

Enthalpy Relaxation of Filled Copolymers

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Synopsis

Excess enthalpy following annealing at various periods of time at $T_g - 10^\circ\text{C}$ was measured by differential scanning calorimetry of electrophotographic toners, copolymers of styrene and butyl methacrylate containing carbon black. An approximate equilibrium enthalpy relaxation after annealing the pure copolymers for one month was 3.30 kJ/kg for a copolymer with 66.5% styrene and 2.72 kJ/kg for a copolymer containing 49.8% styrene. The rate of enthalpy relaxation was reduced by increasing the styrene content of the pure copolymer. The incorporation of a carbon black with high surface area reduces the rate of enthalpy relaxation, increasing in effectiveness with butyl methacrylate concentration.

INTRODUCTION

Random copolymers of styrene and *n*-butylmethacrylate containing carbon black filler are used as commercial toners in the electrophotographic printing process.¹ The quality of printing depends on the adhesion of toner to a latent image and subsequent fixing of the toner by fusion onto paper.² These are affected by the molecular mobility and rheological behavior of the polymer.^{3,4} We suggest that the effect of carbon black on the mobility of the copolymer chains in the vicinity of the glass transition temperature may be inferred from enthalpy relaxation measurements by differential scanning calorimetry.^{5,6}

Random copolymers of styrene and butylmethacrylate at room temperature are polymeric glasses in nonequilibrium states that depend on thermal history and have excess thermodynamic properties such as enthalpy and volume. If such glasses are annealed at temperatures below the glass transition, these properties relax toward values characteristic of an equilibrium amorphous state. The glass improves in molecular packing and becomes more brittle.⁷ When the copolymer is subsequently heated in the differential scanning calorimeter, the amount of enthalpy relaxation is shown by a spontaneous absorption of heat in the vicinity of the glass transition temperature.⁸ For controlled annealing conditions, the rate of enthalpy relaxation is a measure of polymer chain mobility.

EXPERIMENTAL

Materials

Copolymers of styrene and butylmethacrylate were obtained from Hercules, Inc. (PT-1200) and from Scientific Polymer Products (SP²). Their com-

position was determined by elemental analysis (Galbraith Laboratories, Inc., Knoxville, TN) following purification by reprecipitation from tetrahydrofuran solutions. From the amounts of carbon and hydrogen in the copolymer, the styrene composition was found to be 66.5% for PT-1200 and 49.8% for SP². The glass transition temperatures of the pure copolymers were measured by differential scanning calorimetry (Perkin-Elmer Co., Model DSC-2C) at a heating rate of 10°C/min and found to be 68°C for PT-1200 and 54.5°C for SP². From the glass transition temperatures of the homopolymers,^{9,10} the corresponding styrene concentration is calculated as 66.3% for PT-1200 and 49.1% for SP². The molecular weight distribution of the copolymers was estimated by intrinsic viscosity measurements in tetrahydrofuran (Cannon-Ubbelohde) and by gel permeation chromatography (GPC, Waters Associates, Model R-400, five Microstyrigel columns). A "universal calibration" of GPC was determined by measuring the intrinsic viscosity and the elution volume in GPC of fractions of PT-1200.¹¹ The weight average molecular weight was calculated to be 63,000 for PT-1200 with a heterogeneity index approximating 2. For SP², the GPC molecular weight was analyzed using a polystyrene calibration and found to be 46% higher and exhibited a heterogeneity index of 1.8.

The carbon black sample was obtained from Columbian Chemicals Co. and is designated Raven 7000. As reported by the manufacturer, this furnace black has a surface area of 625 m²/g by BET, a particle diameter of 15nm and a structure characterization by DBP absorption of 105 cc/100 g. Thus, the material is of relatively fine particle size and exhibits high surface area and a complex structure.

Mixing

Carbon black and the copolymer in powder form were dry mixed and then melt blended at 130°C in an internal mixer (Brabender Plasticorder). Thin films of pure copolymers and of copolymer containing carbon black were prepared by heating in an oven prior to calorimetric measurements. Similar results were also found for the pure copolymers by heating the compacted powder directly in the calorimeter.

Calorimetric Measurements

A differential scanning calorimeter (Perkin-Elmer DSC-2C) was used to anneal and to measure the heat capacity of all samples as a function of temperature at a heating rate of 10°C/min. The amount of sample was adjusted to include exactly 10 mg of pure copolymer. The calorimeter was calibrated repeatedly with indium and with lead standards. Annealing and DSC measurements were run in a nitrogen atmosphere. In order to maximize the precision of calorimetric measurements, we compensated for baseline drift by placing identical samples in the sample and reference holder of the calorimeter. Both samples were heated at 10°C/min to a temperature 40°C above T_g and then quenched at 320°C/min to a temperature 40°C below T_g . The sample was removed from the reference holder and stored at low temperature ($T_g - 40^\circ\text{C}$) and the sample remaining in the sample holder was heated again at 10°C/min to a temperature 40°C above T_g , quench cooled

at 320°C/min to 10°C below T_g and annealed at this temperature for selected periods of time. Following annealing the sample was quench cooled to 40°C below T_g . The sample that had been previously removed was replaced in the reference holder and both samples were again heated at 10°C/min, and the difference in endotherms between annealed and quenched samples was recorded.

RESULTS

Calorimetric measurements of the heat capacity of quenched copolymer samples, on heating at 10°C/min from well below T_g , yield a characteristic displacement in the endothermic direction. Linear extrapolation of the resulting heat capacity curve above and below this displacement permits identification of the midpoint in temperature as T_g . Using the experimental technique described for measuring difference endotherms in DSC between annealed and quenched samples, a small endothermic peak is observed in the vicinity of T_g . Simple extrapolation of the linear base line on either side of the peak allows determination of the enthalpy relaxation from the area under the curves. The enthalpy relaxation (kJ/kg) is tabulated for pure copolymers and for copolymers containing carbon black in Table I. Since annealing was done at $T_g - 10^\circ\text{C}$, values of T_g are also given.

DISCUSSION

The specific temperature selected for annealing was the result of a compromise between the thermodynamic driving force for enthalpy relaxation, which is very small close to T_g , and the rate of relaxation which becomes

TABLE I
Enthalpy Relaxation (kJ/kg) after Annealing at $T_g - 10^\circ\text{C}$

Copolymer	T_g (°C)	Annealing time					
		15 min	30 min	60 min	100 min	250 min	160 h
Pure PT-1200 ^a	68.0	0.89	1.00	1.13	1.46	1.80	2.38
PT-1200 with 10% carbon black	68.5	0.75	0.96	1.13	1.42	1.76	2.22
PT-1200 with 20% carbon black	68.5	0.67	0.96	1.09	1.38	1.72	2.13
PT-1200 with 30% carbon black	69.5	0.63	0.84	1.00	1.34	1.59	2.01
Pure SP ² ^b	54.5	0.92	1.21	1.38	1.55	2.05	2.51
SP ² with 20% carbon black	55.5	0.71	1.00	1.21	1.38	1.88	2.34
SP ² with 30% carbon black	56.0	0.63	0.84	1.09	1.26	1.76	2.26

Enthalpy relaxation after annealing at $T_g - 10^\circ\text{C}$ for 1 month:

^a 3.30 kJ/kg.

^b 2.72 kJ/kg.

increasingly slow below T_g . By trial and error, $T_g - 10^\circ\text{C}$ was found to give the maximum heat absorption for reasonable changes in time.

A schematic diagram of the enthalpy relaxation process which occurs during isothermal annealing is shown by Petrie.⁸ On "fully" annealing below T_g , the enthalpy of a quenched glass decreases to that of an "equilibrium" glassy state, an extrapolation of the enthalpy line for the liquid to lower temperatures. For a partially annealed glass, the enthalpy has decreased from the quenched line, but has not attained the low value corresponding to equilibrium. Now, when the partially annealed glass is heated, the enthalpy increases slowly until, in the vicinity of T_g , the enthalpy increases rapidly to rejoin the liquid line. With increasing annealing time, the temperature at which a rapid change in enthalpy occurs shifts to higher temperatures and the absolute enthalpy change increases.^{12,13}

The corresponding heat capacity changes as a function of temperature for a quenched and an annealed glass are typically different.⁸ For the quenched glass, a step change in the heat capacity is observed at T_g . For an annealed glass, however, not only a step change but also, an endothermic peak in heat capacity is observed, corresponding to the rapid recovery of enthalpy at T_g . With increasing annealing time, the area of the endothermic peak increases and T_g has shifted to a slightly higher temperature.

It is often convenient to express the enthalpy changes that occur during isothermal annealing of a glassy polymer as deviations from the enthalpy of the equilibrium glassy state—or excess enthalpy.¹⁴ Actually, annealing to infinite time would be required to attain zero excess enthalpy. We attempted to determine the "equilibrium" enthalpy relaxation or excess enthalpy in the quenched state (ΔH_0) by plotting the enthalpy relaxation against reciprocal time. At very long times, the curve becomes very steep and the extrapolation very inaccurate. Another approach was to calculate ΔH_0 from the heat capacity difference between fluid and glass and the annealing temperature.⁶ For PT-1200, ΔH_0 would approximate 2.13 kJ/kg. Actually annealing at $T_g - 10^\circ\text{C}$ for 1 month, we find that, for PT-1200, the enthalpy relaxation was 3.305 kJ/kg and, for SP², 2.72 kJ/kg, respectively. Assuming that annealing at $T_g - 10^\circ\text{C}$ for 1 month yields an approximate "equilibrium" enthalpy relaxation (ΔH_0) and that this "equilibrium" enthalpy relaxation does not change on the addition of carbon black, we can express the excess enthalpy as equal to the equilibrium enthalpy relaxation minus the observed enthalpy relaxation. We suggest that the poor agreement between calculated and measured values of ΔH_0 arises because the heat capacities were observed to depend on temperature and the value of T_g increases on annealing.

The excess enthalpy of an annealed polymeric glass can be described as^{6,15,16}

$$\frac{\Delta H_t}{\Delta H_0} = e^{(-t/\tau_0)^\beta} \quad (1)$$

where ΔH_t is the excess enthalpy at time t , ΔH_0 is the excess enthalpy of the quenched sample, β is a measure of the nonexponentiality, $0 < \beta \leq 1$, and τ_0 is a characteristic relaxation time. If $\beta = 1$, then the process may

be characterized by a single relaxation time. Although β is generally not equal to 1 and $\Delta H_t/\Delta H_0$ also depends on the departure from equilibrium, it is instructive to examine the time at which $\Delta H_t/\Delta H_0 = 0.5$.^{5,6} Accordingly, the excess enthalpy was plotted against log annealing time during isothermal annealing at $T_g - 10^\circ\text{C}$ yielding a series of almost parallel lines and the "half-times" in seconds are listed in Table II.

The rate of enthalpy relaxation is four times faster for the SP² copolymer compared to PT-1200. This was surprising, since the molecular weight of PT-1200 approximated 60,000, while that for SP² was about 90,000.¹⁷ Apparently, a far more important factor is the styrene content of the copolymer, which is 66% for PT-1200 and 50% for SP². Apparently, by increasing the amount of styrene, we increase the half-time for enthalpy relaxation. This is consistent with the styrene units imparting greater rigidity to the copolymer molecules and raising the observed glass transition temperature. An examination of the original differential scanning calorimetry data in the region of the glass transition temperature indicated that the shapes of the curves were very similar for the two copolymers for the same annealing times.

The incorporation of carbon black filler reduces the rate of enthalpy relaxation. Thus, a loading of 30% carbon black increased the corresponding half-times by a factor of 1.9 for PT-1200 and a factor of 2.9 for SP². It is clear that the inclusion of carbon black is more effective in impeding molecular mobility in the SP² copolymer. This is because the SP² copolymer contains 50% butyl methacrylate compared to 34% in PT-1200. Butyl methacrylate is the more polar monomer and interacts more strongly with carbon black providing molecular attachments to the carbon black particles. These data are completely consistent with rheological measurements, in which the effect of shear rate, carbon black surface area and concentration, and copolymer molecular weight and composition were studied.³

Some comments are in order concerning several major assumptions in this work. First, regarding the selection of the equilibrium enthalpy relaxation (ΔH_0) for the pure copolymers, with increasing annealing time these values may increase further. However, both copolymers were annealed at $T_g - 10^\circ\text{C}$ for the same periods of time, and our comparisons are probably valid. More serious is the identification of the long time values of enthalpy relaxation in the pure copolymers with those which would be exhibited by the carbon-black-filled systems. However, for the carbon-black-loaded samples, enthalpy relaxations at 160 h are fairly close to those for the pure copolymers. In fact, in Table II, we examine the relative kinetics of enthalpy relaxation.

TABLE II
Enthalpy Relaxation Half-Times

Copolymer	Amount of carbon black			
	0%	10%	20%	30%
PT-1200	9.6×10^3 s	10.8×10^3 s	12.6×10^3 s	18.0×10^3 s
SP ²	2.4×10^3 s		4.7×10^3 s	6.9×10^3 s

CONCLUSIONS

The rate of enthalpy relaxation in copolymers of styrene and butyl methacrylate containing carbon black and annealed at $T_g - 10^\circ\text{C}$ was measured by differential scanning calorimetry using a direct comparison between annealed and quenched samples. The rate of enthalpy relaxation was sensitive to and was reduced by increasing the styrene content of the pure copolymer. The incorporation of a carbon black with high surface area reduces the rate of enthalpy relaxation, increasingly so with butyl methacrylate content. This is probably due to a specific interaction between the more polar butyl methacrylate units and the carbon black surface, resulting in more effective attachment and immobilization of polymer chains.

Further studies will be directed at measuring enthalpy relaxation in a wider range of copolymer compositions, including corresponding homopolymers, and for various molecular weights, in order to elucidate the nature of these interactions.

Since these copolymers are the polymeric component of toners in the electrophotographic process, a direct measure of interactions with carbon black is of considerable interest. Rheological studies on these materials reported from these laboratories³ have involved static shear measurements on filled systems. These will be extended to transient and dynamic mechanical studies in order to resolve storage and loss components of the viscoelastic response.

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