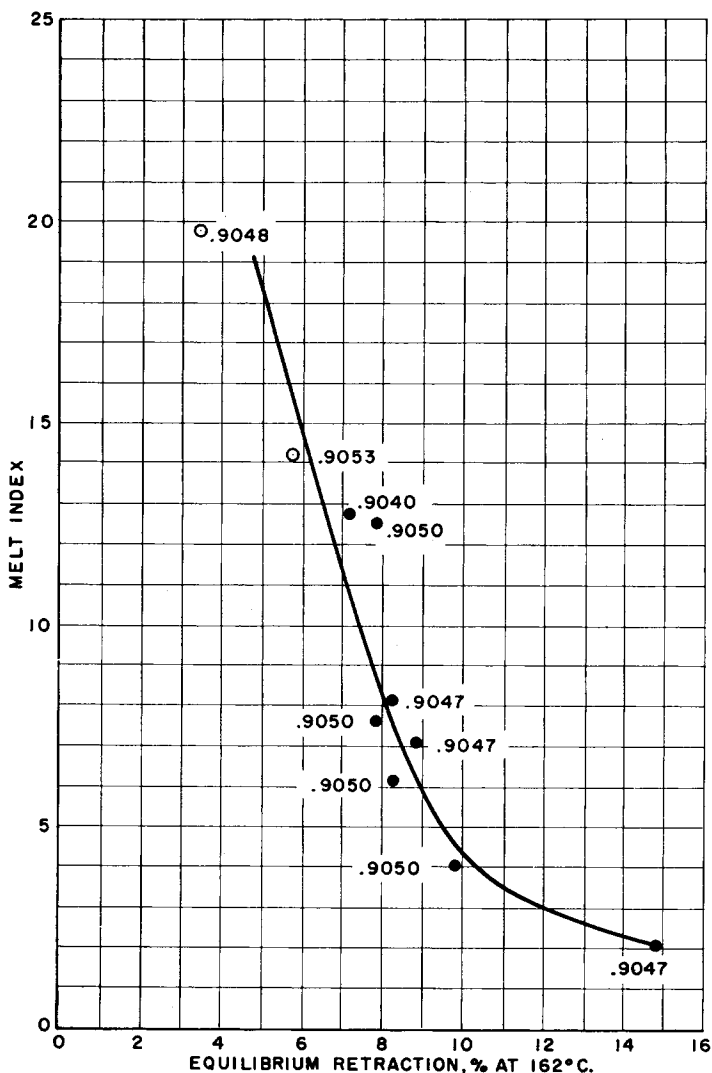


Fig. 3. Equilibrium retraction of thermally degraded polypropylene: (●) devolatilized from xylene solution; (○) degraded in a Banbury. Density indicated for each material.

density of the degraded specimens, a great decrease in equilibrium retraction occurs with increasing melt index. These data, therefore, seem to indicate that the crystallites controlling the retention of molecular orientation can

become increasingly higher melting, at the same level of crystallinity, as the melt index is increased to 20.

Retraction of Polypropylene Blends

Polypropylene can be modified by incorporating other polymers by mechanical blending. Retraction was studied on injection-molded specimens of polypropylene containing either butyl rubber or linear polyethylene. It is apparent from Table III that only relatively large quantities of the second polymer will have a dominating effect on the equilibrium retraction. It seems that the orientation maintenance mechanism in polypropylene remains operative even in the presence of a considerable amount of foreign polymer.

TABLE III
Equilibrium Retraction of Polypropylene Blends

Additive, %		Equilibrium retraction at 154°C., %
Butyl rubber	Linear polyethylene	
10	—	0.0
20	—	0.5
30	—	2.0
40	—	3.5
50	—	5.0
—	10	0.0
—	20	2.0
—	30	2.5
—	40	3.5
—	50	5.5

TABLE IV
Density of Injection-Molded Polypropylene^a

Retraction temp., °C. (30 min. exposure)	Density d^{23} , g./ml.	
	Ambient cooling	4 hr. at 135°C. in air between glass plates
Control	0.9055	0.9067
152	0.9120	—
154	0.9110	—
158	0.9125	—
160	0.9135	0.9135
163	0.9135	0.9139
165	0.9125	0.9122
167	—	0.9140
Total retraction	0.9085	0.9070

^a Injection-molded Pro-fax 6511E (380°F. at 13,000 psi).

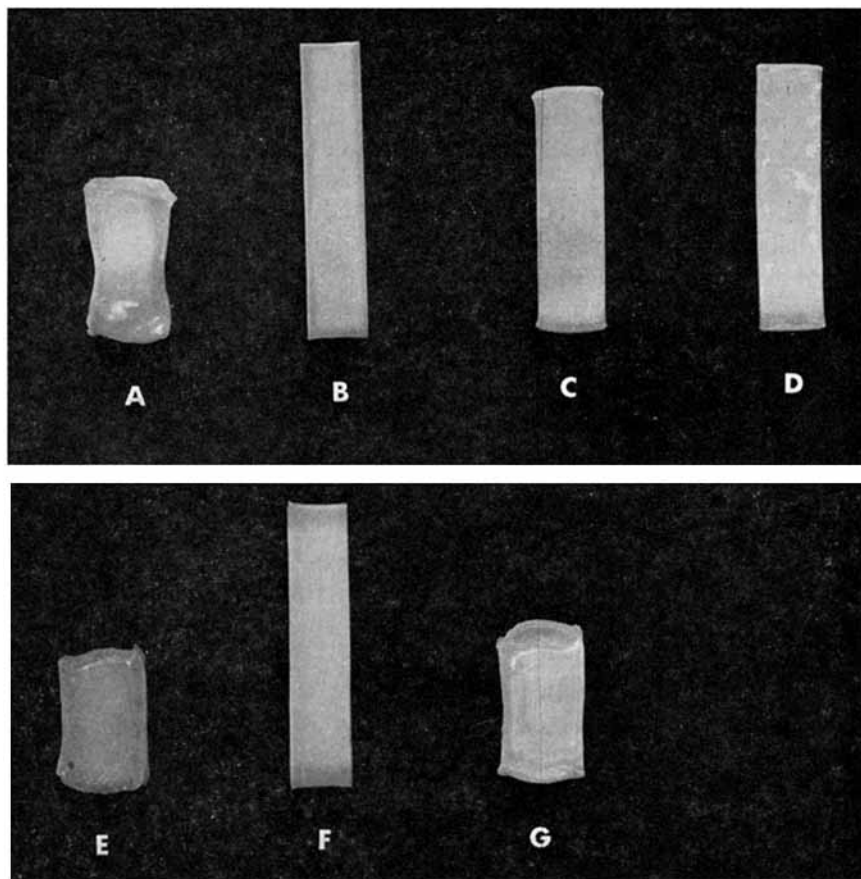


Fig. 4. Retracted polypropylene injection-molded specimens at heating rate $0.8^{\circ}\text{C./min.}$ unless otherwise indicated: (A) $165\text{--}168^{\circ}\text{C.}$; (B) 1 hr. at 155°C. , 1 hr. at 160°C. , 1 hr. at 165°C. , then $165\text{--}168^{\circ}\text{C.}$ at $0.33^{\circ}\text{C./min.}$; (E) 1 hr. at 155°C. , 1 hr. at 160°C. , then $165^{\circ}\text{C.}\text{--}170^{\circ}\text{C.}$; (F) 1 hr. at 165°C. , then $165\text{--}170^{\circ}\text{C.}$; (G) 1 hr. at 160°C. , 1 hr. at 165°C. , then $165\text{--}174^{\circ}\text{C.}$

Density of Retraction Specimens

No extensive density measurements were carried out because of the knowledge that some absorption of glycerine or Dow Corning Fluid had taken place and might give erroneous data. This absorption will be discussed elsewhere. However, the data of Table IV show that some increase in density resulted when partial retraction had occurred, while the density of the completely retracted specimen became almost identical to the starting density.

Melting of Crystallites

Some additional experiments were carried out in order to shed further light on the phenomenon of equilibrium retraction and to lend some support

to the previously proposed explanation of the role of large crystallites. This explanation was, namely, that these crystallites prevent relaxation of the molded-in molecular orientation until completely melted.

In Figure 4, some retraction specimens $2\frac{1}{2}$ in. original length are shown. Pro-fax 6511 (Lot 4067) polypropylene was used in these experiments, showing somewhat improved resistance to retraction compared to the material used earlier. It was also found during this study that still larger differences exist between polypropylenes from different sources.

Sample A was heated from 165 to 168°C. (0.8°C./min.) and showed complete retraction and distortion. After annealing for 1 hr. at each of the temperatures, 155, 160, and 165°C., followed by raising the temperature to 168°C., no such retraction occurred (sample B). The length of the specimen is 2.4 in. In order to have some approximate idea of the rate of perfection of the crystal structure for maintaining molecular orientation, samples C and D were heated to 168°C. at 0.75 and 0.33°C./min. An intermediate amount of retraction was realized.

The next three specimens indicate roughly the limits of heat treatment with this polymer before total melting occurs. Sample E, heat-treated 1 hr. at both 155 and 160°C., when taken to 170°C. retracted completely. Sample F, heat-treated at 165°C., however, showed hardly any shrinkage at 170°C.; the last specimen (G) shows that by 174°C. complete retraction will have taken place. It was interesting to note that in the case of specimens that had received a careful heat treatment up to 165°C., the final shrinkage occurred very fast at a rather specific temperature, indicating that the crystallites remaining had a very narrow melting range. This behavior is in contrast with that of an untreated specimen, which would retract and ultimately melt over a wider temperature range as indicated earlier in this study.

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Résumé

On a étudié le retrait du polypropylène obtenu par injection à l'état fondu, à des températures proches de son point de fusion. A une température donnée au-dessus de 150°C, le retrait atteint une limite en l'espace de quelques minutes. En augmentant la température, cet équilibre de retrait change jusqu'à une valeur caractéristique plus élevée. L'historique du chauffage antérieur influence fortement l'équilibre de retrait. En fait, on peut préparer des échantillons qui présentent un retrait négligeable jusqu'au

point de fusion où une contraction complète du volume apparaît. Un équilibre de retrait à une température donnée est attribué à une fusion des cristallites plus petits que la grosseur spécifique liée à cette température. Les cristallites plus volumineux résiduels empêchent un retrait ultérieur.

Zusammenfassung

Die Retraktion von Spritzgusspolypropylen bei Temperaturen in der Nähe seines Schmelzpunkts wurde untersucht. Bei einer gegebenen Temperatur oberhalb 150°C erreicht die Retraktion innerhalb einiger Minuten einen Grenzwert. Bei Temperaturerhöhung verschiebt sich diese Gleichgewichtsretraktion zu einem höheren charakteristischen Wert. Die Erhitzungsvorgeschichte hat einen grossen Einfluss auf die Gleichgewichtsretraktion. Es können Proben hergestellt werden, welche bis zum Schmelzpunkt eine vernachlässigbare Retraktion zeigen, wo dann eine vollständige Schrumpfung eintritt. Gleichgewichtsretraktion bei einer bestimmten Temperatur wird dem Schmelzen von Kristalliten zugeschrieben, die kleiner sind als der spezifischen, mit dieser Temperatur verbundenen Grösse entspricht. Die zurückbleibenden grösseren Kristallite verhindern eine weitere Schrumpfung.

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