

High-Temperature Aging of Halar Film. I. Study of Physicochemical Changes

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Synopsis

A heat-aging study was undertaken to determine the physicochemical changes in an experimental Halar film [about 80% alternating 1:1 copolymer of ethylene (E) and chlorotrifluoroethylene (CTFE)] as a result of exposure to elevated temperatures in air. This work was intended to evaluate how Halar would behave upon exposure to high temperatures as might be the case in wire and cable coating or other similar applications. Samples of Halar film were aged (unstressed) in air at three different temperatures (150, 175, and 200°C) for a period of up to 1000 h and then characterized with respect to yellowness index, molecular weight, chemical structure changes, crystalline characteristics, thermal behavior, and tensile properties. The results point out no significant deterioration of properties as a result of aging at 150 or 175°C for 40 days. Actually the exposure at 150 or 175°C increases the molecular weight slightly and enhances crystallinity, which improve the dimensional stability of Halar. Extended exposures at 200°C increased the yellowness index and caused physical distortion of the film. The rest of the properties either remained the same or showed some improvement.

INTRODUCTION

Halar is the trademark for Allied Corporation's copolymer products made from ethylene and chlorotrifluoroethylene. These materials, prepared by peroxide catalyst-initiated polymerization, offer a unique combination of properties such as chemical and flame resistance, desirable electrical and mechanical properties, and melt processability. At present, the major application of Halar (50 E:50 CTFE) is in the cable-coating industry where this material could be exposed to high temperatures. A study was, therefore, undertaken to evaluate the physicochemical changes that might occur in Halar upon exposure to elevated temperatures in air.

This article describes the effect of aging time and temperature on chemical structure changes and the thermal and mechanical properties of Halar.

EXPERIMENTAL

All the high-temperature aging experiments were made on an extruded 2-mil Halar film of approximately 50:50 composition of E:CTFE. Following are the details of the various experiments carried out.

Aging Procedure. Halar film samples were aged for various lengths of time at each of the three selected temperatures: 150, 175, and 200°C. The film was freely suspended (i.e., unstressed) in a forced-draft air oven set at the desired temperature.

Yellowness Index. Discoloration of the aged samples was monitored by the ASTM D1925 method using a Hunterlab model D25D color/difference meter.

Viscosity Measurements. The intrinsic viscosity (η) of the film was measured at 135°C using a Cannon Ubbelohde viscometer. The solutions were prepared by dissolving the polymers in 2,5-dichlorobenzotrifluoride at 150°C for 2 h.

Infrared Spectroscopy. The infrared spectra of all the film samples were recorded on Perkin Elmer 283 and 983 models.

Tensile Properties. Tensile property measurements were carried out at 23°C and 50% humidity on a model TTD Instron under the following conditions: 1.0 in./min head speed, 20.0 in./min chart speed, 2.5 in. gage length, and ASTM type IV specimen. The data reported are the average of five experiments.

X-Ray Diffraction. X-ray diffraction (XRD) analysis of the Halar film was carried out on a Phillips goniometer in the transmission mode using $\text{CuK}\alpha$ radiation. Effect of any orientation was eliminated by spinning the sample in its plane at about 70 rpm while scanning 2θ at a rate of $0.1^\circ/\text{min}$. (a) Crystallinity was determined by resolving the area under the peak at $2\theta = 18.2^\circ$ into the crystalline and amorphous scattering. (b) Crystallite dimension (t) perpendicular to the chain axis was determined using the relationship $t = 0.9 \lambda / B \cos\theta$, where λ is wavelength, θ is the Bragg angle, and B is the full width at half-peak height measured from the equatorial 18.2° peak after subtracting the amorphous background.

Thermal Analysis. (a) Thermal stability of the samples was determined by thermogravimetric analysis (TGA). A DuPont 1090 thermal analyzer (automated data processing) with 951 TGA module was used using about a 40-mg sample in a platinum pan, argon atmosphere, and a heating rate of $10^\circ\text{C}/\text{min}$.

(b) Differential scanning calorimetry (DSC) was used to obtain the thermal transitions. A Perkin Elmer DSC-2 with a 3600 thermal analysis data station (TADS) was used. A sample of about 10 mg was crimped in an Al pan and

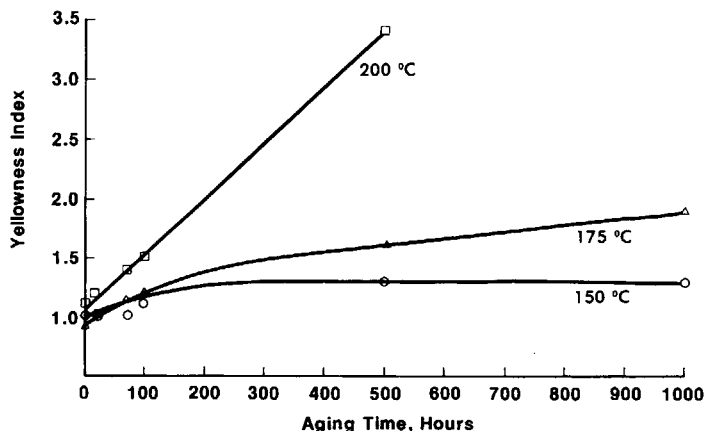


Fig. 1. Effect of time on the yellowness index of Halar film upon thermo-oxidative aging at various temperatures.

heated in argon at a rate of 10°C/min. Following the initial heatup, the samples were held at 280°C for 5 min prior to programmed cooling (10°C/min). A subsequent reheat was carried out under the same conditions as the initial heatup.

(c) Thermomechanical analysis (TMA) was applied in the extension mode to obtain the dimensional changes in the machine and transverse directions of the film. A Perkin Elmer TMS-1 instrument was used under the following conditions: 10°C/min heating rate, helium atmosphere, extension probe with zero load, and a sample strip of 0.31 in. standard length.

RESULTS AND DISCUSSION

The physical and chemical changes in Halar film as a result of heat aging have been determined in order to predict the behavior of Halar at elevated temperatures. Following are the details of some specific properties of Halar as affected by the high-temperature treatment.

Yellowness Index

The changes in yellowness index (YI) as a function of aging time and temperature are shown in Figure 1. The results show that the increase in YI with time becomes dramatic in going from 150 to 200°C aging temperature. In fact, at 150°C the YI appears to have leveled off at a reasonably low value of 1.3 in 500 h or less when compared with a YI of 1.0 for the starting material. However, at 200°C the YI increases linearly with time, reaching a value of 3.4 in 500 h. The discoloration of the films could be visible only after extended exposures at 200°C. The increase in YI probably originates from the development of minor unsaturation along the polymer chain.

Viscosity Measurements

The variations in viscosity of Halar as a result of thermal exposure (time and temperature) conditions are plotted in Figure 2.

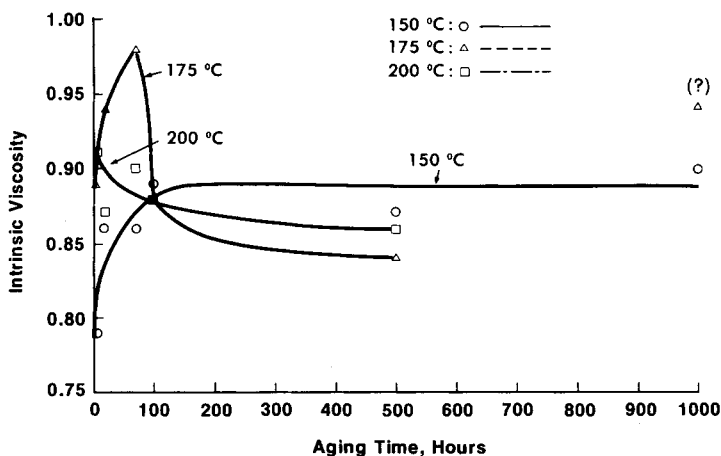


Fig. 2. Effect of time and temperature on the intrinsic viscosity of Halar film upon thermo-oxidative aging.

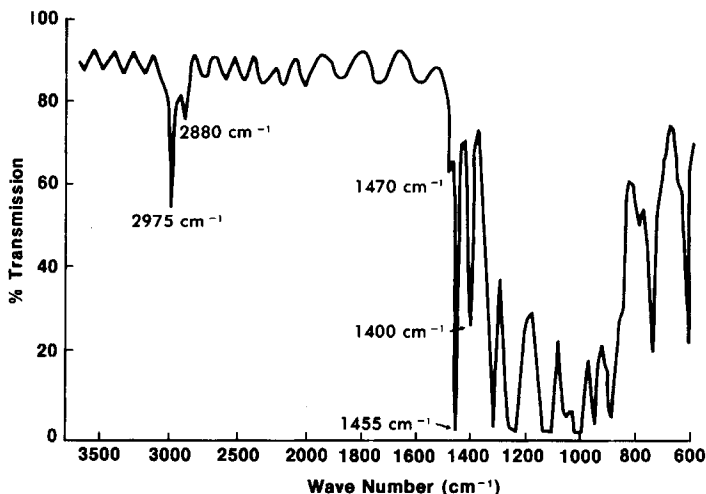


Fig. 3. Infrared spectrum of control Halar film.

It is clearly shown that the thermo-oxidative aging of Halar increases its molecular weight, most likely, as a result of slight crosslinking. At 150°C, the intrinsic viscosity increases from 0.80 to a maximum of about 0.89 in 100 h. A temperature of 175°C appears to be more effective in this respect and increases the viscosity to its highest value of about 0.98 in a 70-h period. Upon continued aging, the molecular weight begins to decrease due to degradation. At an aging temperature of 200°C, the maximum viscosity of 0.91 is achieved in only 5 h. The highest viscosity observed at 175 and 200°C is the result of competing crosslinking and chain-scission reactions. At very long aging times (e.g., 175°C/1000 h, Fig. 2), a further increase in viscosity takes place probably due to enhanced crosslinking.

Infrared Spectroscopy (IR)

The IR spectrum of the control Halar film (Fig. 3) is essentially the same as that of a 1:1 alternating copolymer of ethylene and chlorotrifluoroethylene reported by Sibilia, Roldan, and Chandrasekaran.¹ Using the procedure developed by Tirpak,² this Halar film is shown to have a composition of 48:52 of E:CTFE with the mole fraction of the alternating units being 0.80. The remaining 0.20 fraction is found to consist of blocks of E (0.08) and CTFE (0.12).

The aged film samples do not reveal any additional bands related to unsaturation or oxidized groups, thus implying no significant structural changes upon aging.

The absorbance per centimeter for the 415-cm⁻¹ band, a crystalline absorption, increases with an increase in aging time and temperature. The trend of increasing crystallinity with thermal exposure is essentially the same as that revealed by x-ray and DSC techniques to be described in the following sections.

Tensile Properties

The tensile data of the aged films tested at room temperature is compiled in Table I. There are no major changes in modulus, breaking strength, or

TABLE I
Tensile Properties of Aged Halar Film

Aging Conditions		Tensile Properties ^a						
Temperature (°C)	Time (h)	Viscosity [η]	Test direction	Modulus [(psi) $\times 10^{-6}$]	Break strength [(psi) $\times 10^{-3}$]	Yield strength [(psi) $\times 10^{-3}$]	Break elongation (%)	Yield elongation (%)
—	—	0.80	Mach	2.97	8.83	4.34	140	4.4
			Trans.	2.81	7.33	4.31	250	4.5
150	100	0.89	Mach	2.91	8.59	4.10	140	6.6
			Trans.	2.34	7.58	4.10	330	6.8
	500	0.87	Mach	2.77	8.84	4.04	160	8.0
			Trans.	2.11	7.47	3.92	340	7.9
1000	0.90	Mach	2.60	8.76	4.17	160	9.1	
		Trans.	2.42	7.30	4.05	315	6.3	
175	100	0.88	Mach	2.82	8.81	4.21	140	7.7
			Trans.	2.34	7.94	4.08	360	6.4
	500	0.84	Mach	2.74	8.95	3.97	150	7.8
			Trans.	2.30	7.42	3.95	380	7.1
1000	0.94	Mach	2.97	8.05	4.01	160	6.1	
		Trans.	2.16	7.34	3.92	380	6.6	
200	100	0.88	Mach	2.92	8.45	4.13	115	6.2
			Trans.	2.38	6.22	3.97	420	6.4
	500	0.85	Mach	2.59	6.84	3.99	95	8.4
			Trans. ^b					

^a Data represent average of five measurements.

^b Not available; sample physically distorted.

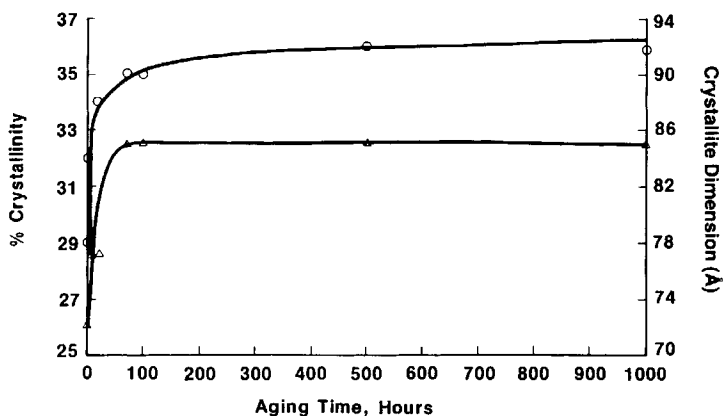


Fig. 4. Effect of time on the (○) percent of crystallinity and (△) crystallite dimension of Halar film upon thermo-oxidative aging at 175°C.

yield strength as a result of 1000 h aging at 150 or 175°C. However, it is interesting to note that in the initial stages of aging, e.g., at 175°C, the modulus decreases slightly. The latter can be explained if we consider that the starting film during processing developed a certain level of molecular orientation which was eliminated during aging. Upon extended exposures, i.e., 1000 h at 175°C, factors such as crosslinking and increased crystallinity dominate and the modulus approaches that of the starting film. Aging at 150 or 175°C tends to increase the breaking and yield elongation of the film which again may be associated with the loss of orientation during the oven treatment. Extended exposures at 200°C caused physical distortion of the film and, therefore, the tensile properties could not be measured. However, short exposures, e.g., 100 h, at 200°C did not affect the tensile data significantly.

For all the film samples, the elongation at break is substantially higher in the transverse direction compared with that in the machine direction; this may be due to the chain orientation in the machine direction which will hinder the extent of elongation relative to that in the transverse direction.

The moduli of these films are in the range reported earlier³ for undrawn Halar films $[(2-3) \times 10^5 \text{ psi}]$.

X-Ray Diffraction

Crystallinity and crystallite dimension⁴ data on the control and some aged Halar films are presented in Figure 4. A typical x-ray diffractometer scan is shown in Figure 5.

Crystallinity of starting film is 29% and it increases upon heat aging to a maximum of $36(\pm 1)\%$. This increase in crystallinity is also accompanied by an increase in the crystallite dimension from 72 Å to a value of 85–90 Å. As described in the Experimental section, crystallite dimensions refer to the direction perpendicular to the chain axis and thus have nothing to do with the lamellae thickness (fold length) of the crystals.

The newly formed crystals are small, i.e., less thick, and less perfect

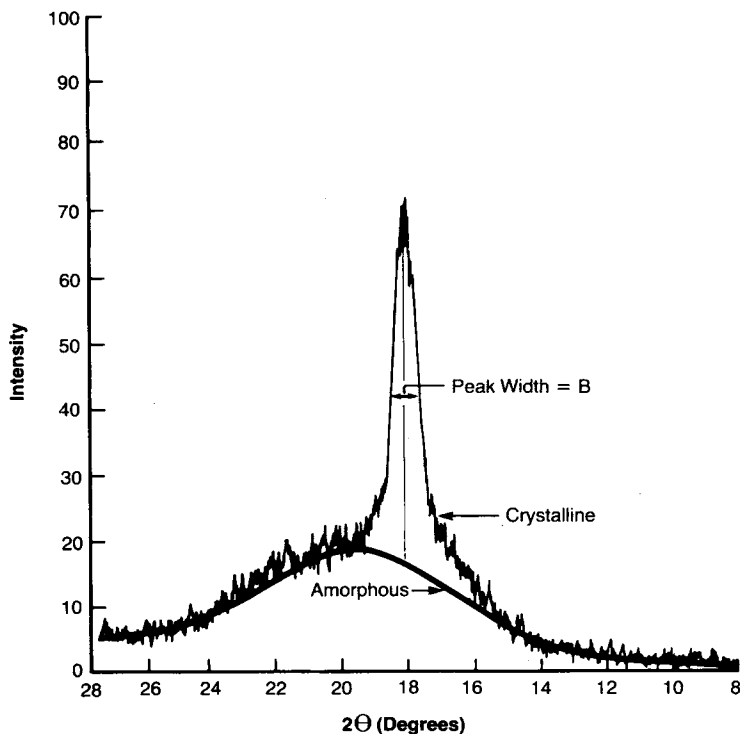


Fig. 5. X-ray diffractometer scan of Halar film aged at 200°C for 100 hr.

compared with the original crystals which themselves do not change during aging. (For evidence see DSC.) In order to account for the above and the increased crystallinity and crystallite dimension, we propose that upon heat aging small crystals grow around the existing crystallites.

TABLE II
Thermal Stability of Aged Halar Film

Aging conditions		Intrinsic viscosity [η]	% Weight loss at (°C):							T_{\max} (°C) ^b
Temperature (°C)	Time (h)		200	300	350	400	450	500	600	
—	—	0.80	0.2	0.3	0.4	0.6	3.3	63	71	482
	100	0.89	0.1	0.2	0.2	0.5	2.2	52	69	494
	500	0.87	0.1	0.1	0.1	0.3	2.2	57	69	491
	1000	0.90 ^a	0.0	0.0	0.1	0.4	3.5	60	68	485
175	72	0.98 ^a	0.1	0.1	0.1	0.5	6.0	64	70	480
	100	0.88	0.1	0.1	0.1	0.5	3.5	61	67	482
	500	0.84	0.1	0.1	0.2	0.5	2.7	63	69	482
	1000	0.94	0.0	0.0	0.0	0.5	4.0	60	68	483
200	5	0.91 ^a	0.0	0.1	0.1	0.3	3.5	63	69	480
	100	0.88	0.0	0.0	0.0	0.3	2.5	58	69	487
	500	0.86	0.2	0.3	0.4	0.8	5.0	55	68	484

^a Represents the highest-viscosity sample aged at a particular temperature.

^b Temperature where maximum rate of weight loss occurs.

TABLE III
Thermal Transitions of Aged Halar Film

Aging Conditions Temperature (°C)	Time (h)	Intrinsic viscosity [η]	Initial heatup			Cooling Crystallization temperature [$T_{c(c)}$](°C)	Reheat	
			Lower Melting endotherm T_{m_l} (°C)	Higher melting endotherm T_{m_h} (°C)	Total ^a heat of fusion, ΔH_f (cal/g)		Melting endotherm T_{m_w} (°C)	Total heat of fusion, ΔH_f (cal/g)
—	—	0.80	—	238	8.4	220	237	8.67 } 8.82 }
150	5	0.79	170	238	8.72	220	238	8.45 } 8.64 }
	20	0.86	178	238	8.71			
	72	0.86	181	238	8.69			
178	100	0.89	178	238	9.24	220	238	8.45 } 8.64 }
					8.76			
					9.30			
188	500	0.87	188	238	9.38	220	237	8.78 } 8.74 } 8.92 }
					9.39			
					9.57			
187	1000	0.90	187	238	9.73	220	238	8.48 } 8.5 }
					9.56			

Thermal Characterization

Thermal techniques were used to determine the aging effects on Halar in terms of thermal stability (TGA), thermal transitions (DSC), and dimensional stability (TMA).

Thermogravimetric Analysis

Thermal stability data of the aged films is compared with that of the control in Table II.

All the films begin to degrade at about 350°C. In spite of the increase in viscosity upon aging, no significant change in thermal stability can be noticed. This implies that the starting material ($[\eta] = 0.80$) falls in a molecular weight range where the effect of molecular weight on the thermal stability is insignificant.

A weight loss of about 0.4% by 350°C for the control sample is probably associated with the loss of additives or impurities. The heat-aged films show somewhat reduced weight loss by 350°C as a result of heat aging which probably eliminates some of the additives.

Differential Scanning Calorimetry

Melting and crystallization temperatures and the heat of fusion data of Halar film samples are summarized in Table III.

The melting behavior of Halar as reflected by the initial heatup (Figs. 6 and 7) is strongly influenced by the thermal treatment. All the aged films exhibit a doublet melting behavior; a lower temperature transition (T_{m1}) depending upon the thermal history, and a higher temperature melting (T_{m2}) always at 238°C. The starting material shows only the higher melting endotherm, T_{m2} , at 238°C. (Note: The specification for commercial Halar product is 240°C. A slightly lower melting temperature reported in this study is probably due to the fact that we are dealing with an experimental melt-processed material.) With the increase in treatment time or temperature, there is corresponding increase in T_{m1} and the total heat of fusion (ΔH_f); the latter being somewhat approximate. Interestingly, there is a good

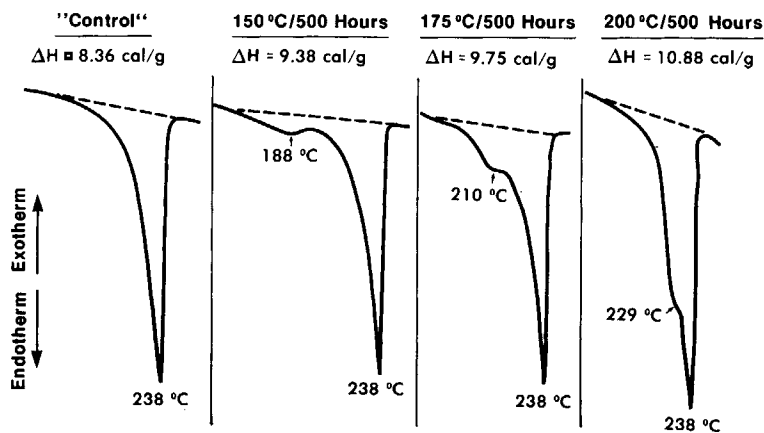


Fig. 6. Effect of aging temperature on the melting behavior of Halar film.

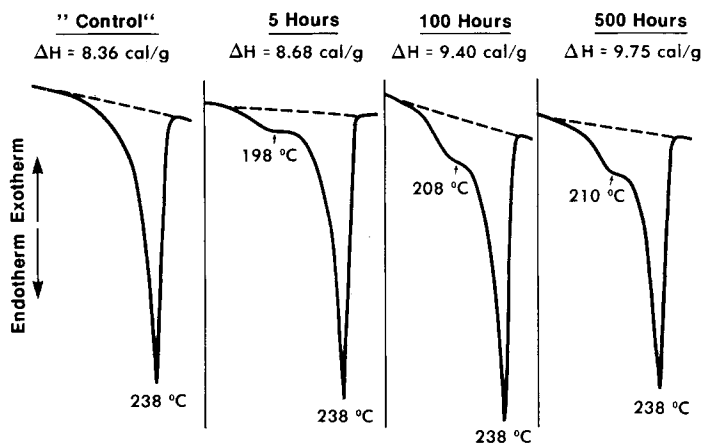


Fig. 7. Effect of aging time at 175°C on the melting behavior of Halar film.

correlation between ΔH_f and percent of crystallinity changes upon annealing, e.g., in 1000 h at 175°C, ΔH_f and percent of crystallinity increase by 19 and 24%, respectively.

After erasing the thermal history, e.g., by a 5-min treatment at 280°C, the aged samples behave similar to the "control." The crystallization temperature upon cooling [$T_{c(c)}$] and the melting temperature (T_{m2}) are found to be about 220 and 238°C, respectively (Table III). Also all the samples exhibit similar ΔH_f values. These results demonstrate that the differences in thermal behavior of heat-aged films, as revealed by the initial heatup, are due to a physical phenomenon (thermal history). Moreover, it can be assumed that the aging does not cause any major degradation of the material as also suggested by IR.

A thorough study of the T_{m1} and T_{m2} transitions will be the subject of a subsequent publication.⁵ However, we wish to mention here that T_{m1} , which

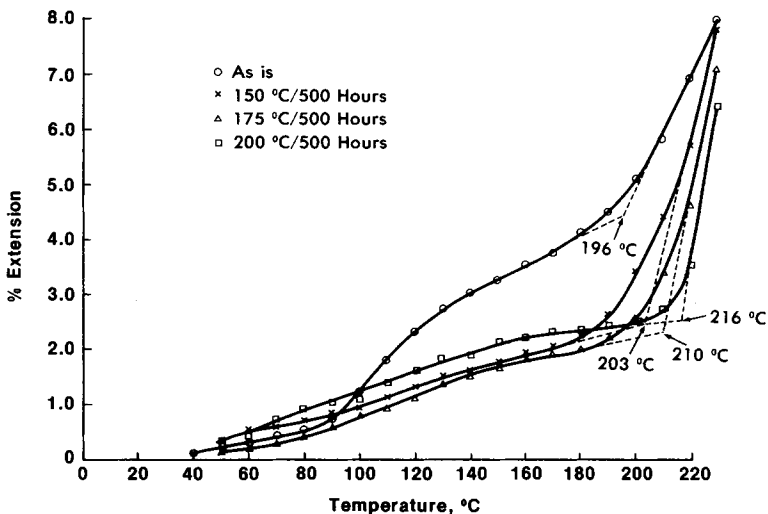


Fig. 8. Effect of aging temperature on the extension versus temperature curves of Halar film (machine direction).

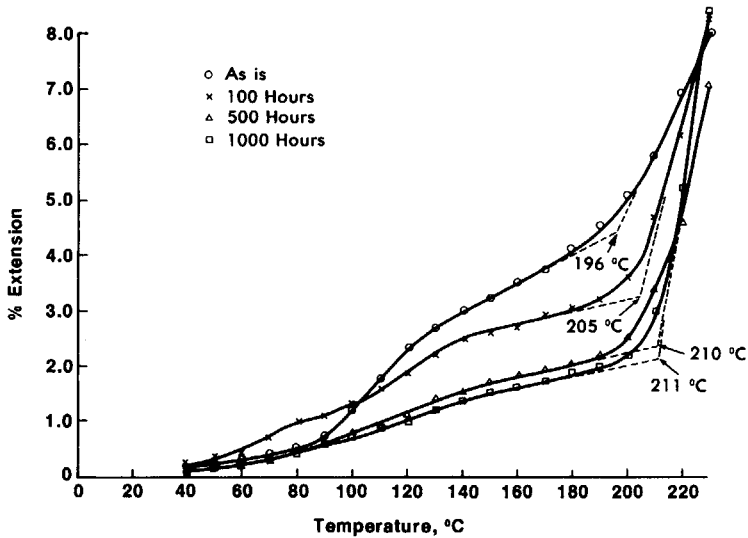


Fig. 9. Effect of aging time at 175°C on the extension versus temperature curves of Halar film (machine direction).

develops upon heat aging is due to the melting of small crystals (i.e., lower melting temperature) formed during the oven aging process.

Thermomechanical Analysis—Extension Data

The extension versus temperature data (machine and transverse directions) for the aged Halar film samples is compared with that of the starting material in Figures 8–11.

In the *machine direction*, the changes in percent of extension versus temperature characteristics of Halar are shown in Figure 8 as a function of the heat-aging temperature. Up to 100°C, no major differences can be observed between the control and the aged samples. Above 100°C, the aged films undergo less elongation than the starting sample. This improvement in dimensional stability can be attributed to the development of lower melt-

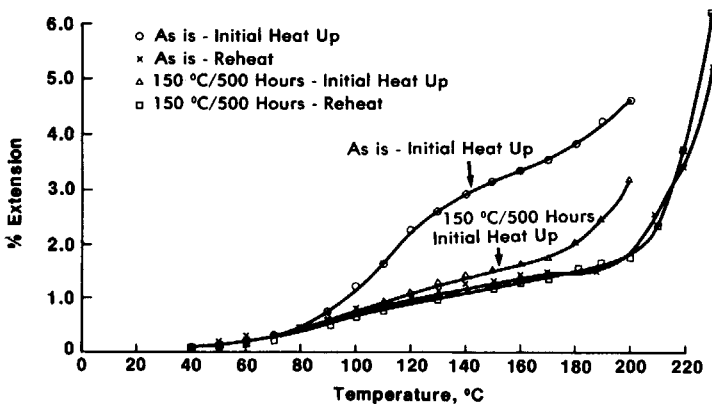


Fig. 10. Influence of thermal history on the extension versus temperature curves of Halar film (machine direction).

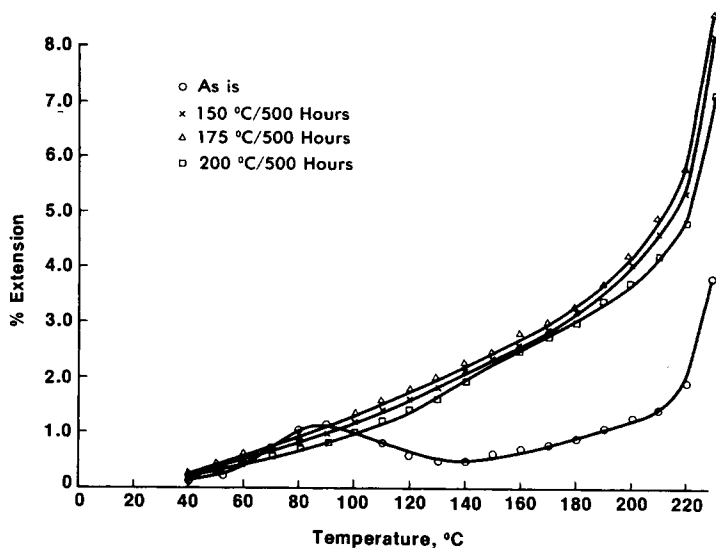


Fig. 11. Effect of aging temperature on the extension versus temperature curves of Halar film (transverse direction).

ing crystallites as a result of heat aging. Interestingly, the effect of aging temperature is also reflected in the dimensional stability of Halar. The extrapolated temperatures (T_e), where the accelerated extension due to molecular flow takes place, are 196, 203, 210, and 216°C for the control, 150, 175, and 200°C aged films. The increase in T_e with the increase in aging temperature is caused by the higher crystallinity due to the newly developed crystallites and, thus, follows the same trend as T_{m1} (i.e., increasing with aging time and temperature). The effect of aging time at 175°C also exhibits somewhat similar behavior (Fig. 9). This again demonstrates that the increase in dimensional stability of Halar as a result of thermal aging is directly related to the new crystallites characteristic of the heat-aging treatment. In fact, our interpretation of increased dimensional stability as a result of newly developed crystallites is fully supported by the data in Figure 10. For example, during the initial heatup, the 150°C/500 h aged film is dimensionally more stable than the control but upon reheating (i.e., after cooling in the TMA unit from 200°C, which being above the T_{m1} of the aged film provides similar thermal history to both the samples), the two films exhibit similar extension versus temperature characteristics. It is important to note that the improvement in stability of the "as is" film upon reheat (Fig. 10) is not in contradiction with our proposition that the new crystals are responsible for the increased dimensional stability. The "as is" film upon initial heatup in the TMA undergoes a certain amount of extension (molecular orientation) by 200°C and when such a sample is reheated, further extension is somewhat restricted which translates into an improvement in dimensional stability upon reheat.

In the *transverse direction*, the aged films behave similarly irrespective of the exposure temperature or time. They elongate gradually with accelerated elongation beginning at about 220°C due to the molecular flow. However, the control Halar film undergoes shrinkage between 90 and 140°C

which is difficult to understand unless it is oriented in the transverse direction (Fig. 11). Further work, e.g., birefringence measurements, would be necessary to explain these results.

Finally we would like to mention that the high-temperature aging of Halar may also result in shrinkage due to an increase in crystallinity. Further studies would be needed to determine the shrinkage effects on aging and its influence on a particular application.

CONCLUSIONS

High-temperature aging of Halar film results in the growth of small crystallites around the original crystalline regions which is reflected in an increase in crystallinity, crystallite dimension, heat of fusion, and the dimensional stability of the product. The molecular weight of Halar also increases slightly upon exposure to elevated temperatures.

No significant deterioration of Halar film can be identified as a result of aging between 150 and 175°C for a period of 1000 h. Even exposure at 200°C for short times (e.g., 100 h) is not detrimental as determined by unsaturation, oxidation, yellowness, thermal properties, and tensile properties. The long-term effect of high temperatures in the proximity of 200°C is expected to depend upon the type of application for Halar.

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