

SHORT COMMUNICATION

The Glass Transition Temperature of Poly(phenylene oxide): Annealing and Filler Effects

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We wish to report some observations on the T_g behavior of "poly(phenylene oxide)" PPO (poly(2,6-dimethyl-*p*-phenylene oxide), both unfilled and containing varying amounts of glass beads as filler.

The T_g of unfilled PPO is usually given as 210°C.¹ But this is for specimens which have been molded from the powder supplied by the manufacturer. If this powder is used in DTA experiments, *without* prior heating, a transition is found at 234°C. On cooling and reheating the same specimen in the apparatus, the transition occurs at a lower temperature and with reduced intensity, as shown in Figure 1. If the sample is annealed at 300°C for varying amounts of time, T_g drops rapidly in the first few minutes and tend to level off at the usual value, as seen in Figure 2. The curves of Figure 1 were obtained with a du Pont Thermo-analyzer, model 900, using a heating rate of 20°C/min. The samples, previously dried in a dessicator for at least 24 hr at room temperature, were exposed to air during the measurements. Just above the *endo*-thermic peak, which we believe represents T_g , an apparent *exo*-thermic peak occurs. It is apparently this peak which is reported² as a melting point, with $T_m=270^\circ\text{C}$.

Since it is unwise to base T_g estimates solely on DTA data, DSC measurements were also

made (Perkin-Elmer DSC-1) with a similar heating rate of 16°C/min and with more careful control of the baseline. A nitrogen blanket was employed, which reduced but did not eliminate oxygen. A typical first heat cycle is shown in Figure 3. The DSC results confirm the DTA measurements: T_g at about 230°C with an *exo*-thermic peak at 270°C, and the same shift in T_g after exposure to 300°C. These results raise a number of questions: Why is T_g decreased by the heating, what is the origin of the high temperature peak and does one "transition" effect the other. There are

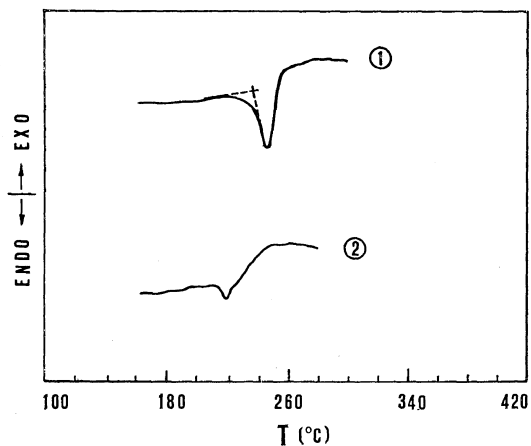


Figure 1. DTA curves for ① powder, as supplied, and ② same sample after a 2 min annealing at 300°C, cooling to 150°C and immediately rerun. T_g estimated from base line and low-temperature side of peak as shown.

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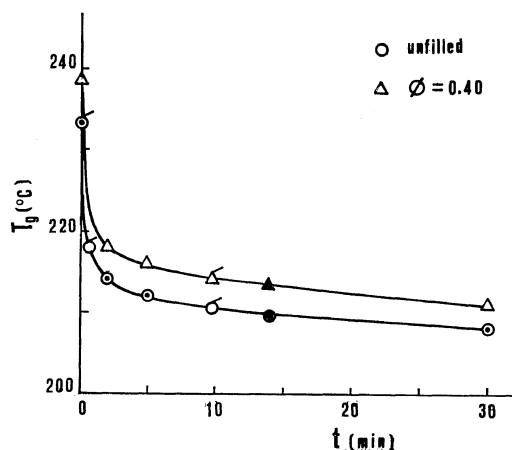


Figure 2. Change in T_g with time of annealing at 300°C , as determined by DTA (unflagged points) and DSC (flagged). Filled point—sample shaved from a conventionally molded sheet.

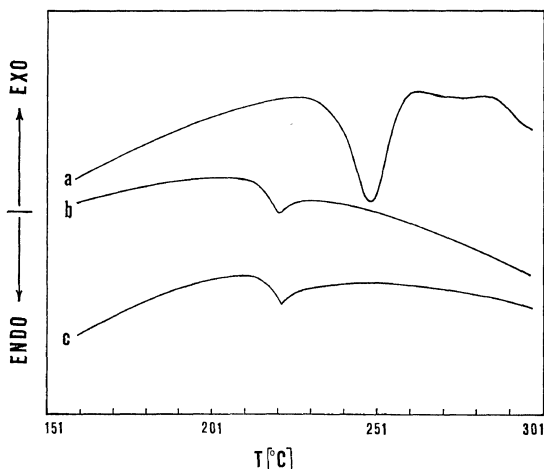


Figure 3. Portion of the DSC curve for the powdered PPO, showing (a) the high-temperature peak, (b) the same region after heating to 300°C , cooling and re-running, and (c) the same region after annealing 1 hr at 272°C , cooling to 150°C and re-running.

several possible answers to each of these, which can be checked by appropriate experiments.

T_g can be changed by frozen-in stresses and by the presence of small-molecule impurities, either preexisting or induced by the heating. It might possibly be affected by the degree of crystallinity of the sample. On the other hand the apparent change in T_g might be only an

artifact, since the experimentally observed quantities of temperature difference (DTA) and rate of heat input (DSC) depend on heat transfer, thermal conductivity and specific heat as well as on the changes in phase or in heat capacity *per se*.

If T_g has been altered by the relief of frozen-in stresses, the magnitude of the drop would have to imply enormously high compressive stresses in the powder granules. The point is easily checked by heating just below T_g , to 234°C and immediately cooling. Although the material is still in the glassy state at this temperature, it is now so close to T_g that such high stresses must relieve themselves. Thus when the powder is reheated, T_g should again be reduced. However, experiment shows that it is not, which eliminates this source of change. The presence of pre-existing small molecule impurities is also an unlikely source of the change in T_g . They normally plasticize a polymer or lead to separate transitions. In the first case, their removal by heat would shift T_g to higher, not lower temperature (unless they act as antiplasticizers); in the second case, the main chain T_g should remain unchanged.

The use of two different (though admittedly related) experimental techniques for determining T_g strongly argues against experimental artifacts. Moreover, the value of 210° for the heated material agrees well with that deduced from mechanical property tests on molded specimens. Clash—Berg $G(10)$ data are shown in Figure 4 where it can be seen that the Tobolsky T_i value is about 210°C .

The lower T_g of the heated material probably results from degradation. Thus, Ehlers, Frish and Powell³ and Davis⁴ show that an initial weight increase occurs as samples are heated in air or oxygen, the amount of the increase being in accord with an oxygen uptake of $1.8 \times 10^2 \text{ cm}^3/\text{g}/\text{hr}$ at 300°C , a value obtained by extrapolation from Davis' Figure 3. Conley⁵ has also pointed out the rapid oxygen attack on specimens (presumably in the form of films), noting that at 225°C an induction period is followed by very vigorous reaction. We calculate from Davis' data that the uptake amounts to roughly one mole of oxygen per chain, which should suffice to give the few percent of low-

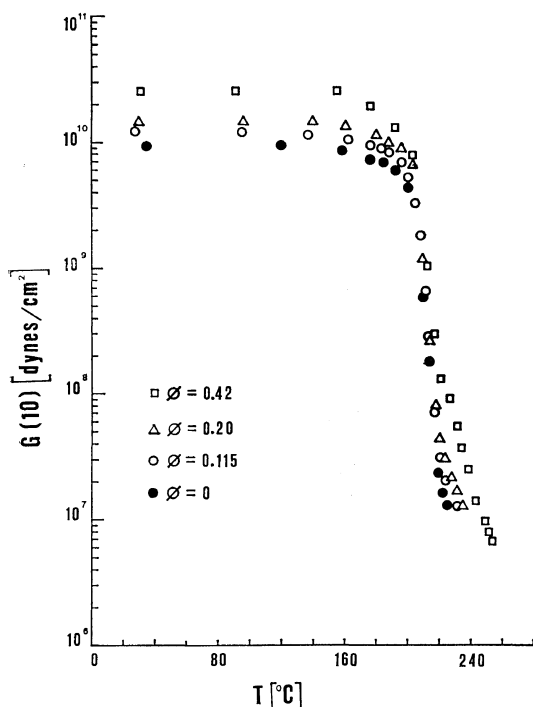


Figure 4. Clash-Berg $G(10)$ modulus data for molded specimens of PPO, for different filler levels.

molecular-weight products which would be required to lower T_g by 25°C.

The fact that the same initial value of T_g of about 234°C is found in experiments run in both air (DTA) and under a nitrogen blanket (DSC) indicates that only traces of oxygen are required. If oxydative degradation is the culprit, compressing the powder at room temperature before test should reduce the effect. Thin sheets were therefore prepared in this way and material for the DTA test was obtained by shaving in the usual way. An even higher T_g of 243°C was obtained. This same specimen was rerun after holding it at 300°C in the apparatus for 5 min. T_g again decreased—to 220°C; presumably its T_g would also drop to about 210°C with further annealing at 300°C.

The high temperature peak, seen in Figure 3a, could be interpreted as a crystalline melting, for when the sample is reheated the peak has disappeared, as in Figure 3b, *i.e.*, as if the crystallites had melted but not reformed in the time available.

To investigate this region more closely, samples were heated to 258°C, *i.e.*, well below the beginning of the upper peak, immediately cooled and then heated to 300°C. A second sample was heated to 272°C, the temperature of the peak, and annealed for 1 hr before cooling and reheating to 300°C.

If the peak is due to crystallinity, the first experiment should not change it, while in second case annealing should permit further crystallization if the preexisting crystallinity were not the equilibrium value for that temperature. Subsequent reheating to 300°C should then show either no or an enhanced thermal effect, depending on whether the crystallinity remains constant or increases. In actual fact, the first experiment leads to a virtual disappearance of the peak while in the annealed sample it disappeared completely, Figure 3c. These results argue that the peak is not due to crystallinity at all. The 258°C exposure could only have changed the peak if the crystallites were in a highly metastable condition. However, the annealing should then have permitted regrowth on the residual stable nuclei. As a further check, X-ray diffraction patterns were taken on the fresh powder, before and after heating to 300°C and after annealing at 272°C for 1 hr. No evidence for crystallinity could be seen by this admittedly less sensitive technique.

Prior experience with the analysis of inorganic glasses and semicrystalline materials⁶ suggests that this peak is simply due to the change of heat transfer to the sample as the sample flows above T_g . All of the results are consistent with this mechanism—heating to 172°C and immediate cooling permits only partial fusion with a correspondingly small decrease in “*endo-thermicity*,” annealing for 1 hr permits added flow and elimination of the peak (Figure 3c).

Finally, we note that in these two experiments the value of T_g after reheating is nearly constant, showing that changes in the high-temperature peak have had no effect on it. Having established T_g for the powder and molded material, we now consider the effect of a filler. When 40 vol% of glass beads is added to the polymer, the glass temperature is raised about 4°C. This effect is independent of the anneal-

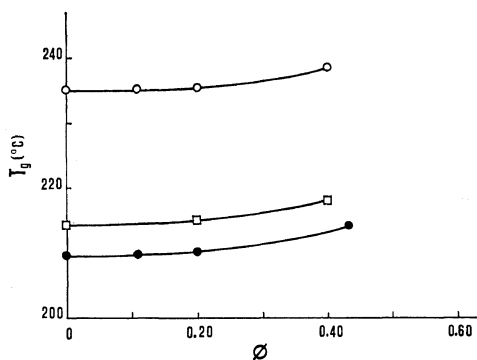


Figure 5. Increase in T_g of PPO (DTA measurement) with filler content for \circ the powdered material; \square the same material after heating to 300°C for 3 min; \bullet samples shaved from molded pieces.

ing time and, more importantly, occurs in the simple physical mixture of the two components (Figure 2). This means that since the PPO is in the glassy state until T_g , there cannot be polymer adsorption on the glass. Hence the usual explanation of a modification of chain motion and free volume by the filler particles cannot be invoked here.

When varying bead concentrations are employed, results such as shown in Figure 5 are obtained. Here the results of the first and second heating of the mixed powders are compared with results from specimens which were prepared by mixing and molding at 285°C in the usual way. The material used for the DTA measurements was shaved off the molded piece with a razor blade. The much higher T_g of the virgin powder is evident in all compositions. Moreover, the effect of the glass on the apparent T_g is the same in all cases and again argues against a real effect by the beads.

We can offer no convincing explanation for the effect of the beads. Since the DTA apparatus measures the temperature difference between a reference (glass beads) and the sample, perhaps it is a question of heat capacity and heat transfer plus thermal conductivity in the mixed system. The latter seems doubtful however because the same T_g is found with the sample temperature leading and lagging the reference temperature. Moreover, DSC gives the same result (Figure 2). More experiments

with three-phase systems (two powders and air) are indicated.

As a first step, differential DSC has been attempted, using powdered PPO in the reference cell instead of air, and the 20% beads—80% PPO in the sample holder. A slight change in the slope of the base line occurs in the region of T_g , but with the present sensitivity of the apparatus it is impossible to distinguish whether there is a change in T_g , even if much reliance could be placed on the small change observed. The high temperature peak shows clearly, however, though with reversed sign because of the larger amount of polymer in the reference cell.

The negligible effect of the filler on T_g is also shown in the modulus data, Figure 4. The beads clearly enhance the glassy modulus, as expected, and are tending to increase the modulus at the foot of the transition zone, as it should. The location of the transition zone is unchanged, however. Analogously no effect of the glass beads on the T_g of polystyrene has been reported by Mills⁷ while small effect of a filler on the transition temperature have been reported by Landel⁸ for glass beads in PIB or by Schwarzl⁹ for potassium chloride in a polyurethane rubber. Droste and Di Benedetto¹⁰ using DTA also report only a small effect on T_g —4 or 5°C at 40%—for beads in a phenoxy polymer.

This small change in T_g is in contrast to earlier data of Landel¹¹ reporting a large increase of T_g for ammonium perchlorate in polyurethane rubbers similar to that used by Schwarzl, using linear expansion coefficient measurement to determine T_g .

In this case, the postulated attachment of the chains to the filler could well be real, since the NH moiety of the urethane group or of any traces of urea groups can fit into the crystal lattice, replacing the NH_4^+ group. The possibility cannot be ruled out, however, that small amounts of the salt have dissolved in the polymer and modified its T_g , as can happen with lithium salts in poly(propyleneoxide).¹²

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