

Using the Essential Work of Fracture Method for Studying Physical Aging in Thin, Ductile, Polymeric Films

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Water-filled, drop impact tests on full-scale, blow-molding polyester bottles showed that impact properties change significantly after 30 days of aging at 50°C. To quantify this deleterious effect of aging, we did small-scale laboratory experiments using the essential work of fracture method (EWFm). We measured the essential work of fracture of thin specimens cut from the sides of blow-molded bottles and aged under various conditions. Similar to the impact results, significant drops in essential work occurred after relatively short amounts of aging. Additional experiments confirmed that the decreases in essential work were due to physical aging and not to chemical degradation. A comparison of the essential work results to the full-scale, bottle-drop impact tests showed some inconsistencies that need to be resolved before EWFm can be recommended as a quantitative method for studying physical aging of blow-molding polyester resins.

I. INTRODUCTION

Many types of blow-molding, plastic bottles are manufactured from polyester resins. Regardless of whether the resin has the potential for crystallization or not, the rapid cooling of the blow-molding process leads to an amorphous solid. The glass transitions of typical blow-molding, polyester bottle resins are in the range of 70 to 80°C. Because bottles are commonly stored in warehouses that might reach 50°C, there is a concern about the effects of physical aging on the mechanical properties of blow-molded bottles.

Full-scale, water-filled, drop impact tests on bottles from a series of polyester resins showed that impact properties can degrade significantly after only 30 days of aging at 50°C (1). Because these impact tests were on full-scale specimens, there is no question that aging is an important factor. Two problems with drop impact tests, however, are that they require much material (more than 25 bottles for each data point) and that they rely on qualitative data (break/no break observations). For an additional test method, this paper

describes use of the essential work of fracture method (EWFm) for monitoring aging in polymer resins. EWFm was originally developed by Cotterell and Reddel (2) to characterize the fracture of metals in plane-stress conditions. It was later extended to analyze the fracture of ductile polymers in plane-stress conditions (3-5) or plane-strain conditions (6). There is currently an international effort to develop EWFm as a standard method for characterizing the toughness of thin, ductile polymers (7). Our goal was to use EWFm to get quantitative results for aging of bottle resins with far less material than required for full-scale drop impact testing. These results could then potentially be used to screen and develop new resins. In the long range, more extensive results could be used to make predictions about bottle durability as a function of storage time and temperature.

II. MATERIALS AND METHODS

The DuPont Company provided five different types of copolyester resins in the form of cylindrical bottles, which were designated as resins X, A, B, C, and D

Table 1. The Bottle Resins Were All Copolyester Resins With Various Compositions and Types of Glycols and Diacids. The Trade Names for Resins X, A, B, C, and D Are Listed in This Table.

Resins	Trade Name*
X and A	Selar PT X290 polyester resin
B	Selar PT X279 polyester resin
C	Kodak PETG copolyester 6763 resin
D	Selar PT 7076 polyester resin

*Selar is a registered trademark of E. I. DuPont de Nemours and Company. Kodak is a registered trademark of Eastman Kodak Company.

(see Table 1). Resin X is identical to resin A except that the bottles were prepared in a different molding run. Resin C is an amorphous polymer. Resins X, A, B, and D are amorphous in bottles, but with proper conditioning may crystallize and become semicrystalline. Resins X and A, however, crystallize much less than resins B and D, and are therefore predominantly amorphous. Full-scale bottles molded from each of these resins have been subjected to water-filled drop impact tests (1). The drop impact tests were conducted as follows. A bottle made from resin X, A, B, C, or D was filled with water and dropped from some initial height, in feet, at room temperature. If the bottle did

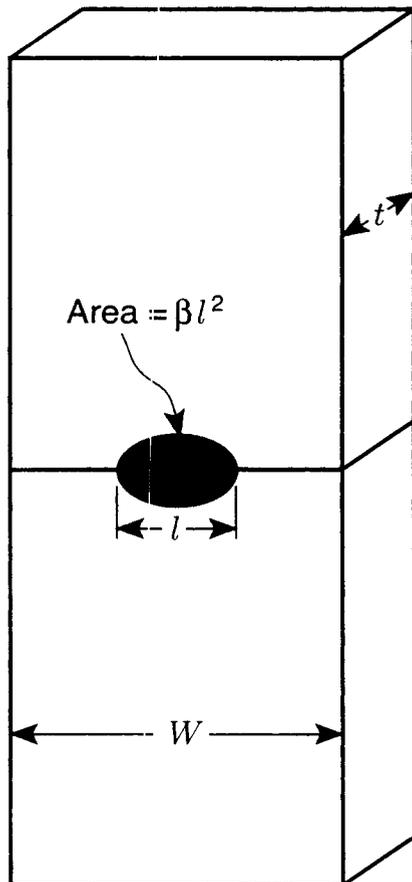


Fig. 1. Specimen geometry for deeply, double-edge notched tensile (DDENT) specimens. The specimen width is W and thickness is t . The ligament length is l .

not break at that height, the next bottle would be dropped at a height 15.24 cm (0.5 ft) higher than the previous height. Alternately, if the bottle broke at that height, the next bottle would be dropped at a height 15.24 cm lower than the previous height. Twenty-five bottles for each resin were dropped to obtain reliable data. The minimum height, at which all bottles did not break; the maximum height, at which at least one bottle passed the test; and the average height, predicting the height at which 50% of the bottles will break were recorded. The same experiment was repeated for additional bottles kept at 50°C for 60 days. These experiments monitored the changes of the properties of the bottle resins due to aging, at temperatures below the glass transition temperature.

Monitoring the effect of aging using small-scale laboratory tests was done using EWFM. In EWFM specimens, the crack tip region or yield zone is divided into two parts—an end region, where the crack initiation process takes place, and an outer region, where plastic deformation accommodates the larger strain. The total work of fracture, W_{total} , can be considered as the sum of work that goes into the end region, which is referred to as W_e , and work that goes into the outer region, which is labeled as W_p . Thus,

$$W_{total} = W_e + W_p$$

Consider a deeply double edge notched tension (DDENT) specimen of a ductile polymer as shown in Fig. 1. It is assumed that W_e is proportional to the ligament area and W_p is proportional to yield-zone volume (6). The total work becomes

$$W_{total} = w_e l t + w_p V_p \quad (1)$$

where l is ligament length, t is the sample thickness, V_p is yield zone volume, w_e is the essential work per unit ligament area, and w_p is the nonessential work per unit volume. When plane-stress conditions apply for all ligament lengths, it is further assumed that w_e is constant and V_p is proportional to $l^2 t$ (6). The specific work of fracture, i.e., $W_{total}/l t$, becomes

$$\frac{W_{total}}{l t} = w_{specific} = w_e + \beta w_p l \quad (2)$$

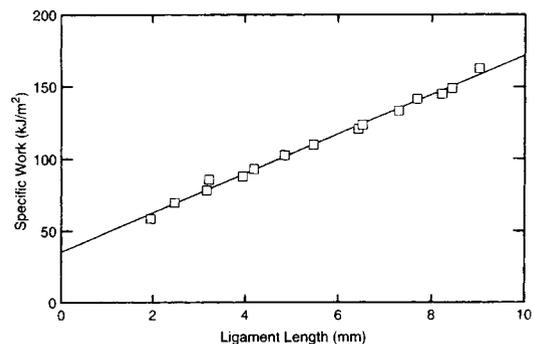


Fig. 2. Typical experimental results for measuring the essential work of fracture. The plot is specific work as a function of ligament length. The intercept of the best linear fit at zero ligament length is the essential work of fracture, w_e .

where β is a proportionality constant or shape factor associated with the yield zone volume. The plane-stress w_e may thus be determined from a plot of w_{specific} vs. l . Typical experimental results are shown in Fig. 2. The intercept of a linear fit to w_{specific} vs. l is w_e ; the slope is βw_p . Besides DDENT, a variety of sample geometries such as deeply center-notched tension specimens (DCNT), deeply single edge-notched tension specimens (DSEN), and modified double edge-notched tension specimens (MDENT), have been developed for specific material tests (8).

The sample geometry restrictions to ensure plane-stress conditions are empirically recommended to be (6)

$$(3t-5l) < l < \min(W/3, 2r_p) \quad (3)$$

where r_p is the radius of the plastic zone at the crack tip and $\min(W/3, 2r_p)$ implies the minimum of the enclosed quantities. The thickness restriction ($l > 3t-5l$) is used to avoid the plane-strain/plane-stress transition region at short ligament length where Eq 2 cannot be applied since both w_e and w_p may depend on the stress state (6). The width restriction ($l > W/3$) is used to confine plastic deformation to the ligament area thereby preventing the deformation from extending to the lateral boundaries of the specimen. The final restriction ($l < 2r_p$) is used to ensure complete yielding of the ligament before crack growth so that the plastic zone size, V_p , is controlled by the ligament length.

Our EWFM specimens were cut from sides of cylindrical bottles. Each 80 cm diameter bottle was cut into ten pieces. The specimens were 150 mm long (6 inches) and oriented parallel to the axis of the bottle. The specimens were 25 mm wide (1 inch). The notches were cut perpendicular to the long axis of the specimens and thus perpendicular to the axis of the bottles. The specimen thicknesses varied from bottle to bottle between 0.3 to 0.6 mm. A single EWFM experiment required 15 to 20 specimens and thus needed only two bottles.

Aging was done in ovens at 50°C or 65°C with specimens either in a dry environment or immersed in water. After removal from the oven, specimens were kept dry until testing. Samples with zero days of aging, or in other words no aging, were kept in a dry environment at 22°C until testing.

All bottle specimens had been at room temperature from a few days to about a month prior to testing. There was thus a possibility of room-temperature aging effects in addition to the high-temperature aging. We assumed, however, that the aging at room temperature was slow enough that it could be ignored relative to the aging times at elevated temperature. We did not have the option of erasing room-temperature aging by heating above T_g and cooling because that process would change the structure of the bottles. We wanted to study the aging of "as-molded" bottles.

DDENT specimens (see Fig. 1) were prepared using a knife with special care being taken to ensure that the notch tips were perfectly aligned. The ligament

length, l , was chosen to be within the upper and lower bounds defined by Eq 3. Ligament lengths were measured using a traveling microscope after the samples were fractured. A higher accuracy in the measurement of the ligament length was possible by this procedure because the fractured ligament surface whitened and could easily be observed and measured. Measuring the ligament length before fracture gave erroneous results because the crack tips partially closed after the blade was extracted. Errors in ligament length measurement will lead to errors in the calculation of specific work. The problem is most severe for small ligament lengths where the error induced can be high.

The measurements for W_{total} and σ_y were done on a 25 kN MTS servohydraulic testing system. The sample was held between two wedge grips and loaded at a constant displacement rate of 0.01 mm per second. Load and displacement data were recorded using custom IBM PC software interfaced to an MTS 464 data display device. The peak load in the load-displacement plot divided by the initial ligament length was taken as the yield stress, σ_y . The area under the load-displacement curve represents the total work of fracture, W_{total} , for a given ligament length.

Measurement of the glass transition temperature, T_g , and crystallization temperature, T_c , of samples with different periods of aging was carried out using a Perkin-Elmer DSC-2 differential scanning calorimeter. Aged specimens were cooled to room temperature, transferred to the DSC machine, and heated to above 200°C at 20°C per minute. The crystalline temperature is the peak of the crystallization exotherm that occurred between T_g and the melting point.

The densities of the specimens with varying periods of aging were measured using a density column. A standard density column was set up according to the guidelines of ASTM-1505-85, Method C (9). A water-calcium nitrate system was used to cover the density range of 1.27 g/ml to 1.35 g/ml.

III. RESULTS AND DISCUSSION

Aging at 50°C

A series of X, A, B, C, and D specimens were placed in an oven at 50°C. After 0, 30, 45, and 60 days of aging, we measured the essential work of fracture (w_e), the nonessential work of fracture (w_p), the glass-transition temperature (T_g), crystallization temperature (T_c), the tensile yield strength (σ_y), and the density (ρ). The results for w_e , T_g , T_c , and σ_y are given in Tables 2 to 4. T_c was clearly defined only for semicrystalline resins B and D. Resins X and A showed a much broader and smaller crystallization exotherm than did resins B and D. Resins X and A will be considered as only slightly crystalline or rather mostly amorphous. As a result, the T_c 's for resins X and A are not reported. The w_p results are not listed because they did not show any identifiable trends. The results for ρ are not listed because there were no resolvable changes in density due to any aging conditions.

A plot of w_e vs. time for resins A, B, C, and D for aging at 50°C is given in Fig. 3. A decrease in w_e and for all samples after aging is apparent. Most of the changes in w_e occurred during the first 30 days of aging. The decrease of w_e for resins B and D was about 50%, which is almost four times the percentage decrease observed for resins A and C. This result was probably caused by the different chemical structure of

the bottle resins. Resins B and D are semicrystalline polymers and resins X, A, and C are mostly or totally amorphous polymers. Because all bottles were quenched to an amorphous state during manufacturing, resins B and D might be farther from the equilibrium state than the resins X, A, and C. Thus, aging proceeds faster and more dramatically in resins B or D than in resins X, A, and C. Resins B and D, however, were ini-

Table 2. The Essential Work of Fracture, w_e (in kJ/m²) for Resins X, A, B, C, and D as a Function of Aging Time at 50°C or 65°C. Some Results for Resin X Were Also Done for Aging at 50°C While Immersed in Water.

Time (days)	Temp. (°C)	Environment	X kJ/m ²	A kJ/m ²	B kJ/m ²	C kJ/m ²	D kJ/m ²
0	—	—	17.92	17.11	35.43	26.25	29.90
30	50	air	15.37	16.07	17.11	21.80	15.52
30	50	water	12.99	—	—	—	—
45	50	air	—	17.05	16.72	20.12	17.55
60	50	air	14.03	14.74	21.16	19.82	22.63
60	50	water	15.58	—	—	—	—
1	65	air	—	21.92	26.25	24.16	26.80
7	65	air	—	20.76	28.82	23.24	24.06
14	65	air	—	21.40	25.42	24.32	25.68
28	65	air	—	21.22	24.88	21.67	23.96

Table 3. The Glass-Transition Temperature, T_g (in °C) and Crystalline Temperature, T_c (in °C) for Resins X, A, B, C, and D. The T_c Which Are Listed in Parentheses, Were Obtained Only for Resins B and D.

Time (days)	Temp. (°C)	Environment	X	A	B	C	D
0	—	—	72	72	73 (146)	78	72 (144)
30	50	air	79	80	79 (145)	81	80 (143)
30	50	water	80	—	—	—	—
45	50	air	—	82	81 (146)	82	82 (143)
60	50	air	80	82	82 (145)	84	82 (142)
60	50	water	80	—	—	—	—
1	65	air	—	79	79 (146)	81	80 (145)
7	65	air	—	80	81 (145)	84	80 (144)
14	65	air	—	81	81 (146)	83	83 (143)
28	65	air	—	82.76	81 (148)	85	83 (146)

Table 4. The Results for Yield Stress, σ_y (in MPa) for Resins X, A, B, C, and D as a Function of Aging Time at 50°C or 65°C. Some Results for Resin X Were Also Done for Aging at 50°C While Immersed in Water.

Time (days)	Temp. (°C)	Environment	X	A	B	C	D
0	—	—	50.16	46.50	51.12	42.84	50.21
30	50	air	55.29	55.69	58.95	51.92	56.76
30	50	water	56.27	—	—	—	—
45	50	air	—	55.99	57.82	52.74	57.99
60	50	air	56.74	57.11	59.93	53.63	59.04
60	50	water	59.70	—	—	—	—
1	65	air	—	57.03	59.39	52.75	59.21
7	65	air	—	59.21	60.41	53.96	59.88
14	65	air	—	59.39	61.00	55.21	60.53
28	65	air	—	59.07	61.56	55.20	61.41

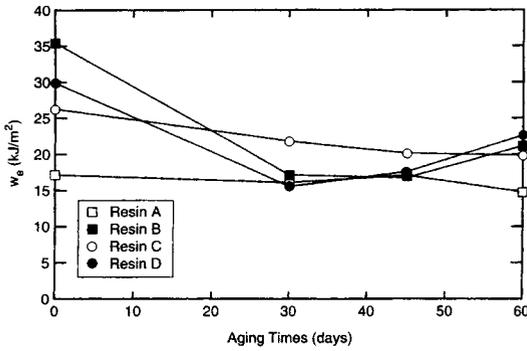


Fig. 3. The essential work of fracture, w_e , for resins A, B, C, and D as a function of aging time at 50°C. The solid symbols are semicrystalline resins (B and D). The open symbols are mostly amorphous or amorphous resins (A and C).

tially tougher than resins X, A, and C. Although they showed more dramatic aging effects their toughness only decreased to a level comparable to that of resins X, A, and C after aging. There was even a hint that resins B and D increased in toughness after longer aging times.

Bottle resins are typically used as liquid containers. To check for any possible influence caused by aging in the presence of a liquid, particularly water, we did additional aging experiments with specimens immersed in water. Samples of resin X, which has the same chemical structure as resin A, were immersed in water and subjected to identical aging treatments. After aging they were exposed to open air for about 2 hours before testing. The w_e , T_g , and σ_y results of the tests are given in the Tables 2 to 4. No significant differences in the changes in w_e and T_g were observed between samples aged in dry air or in water. These results indicate that the effect of water on aging of these polyester-copolymer resins can be neglected. Thus, all other results were done using aging in air.

As seen in Tables 3 and 4, T_g and σ_y increased for all samples after aging. The increases in T_g and σ_y were similar for all resins and thus cannot be used to distinguish among the various resins. These changes were about an 8°C increase in T_g and 16% increase in σ_y . Similar to w_e , most of the changes in T_g and σ_y occurred during the first 30 days of aging; the changes after 45 and 60 days of aging were much smaller than the changes in the first 30 days of aging. There was no decrease in T_g or σ_y for resins B and D at longer aging times that might correspond to the previously mentioned increase in w_e .

Aging at 65°C

The physical aging process occurs faster at higher temperatures. The effect of aging temperature was investigated by doing additional tests after aging at a temperature closer to the polymer T_g , i.e., 65°C. Similar to the 50°C aging experiments, a series of specimens were placed in an oven at 65°C. After 1, 7, 14, and 28 days of aging, we measured w_e , w_p , T_g , T_c ,

σ_y , and ρ . Experimental results obtained for w_e , T_g and σ_y for resins A, B, C, and D are listed in Tables 2 to 4. The time dependencies of w_e are plotted in Fig. 4. All results are similar to aging at 50°C except that the changes occurred faster. In Fig. 4, resins B, C, and D aged for only 1 day had an obvious decrease in w_e and an increase in T_g and σ_y compared with non-aged samples. The decrease of w_e for samples B and D was about 20% and was about 8% for resin C. The probable reasons for the larger change in semicrystalline polymers B and D are the same as were discussed for aging at 50°C. The increases in T_g and σ_y for samples aged one day were 6°C and 20%, respectively. Further aging beyond one day did not alter w_e , T_g , or σ_y significantly. All resolvable changes in w_e , T_g , and σ_y thus occurred within one day. In contrast to the 50°C results, there was no increase in w_e for resins B and D at long aging times.

An anomalous result occurred for resin A. Instead of decreasing, w_e increased after one day of aging and thereafter remained constant. This unusual result was the only resin to show an increase in w_e at the onset of aging. Because this increase was not matched by a physically similar decrease in T_g and σ_y , we suggest the increase may not be real.

The aging time needed to cause changes in w_e , T_g , and σ_y of samples aged at 65°C (only one day) was less than what was needed to show similar changes at 50°C (30 days or possibly less). A question arises about how much faster aging proceeds at 65°C than at 50°C. According to Struik (10), relaxation time is an important factor determining the rate of physical aging. To predict the relaxation time of polymers at various aging temperatures below T_g , he started with a first order isothermal volume relaxation equation given as (10)

$$\frac{dV_f}{dt_a} = \frac{V_{f\infty} - V_f}{\tau(T, V_f)} \quad (4)$$

where V_f is the free volume at a given instant at temperature T , $V_{f\infty}$ is the free volume at temperature T after reaching equilibrium, t_a is the aging time (here

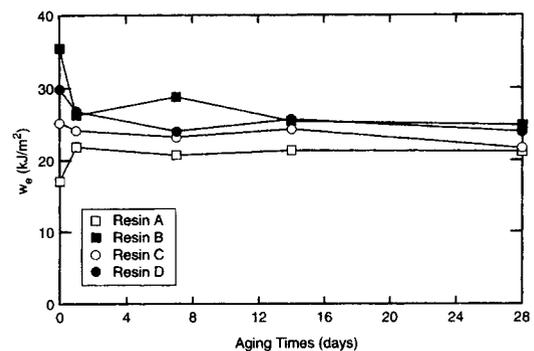


Fig. 4. The essential work of fracture, w_e , for resins A, B, C, and D as a function of aging time at 65°C. The solid symbols are semicrystalline resins (B and D). The open symbols are mostly amorphous or amorphous resins (A and C).

assumed to be time at 50°C or 65°C), and τ , which is a function of T and V_f , is the relaxation time at the instant of interest.

The variation of τ with V_f is assumed to be described by the following equation

$$\ln \frac{\tau}{\tau_\infty} = c(V_{f_\infty} - V_f) \quad (5)$$

where c is a constant and τ_∞ is τ at equilibrium. Rewriting Eq 5 as

$$V_f = \frac{1}{c} \cdot \ln \frac{\tau_\infty}{\tau} + V_{f_\infty} \quad (6)$$

and inserting into Eq 4, Struik obtained

$$\frac{d \ln \left(\frac{\tau_\infty}{\tau} \right)}{dt_a} = \frac{\tau_\infty}{\tau} \cdot \ln \frac{\tau}{\tau_\infty} \quad (7)$$

Solving this differential equation using several approximations for aging sufficiently far below T_g , Struik derived

$$\frac{\tau}{\tau_a} \approx \left[0.77(T_g - T) - \ln \frac{\tau_a}{100} \right] \quad (8)$$

where τ at T_g has arbitrarily been taken as 100 seconds. Equation 8 predicts that τ is a linear function of temperature at constant t_a .

From Table 3, the T_g of the resins A, B, C, and D before aging was about 74°C and after aging was about 82°C. If Eq 8 can be applied for aging at 50°C and 65°C, the ratios of relaxation times at 50°C and at 65°C before and after aging are about $\tau_{50}/\tau_{65} = 1.77$ before aging and $\tau_{50}/\tau_{65} = 3.93$ after. The prediction is that aging proceeds at 65°C about 2 to 4 times faster than at 50°C. Unfortunately, we do not have enough data to precisely determine the relative aging times. Because the first data point at 50°C was only after aging for 30 days and most aging had occurred within those 30 days, all we know is that τ_{50} is less than 30 days. Similarly, all we know about aging at 65°C is that τ_{65} is less than one day. These results are not inconsistent with the predictions from Struik, but we would need more data at early aging times to determine the accuracy of the prediction.

Evidence of Physical Aging

Physical aging is distinct from chemical aging or degradation because it does not involve any change in the chemical structure of the polymer. We have assumed that our experiments observed effects of physical aging. It is important to verify this assumption; we cite three results that support it.

One method to look for changes in chemical structure is to look for changes in molecular weight before and after the aging treatment. Because molecular weight is directly related to solution viscosity, we looked for changes in solution viscosity. Solution viscosity experiments were done on resins A and C in

phenol solutions. The relative viscosities for three different concentrations of resins A and C both before and after aging for 60 days at 50°C were obtained by using a two-tube viscometer and repeated three times. The ratio of the relative viscosities before and after aging were all 1.000 ± 0.003 . These results imply that the molecular weight, which is correlated with viscosity, does not change during the aging treatment.

A decrease in molecular weight normally causes T_g and σ_y to either decrease or remain unchanged but never to increase. All aging experiments, however, caused both T_g and σ_y to increase (see Tables 3 and 4). The T_g and σ_y results are thus consistent with there being no loss in molecular weight during the aging process.

Typical DSC results for T_g , tracing the thermal history of resin A samples with different aging periods during heating, are shown in Fig. 5. It can be observed that samples with aging treatments have a DSC peak near T_g . The height and position of this peak increased with longer aging times. Similar DSC peaks have been identified in the literature (11, 12) as a consequence of physical aging before reheating. They are a kinetic effect that arises from changes in the relaxation time of the aged glass. Such an effect is purely physical and not associated with chemical degradation. The effect is accentuated by rapid cooling (bottle molding) followed by slow heating (our DSC experiments) after aging (11, 12).

In summary, the lack of changes in solution viscosity, the increases in T_g and σ_y , and the peaks in the DSC plots all suggest that the changes in mechanical and physical properties of these copolyester bottle resins were caused by physical aging and not by chemical degradation.

Drop Impact Test Results

Besides the EWFm experiments, resins X, A, B, C, and D were tested in full-scale, water-filled, drop impact tests (1). The results for no aging and after aging for 60 days at 50°C are given in Table 5. The impact resistance is characterized here using the average height to cause bottle failure.

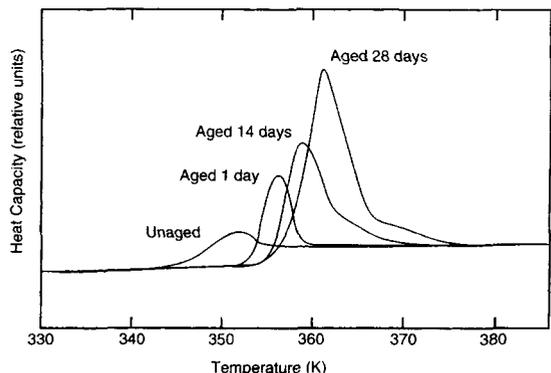


Fig. 5. Differential scanning calorimetry results (DSC) for resin A as a function of aging time at 65°C.

Table 5. Results of Bottle-Drop Impact Tests and the Essential Work of Fracture Tests for Resins X, A, B, C, and D Before and After Aging at 50°C.

Resins	Condition (days)	The Avg. Height (m)	Change in Avg. Height	w_e (kJ/m ²)	Change in w_e
X	0 at 22°C	1.74 (5.7 ft)	—	17.92	—
	30 at 50°C	0.61 (2.0 ft)	-64.91%	15.37	-14.23%
	60 at 50°C	0.49 (1.6 ft)	-71.93%	14.03	-21.71%
A	0 at 22°C	1.83 (6.0 ft)	—	17.11	—
	60 at 50°C	0.67 (2.2 ft)	-63.35%	14.74	-13.85%
B	0 at 22°C	1.07 (3.5 ft)	—	35.43	—
	60 at 50°C	0.49 (1.6 ft)	-54.29%	21.16	-40.27%
C	0 at 22°C	1.58 (5.2 ft)	—	26.25	—
	60 at 50°C	0.73 (2.4 ft)	-53.85%	19.80	-24.57%
D	0 at 22°C	0.98 (3.2 ft)	—	29.90	—
	60 at 50°C	0.46 (1.5 ft)	-53.13%	22.63	-24.31%

Note: Changes in the average impact height and w_e on resins X, A, B, C, and D after aging at 50°C in dry air were normalized by dividing by their unaged value.

Because both w_e and impact height are measures of material toughness, it is appropriate to compare them. Prior to aging, the impact results rank in the resin order AXCBD; after aging, the resin rank changes to CAXBD. The impact results thus always rank the mostly amorphous or amorphous resins (X, A, and C) higher than the semicrystalline resins (B and D). The w_e rankings are different. Before aging, the w_e results rank in the resin order BDCXA; after aging the resin rank changes to DBCXA. In contrast to the impact results, the w_e results always rank the semicrystalline resins (B and D) higher than the mostly amorphous resins (X, A, and C).

To visualize the correlation between w_e and impact height, we plotted w_e vs. the average impact height for polymers before and after aging at 50°C. The plot is shown in Fig. 6. The semicrystalline and the mostly amorphous or amorphous polymers segregate into two different regions. Thus, within a single resin type, there is a reasonable correlation between w_e and im-

pect height. But for different resin types, w_e cannot be used to predict bottle-drop results. More work is needed before we can speculate on why the correlation depends on the resin type. Some possible reasons are testing rate (impact rates in drop tests vs. slow static testing rates in EWFM test), specimen geometry (bottles vs. tensile coupons), dynamic liquid effects (filled bottles vs. tensile coupons), or inadequacy of the EWFM method. Although it is possible that w_e is not a valid measure of toughness, the fact that we observed consistent aging effects in w_e and that w_e correlates with impact results within a single resin type suggests that the EWFM method has potential.

IV. CONCLUSIONS

The EWFM method was successful in monitoring effects of aging on fracture toughness. EWFM is a very sensitive technique. The percentage changes in w_e were larger than the percentage changes in T_g , σ_y , and ρ . Furthermore, changes in w_e reveal differences between resins that were not apparent from the other properties. If those differences can be better related to real-world performance, EWFM will be a valuable tool for selecting bottle resins. From a comparison of the results of the bottle-drop tests and the EWFM results, however, it is concluded that the inconsistencies between these two tests need to be resolved before EWFM can be recommended as a quantitative method for studying physical aging.

Because EWFM uses less material than full-scale testing methods, there is thus the potential for larger scale testing that could lead to methods for predicting the temperature dependence of the aging process. One could envision monitoring w_e as a function of aging time and attempting to use time-temperature-superposition (12) to construct a master curve for aging at some reference temperature for any amount of time. If time-temperature superposition can be used to follow large-strain properties like fracture toughness, the results could be used to predict the durability of bottles at any storage temperature.

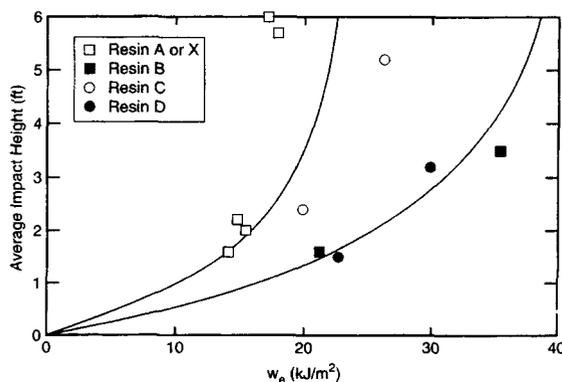


Fig. 6. A cross-plot of the average impact height in drop impact tests as a function of essential work of fracture, w_e , for resin X, A, B, C, and D. Each point corresponds to two experiments on samples that were unaged or exposed to identical aging treatments at 50°C. The solid symbols are semicrystalline resins (B and D). The open symbols are mostly amorphous or amorphous resins (X, A, and C).

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NOMENCLATURE

c	a constant.
l	ligament length of a DDENT sample.
r_p	radius of the plastic zone at the crack tip.
T	temperature.
T_g	glass-transition temperature.
T_c	crystallization temperature.
t	thickness of a DDENT sample.
t_a	aging time.
V_f	free volume at a given instant.
$V_{f\infty}$	free volume at temperature T after reaching equilibrium.
W	width of a DDENT sample.
W_{total}	total work of fracture in the EWFM analysis.
W_e	work of fracture that goes into the end region at the crack tip in the EWFM analysis.
W_p	work that goes into the outer region at the crack tip in the EWFM analysis.
w_e	essential work per unit ligament area.
w_p	nonessential work per unit yield zone volume.

Greek Symbols

β	a proportionality constant or shape factor associated with the yield zone volume.
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σ_y	tensile yield strength.
ρ	density.
τ	relaxation time at a given instant.
τ_∞	relaxation time at equilibrium.
τ_{50} and τ_{65}	relaxation times at 50°C and 65°C, respectively.

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