

Physical Aging in Isotactic Polypropylene

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SYNOPSIS

Physical aging studies were made using commercial and laboratory samples of isotactic polypropylene. Linear and nonlinear viscoelastic responses were measured after quenching the glass from above the glass transition temperatures to below the glass transition. Results show that aging is not eliminated by large mechanical deformations; rather, the time required for the glass to age into equilibrium is independent of the applied stress. Results obtained are purely kinetic and interpreted as the effects accompanying the process of glass formation in a semicrystalline polymer. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Quenched polymer glasses, unlike liquids and crystalline solids, are not in equilibrium with their environment but are in metastable states. The mechanical and thermal properties of such polymer glasses are time-dependent and therefore change abruptly at temperatures close to but below the glass transition. This process is called physical aging and arises as a result of the relaxation processes in the glass state.

Physical aging is the slow and gradual continuation below the glass transition¹ temperature of the glass formation process that starts at T_g . After the transition from liquid-like to glass-like behavior, the material is in a nonequilibrium state, and its structure spontaneously moves towards equilibrium. Accompanying the change in volume with increasing aging time, the relaxation spectrum of the glass shifts to longer times. Temperature-dependent properties of the materials, such as specific volume and heat capacity, are affected, and these change abruptly at the T_g .

The model of an extended glass transition was proposed many years ago by Struik²⁻³ to explain physical aging in semicrystalline polymers. The main conclusion of this model is that the crystals in the material inhibit molecular motion in the amorphous phase and reduce the segmental mobility,

which sets in at the glass transition. In the immediate vicinity of the crystals, the reduction will be at its maximum, and only at large distances from the crystals will the properties of the amorphous phase approximate those of the bulk amorphous material.

The consequence of the above reduction in mobility is that the T_g is broadened and extended to higher temperatures. Below the T_g , the amorphous phase will be completely glass-like and, as such, exhibit the same aging effects as a purely amorphous polymer. Above the T_g of the amorphous regions, part of the semicrystalline polymer will still be glassy, and aging will persist above the T_g .

EXPERIMENTAL SECTION

Commercial samples of polypropylene obtained from manufacturers, as well as research samples, obtained by direct synthesis in the laboratory were used in this study. In the case of this paper, the crystallinity of the samples used ranged from 47 to 15%, the weight average molecular weight varied from 10^5 to 10^6 , while the density was about 935 kg/m^3 and had a typical yield stress of 50 Mpa.

Samples of a 47 and 15% crystalline PP were aged at various temperatures below the T_g for different lengths of time in a cryogenic chamber fed with liquid nitrogen. Any orientation or thermal history in the sample was removed by heating at 470 K for 15 min and quenching at 320 K/m to the aging tem-

peratures. Aged samples were examined using a differential scanning calorimeter DSC-2 at a sensitivity setting of 20.92 mJ/s.

Samples weighing between approximately 24 and 33 mg were used at heating rates from 2.5 to 20 k/min and a sensitivity of 83.6 mJ/s. Sapphire was used as a comparative heat capacity standard since this allowed for variation in calorimeter sensitivity with temperature. Each sample was run at different heating rate settings, and the heat capacity values were extrapolated to zero heating rate. This corrects for errors which could arise because of previous thermal history effects.

Over the range of thermal transitions and over limited temperature ranges, the heat capacity vary linearly with temperature according to the expression

$$C_p = a + bT \quad (1)$$

where a and b are constants, and T is temperature

The extent of aging was determined using the method of Cowie et al.⁴ This method consists of measuring the enthalpy difference between the aged and unaged samples. Subtraction of the quenched thermogram baseline from that of the aged produces an aging peak that is integrated between two fixed temperature limits according to the equation.

$$\Delta H(T_a, t_a) = \int_{T_\beta}^{T_\infty} [C_p(\text{aged}) - C_p(\text{unaged})] dt \quad (2)$$

where T_∞ and T_β are suitably chosen temperature limits, and ΔH is the enthalpy of aging.

RESULTS AND DISCUSSION

The glass transition of samples held at various temperatures close to but below the transition temperatures exhibited marked endothermic peaks as seen from the DSC traces on heating through the glass transition. These peaks are indicative of an overshoot of the glass transition temperature associated with and characteristic of physical aging. Essentially, they have no real thermodynamic significance because these samples were not annealed. The T_g changes may thus be an indication of previous thermal history in the sample. It is, however, possible that heating the sample for the period indicated in this paper is able to eliminate most of the previous history in the samples.

The extent of the endothermic peaks increases logarithmically with time, as has been observed in other polymeric systems.⁵⁻⁷ The absorption of energy resulting from enthalpy relaxation increased with increasing aging temperature. This is evident from the plots of aging enthalpy ΔH against aging time (Fig. 1).

The fractional extent of aging in the samples at the same supercooling were similar, despite the differences in sample crystallinity and molecular weight. This indicates that the aging is restricted to the amorphous regions, as has been observed in other polymers. A rate expression for the isothermal volume relaxation of a glass by which free volume holes in the glass change and move slowly to the outside was proposed by Hirai and Eyring.⁸ This expression is

$$\begin{aligned} -dp/dt &= 1/\tau(kT/V_h) \\ &\times \exp PV_h/2RT(2 \sinh)(PV/RT) \quad (3) \\ \text{where } p &= 1/(AB)(\Delta V/v) \quad (4) \end{aligned}$$

and AB is the compressibility difference between the glass and liquid, ΔV and v are the change in specific volume of the glass, τ is the relaxation time, and V_h is the volume of a hole.

If processes similar to volume relaxation occur during physical aging, then the percentage of material that did not go through the aging process is given by

$$\begin{aligned} 1 - \Delta H/\Delta Cp\Delta T &= 1 - \Delta H/\Delta H_\infty \\ &= A \ln 3t/2\tau \quad (5) \end{aligned}$$

The relaxation time during the aging process can be obtained from the intercept of a plot of the left hand side of eq. (5) against time (Fig. 2). The relaxation times during the aging process were observed to increase progressively with decreasing temperatures, i.e., an increase in supercooling, given by $\Delta T = T_a - t_a$. The relaxation time at a given value of supercooling were similar. This indicates that the shift in the T_g on aging results from the entropy term A_0 , as in eq. (6). This is in agreement with the theoretical predictions of Gibbs and DiMarzio.⁹

The relaxation time may be considered to be inversely proportional to the overall rate of aging. Its relationship with the activation energy of aging can be expressed as

$$1/K_\infty = \tau = A_0 \exp(E_a/RT) \quad (6)$$

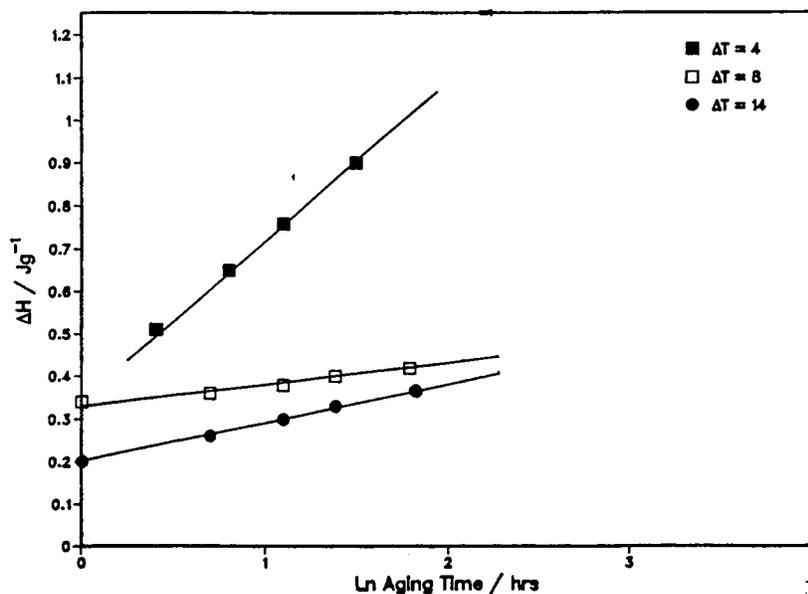


Figure 1 Aging enthalpy against time.

where A_0 includes the proportionality, frequency, and entropy of aging terms. Plots of $\ln \tau$ against temperature are linear (Fig. 3). The activation energy E_a was calculated from the slope to be $2.14 + -0.031$ mJ/mol. The sample having the higher degree of crystallinity has a higher activation energy of aging, and this implies greater barrier to molecular motion.

CONCLUSION

Physical aging in polypropylene compared to ethylene-propylene copolymers and fully amorphous polymers is accompanied by small aging peaks. The activation energy for aging within the limits of experimental errors were similar for the various PP samples. The similarity in the values of the acti-

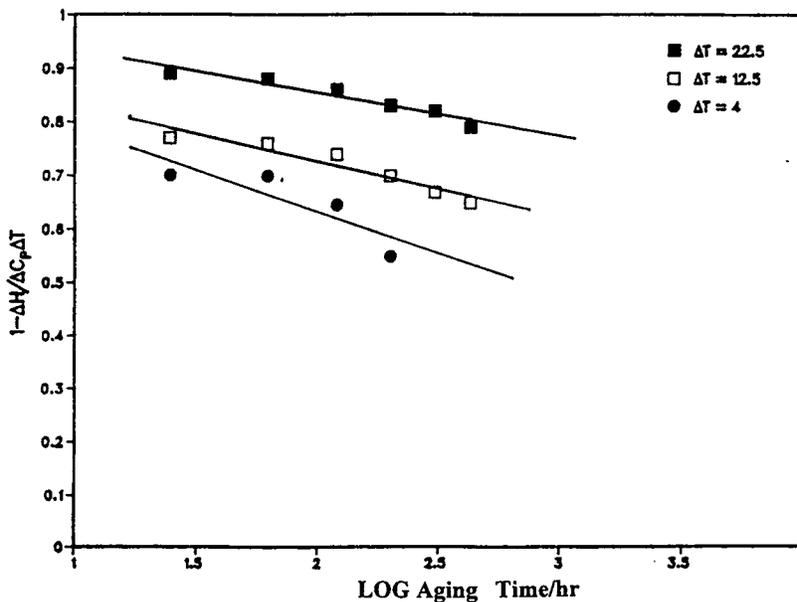


Figure 2 Physical aging kinetics, 47% crystalline PP.

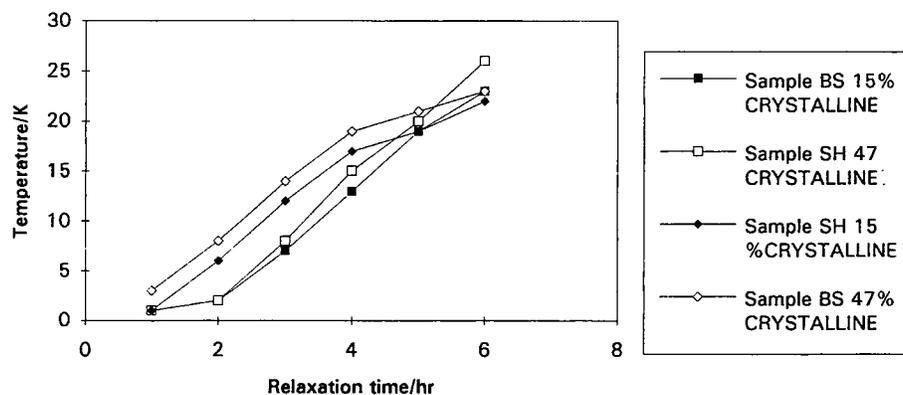


Figure 3 Relaxation time against temperature.

vation energies for samples of the same material suggests a fundamental similarity in the conformational changes occurring in physical aging and the glass transition process. Physical aging of annealed samples of PP should result in larger endothermic peaks than were obtained in this work. This is common with such samples, and indeed this study has been published elsewhere by this author.¹⁰

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