

Crystallinity Index of Poly(ethylene Terephthalate) by X-Ray Diffractometry and Differential Scanning Calorimetry

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Synopsis

The crystallinity of a variety of poly(ethylene terephthalate) (PET) specimens, produced by thermal annealing, has been measured by three x-ray diffractometric index methods and by an index method for differential scanning calorimetric data. The measurement procedures are termed indices since they involve various methods of ranking specimens in a relative manner between maximum and minimum crystallinity standards. Statistically different index values are determined by the various physical methods and procedures of calculation for many types of specimens. The integral index method, which utilizes x-ray diffractometric data, corresponds in a more precise manner to the calorimetric index than to the other two x-ray methods, for the cases in which oriented film is annealed in a vacuum oven and is subject to a continuous pumping environment. This treatment also produces a threefold increase in number-average molecular weight of PET film. Annealing in sealed ampules, M_n constant, produces substantially the same results for all three x-ray methods but different results for the calorimetric procedure. A relatively simple two-point procedure yields virtually the same trend as the more complicated indicial methods.

INTRODUCTION

The property of crystallinity has been inferred from a variety of physical techniques including x-ray diffraction, density measurements, heat content, diffusion of penetrants, infrared absorption, and nuclear magnetic resonance.^{1,2} The x-ray diffraction method itself is subdivided into numerous techniques, both camera and diffractometric, and different methods of calculating the property. Two main divisions are the absolute separation of the scatter into crystalline and amorphous contributions and the ranking of diffractograms in a relative manner by means of one of the index procedures. One desirous of measuring the crystallinity of a polymeric system is thus faced with a plethora of physical techniques, nuances, and methods of calculation. Little is known of the degree of correspondence among the various ways of arriving at an estimate of crystallinity or if, in fact, this property is a function of the manner of measurement or calculation.

Since workers in x-ray diffraction seem to feel that the x-ray method(s) is the measure of crystallinity, and workers in other physical techniques

doubtless advocate their specialization, it was decided to measure a variety of PET specimens by the diffractometric x-ray method and also by a method based upon an entirely different physical principle but which appears to be very direct—differential scanning calorimetry. Of the x-ray measurements, the formalized ranking of specimens between amorphous and crystalline standards, which does not involve a difficult and perhaps arbitrary division of a diffractogram into areas of crystalline and amorphous scatter, to produce an index rating analogous to the octane rating of hydrocarbons intuitively seems the more direct approach. Statton³ has adapted the integral and correlation indices of Wakelin et al.⁴ to the study of crystallinity in poly(ethylene terephthalate) by x-ray diffraction. Bosley⁵ has proposed a very simple two-point procedure for the same determination. Since all three x-ray index methods utilize the same data and thus differ only in method of calculation, all three indices will be compared among each other and also with an index based upon the heat of fusion for specimens of PET heated in different ways to produce a range of crystallinity values. The intrinsic viscosity and number-average molecular weight were also determined for selected specimens.

EXPERIMENTAL

Specimen Preparation

In an effort to obtain samples of differing crystallinity in order to ascertain the comparative behavior of the three x-ray crystallinity indices and an index based upon differential scanning calorimetric data, quenched melt PET, and commercial, 1-mil, biaxially oriented film were subjected to a series of constant temperature thermal vacuum treatments. Three series of tests were performed with the samples contained in open tubes (samples subjected to the 1 torr pressure, constant temperature, and continuous pumping environment of a vacuum oven) while another was performed with the samples contained in sealed ampules (vacuum oven used solely for isothermal treatment, sample plus unsealed ampule outgassed at 80°C. for 72 hr. and then the sample sealed in the ampule while the total pressure over the polymer was 10^{-6} torr). The test series are listed in Table I.

There were also experiments performed with random combinations of the conditions in an effort to produce the maximum crystallinity standards.

After the specimens were prepared by the isothermal treatments, they

TABLE I

Series no.	Material	Containment	Temperature, °C.	Time, hr.
S1	Quenched melt	Open tubes	80-245	72
S2	1-mil film	Open tubes	80-245	72
S3	1-mil film	Open tubes	200	0-304
S4	1-mil film	Sealed ampule	200	0-329

were ground to 60 mesh in a Wiley mill at Dry Ice temperature. This grinding was an attempt to produce randomly oriented specimens for the diffractometer and easily achieved similar masses for the calorimeter and solution property techniques. It was also used to produce a flat surface through packing in a flat sample holder, since the thermal treatments deformed the film into a nonplanar material.

X-Ray Diffractometry

After the thermal vacuum annealing and grinding, the 60-mesh powder was pressed into a flat sample holder and the intensity of the diffracted nickel-filtered copper radiation was recorded on paper tape (digital printer reading from a scaler) at every 0.3 degree (2θ) increment in the angular range from 10.0 to 34.0 degrees. The data used were the best three of five 10-sec. counts at each $2\theta_i$. All 81 points ($2\theta_i$: $i = 1, 2, \dots, 81$) were used for integral and correlation indices; however, only two points ($2\theta_i$: $i = 54, 63$) were used for the remaining index.

The attempt at producing randomly oriented specimens by grinding proved to be a failure. Evidently the 60-mesh powder of the ground 1-mil biaxially oriented film layered during compaction, necessitating separate maximum crystallinity standards for the quenched melt and 1-mil film experiments. This difference in standards was required only for the x-ray diffraction methods. The amorphous standard was quenched, melt-cast PET and the crystalline standard for films was a film specimen which had been heated at 200°C. for 160 hr. while enclosed in a sealed ampule. The crystalline standards for the quenched melt series were melt-cast specimens which had been heated in sealed ampules at 245°C. for 116 hr. for the correlation and two-point procedures and 72 hr. for the integral index. This latter time and temperature is in accord with Statton's recommendation.³

Differential Scanning Calorimetry

An adequate description of the theory and operation of a differential scanning calorimeter has been presented elsewhere.^{6,7} Sample weights were approximately 7.30 mg. and were obtained on an electrobalance to the nearest 0.01 mg. The fusion area of each thermogram was determined with a planimeter, and the arithmetic mean of the best two of three samples of each specimen was taken as the estimation of the crystallinity of a particular specimen. The maximum crystalline standard (greatest heat of fusion) for the entire series was a quenched melt specimen which had been heated at 225°C. for 72 hr. The amorphous standard was identical to the one used in the x-ray diffraction determinations. Values for the heat of fusion varied from essentially zero to 14.00 mecal./mg.

Solution Properties

Number-average molecular weight and intrinsic viscosity determinations were performed on certain specimens of 1-mil film from the series heated as a function of time at 200°C.; the specimens came from both the sealed

ampule and 1 torr, continuously pumped series. The solutions used were prepared by extracting 0.5 g. of polymer with 50 ml. of *o*-chlorophenol at 90°C. for 16 hr. All samples were completely soluble. Intrinsic viscosity determinations were made at 25°C. using Ubbelohde viscometers. Number-average molecular weights were measured at 37°C. with a dynamic osmometer with type 450 gel cellophane membranes.

METHOD OF INDICIAL CALCULATION

Three X-Ray Crystallinity Indices

In essence, the index procedure is a formal method of ranking specimens between experimentally determined maximum crystalline and minimum crystalline standards. The two-point procedure, although requiring judgement as to the choice of one point (at one angle, 2θ) representative of the crystalline scatter and one point representative of the amorphous scatter, is a true indicial procedure, since the unknowns are interpolated between a crystalline and an amorphous standard. Statton³ offers argument for the use of the term index for these ranking procedures.

In the integral index procedure the absolute intensity differences (at the programmed 2θ 's, with all data normalized for constant area) between the unknown sample and the amorphous standard, $(I_u - I_a)_i$, and those between the crystalline and amorphous standards $(I_c - I_a)_i$, are collected, the differences summed, and the ratio taken. The index is defined as

$$\frac{\sum_i^n (I_u - I_a)_i}{\sum_i^n (I_c - I_a)_i} \times 100 \quad n = 81$$

The correlation index procedure utilizes the same absolute differences, but this index is calculated by extracting the slope of the least-squares line to a plot of $(I_u - I_a)_i$ versus $(I_c - I_a)_i$. The index is 100 times m in the following least-squares line:

$$\widehat{(I_u - I_a)} = m(I_c - I_a) + b$$

On defining $(I_u - I_a)_i$ as y_i , $(I_c - I_a)_i$ as x_i , and denoting their arithmetic means as \bar{y} and \bar{x} , the integral index in essence amounts to

$$100(\bar{y}/\bar{x}) = 100(\bar{y} - 0)/(\bar{x} - 0) = 100m_I$$

or the slope of the line through (\bar{x}, \bar{y}) and $(0, 0)$ while the correlation index is

$$100 m_c = 100(\bar{y} - b)/(\bar{x} - 0)$$

or the slope of the line through (\bar{x}, \bar{y}) and $(0, b)$, the constant b being the least-squares determined y intercept. Since the two indices are thus identical if $b = 0$, the idea that the correlation index is to be preferred (more

precise) over the integral index and that the intercept b in the correlation method should be zero if the normalization is properly performed, as presented by Statton,³ does not fit the mathematics of the situation, in the sense that both ideas cannot be true.

The two-point procedure involves the measurement of a point, I_c , representative of the 100 diffraction peak (dominant feature of the diffractogram of PET) and of a point, I_a , representative of the amorphous halo.^{5,8} The ratio of the two, I_{cu}/I_{au} , is then interpolated between the two-point ratios of the crystalline and amorphous standards, the index being

$$\frac{(I_{cu}/I_{au}) - (I_{ca}/I_{aa})}{(I_{cc}/I_{ac}) - (I_{ca}/I_{aa})} \times 100$$

and, if the amorphous halos are constant, or almost constant, we have an index of the same general form as the other two, but based only upon the magnitude of the characteristic peak,

$$\frac{I_{cu} - I_{ca}}{I_{cc} - I_{ca}} \times 100$$

If the ratio of the arithmetic means of the differences, based upon many angular points, is thus the principle of the measurement, one can suppose that the utilization of fewer and fewer points will increase the standard deviation of the means but not degrade the position of the means, at least as long as there are sufficient points for the statistical ideas to hold. The comparative determinations of the three indices should show how well an intelligent choice of a representative peak can compensate for the "poor" statistics of the two-point method.

The DSC Crystallinity Index

The DSC index is again based upon the ranking of specimens between maximum crystalline and minimum crystalline experimentally determined standards. This method of ranking is dependent on the heat of fusion of the various thermally treated PET samples. The crystallinity index is given by

$$\frac{H_{fu} - H_{fa}}{H_{fc} - H_{fa}} \times 100$$

where H_{fu} , H_{fa} , and H_{fc} are the heats of fusion of the specimen, the amorphous standard, and the crystalline standard, respectively.

RESULTS AND DISCUSSION

The indicial data for the four series of tests are presented in Table II. Figures 1-4 are graphs of the data in Table II with the data points joined linearly in order to indicate (pointwise) in a clearer manner the relationship between the two experimental techniques and the various methods of calculating the diffractometric indices.

TABLE II. Values of the Crystallinity Indices

Series	Film and treatment	Time, hr.	Temperature, °C.	(M1) Integral index	(M2) Correlation index	(M3) Two-point index	(M4) DSC index
S1	Quenched melt	72	245	76.2	71.0	58.2	87.1
		72	225	90.2	57.4	32.2	100.0
	film, continuous pumping	72	200	75.1	55.1	43.7	84.5
		72	175	61.8	42.6	42.8	29.0
		72	150	60.9	46.9	41.6	23.8
		72	120	41.6	28.7	25.1	27.4
		72	100	36.5	24.0	22.6	14.5
		72	80	7.7	0.0	1.1	0.1
S2	1-mil film, continuous pumping	72	245	72.9	69.3	53.1	99.1
		72	225	77.6	67.7	50.4	90.0
		72	200	71.6	62.3	52.9	71.3
		72	175	63.0	49.1	37.5	57.4
		72	150	64.3	47.6	39.5	50.4
		72	120	51.8	36.0	29.1	45.8
		72	100	59.8	44.8	36.9	52.1
		72	80	59.8	43.0	34.6	46.3
S3	1-mil film, continuous pumping	304	200	64.8	53.8	40.0	72.6
		240	200	66.1	55.1	45.5	76.3
		144	200	59.9	46.2	39.8	70.8
		115	200	70.0	60.0	46.8	71.7
		100	200	68.4	57.5	46.7	80.5
		72	200	71.6	62.3	52.9	71.3
		64	200	66.3	55.6	45.0	70.3
		48	200	60.8	48.6	40.1	69.4
24	200	64.6	52.4	41.2	54.9		
S4	1-mil film, sealed ampule	329	200	81.0	78.7	72.9	77.7 ^a
		304	200	81.3	77.5	69.6	71.7 ^a
		260	200	96.7	97.1	94.9	78.9 ^a
		210	200	97.0	96.5	91.4	67.8 ^a
		160	200	100.0	100.0	100.0	62.4 ^a
		115	200	90.5	85.8	86.4	45.3 ^a
		60	200	92.5	90.9	85.2	37.7 ^a
		24	200	89.2	84.6	80.7	30.1 ^a
Other	Quenched melt, sealed ampule	72	245	100.0	91.8	74.9	
		116	245	98.6	100.0	100.0	
	Quenched melt, sealed ampule	115	245	84.4	69.3	44.9	
		72	245	67.4	68.4	65.1	
	1-mil film, sealed ampule	116	245	74.3	76.8	94.7	
		—	—	55.3	39.8	27.8	43.7

^a Assuming three fusion endotherms.

The data for the untreated film specimens (average of 5 determinations) are as follows: integral, 55.3; correlation, 39.8; two-point, 27.8; and DSC, 43.7.

For convenience, the four series are designated by S1, S2, S3, and S4, respectively, and M1, M2, M3, and M4 were the four methods within each set. (These are so designated on Table II.) With the aid of the analysis of variance for the "randomized block" design, along with a method by Scheffé,⁹ that makes individual comparisons of methods when differences are present, the following statistical conclusions were reached.

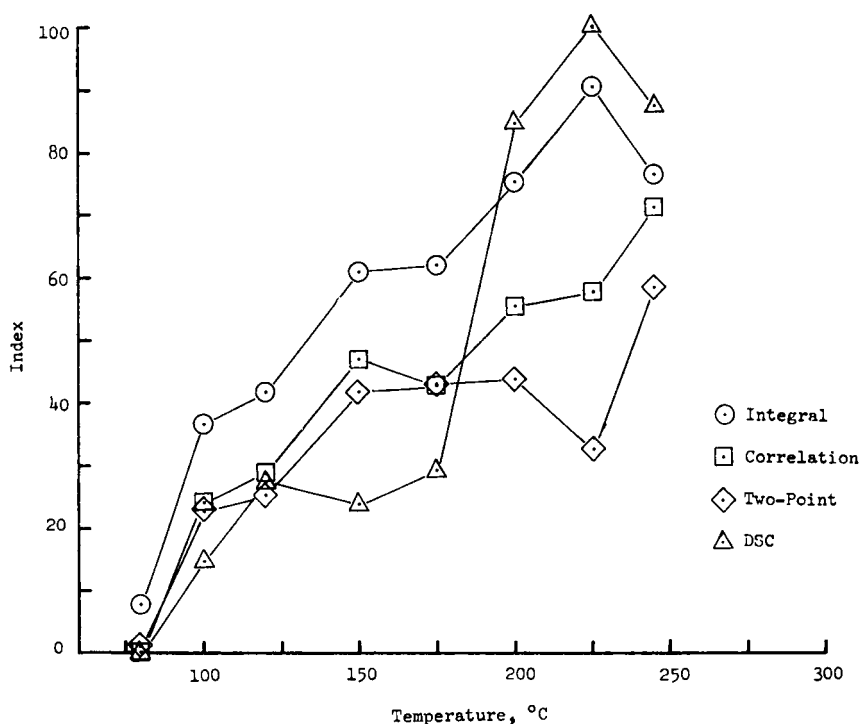


Fig. 1. Variation of crystallinity indices with temperature for quenched melt PET heated for 72 hr. with continuous pumping.

(1) For S1, at least one of the methods was significantly different from the rest; however, because the level of confidence was less than 0.99, no further inferences were made on the methods.

(2) For S2, with a very high degree of confidence (greater than 0.99), a significant difference was detected among the four methods. M1 and M4 are essentially the same, while M2 and M3 are alike but different from M1 and M4.

(3) In S3, M1 and M4 were alike and significantly different from M2 or M3. Furthermore, M2 was found to be different from M3. The confidence level was, again, higher than 0.99 for all conclusions in S3.

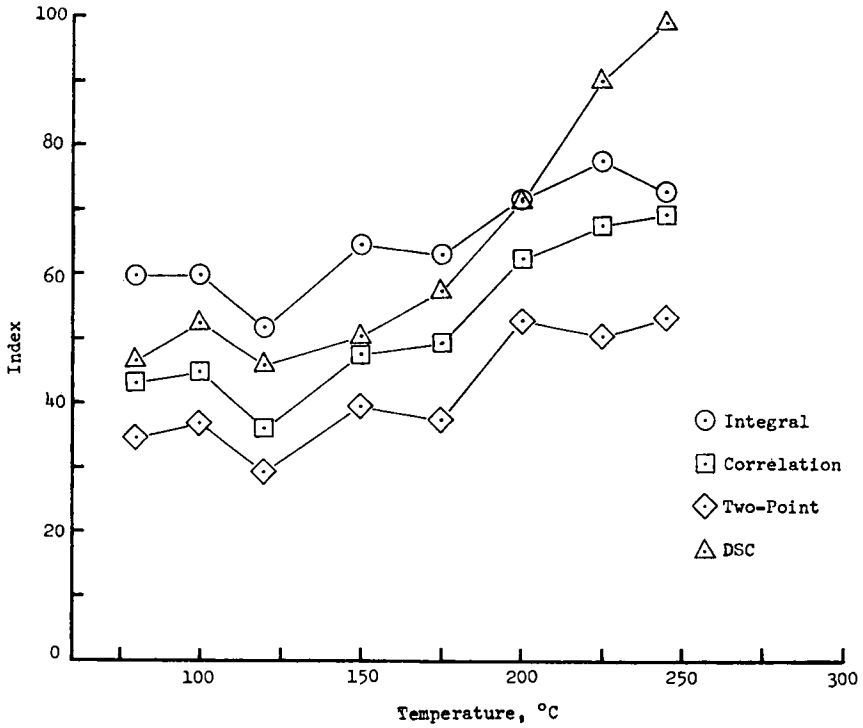


Fig. 2. Variation of crystallinity indices with temperature for 1-mil PET film heated for 72 hr. with continuous pumping.

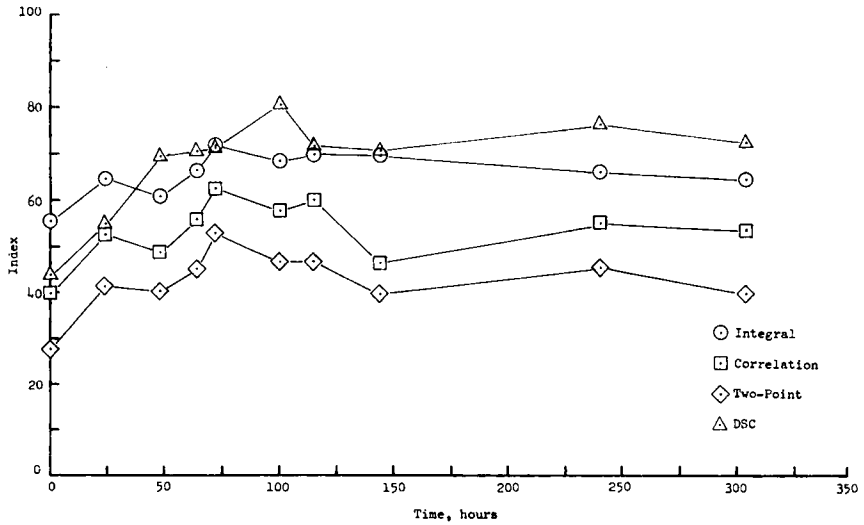


Fig. 3. Variation of crystallinity indices with time for 1-mil PET film heated at 200°C. with continuous pumping.

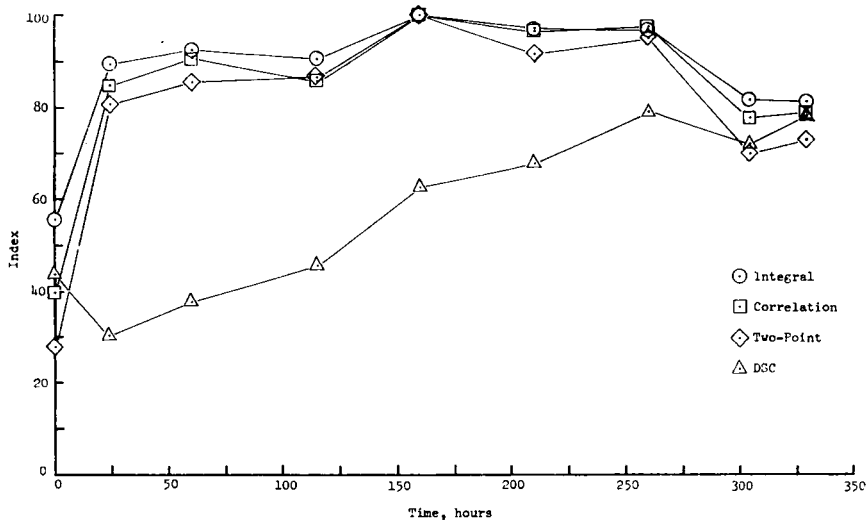


Fig. 4. Variation of crystallinity indices with time for 1-mil PET film heated at 200°C. in sealed ampules.

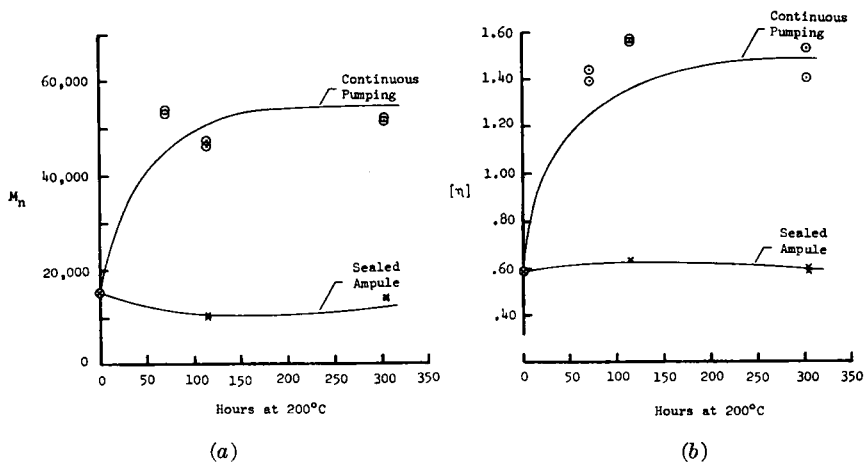


Fig. 5. Variation of (a) number-average molecular weight and (b) intrinsic viscosity of 1-mil PET with time at 200°C.

(4) In S4, no significant difference could be detected in methods M1, M2, and M3; however, they are highly different from M4 with a confidence level of higher than 0.99.

Although the assumption of normality is present, that is, the data are normally distributed, one can safely say that differences in methods do exist based on high confidence levels.

Post-Polymerization of PET Film

The number-average molecular weight and intrinsic viscosity were determined for selected specimens from experimental sets of commercial, 1-mil PET film which had been heat-treated in a vacuum oven at $200 \pm 1^\circ\text{C}$. for periods of time varying from 24 to 329 hr. One set (S3) of the specimens had been subjected to the 1 torr pressure and continuous pumping environment of the oven, while the other set (S4) was contained in sealed ampules and thus was in contact with its gaseous effluent during the heat-treatment sequence. Figures 5a and 5b present the results of the number-average molecular weight and the intrinsic viscosity determinations, respectively, the abscissae being the number of hours each specimen was maintained at 200°C . While the specimens of each series were heated in a substantially similar manner, the only difference being their manner of containment, the continuous pumped specimens tripled their number-average molecular weight, the M_n of the sealed ampule specimens remaining essentially the same. The intrinsic viscosity of the continuously pumped specimens increased from about 0.6 to 1.4 dl./g., the sealed ampule specimens remaining at about 0.6 dl./g.

Figure 6, which is a plot of the least-squares fits to the integral indices of the two data sets, shows that the sealed ampule specimens attained a crystallinity about 20% greater than the specimens subjected to continuous pumping. Also presented in Figure 6 are representative thermograms showing three possible fusion endotherms for the more crystalline, lower

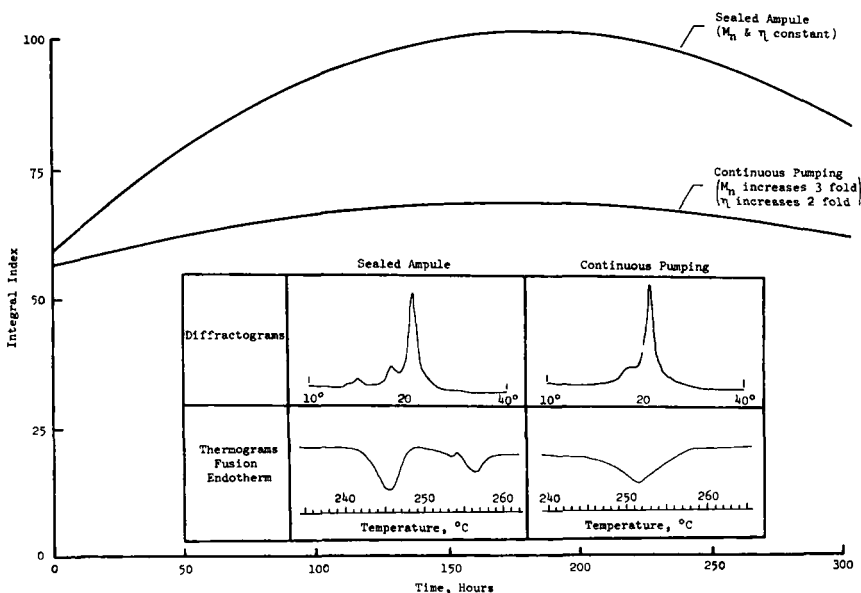


Fig. 6. Variation of integral index for two series of 1-mil PET film heated at 200°C . for various periods of time.

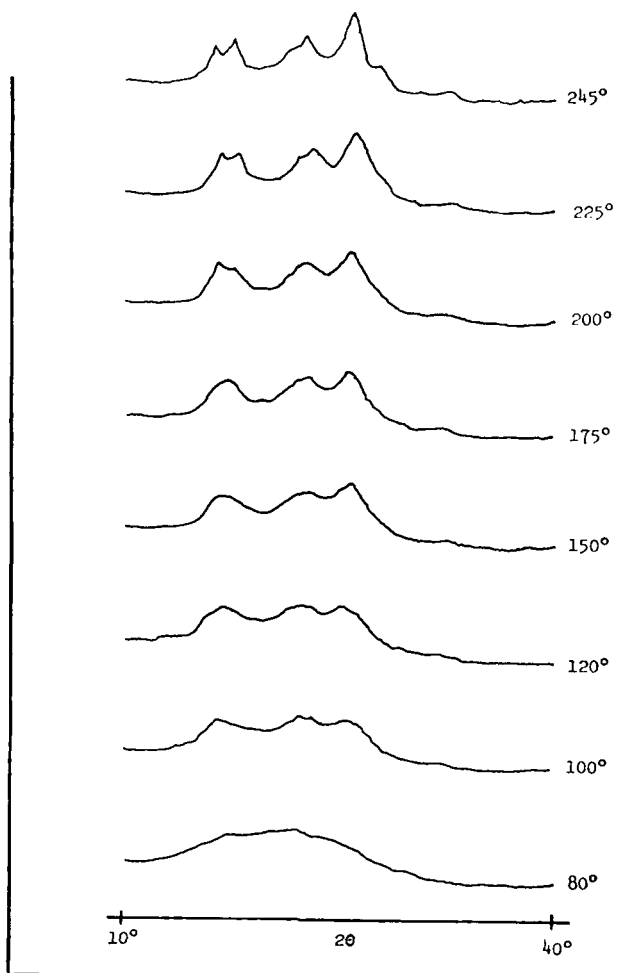


Fig. 7. Variation of diffractogram for quenched PET heated for 72 hr. at various temperatures.

molecular weight specimens and one fusion endotherm for the less crystalline, tripled molecular weight specimens. Completing this figure and continuing the display of the differential properties bound to the containment parameter, the diffractogram of a continuously pumped and that of a sealed ampule specimen are presented along with the thermograms. The feature to observe is the incidence of a pronounced diffraction peak in the 15–18° (2θ) region of the sealed ampule diffractogram. (Since this region is more sharply defined in the specimens treated at 245°C., 72 hr., these specimens were used in order to show the difference in a more obvious manner. The difference in this region of the diffractograms of the two series increases with time at 200°C. and is definite for longer duration specimens, but is of a more diffuse nature than those presented.) All secondary find-

ings presented within this section are consistent with the concept of a longer polymer chain being more liable to entanglement and thus undergoing less crystallization under a specific set of circumstances. The extra peaks in the diffractograms and thermograms also suggest the possibility of a new crystalline phase in the PET film.

There is a confusing aspect to the above, however. On examining the change of shape of the quenched melt diffractogram as a function of temperature (Fig. 7) one would notice the development of a very similar crystalline diffraction peak in the $15\text{--}18^\circ$ (2θ) region. Yet, the high temperature specimens (175°C. up) of this series were completely insoluble in *o*-chlorophenol (even at 90°C. for 72 hr.), and their thermograms did not display the three fusion endotherms. (These quenched melt specimens were also insoluble in 40% tetrachloroethane + 60% phenol.)

Interpretation of Thermograms

Figures 8 and 9 show the thermograms obtained for the four series of samples.

The quenched melt-cast PET sample experienced a glass transition and cold crystallization¹⁰ (Fig. 8). The present findings are in accord with Hughes and Sheldon's with respect to a secondary premelt crystallization.¹¹ The actual fusion area for the amorphous standard was obtained by subtracting the cold crystallization area from the sum of the areas pro-

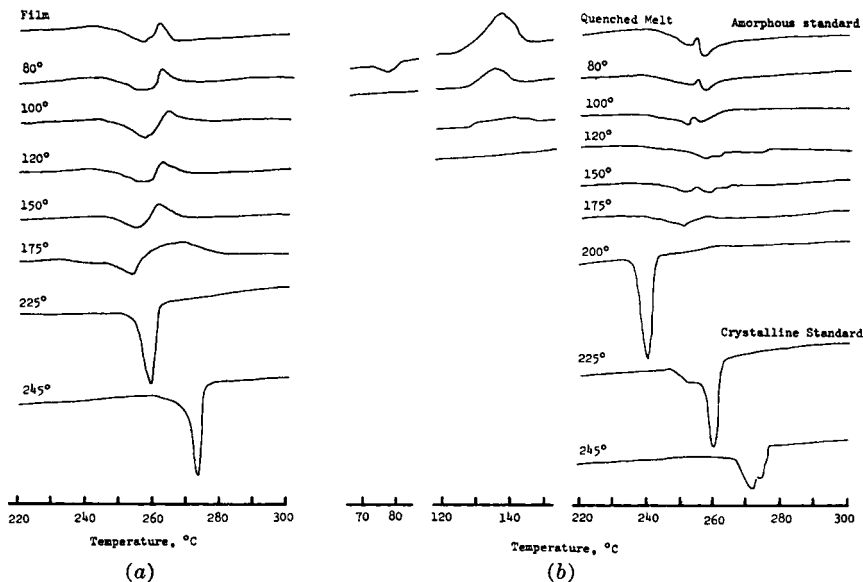


Fig. 8. Thermograms of PET: (a) fusion thermograms for film samples heated for 72 hr. with continuous pumping at the indicated temperatures; (b) thermograms showing glass transition, cold crystallization, and fusion for quenched melt samples heated for 72 hr. at the indicated temperatures.

duced by the glass transition and fusion. It was also necessary to subtract out the effect of cold crystallization for the quenched melt-cast samples heated at 80°C. for 72 hr. and 100°C. for 72 hr.

The nature of the thermograms for the film samples treated in sealed ampules, constant temperature, variable time (Fig. 9a) suggests three possible interpretations. This arises from the fact that the thermogram fusion curves exhibit more than one minimum point. The first possibility is to consider all the area to be one fusion (Fig. 10). The second is to consider two crystalline regions present in the polymer with a cold crystallization occurring between them (Fig. 10b). The third possibility, and the

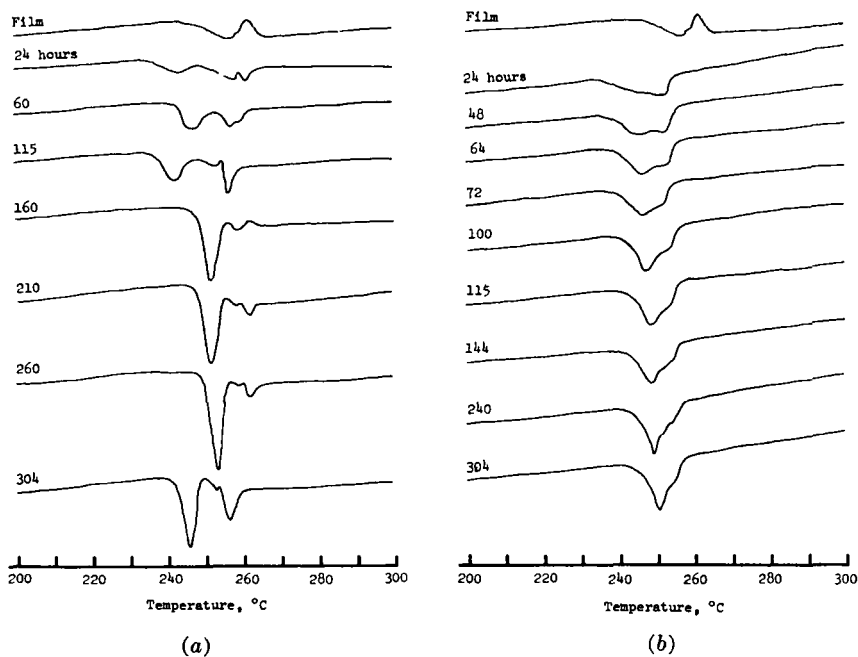


Fig. 9. Fusion thermograms for PET film samples heated at 200°C. for indicated time (hours): (a) sealed ampules; (b) continuous pumping.

interpretation used in the correlation of DSC and x-ray data, is the existence of three fusion endotherms (Fig. 10c). This appears to be supported by x-ray diffractograms as shown by Figure 6. The possibility of artifactual fusion endotherms is recognized for polyolefins;¹² however, the thermograms of Figures 9a and 9b were of samples produced four at a time, with random mixing between the two series, by insertion into cavities within a hot massive metal block mounted in the oven. The block would decrease several degrees in temperature immediately upon insertion of the samples and require several hours to return to the programmed temperature of 200°C. Multiple endotherms are thus possible, but these are observed only in the constant M_n situations.

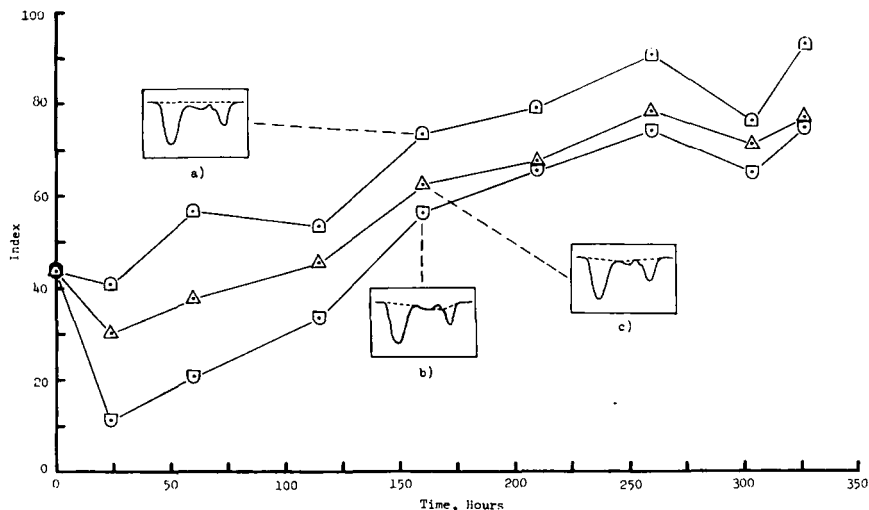


Fig. 10. Index values for sealed ampule samples depending on interpretation given thermograms.

The Three X-Ray Indices

While the integral index was conceived as involving a numerical integration of the difference between two diffraction curves,³ (a Simpson's or trapezoidal rule method would have been a better attempt at such a calculation, but as has been shown it is actually an average difference method), and the correlation index involves the determination of the slope of the best (least-squares) fit of 81 points, to a linear form, the two-point index involves only the slide rule calculation of a ratio. Even though Bosley⁵ offers rather convincing argument for his method, those who have used the far more arduous integral and correlation indices will perhaps doubt that such a simple system can provide meaningful determinations. However, while the chance for error in estimating the mean over the entire diffractogram by the measurement of one or two points in the angular range is high, the effect of averaging many points at d spacings which have little or nothing to do with the crystalline state of the polymer along with those relatively few points concerned with the crystalline phase is such as to muddle understanding of what is truly estimated by those methods based upon the average point (integral and correlation).

An idea of the pointwise variation of the methods can be obtained by reference to Figures 1-4. Figure 1, the data for the quenched melt at constant time and varying temperature, presented a rather confused relationship between the various methods, perhaps because the lack of orientation in this material allows more complicated interactions to occur. Figures 2 and 3, which show data for biaxially oriented film heated for constant time at various temperatures and heated at 200°C. for various times, present variations such that with proper calibration, it should be possible

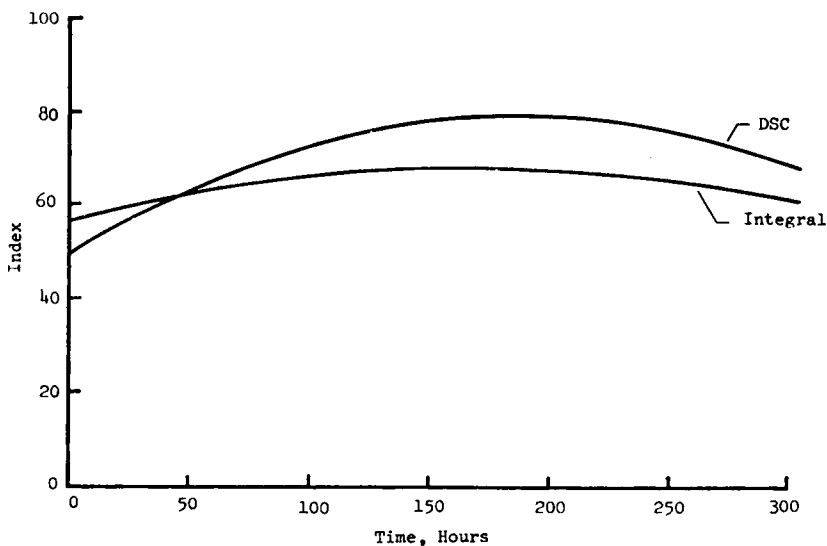
to infer either of the two indices which are based upon the mean point from the relatively simple two-point procedure by means of an additive constant. While the previous two situations represent conditions under which further polymerization can occur, Figure 4, representing a relatively constant M_n situation yields virtually the same indicial result for all three x-ray indices. In any event, for all four experimental situations the two-point index represents the crystallinity minimum of the x-ray index methods. Whatever the result of the x-ray methods means physically, these methods do allow for a ranking of specimens of different kinds as to the property of crystallinity, or, in other words, can answer the question, which sample is the more crystalline, but not perhaps the question of how crystalline.

X-Ray Diffractometry Versus Differential Scanning Calorimetry

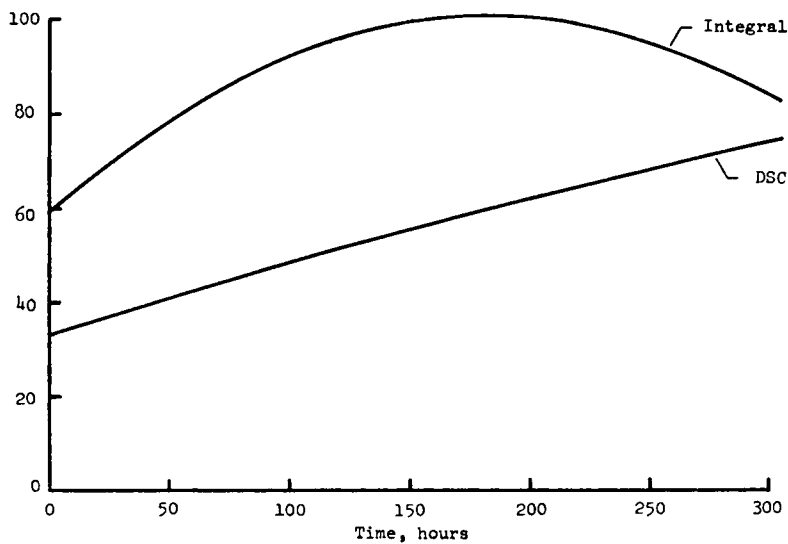
From the statistical analysis of the four data sets it has been shown that the differential scanning calorimetric index seems to be measuring the same population as the x-ray integral index for the two continuously pumped, film experiments (72 hr., varying temperature; and 200°C., varying time). It might also be mentioned that these were the two methods of determining crystallinity index which yield a maximum in the indicial curves between 200 and 245°C. for the quenched melt experiment. The existence of a maximum is consistent with the rough 8/9 T_m rule.¹³ However, as has been discussed, the three x-ray diffraction procedures yield substantially similar results for the film experiment in which the samples were contained in sealed ampules, while the DSC-based index continued increasing with time at 200°C., not reaching the magnitude of the x-ray-based determinations until after about 280 hr. of annealing (Figs. 11). Thus, the case in which the crystallization is unimpaired by further polymerization presents the problem of accounting for such a difference in methods, which yield similar results for other test series.

Initially (Fig. 11b) it can be said that there is orientation of the polymer chains with respect to the polymer surface (which is also the diffraction plane) such that x-ray method senses more order than is representative of the material on a volume basis. If it can be assumed that crystalline growth occurs predominately in the oriented crystalline regions, then this assumption would explain the increased differential with time between the crystallinity that is indicated by the measured x-ray scatter and the crystallinity on a volume basis. The diffraction plane rapidly becomes almost completely crystalline (based upon a film standard) while the bulk crystallinity increases at a rate indicated by the DSC curve. In any event, any incremental increase in order in the diffraction plane would affect the x-ray method more than DSC. After prolonged annealing, the two curves approach a common value, indicating achievement of the maximum crystalline state for oriented PET treated at 200°C. in a sealed ampule.

In a sense, the issue is confused by the fact that failure to achieve complete randomization of the powdered film necessitated the institution of separate x-ray indices for the oriented and unoriented PET and resulted



(a)



(b)

Fig. 11. Least-squares plots of integral and DSC indices for PET film heated at 200°C. for various times: (a) continuous pumping; (b) sealed ampule.

in the maximum crystallinity standard for the integral index for films being part of the above data set (S4) while the maximum for the DSC index (based upon all samples) was an annealed quenched melt specimen. Since the highest DSC specimen in this set is less than the DSC crystalline standard, there results a certain calibration between the x-ray film and quenched

melt data sets which in effect indicates that maximum crystallinity (in the absolute sense) cannot be achieved with oriented material. This leads to an observation that in some way orientation aids crystallization, but is, in a sense, a destructive phenomenon which denies the achievement of maximum crystallinity. This interpretation seems a synthesis of the observation of Statton³ that it is the preconceived notion of polymer workers that orientation aids crystallization and his finding that maximum crystallinity cannot be achieved with oriented material.

In addition to the uncertainty introduced into the x-ray indices, which are based upon the mean point, by adding the contribution from other than crystalline phases, there is uncertainty in the DSC index due to factors such as the implied assumption of negligible contribution from any configurational changes in the amorphous component, as discussed in a recent paper by Dole.¹⁴ Be that as it may, with the limitations of the various techniques recognized, measurements of crystallinity by different physical methods are of value in that grossly discordant determinations can point to material characteristics which may not be observed if only one type of measurement were performed. It is also conceivable that the different crystallinities, as determined by different techniques, may vary in their applicability to the various polymeric properties.

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Résumé

La cristallinité des différents échantillons de téréphtalate de polyéthylène (PET), produite par recuit thermique, a été mesurée au moyen de trois méthodes de détermination de l'indice, la diffractométrie aux rayons-X et par une méthode d'indice pour

l'enregistrement différentiel et des données calorimétriques. Les méthodes de mesures sont appelées des indices car elles impliquent diverses méthodes de classement des échantillons d'une manière relative entre des standards de cristallinités minima et maxima. Les valeurs statistiquement différentes des indices sont déterminées par de nombreuses méthodes physiques et procédés de calcul pour plusieurs types d'échantillons. Les méthodes de l'indice intégral qui utilisent les données diffractométriques aux rayons-X correspondent de manière la plus précise à l'indice calorimétrique et meilleure que les deux autres méthodes aux rayons-X pour lesquelles le film orienté est recuit dans un four sous vide et est sujet à pompage sous vide continu. Ce traitement produit également une augmentation triple du poids moléculaire en nombre du film de polyéthylène. Le recuit en ampoule scellée produit substantiellement les mêmes résultats pour les trois méthodes aux rayons-X mais différent pour les mesures calorimétriques, le poids moléculaire en nombre étant gardé constant. Un procédé à deux points relativement simple fournit virtuellement la même allure générale que les méthodes aux indices nettement plus compliquées.

Zusammenfassung

Die Kristallinität einer Vielfalt, durch thermische Temperung erzeugter Polyäthylenterephthalat-(PET)-proben wurde nach drei röntgendiffraktometrischen Indexmethoden und nach einer Indexmethode zur Differentialabtastung kalorimetrischer Daten bestimmt. Die Messverfahren werden als Indexmethoden bezeichnet, weil sie in verschiedener Weise eine relative Einordnung der Proben zwischen Standards mit Höchst- und Mindestkristallinität erlauben. Nach den verschiedenen physikalischen Methoden und Berechnungsverfahren werden für viele Proben typen statistisch verschiedenartige Indexwerte bestimmt. Die integrale Indexmethode auf Grundlage röntgendiffraktometrischer Daten entspricht für die Fälle, in welchen ein orientierter Film im Vakuumtrockenschrank unter kontinuierlichem Abpumpen getempert wird, enger dem kalorimetrischen Index als dem anderen beiden Röntgenmethoden. Diese Behandlung führt auch zu einer Zunahme des Zahlenmittelmolekulargewichts eines PET-Films auf das dreifache. Eine Temperung in abgeschmolzenen Gefäßen führt, bei konstantem M_n , bei allen drei Röntgenmethoden zum gleichen Ergebnis, jedoch zu abweichenden Ergebnissen beim kalorimetrischen Verfahren. Ein verhältnismäßig einfaches Zwei-Punkt-Verfahren liefert praktisch den gleichen Trend wie die komplizierteren Indexmethoden.

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