

PHYSICAL AGING STUDIES IN AMORPHOUS POLY(ETHYLENE TEREPHTHALATE) (PET) BLENDS *

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(Received 16 February 1990)

ABSTRACT

Physical aging phenomena of amorphous poly(ethylene terephthalate) (PET) blends have been investigated. Blends modified with dioctylphthalate (DOP), a miscible plasticizer, have shown a significant reduction in the glass transition temperature, while rubber modified blends exhibit no change in T_g . Enthalpy relaxation kinetics are well represented by $\Delta H = \Delta H_a [k - \exp(-t/\tau)]$. The apparent recoverable enthalpy ΔH_a reaches a maximum at about 18°C below T_g . The slope of the relaxation curves decreases exponentially with $T_g - T_a$. Addition of rubber modifiers strongly suppresses the extent of enthalpy relaxation. High pressure treatment of fully aged samples leads to temporary erasure of the aging endotherm. Concomitant changes in mechanical properties have been detected by dynamic mechanical analysis and mechanical testing coupled with scanning electron microscopy.

INTRODUCTION

Glycol modified poly(ethylene terephthalate) (PETG) or amorphous PET is widely used in the medical device industry, mainly owing to many of its attractive properties: high modulus, optical transparency, relatively high toughness, and capability of withstanding ionizing radiation for sterilization. Also, owing to its amorphous nature, it is subject to physical aging.

We are interested in fundamental understanding as to how processing may induce the aging process and thus affect the properties. Many steps in medical device manufacture are carried out under temperature conditions approaching the glass transition temperature of the material, about 80°C. For example, in preconditioning for ethylene oxide sterilization temperatures could reach 120°F (or about 50°C). Drying operations after aqueous cleaning could involve temperatures as high as 70°C for a variable period of time. Furthermore, during the shelf life and transport of the devices, exposure to elevated temperatures is very common. In most cases, we saw

* Presented at the 18th Annual NATAS Conference, San Diego, CA, U.S.A., 24–27 September 1989.

few dimensional distortions resulting from softening near T_g . However, in some cases we encountered dramatic losses in physical properties. Since physical aging is suspected of playing a major role in this process, we decided to study the process as a function of the T_g value. For a systematic variation in T_g , a miscible plasticizer, dioctyl phthalate (DOP), was incorporated. In this way, the kinetics of physical aging were determined as a function of the parameter ($T_g - T_a$), where T_a is the aging temperature.

In addition, rubber modification using elastomers having different degrees of compatibility was studied. At the levels used (maximum 20%) isolated spherical domain morphologies were expected. Owing to compatibility differences, very different interfacial transition zones should result. Since the domains determine the impact properties of the material, it will be interesting to compare the behavior of the aging kinetics in this regard. Moreover, mechanical stresses can often induce profound changes in the thermodynamic states of materials. The effects of high pressure (exceeding 40 atm) on the aging phenomena will be examined.

EXPERIMENTAL

Glycol modified PET, PETG-6763, and plasticizer DOP were obtained from the Eastman Chemical Co., Stereon 840, a styrene butadiene block copolymer, was obtained from the Firestone Tire and Rubber Co., and Gaflex, a polyester-based thermoplastic elastomer, was obtained from GAF Co. Compounding was carried out in two ways. Small sample sizes (ca. 40 g) were prepared on a Brabender melt mixer at about 190°C melt temperature and about 50 rpm. In the case of liquid plasticizer, the DOP was added dropwise to a fully fluxed melt. For larger quantity samples, a Killion 1.5 inch single screw extruder was used. The melt temperature was about 210°C and the screw r.p.m. was set at 50. A special screw with a melt mixing section (Meddox) was employed in this experiment. Prior to compounding, the PETG resin was dried at about 70°C in an air circulated convection oven for at least 18 h to reduce the moisture content to less than 0.1%. For the Brabender samples, a 0.5 mm sheet was pressed from the compound immediately upon blending with a Pasadena compression molding press at about 200°C and 15 ton hydraulic pressure. The extruder prepared samples were pelletized, dried and injection molded into ASTM type tensile specimens, also pressed into 0.5 mm sheets for analysis.

Aging experiments were carried out in a Blue M forced air convection oven at various temperatures, with the actual sample temperature being measured by a calibrated glass thermometer. The enthalpy recovery experiments were conducted with a Du Pont 1090 thermal analyzer with a 910 DSC cell. Typically, the samples were scanned from about 5°C to 120°C at a scan rate of 20°C min⁻¹. To avoid artifacts from sample movement

resulting from stress relief and from changing contacts with the sample pan, a modified procedure adopted from precision heat capacity measurement was used: in an open aluminum sample pan, the bottom of which was coated with thermally conductive silicone grease, the sample was pressed in the form of a thin flat section. In this way, during the stress relieving process, the sample can “float” in the sample pan while the silicone grease maintains full thermal contact with the calorimeter. Also, leaving the pan unsealed prevented disturbance of the sample’s history from mechanical dilation.

Dynamic mechanical measurements were obtained on a Dupont 981 DMA in the quantitative mode, with a temperature scan rate of $5^{\circ}\text{C min}^{-1}$. Tensile experiments were conducted on a MTS 810 servo-hydraulic physical tester at a testing rate of 50 cm min^{-1} . Fracture morphologies were examined on a JEOL 35 CF scanning electron microscope. For rubber modified samples, the fracture surfaces were first subjected to an oxygen plasma etch at about 100 W of r.f. power for 5 min, to bring out the rubber particle morphology.

For the high pressure gas plasticizing experiment, a Parr one-liter high pressure reactor was used. Samples of fully aged PETG sheets were first introduced into the reactor which was then sealed. High purity dry carbon dioxide CO_2 was then introduced through a high pressure regulator. Pressure inside the reactor was maintained at 4.14 MPa (600 lbf in^{-2}) for up to several hours while the samples were held at ambient temperature. Upon completion of the experiment, the reactor was vented to atmospheric pressure in about 2 min and the samples were removed for examination.

ENTHALPY RELAXATION

Amorphous polymers below their glass transition temperatures are in a glassy (non-equilibrium) state, where changes in structure-dependent properties such as refractive index, dielectric constant, stress relaxation modulus, and creep compliance are manifestations of molecular relaxation towards equilibrium. Physical aging is generally defined as the process by which the intensive thermodynamic properties such as enthalpy and entropy of a glassy material, raised by external perturbations such as heat or stress, decay to a stable state of lower free energy. The rate of the relaxation processes involving the cooperative movement of polymer segments determines the kinetics of physical aging. One of the most powerful techniques employed to study structural relaxation is monitoring of the time dependence of the enthalpy using differential scanning calorimetry (DSC). The reduction in enthalpy brought about by aging is seen as an endothermic peak, often described as the “overshoot” phenomenon, in a DSC scan of an aged material that is heated above the T_g value. Petrie [1] derived the following

principles governing enthalpy relaxation kinetics: (1) the recoverable enthalpy (endotherm) for a material annealed at a temperature T_a will increase with annealing time and will approach an equilibrium value which is proportional to $T_g - T_a$; (2) both the area of the endotherm and the endothermic peak temperature increase with heating rate.

The phenomenology of enthalpy relaxation kinetics has been extensively studied [2–4]. Probably the most often cited model is Moynihan's description [2] of the relaxation function towards equilibrium as being both non-linear and non-exponential. During aging, the enthalpy relaxation function $\Phi(t)$ is defined by

$$\Phi(t) = [H(t) - H(\infty)]/[H(0) - H(\infty)] \quad (1)$$

where $H(\infty)$ is the equilibrium enthalpy at T_a . The William–Watts function is used to model the enthalpy relaxation as shown below:

$$\Phi(t) = \exp\left[-(t/\tau)^\beta\right] \quad (2)$$

where $0 < \beta \leq 1$ is a measure of the width of the relaxation spectrum and of non-exponentiality, and τ is given by [5]

$$\tau = A \exp\left[x \Delta h/RT + (1 - x) \Delta h/RT_f\right] \quad (3)$$

where A is a fitting constant, R is the gas constant, $0 < x \leq 1$ is a nonlinearity parameter, Δh is an activation enthalpy, and T_f is the fictive temperature, often used to characterize the structure of a glass and first introduced by Tool [6]. In this case, T_f is defined as the temperature at which the measured enthalpy would be the equilibrium value. Obviously, the equilibrium state well above T_g is characterized by the identity $T_f = T$, and enthalpy relaxation from a nonequilibrium state resulting from physical aging is described by the decay of T_f towards T . An important physical consequence of the above model is that the kinetics of aging/relaxation are strongly dependent on the departure from equilibrium. This nonlinearity is expressed by eqn. (3) in which the average relaxation time τ is treated as a function of structure T_f and temperature T .

It has been firmly established that the primary rate controlling factor for enthalpy relaxation is the departure from equilibrium, or $T_g - T_a$. However, some of the secondary effects, including molecular weight, molecular weight distribution or the polydispersity effect, subsidiary modes of motion and structure forming capabilities, and in the case of polymer blends, thermodynamic miscibility, also play a dominant role in influencing the aging characteristics of amorphous polymers. Yoshida and Kobayashi [7], who studied the effect of the size of the side group of poly(alkyl methacrylates) on the rate of relaxation, have concluded that the relaxation time increases with larger side groups. The pioneering work of Bosma and coworkers [8] on polymer blends has demonstrated that enthalpy relaxation is greatly affected by polymer–polymer miscibility. Based on the findings of Yoshida et al. [9],

the relaxation time for a series of amorphous styrene/4-hydroxystyrene copolymers is strongly dependent on the hydroxystyrene content in the polymer. They concluded that the formation of hydrogen bonds between hydroxyl groups in these copolymers restrict mobility of the main chain and thereby retard enthalpy relaxation.

The effects of mechanical and vapor treatments on the enthalpy relaxation kinetics of glassy polymers have been investigated [10–12]. Berens and Hodge [10] have found that aging of poly(vinyl chloride) (PVC), as monitored by DSC, is greatly suppressed by the presence of methylene chloride or CO₂ vapor. Matsuoka [11] has theorized that mechanical stresses such as dilation increase the enthalpy of a glass, which would reduce the magnitude of relaxation and thereby accelerate the enthalpy relaxation kinetics. Chan and Paul [12] have observed that exposure of aged polycarbonate (PC) to high carbon dioxide pressures reduces the magnitude of the enthalpy relaxation, and for sufficiently high pressures the endotherm completely disappears and the DSC trace resembles that of an unaged sample with a highly depressed T_g . More interestingly, the presence of CO₂ in PC significantly lowers the glass transition temperature of PC and erases the effect of aging, thus making the material more ductile than the untreated polymer.

RESULTS AND DISCUSSION

Enthalpy relaxation kinetics

The glass transition temperatures of dioctyl phthalate (DOP) modified polyethylene terephthalate glycol (PETG) blends are shown in Fig. 1. As expected, the glass transition temperature decreases almost linearly with

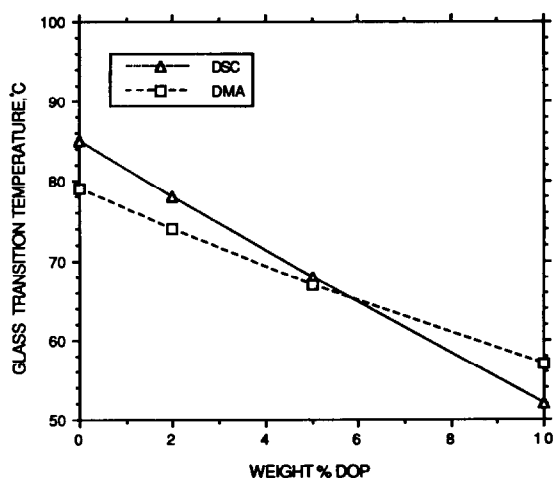


Fig. 1. Glass transition temperature for DOP modified PETG.

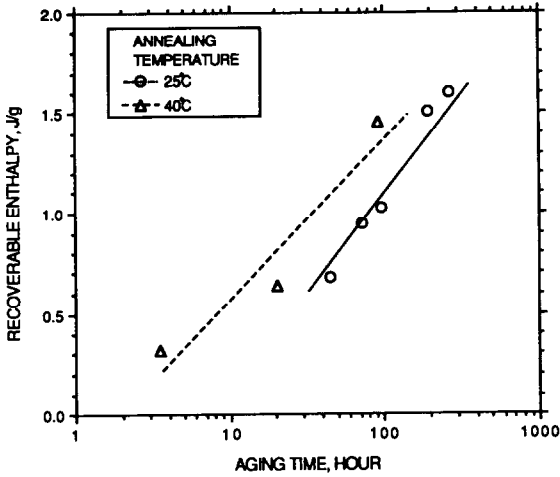


Fig. 2. Enthalpy recovery for PETG blended with 10% DOP.

increasing concentration of DOP. Measurements obtained from DSC and dynamic mechanical analysis (DMA) are in good agreement. The enthalpy recovery plots for 10%, 5%, 2% and 0% DOP PETG blends are shown in Figs. 2–5, respectively. The effects of aging temperature and aging time are clearly displayed in these plots. In accordance with Petrie's findings, the recoverable enthalpy, irrespective of the annealing temperature, increases with aging time and approaches a limiting value that is strongly dependent on the annealing temperature. The following equation was used to fit the recovery curves

$$\Delta H = \Delta H_a [k - \exp(-t/\tau)] \quad (4)$$

where ΔH_a is the apparent limiting value of the recoverable enthalpy at an

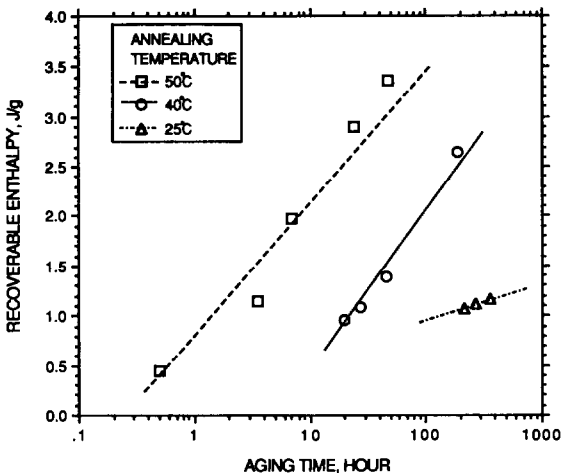


Fig. 3. Enthalpy recovery for PETG blended with 5% DOP.

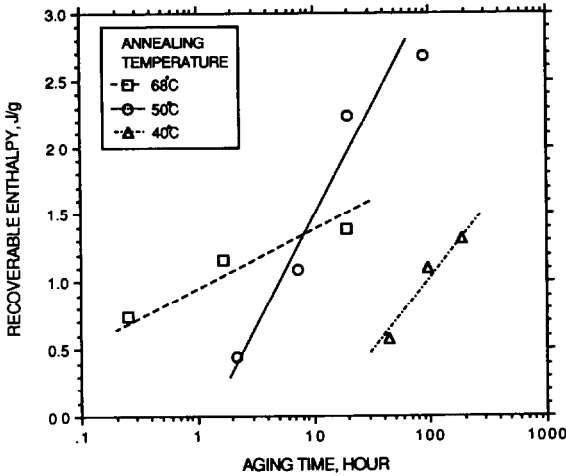


Fig. 4. Enthalpy recovery for PETG blended with 2% DOP.

aging temperature T_a , and τ is the time constant. Obviously, a plot of $\ln(\Delta H/\Delta H_a)$ versus t should yield a straight line whose slope is $1/\tau$. A least squares fit was used to extract the time constant for each of the recovery curves. The half life time constant, $\tau_{1/2}$, corresponding to the time required to attain 50% of the apparent recoverable enthalpy, is plotted in Fig. 6 against the departure of the aging temperature from the glass transition temperature or $T_g - T_a$. T_g values in these cases are those of the blends measured by DSC. This plot suggests that the half equilibration time constant increases exponentially with $T_g - T_a$. The exponential relationship holds well within a given type of blend. However, the scatter observed in the master plot

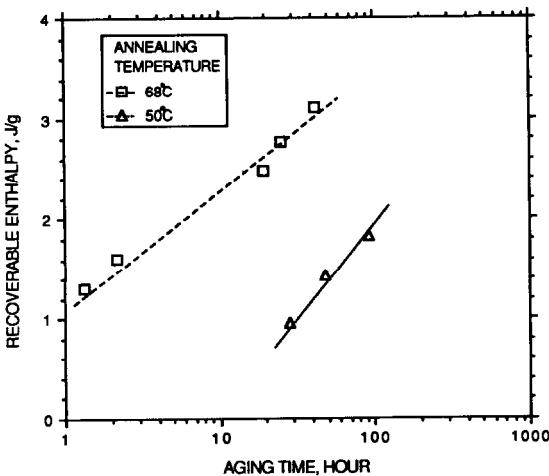


Fig. 5. Enthalpy recovery for PETG.

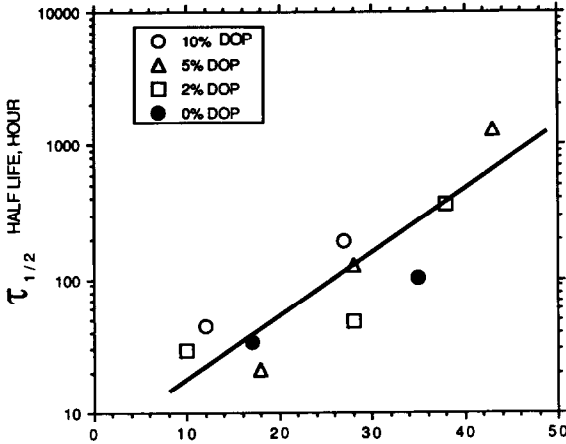


Fig. 6. Master plot for half life time constant vs. $T_g - T_a$.

indicates that the enthalpy relaxation kinetics for the different blends are not quite superimposable, thereby suggesting that there may be structural differences in these blends. It should be noted also that the fitting function appearing in eqn. (4) fails to account for the nonexponentially and nonlinearity inherent in enthalpy relaxation.

Figure 7 shows a plot of apparent recoverable enthalpy and equilibrium enthalpy versus $T_g - T_a$. The equilibrium enthalpy, derived by Petrie [1], is given by

$$\Delta H_E = C_f - C_g(T_g - T_a) = \Delta C_p(T_g - T_a) \quad (5)$$

where C_f is the heat capacity at the fluid state, and C_g is the heat capacity at

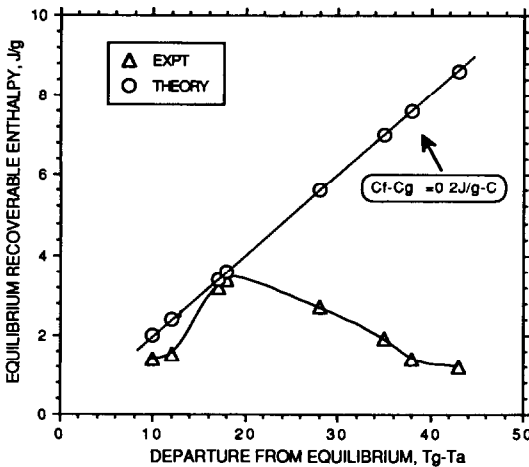


Fig. 7. Apparent and equilibrium enthalpy vs. $T_g - T_a$.

the glassy state. The equilibrium enthalpy was calculated using a value of $\Delta C_p = 0.2 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$. It is interesting to note that the experimental apparent recoverable enthalpy, obtained from samples aged at a fixed annealing temperature for an aging period ranging from days to about a month, shows a maximum at about 18°C deviation from equilibrium. This type of functional behavior is analogous to that observed for the maximum crystallization temperature bounded between the melting point and glass transition temperature. The maximum apparent enthalpy is a direct result of the two competing forces, namely, kinetics and thermodynamics, operative in a relaxation process. At aging temperatures close to T_g , the enthalpy relaxes to the equilibrium value very quickly and the energy adsorbed is very small because the excess enthalpy is very close to the equilibrium value. At aging temperatures far below T_g , the thermodynamic force is very large but molecular mobility is practically frozen. Based on the continuity principle, there exists an optimum aging temperature, for a fixed aging period, for which the apparent recoverable enthalpy is at a maximum. For the one month aging period we have used to conduct this study, the optimum temperature for yielding the maximum enthalpy is about 18°C below T_g .

Effects of rubber modification on the aging kinetics of PETG were examined using two copolymers: Gaflex, a polyester-based thermoplastic elastomer, and Stereon, a poly(butadiene co-styrene) block copolymer. The enthalpy recovery plots, apparent recoverable enthalpy, and the half life time constant are shown in Figs. 8, 9 and 10, respectively. Several striking features can be observed from these plots. First, the apparent recoverable enthalpy for these materials is about two times lower (1.5 J g^{-1} versus 3.0 J g^{-1} at an annealing temperature of 70°C) compared with that of the unmodified PETG. Furthermore, the half time constant for the Gaflex

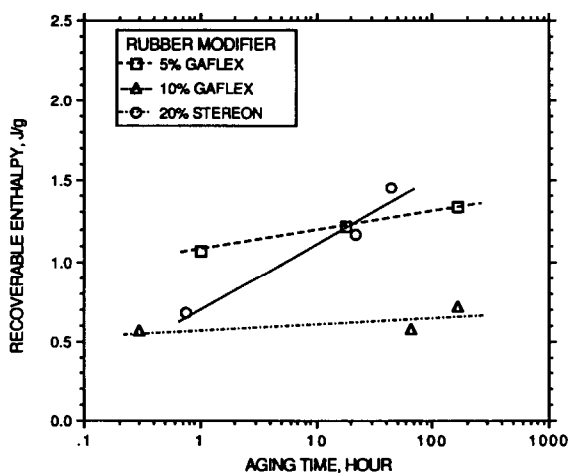


Fig. 8. Enthalpy recovery for PETG blended with rubber modifiers annealed at 70°C .

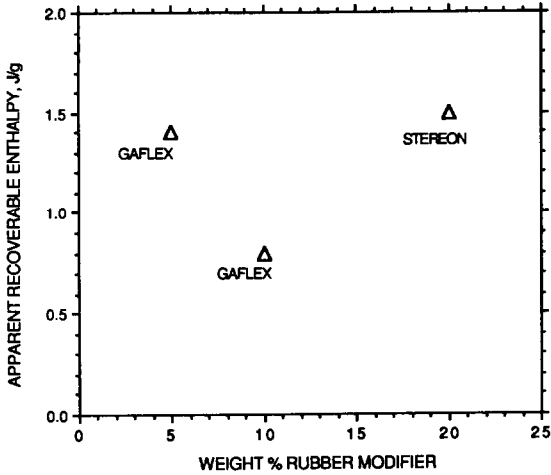


Fig. 9. Recoverable enthalpy for PETG/rubber systems annealed at 70 °C.

system is an order of magnitude higher than that of the unmodified material. In order to gain more insight into these rubber modified systems, the oxygen plasma etched fracture surfaces of these materials were examined using scanning electron microscopy (SEM). The SEM micrographs shown in Figs. 11–13 clearly indicate that there is a marked difference in the blend morphology between the Gaflex and Stereon system. These micrographs demonstrate that the Gaflex modifier was selectively etched by the oxygen plasma while the Stereon particles remained intact. More interestingly, the effective volume of the modifier present in the 10% Gaflex material seems to far exceed 10%, thus suggesting that there was a high degree of interfacial

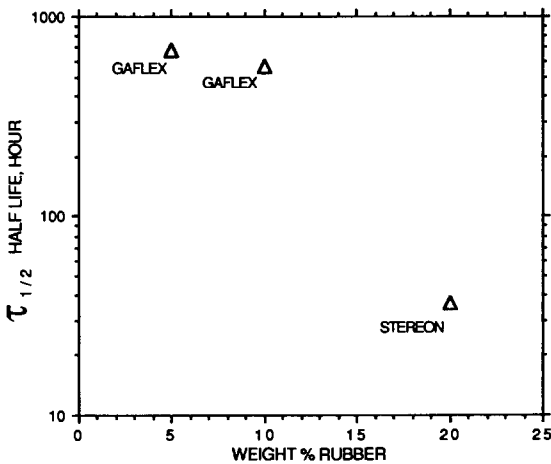


Fig. 10. Half life time constant for PETG/rubber systems annealed at 70 °C.

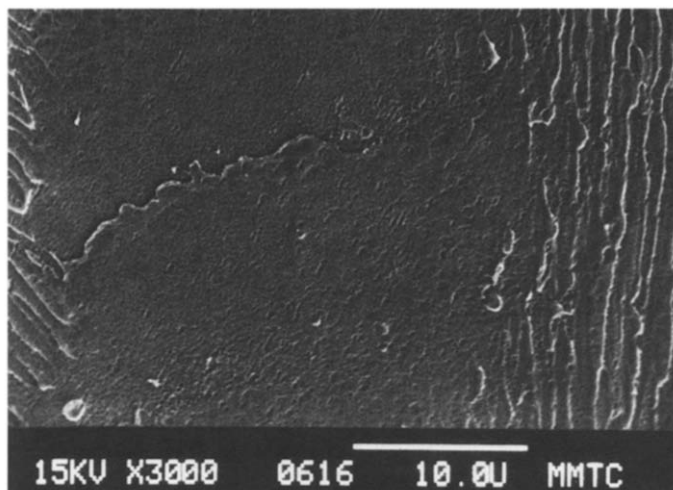


Fig. 11. Fracture morphology for PETG modified with 5% Gaflex.

interaction between the modifier and the matrix. Based on the half life time constant and apparent recoverable enthalpy coupled with the SEM finding, we concluded that enthalpy relaxation is greatly retarded, especially for the Gaflex system, by the addition of these copolymers. This possibly may result from partial compatibility between the modifier and the matrix.

In agreement with the findings of Chan and Paul [12], exposure of fully aged PETG to high pressure CO_2 causes a significant reduction in its glass transition temperature, as shown in Fig. 14, owing to the plasticizing action of the penetrant. The endotherm also totally disappears, as if the polymer

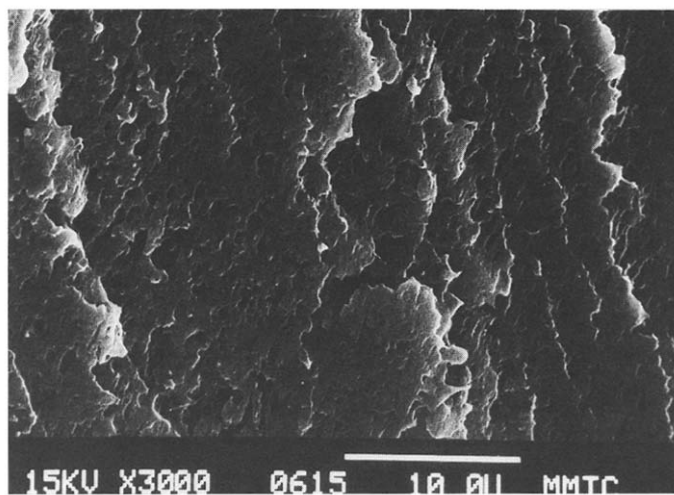


Fig. 12. Fracture morphology for PETG modified with 10% Gaflex.

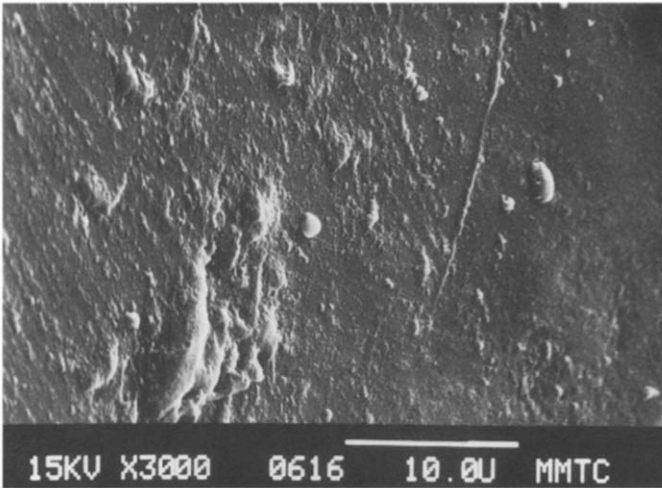


Fig. 13. Fracture morphology for PETG modified with 20% Stereon.

has been fully “rejuvenated”. The erasure of the endotherm brought about by high pressure treatment has been attributed to the increase in the equilibrium enthalpy caused by mechanical dilation. Surprisingly, we discovered that the disappearance of the aging endotherm is only a transient phenomenon, and the pressure treated samples stored at room temperature for a short period (2–3 days) undergo enthalpy relaxation exhibiting recovery identical to fully aged polymer without pressure treatment. This observation suggests that the elevation in enthalpy induced by high pressures is a time dependent process where the enthalpy decays or reverts back to its original (fully aged) state. This reversal in thermodynamic state is postulated to be a clear manifestation of the memory phenomena inherent in polymers.

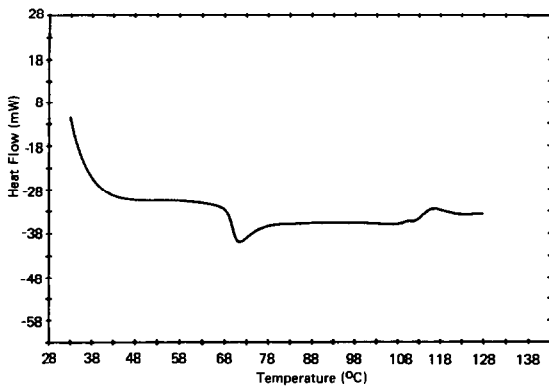


Fig. 14. High (600 lbf in^{-2}) pressure treated PETG showing a highly depressed T_g .

Dynamic mechanical analysis

As a polymeric glass undergoes aging, it becomes more brittle (reduced elongation at break) and stiffer (higher modulus). The mechanical $\tan \delta$ is often used to assess the degree of fluidity in a material. A low $\tan \delta$ implies that the material is more solid-like or more rigid. As expected, Fig. 15 shows that aging results in the reduction of $\tan \delta$. Poly(ethylene terephthalate) (PET) is known to exhibit a β transition centered around -60°C [13]. This β process is generally accepted to have originated from both the crystalline and noncrystalline regions of the polymer. The DOP and rubber modified PETG blends examined in this study also undergo a β relaxation at this temperature. Based on the half β peak width measurements, we found that both addition of DOP and rubber modifiers, and aging lead to a narrowing of the β peak. This narrowing in the β transition could be qualitatively explained on the premise that aging may restrict certain modes of molecular motion which would reduce the breadth of the relaxation.

Ultimate properties and fracture morphologies

The most catastrophic effect of physical aging is the degradation of ultimate properties which would invariably lead to premature failure. The stress-strain curves displayed in Figs. 16 and 17 clearly demonstrate the detrimental effect of aging. Ordinarily, PETG is a fairly ductile material with fracture strain greater than 150%. Upon aging, PETG behaves almost like a glass and shatters at very small elongation. The fracture strain is reduced by more than 5-fold. Such pronounced degradation in tensile

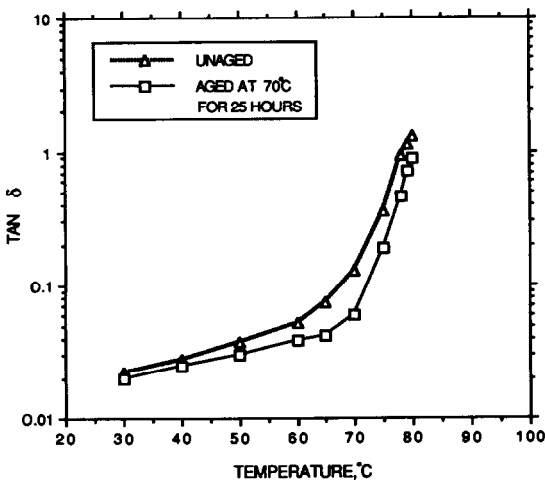


Fig. 15. Dynamic mechanical $\tan \delta$ for PETG modified with 10% Gaflex.

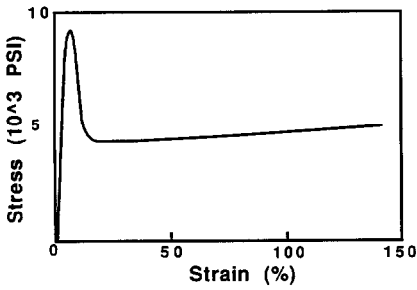


Fig. 16. Stress-strain curve for unaged PETG.

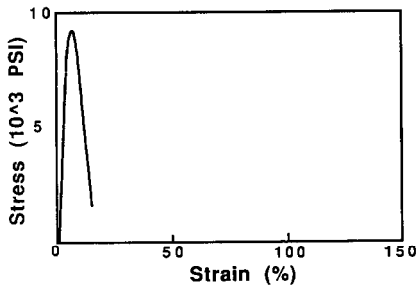


Fig. 17. Stress-strain curve for aged PETG.

property is obviously caused by the reduction in molecular mobility which accompanies physical aging. Densification of material is mediated by the reduction in free volume. SEM micrographs, found in Figs. 18 and 19, clearly illustrate the difference in the failure mechanisms operative in the

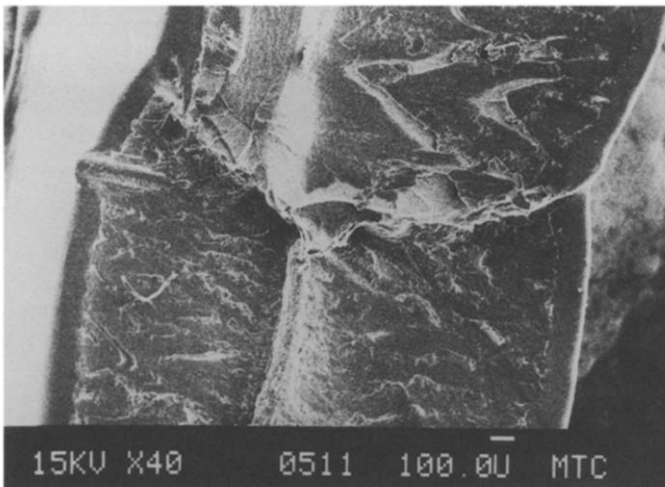


Fig. 18. SEM micrograph for unaged PETG.

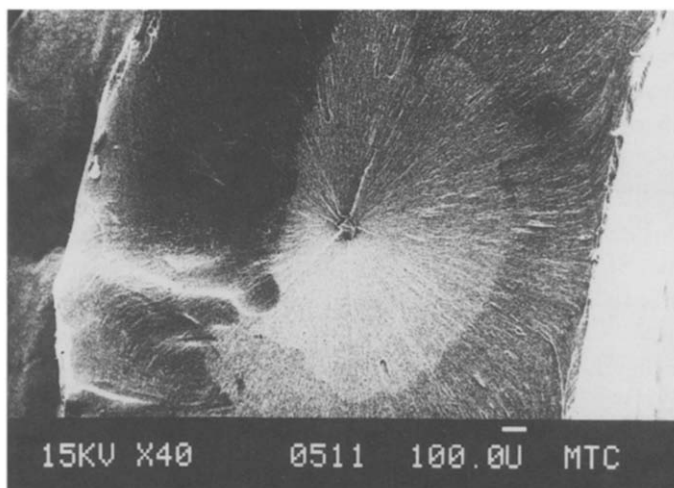


Fig. 19. SEM micrograph for aged PETG.

unaged and aged materials. The fibrils and peaks observed in Fig. 18 indicate that the material has experienced a high degree of plastic deformation which is indicative of ductile failure. The planar surface and concentric beach marks shown in Fig. 19 are clear signatures of brittle failure.

CONCLUSION

The effects of annealing time, annealing temperature and pressure, plasticizer and rubber modifier on the aging phenomena, especially enthalpy relaxation kinetics, of PETG have been investigated. Multiple annealing temperatures were applied to PETG blends modified with 10%, 5%, 2% and 0% DOP. As expected, the glass transition temperature of the blends decreased monotonically with increasing concentration of DOP. However, the glass transition temperature of the Gaflex and Stereon modified PETG remained unaltered and did not show any dependence on either the concentration or the type of rubber modifier. Enthalpy relaxation curves were well modified by the function $\Delta H = \Delta H_a [k - \exp(-t/\tau)]$. The apparent recoverable enthalpy ΔH_a reached a maximum at about 18°C below T_g . The half life time constant $\tau_{1/2}$ varied exponentially with $T_g - T_a$. The addition of rubber modifiers suppressed the extent of enthalpy relaxation, as evidenced by the lowering of apparent recoverable enthalpy relative to unmodified PETG. Gaflex copolymer was seen to strongly retard the enthalpy relaxation kinetics while Stereon showed no apparent effect on the relaxation kinetics. This difference in the aging kinetics is attributed to the compatibility difference of the rubber modifiers with the PETG matrix. Exposure of fully aged PETG to high pressures completely eliminated the aging endotherm

and caused a significant reduction in the glass transition temperature. This erasure was found to be reversible where pressure treated samples undergo enthalpy relaxation with recovery identical to the fully aged samples without pressure treatment. Such remarkable recovery was postulated to be a manifestation of the memory phenomena inherent in polymers. DMA study indicated that aging results in reduction in $\tan \delta$. Addition of DOP and rubber modifier to the PETG matrix, and aging of the blends led to a narrowing of the β peak. SEM and mechanical testing unequivocally demonstrated that aging leads to dramatic degradation in ultimate properties.

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