# Thermal Behavior of Carbon Black Filled Polymers*

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## Synopsis

DSC measurements suggest that polybutyl methacrylate interacts more strongly with carbon black than polystyrenes and corresponding random copolymers do, showing an increase in $T_g$ of 8.6°C, compared to 2-3°C, by the inclusion of 20% carbon black of surface area 625 $m^2/g$, in agreement with rheological studies. Enthalpy relaxation in the vicinity of $T_g$ is increased by annealing at $T_g - 10°C$, attaining a maximum of 1.65 kJ/kg for polybutyl methacrylate and 2.6 kJ/kg for polystyrene. At constant annealing temperature, the rate of enthalpy relaxation in polybutyl methacrylate was reduced by a factor of about two by the addition of carbon black. However, both pure polystyrene and polybutyl methacrylate show the same rate of enthalpy relaxation as the corresponding filled polymers, following annealing at the appropriate $T_g - 10°C$.

## INTRODUCTION

Recent rheological studies of carbon black filled polymers have shown yield effects at low shear rates and frequencies.[1-5] In steady shear measurements, the viscosity became unbounded below a critical shear stress. Analogously, in dynamic mechanical measurements, G′ and G″ became frequency-independent at low frequencies. Apparently, an independent network of carbon black was formed within the composite, hence, yield stresses and low-frequency moduli were temperature-independent and almost independent of the polymer matrix. Yield was most readily shown for low matrix viscosities, high surface area and concentration of carbon black, and minimal polymer/carbon black interaction.

At high shear rates and low carbon black loadings, plasticization was observed for high molecular weight polystyrene and copolymers.[2,3] Plasticization behavior was not observed in dynamic experiments. Therefore, plasticization was believed to be a structure effect in which high shear rates completely broke down the carbon black network. Factors minimizing polymer–carbon black interaction facilitated plasticization. Unlike polystrene, polybutyl methacrylate had strong interactions with the filler. Random copolymers of styrene and butyl methacrylate behaved more like polystyrene. It was inferred that long sequences of butyl methacrylate were essential for effective carbon black–polymer interaction.

In order to examine some of the inferences from viscosity and moduli measurements, thermal analysis of the filled systems was undertaken. As a rule,

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the glass transition temperature of polymers increases on the addition of rigid filler.[6] Polymer molecules may adsorb on the surface of the filler, forming a layer where the molecular mobility is substantially reduced; this leads to a higher glass transition temperature. Therefore, the extent of polymer/filler interactions can be monitored by measuring the change in glass transition temperature on filling. Another indication of molecular mobility is the rate of enthalpy relaxation of a polymeric glass, annealed at a temperature just below the glass transition. It has been shown[7,8] that, by careful control of the thermal history, the amount of enthalpy relaxed and the excess enthalpy can be obtained as a function of annealing time by differential scanning calorimetry. From glass transition temperatures and rates of enthalpy relaxation, we hope to infer the extent of polymer-filler interactions in carbon black filled systems.

The most important thermal property of amorphous high polymers is the glass transition temperature ($T_g$). Below $T_g$, the polymer behaves as a glassy solid, and above $T_g$ it becomes rubbery. $T_g$ is the temperature at which large scale segmental motion becomes possible. Below $T_g$, polymer chains are frozen and molecular motion is restricted. Hence, the elastic modulus is high and the viscous modulus low. As $T_g$ is approached, large scale segmental motion occurs and the elastic modulus drops, usually by 2–3 orders of magnitude. The viscous or loss modulus goes through a maximum through the glass transition, because energy input is easily dissipated in inducing segmental flow. $T_g$ is usually taken as the temperature where tan $\delta$ ($G''/G'$) reaches a maximum in dynamic mechanical analysis. In thermal analysis, the volume expansion coefficient and the heat capacity undergo a step change at $T_g$. Since the expansion coefficient and heat capacity are second derivatives of the free energy, the glass transition resembles a second-order thermodynamic transition. Careful measurements have demonstrated that $T_g$ is a function of the rate of measurement. $T_g$ increases with heating rate in calorimetry and with frequency in dynamic mechanical measurements on heating. Since the glass transition is kinetically controlled, and the definition somewhat arbitrary, there are differences in $T_g$ when measured by different methods. Dynamic mechanical measurements give higher values of $T_g$ than calorimetry.[9]

$T_g$ is a sensitive indicator of the molecular mobility of polymer chains. Stiff and rigid polymer molecules have higher $T_g$, and molecules with bulky side groups may have increased $T_g$ as free rotation of the polymer molecules is prevented.[10] $T_g$ can be correlated to free volume, because an increase in free volume enhances the mobility of polymer chain segments and lowers $T_g$. Sometimes, chains with bulky side groups are prevented from close packing; thus increasing free volume and decreasing $T_g$. The addition of plasticizers also decreases $T_g$, because polymer chains are separated by plasticizers, increasing the free volume. A large free volume is also associated with chain ends, and an increase in the number of chain ends increases free volume. Therefore, $T_g$ of polymers can be simply correlated with the number average molecular weight.[10]

The addition of rigid fillers usually increases $T_g$,[6] because of immobilization of polymer molecules by adsorption on the filler surface. The amount of immobilization depends on the nature of polymer/filler interaction, volumetric filling, and the specific surface area of the filler. Efforts have been made to correlate increases in $T_g$ with the extent of polymer/filler interaction, as measured by heats of adsorption in a gas chromatograph.[11] Further, $T_g$ has been correlated with the thickness or volume fraction of an immobilized polymer layer.[11,12] Usually, immobilized thicknesses of 20–100 Å have been suggested,[11] but a larger thickness, of the order of several hundred angstroms, is also possible.[13,14] The thickness of an adsorbed polymer layer can also be estimated by monitoring the change in heat capacity at $T_g$.[6] A simple way to estimate the extent of polymer/filler interactions would be to measure the increase in $T_g$ on filler loading.

Because of the kinetic character of the glass transition, a polymer melt cooled below $T_g$ is, ordinarily, not in its equilibrium state. Excess thermodynamic quantities, such as volume and enthalpy, depend primarily on thermal history. If a polymer glass is annealed at a temperature near, but below $T_g$, it tends to relax and approach equilibrium values of enthalpy and volume. On annealing, ordering occurs in the amorphous glass,[7] leading to a change in mechanical properties.[15–17]

From differential scanning calorimetry (DSC), the rate and amount of enthalpy relaxed in a polymer glass can be monitored.[7,8] On heating an annealed glass at $T_g$, the relaxed enthalpy is absorbed, showing an endothermic peak. From the area under the peak, it is possible to calculate the enthalpy relaxed during annealing. If $T_g$ is changed by annealing, an analysis due to Petri[7] is used to calculate the amount of enthalpy relaxed. Another analysis, to account for the change in $T_g$ on annealing, has been given by Yoshida and Kobayashi.[18] Here, the assumption that the heat absorbed should be instantaneous is not necessary. Since the enthalpy is the integral of the heat capacity over temperature, the enthalpy relaxed on annealing is obtained by integrating the thermograms of annealed and quenched samples, taking the difference between the two. This method eliminates the need for a correction to the enthalpy relaxation resulting from a change in $T_g$.

The rate of enthalpy relaxation is a measure of chain mobility under controlled annealing conditions.[19] A decrease in chain mobility is seen as a decrease in the rate of enthalpy relaxation. The rate is also dependent on the proximity to $T_g$. To achieve reasonable rates and measurable amounts of heat absorbed, annealing is usually performed about 10°C below $T_g$.[19]

## EXPERIMENTAL DETAILS

### Materials

Polystyrenes were obtained from the Dow Chemical Co.; the high molecular weight polymer was a commercial sample (Dow Styron 685) and the low molecular weight sample was experimentally prepared. Gel permeation chromatography (GPC), calibrated with narrow distribution polystyrene standards, yielded weight average molecular weights of 255,000 and 43,000, respectively. Polybutyl methacrylate was purchased from Scientific Polymer Products ($SP^2$) and had a weight average molecular weight that approximated 320,000. Random copolymers of styrene and butyl methacrylate were obtained from Scientific Polymer Products ($SP^2$ 50/50) and Hercules Inc. (PT1200). The styrene content of the copolymers was 50 and 66.5 wt %, respectively. Weight average molecular weights approximated 170,000 and 85,000, respectively. Carbon black powder was obtained from Columbian Chemicals Co. and designated Raven

7000. The specific surface area of the carbon black was reported to be 625 $m^2/g$, as measured by nitrogen adsorption.

Polymer beads and carbon black powder were dry-blended and then mixed in an internal mixer (Brabender Plasticorder) at about 150°C for 15 min at 100 rev/min. Composites containing 20% by weight of carbon black were prepared.

### Differential Scanning Calorimetry

Glass transition temperatures and enthalpy relaxation measurements were performed on a differential scanning calorimeter (Perkin-Elmer, Model DSC-4). The DSC was interfaced to a microcomputer for data acquisition and analysis. Programs were written for baseline subtraction, $T_g$ measurement, and area under peak calculations. The DSC was repeatedly calibrated with indium standards for maximum accuracy. Sub-ambient experiments were done by filling the DSC reservoir with a mixture of dry ice and ethanol. Experiments were conducted at a heating rate of 10°C/min, while quenching was achieved by cooling at 200°C/min. The effects of prior thermal history were minimized by keeping the samples in the DSC for 2 min at a temperature about 50°C above $T_g$. For enthalpy relaxation measurements, annealing was ordinarily performed in the DSC. After holding the temperature at about 50°C above $T_g$ for 2 min, the sample was quickly cooled at 200°C/min to the annealing temperature. Annealing times varied between five minutes and eighteen hours. At the end of the annealing period, the sample was again rapidly cooled to a temperature 60–70°C below $T_g$. The sample was then heated through $T_g$ at 10°C/min, and the endothermic enthalpy relaxation peak was monitored. Long term annealing of polystyrene was performed in an oven with temperature control better than ± 0.5°C.

## RESULTS

Two kinds of experiments were conducted in the DSC. First, $T_g$ of pure and carbon black filled polymers and copolymers was measured. The results are shown in Table I. For all the polymers and copolymers, except for polybutyl methacrylate, the addition of 20% carbon black of surface area 625 $m^2/g$ in-

TABLE I
Glass Transition Temperature of Pure and Filled Polymers

| | $T_g$ (°C) | |
|---|---|---|
| Polymers | Pure | Filled |
| High molecular weight polystryrene Dow Styron 685 | 103.4 | 106.6 |
| Low molecular weight polystryene | 101.2 | 103.5 |
| Polybutyl methacrylate | 22.9 | 31.5 |
| $SP^2$ 50/50 copolymer | 54.4 | 56.5 |
| PT1200 copolymer | 67.5 | 69.9 |

creased $T_g$ by about 2–3°C. The increase in $T_g$ for polybutyl methacrylate was 8.6°C.

The second type of experiment was a study of the enthalpy relaxation of a polymeric glass held at a temperature slightly below $T_g$. The enthalpy relaxed is plotted against annealing time for polybutyl methacrylate, both pure and filled with 20% carbon black of surface area 625 $m^2/g$, in Figure 1. The annealing was carried out at 12.9°C for both unfilled and filled polymer, as well as at 21.5°C for the filled polymer. These two temperatures are 10°C below $T_g$ of pure and filled polymer, respectively. The enthalpy relaxed was calculated by integrating the difference of the DSC thermograms of the annealed and quenched samples. As described, this eliminates the need for monitoring the change in $T_g$ with annealing time. From Figure 1, the maximum enthalpy relaxed for pure polybutyl methacrylate approximates 1.65 kJ/kg at long times. Filled polybutyl methacrylate annealed at 21.5°C levels off at about 1.25 kJ/kg. For filled polybutyl methacrylate annealed at 12.9°C, the amount of enthalpy relaxed is somewhat higher.

In Figure 2, the results of annealing high molecular weight polystyrene are shown. Annealing was carried out at $T_g - 10°C$ i.e., 93.4°C for pure polystyrene and 96.6°C for filled polystyrene. Since $T_g$ for pure and filled polystyrenes were not far apart, annealing of the filled polymer at 93.4°C was not undertaken. Enthalpy relaxation was determined by integration of the difference between the DSC traces of quenched and annealed materials and by direct calculation of the area under the relaxation peak and then correcting for the change in $T_g$ on annealing. Both methods gave almost identical results. The maximum change in $T_g$ on annealing was 4.7°C, observed for filled polystyrene annealed for 168 hours. From Figure 2, we find that the maximum enthalpy relaxed for pure polystyrene is 2.6 kJ/kg and for filled polystyrene it is 2.0 kJ/kg. The theoretical maximum is predicted to equal $\Delta C_p(T_g - T_a)$, where $\Delta C_p$ is the change in heat capacity at $T_g$ and $T_a$ is the annealing temperature.[7,18] $\Delta C_p$ was calculated from

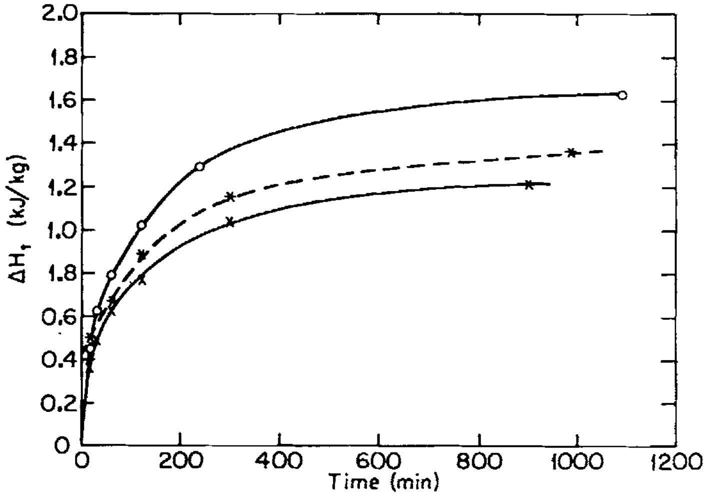

Fig. 1. Enthalpy relaxation of polybutyl methacrylate: (O) pure, annealed at 12.9°C; (∗) filled, annealed at 12.9°C; (×) filled, annealed at 21.5°C.

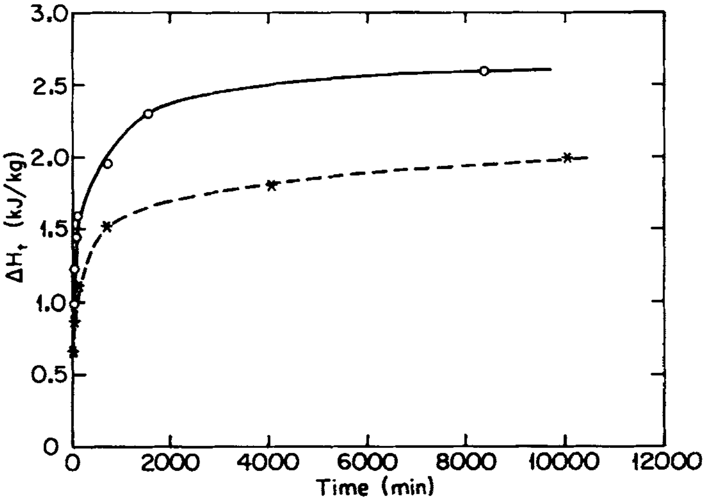

Fig. 2. Enthalpy relaxation of polystyrene (high molecular weight): (O) pure, annealed at 93.4°C; (*) filled, annealed at 96.6°C.

DSC traces to be 0.271 and 0.209 kJ/kg°C for pure and filled polystyrene, respectively.

## DISCUSSION

As a rule, $T_g$ increases with the addition of rigid fillers.[6] The magnitude of the increase depends on the nature of the filler, the polymer and the method of measurement.[6] Increases of up to 20°C were observed for a 10 volume percent loading of aerosil in polymethyl methacrylate or polystyrene.[6,14] In other cases, little or no change in $T_g$ was observed for sodium chloride in polyurethane[20] and carbon black in butadiene–styrene copolymer.[21] On the other hand, the addition of small amounts (1–3 volume %) of $TiO_2$ to poly(vinylchloride–vinylacetate) lowered $T_g$ by 4–15°C.[22] It was suggested that the adsorption of acetate groups on the filler surface broke interchain hydrogen bonds, increased the chain mobility, and reduced $T_g$. Usually, the adsorption of functional groups from the polymer chain onto the filler surface reduces the number of conformations of the polymer molecule. This produces a surface layer in which polymer molecules have considerably less mobility.[6] Adsorption of polymer onto the filler surface also affects supermolecular packing, reducing the free volume and the mobility of polymers in the bulk.[6] Therefore, $T_g$ is usually shifted to higher temperatures. In rare cases, two distinct values of $T_g$, for the surface layer and the bulk polymer, have been identified.[23]

In the present investigation we have observed modest increases in $T_g$ in the range of 2–3.2°C, for polystyrenes and copolymers, on the addition of 20% of the carbon black of high surface area. This indicates that the filler induces some loss of mobility in the quiescent polymer. For polybutyl methacrylate, the increase in $T_g$ for the addition of 20% of the carbon black was 8.6°C, indicating a much stronger interaction between filler and polymer. We suggest that polar polybutyl methacrylate groups adsorb preferentially on the carbon black surface. These polar groups are also present in the copolymer, but since these are distributed randomly,[24] long sequences of butyl methacrylate residues are absent. Presumably long sequences of such residues are essential for polar bonding to the filler. If this study were extended to block copolymers, it would shed more light on this aspect.

Polymer glasses are not in equilibrium and have excess volume and enthalpy. The size of these excess properties depend on the method of preparation and thermal history of the glass. By annealing a quenched glass at temperatures approaching $T_g$, the enthalpy and volume relax towards equilibrium values. By studying the extent of relaxation and the rate at which different polymeric systems relax, we can gain some insight into the mobility of polymer molecules.

The amount of enthalpy relaxed after annealing for long periods of time at $T_g - 10°\mathrm{C}$ is reduced by the inclusion of carbon black filler (Figs. 1 and 2). The addition of 20% carbon black of surface area 625 $\mathrm{m}^2/\mathrm{g}$ reduced the enthalpy relaxed at long times by about 24% for polybutyl methacrylate and about 23% for polystyrene. Within experimental error, the reduction of enthalpy relaxed simply corresponds to the reduction in weight fraction of polymer by the addition of carbon black.

For the polymers examined in this study, the long time annealing behavior was used to determine the enthalpy relaxed at infinite time, $\Delta H_\infty$. These values agreed well with theoretical maximum values, predicted by $\Delta C_p$ measurements.[7,18] $\Delta H_\infty$ is then the enthalpy relaxation in a polymeric glass needed to achieve equilibrium. The excess enthalpy present after annealing for time $t$ is therefore

$$\Delta H_{\mathrm{ex}} = \Delta H_\infty - \Delta H_t$$

where $\Delta H_t$ is the enthalpy relaxed after annealing for time $t$. The fractional excess enthalpy is the ratio, $\Delta H_{\mathrm{ex}}/\Delta H_\infty$, and varies between 1.00 at zero time and 0 at infinite time. A plot of the fractional excess enthalpy versus log time was linear over the annealing time range.[8,18] The slope of this plot reflects the rate of enthalpy relaxation. We have observed that the absolute value of the slope for pure polybutyl methacrylate exceeds that of filled polybutyl methacrylate, annealed at the same temperature, 12.9°C. Indeed, at the constant annealing temperature, the rate of enthalpy relaxation was reduced almost in half for filled, compared to pure, polybutyl methacrylate. However, if the filled polymer is annealed at 21.5°C, which is 10°C below $T_g$ (31.5°C), then the lines for pure and filled polybutyl methacrylate superpose. This suggests that, at the same temperature interval below $T_g$, the molecular mobility in corresponding pure and filled systems is about the same. In the case of polystyrene, both pure and filled polymers had $T_g$ very close together (103.4 and 106.6°C). Annealing pure and filled polystyrene was carried out at $T_g - 10°\mathrm{C}$ for both systems. The plots of fractional excess enthalpy versus log time for both pure and filled polystyrene are very close and have the same slope. If filled polystyrene were annealed at 93.4°C, the same temperature as pure polystyrene, we suggest that the curve would not be significantly different, as the temperatures of annealing are so close. The absolute value of the slope for the decrease in fractional excess enthalpy with log time at $T_g - 10°\mathrm{C}$ in polybutyl methacrylate exceeds that for polystyrene by almost 50%. This suggests that the rate of enthalpy relaxation is higher for polybutyl methacrylate. Apparently, polybutyl methacrylate is a more flexible molecule than polystyrene, even when both polymers are compared at $T_g - 10°C$.

## CONCLUSIONS

$T_g$'s of several polymers measured by DSC are increased by the addition of 20 weight % carbon black of surface area 625 $m^2/g$. For low and high molecular weight polystyrenes, and for two random copolymers of styrene and butyl methacrylate, $T_g$ was increased by about 2–3°C. For polybutyl methacrylate homopolymer, the increase in $T_g$ was 8.6°C. These observations are consistent with rheological measurements.[1-5] Pure polybutyl methacrylate interacts most strongly with carbon black, producing the largest enhancements in steady shear viscosity and dynamic mechanical moduli. Polystyrenes show a much weaker interaction with carbon black. The corresponding random copolymers behave like polystyrene; this implies that long sequences of polar butyl methacrylate residues are required for extensive bonding to carbon black.

Changes in absolute values of $T_g$ are accompanied by enthalpy relaxation in the calorimetry of polymer glasses which had been annealed at temperatures below $T_g$. Following annealing at $T_g - 10°C$, the maximum enthalpy relaxed at long annealing times approximates 1.65 kJ/kg for polybutyl methacrylate and 2.6 kJ/kg for polystyrene. This agrees well with theoretical maxima calculated for these polymers.[7,18] Moreover, on annealing at $T_g - 10°C$, the rate of enthalpy relaxation is about 50% higher for polybutyl methacrylate than for polystyrene. Even after adjusting for $T_g$, polybutyl methacrylate appears to relax more readily than polystyrene. After adding 20% carbon black of surface area 625 $m^2/g$, the rate of enthalpy relaxation in filled polybutyl methacrylate annealed at 12.9°C is reduced by a factor of about two, compared to pure polybutyl methacrylate annealed at 12.9°C. The large change in rate of enthalpy relaxation, following the addition of carbon black to polybutyl methacrylate, results from strong interactions between the polar polybutyl methacrylate and the high surface area carbon black. However, both pure polystyrene and polybutyl methacrylate exhibit the same rate of enthalpy relaxation as the corresponding filled polymers, following annealing at 10°C below their respective $T_g$. The absolute shift in $T_g$ appears to be the primary indicator of polymer/filler interaction.

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