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-molded polyester bottles showed that the impact properties change dramatically after about 30 days of aging at realistic storage temperatures. We used the essential work of fracture technique to study the effect of physical aging on the fracture toughness of thin specimens cut from the sides of blow-molded bottles. Significant drops in toughness were found to occur after relatively short amounts of aging. Additional experiments confirmed that the drop in toughness was due to physical aging and not to chemical degradation.

INTRODUCTION

Many types of blow-molded, 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 transition of typical polyester resins is in the range of 70 to 80˚C. Because bottles are commonly stored in ware houses that might reach 50˚C, there is a concern about the effects of physical aging on the mechanical properties of blow-molded bottles.

Some recent water-filled, drop impact tests on bottles from a series of polyester resins show that impact properties can degrade significantly after only 30 days of aging at 50˚C (Smilie (1)). Because these impact tests were on full-scale specimens, there is no question that aging is an important factor. Two problems with the impact tests are that they require much material (more than 25 bottles for each data point) and that they rely on break/no break observations. This paper describes use of the essential work of fracture method (EWFM) (Cotterell and Reddell (2), Mai *et al*. (3), and Saleemi and Nairn (4)) as an alternative method for monitoring aging. Our first goal was to get quantitative and more extensive results with far less material. 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 temperature.

MATERIALS AND METHODS

The DuPont company provided us with cylindrical, blow-molded bottles manufactured from four different polyester resins. The resins are labeled here as resins A, B, C, and D. All resins are copolyester resins polymerized from some mixture of glycols and some mixture of diacids. Resin A uses a glycol mixture that is 92 mole % ethylene glycol and 8 mole % cyclohexane dimethanol. Its acid is 100% terepthalic acid. Resin B uses 100% ethylene glycol . Its acid is 97 mole % terepthalic acid and 3 mole % isothalic acid. Resin C uses a glycol mixture that is 70 mole % ethylene glycol and 30 mole % cyclohexane dimethanol. Its acid is 100% terepthalic acid. Resin D uses 100% ethylene

glycol. Its acid is 100% terepthalic acid. When cooled slowly, resins B and D are semicrystalline while resins A and C are amorphous.

The fracture characterization was done using EWFM (2-4) which is a method specifically designed for measuring plane-stress fracture toughness in thin ductile materials. In brief, a series of deeply, double edge notched specimens were loaded until failure and the total work of fracture was recorded. The series of specimens varied only in ligament length. To insure plane-stress conditions in all specimens, the ligament was restricted to being longer then four times the thickness and shorter than the plastic zone size or 1/3 the width, whichever was shorter (2-4). By EWFM, a plot of work of fracture per unit ligament area as a function of ligament length should be a straight line. The intercept defines the essential work of fracture, w_e, and the intercept defines the nonessential or plastic work of fracture, w_p. w_e is associated with plane stress fracture toughness; we looked for changes in w_e with aging. w_p is associated with yielded around the crack tip that does not lead to fracture.

Our EWFM specimens were cut from the sides of the cylindrical bottles. The long axis of the specimens were nominally 150 mm long and were parallel with the axis of the bottle. The samples were 25 mm wide. 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 but were in the range of 0.3 to 0.6 mm. We were able to cut ten specimens from each 80 mm diameter bottle. A single EWFM experiment required 15 to 20 specimens and thus needed only two bottles.

RESULTS AND DISCUSSION

A series of specimens were placed in ovens at 50˚C. After 0, 30, 45, and 60 days of aging, we measured the essential work of fracture (w_e), the glass-transition temperature (T_g), the yield strength (σ_y), and the density (ρ). Figure 1 shows all w_e results as a function of aging time. All resins showed a significant drop in toughness after only 30 days of aging. Between 30 and 60 days of aging there was little change in toughness or perhaps a small increase. Resins B and D, the semicrystalline resins, showed the highest toughnesses before aging, but decreased the most (about 50%) after 30 days of aging. We suggest that semicrystalline resins quenched to an amorphous state are farther from the equilibrium state than an amorphous resin and thus more susceptible to physical aging. Resins A and C, the amorphous resins, started with a lower toughness, but decreased only 15 to 20% after aging for 30 days. We also aged samples at 65˚C for 0, 1, 14, and 28 days. At this higher temperature, the effects of aging are similar, but most changes occur within one day of aging.

Besides changes in toughness, aging also caused T_g to increase 5-10˚C, σ_y to increase 15-20%, and ρ to increase slightly. The changes in ρ were consistently increases, but they were almost unresolvable. The changes in T_g, σ_y, and ρ were similar for all resins and thus not suitable for differentiating among the resins. The changes in ρ were too small to be a useful tool for monitoring aging.

We claim that all the changes were due to physical aging and that there were no chemical degradation effects. The direct evidence to support this claim was that there was no change in solution viscosity (with phenol as the solvent) as a function of aging time. A decrease in molecular weight due to chemical degradation should have led to a decrease in solution viscosity. Some indirect results supporting physical aging were the increase in T_g, the increase in σ_y, and peaks in the DSC curve near the glass transition region (see Fig. 2). A loss in molecular weight due to chemical degradation should cause either no change or a decrease in T_g and σ_y, contrary to the observed increase. Peaks in the DSC curve near the glass transition region are a kinetic effect associated with aging before heating. The longer the aging before heating, the larger should be peaks; this prediction agrees with our observations (see Fig. 2).

Figure 3 is a cross-plot of the w_e results as a function of the water-filled, drop impact results. The data include both unaged and aged specimens. The aged specimens were all aged at 50˚C for 60 days. The numbers for the impact results are the statistically predicted drop height for which 50% of the bottles break upon impact. The lines indicate that there is a reasonable correlation between w_e and impact height for each class of resins (amorphous or semicrystalline), but that the correlation is resin dependent. Among all resins groups, we find that w_e is not necessarily a good predictor of impact

height. For example, the semicrystalline resins have a higher w_e than the amorphous resins, but a lower impact height before aging and a comparable impact height after aging. More work is needed before we can relate w_e results for real-world bottle performance.

CONCLUSIONS

The essential work of fracture technique is capable of monitoring changes in mechanical properties caused by physical aging. 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 other properties. If those differences can be related to real-world performance, EWFM will be a valuable tool for selecting bottle resins. Another benefit of EWFM is that we can get results with much less material. There is thus the potential for larger scale testing that could lead to methods for predicting the temperature dependence of the aging process. Perhaps time-temperature superposition can be applied to fracture toughness and limits can be placed on acceptable bottle storage conditions.

SYMBOLS

EWFM = essential work of fracture method
w_e = essential work of fracture (J/m^2)
w_p = nonessential or plastic work of fracture (J/m^3)
T_g = glass transitions temperature (°C)
σ_y = yield strength (MPa)
ρ = density (g/cm^3)

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4. Saleemi, A. S., and Nairn, J. A., 1990, Polym. Eng. and Sci. 30, 211.

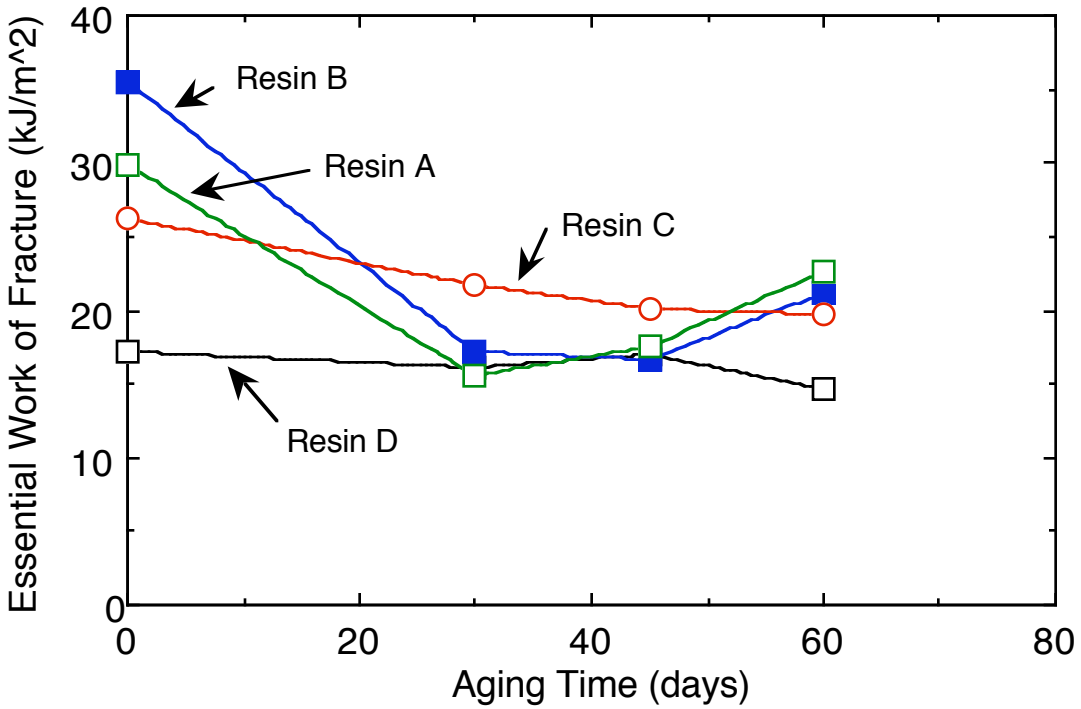

Figure 1: The essential work of fracture for a series of polyester resins as a function of aging time at 50˚C. The filled symbols are for semicrystalline resins and the open symbols are for amorphous resins.

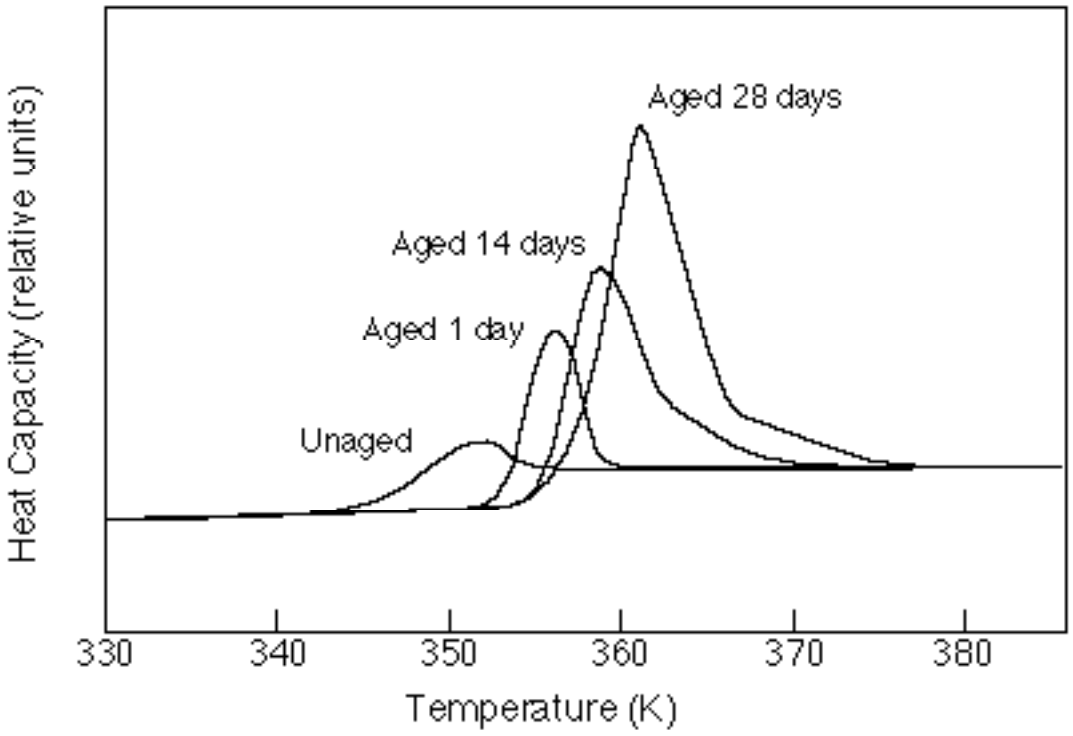

Figure 2: The glass transition region from the DSC of resin A as a function of aging time at 65˚C. The peaks are a kinetic effect caused by aging before doing the DSC experiment.

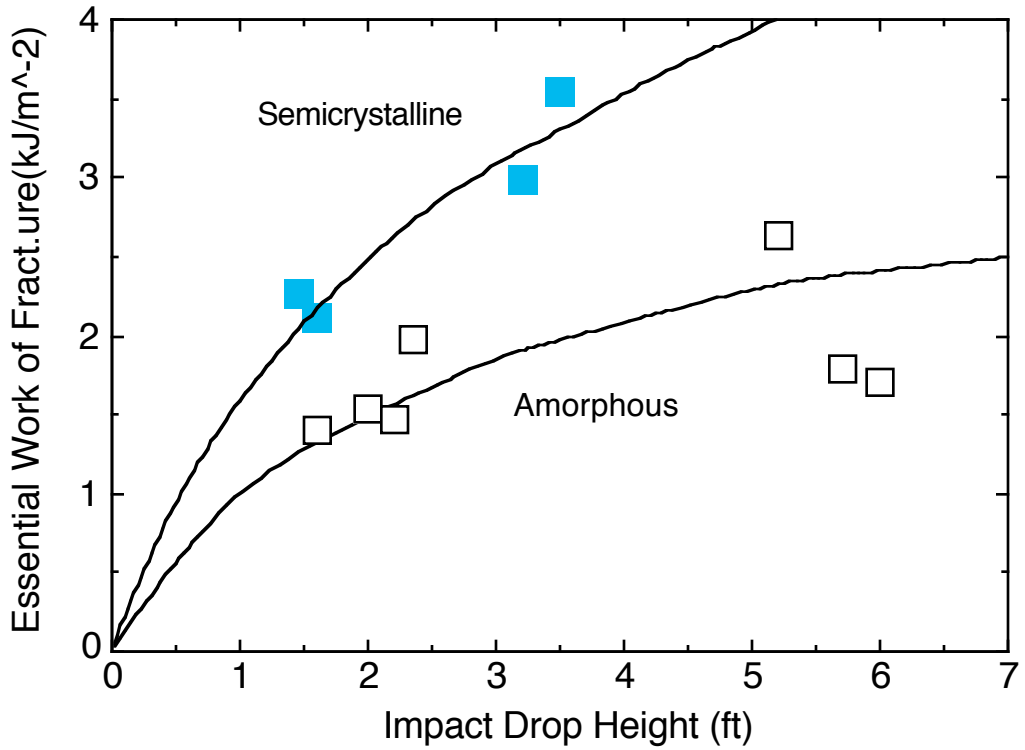

Figure 3: Cross-plot of the essential work of fracture as a function of the impact drop height. The data points are for all resins and include both unaged and aged specimens. The filled symbols are for semicrystalline resins and the open symbols are for amorphous resins