

Effect of silica nucleants on the rates of crystallization of poly(ethylene terephthalate)

Giulio Turturro*, G. R. Brown and L. E. St-Pierre

Department of Chemistry, McGill University, Montreal, PQ, H3A, 2K6, Canada

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Studies of the crystallization of poly(ethylene terephthalate) (PET) by d.s.c., both isothermally and non-isothermally, show that the addition of silica causes marked increases in rate at loadings < 1 part filler in 100 parts polymer. At higher loadings the overall rate of crystallization decreases until it becomes less than that of un-nucleated PET. Modified silica, with an alkoxy-coated surface, causes similar but less pronounced changes in rate. The retardation in rate in spite of an increase in the number of spherulites is attributed to an increase in the viscosity of the polymer melt due to strong adsorption onto the silica particles.

(Keywords: Poly(ethylene terephthalate); crystallization; silica; retardation; adsorption)

INTRODUCTION

For crystallizable polymers primarily nucleation is known to affect the number of nuclei per unit volume, their size, the overall rate of crystallization and the total crystallinity than can be attained^{1,2}. These factors, in turn, determine certain physical properties such as impact resistance and dimensional stability of parts fabricated from these polymers.

Poly(ethylene terephthalate) (PET) is widely used as a molding powder but increases in its use have been limited by a tendency of the parts to distort in shape over long periods of time. These changes have been attributed to a very slow crystallization process and have resulted in numerous studies of its bulk crystallization in hopes of solving these problems³⁻⁷.

Work in this laboratory has demonstrated that it is possible to achieve control of certain aspects of crystallization in polymer melts by the addition of well-characterized silica nucleants. This paper describes the application of these techniques to the PET system. The crystallization of PET, both un-nucleated and nucleated with silica, has been studied under isothermal and temperature-programmed conditions. The role of the silicas in controlling the rate of growth of PET spherulites, i.e. in retarding crystallization in the same manner seen in other systems⁸⁻¹⁰, was of special interest in this study.

EXPERIMENTAL

Materials

Poly(ethylene terephthalate). Commercial PET, supplied by Rohm and Haas Ltd., was purified by dissolving it in *o*-chlorophenol, precipitating it by

addition of methanol and drying under vacuum before use. The intrinsic viscosity in *o*-chlorophenol at 25°C was 0.62 yielding a viscosity average molecular weight of 2.02×10^4 ¹¹. The polymer had a maximum of 40 carboxyl end groups per 10⁶ g of polymer and 0.60 ± 0.10 diethylene glycol groups, as quoted from the manufacturer. The equilibrium melting temperature, determined by d.s.c., was 268°C.

Silicas. An amorphous, thermal silica (Cab-O-Sil M5) with particle size 12 nm and 99.8% pure was obtained from Cabot Corp. (Boston, Mass.). The nitrogen BET surface area, determined by Chahal¹², was $200 \pm 10 \text{ m}^2 \text{ g}^{-1}$.

A silica sample with a trimethylsilylated surface, also prepared by Chahal¹², was also used. The surface treatment was achieved by the following procedure. A quantity of silica was degassed in an aluminum bomb. After a known volume of trimethylchlorosilane had been added, the bomb was heated to cause reaction with the silica. The modified silica was then dried at 230°C in a stream of dry helium for 3 h. Total carbon content (Schwartzkopf Microanalytical Lab., Woodside, NY) indicated a surface coverage of 1.7 ± 0.2 trimethylsilyl groups/100 Å².

Dispersions. The polymer-nucleant composites were prepared by addition of known quantities of the silica, previously dried under vacuum (< 0.1 Pa) at 110°C for ≈ 10 h, to a 10% solution of PET in *o*-chlorophenol [Spectroanalytical quality, dried over molecular sieves (Linde Type 3A, Matheson, Coleman and Bell Ltd., Ohio)]. The mixtures were agitated with a stainless-steel spatula until most of the solvent had evaporated. The remaining solvent was removed by freeze-drying. The composites were stored over silica gel in a vacuum desiccator.

* Present address: Wiik and Hoeglund, Canada, Huntsville, Ontario, POA 1K0, Canada

Methods

A Perkin-Elmer Differential Scanning Calorimeter (model DSC-1B) was used to measure the rates of crystallization of pure PET and its composites. Calibrations for temperature and heat release (peak area) were made in the usual manner^{13,14}.

RESULTS AND DISCUSSION

Non-isothermal crystallization of PET

When PET is cooled from the melt with the d.s.c., it exhibits an exotherm indicative of the enthalpy of crystallization. The temperature at the peak of the exotherm, taken to be the optimum crystallization temperature, T_{op} , corresponds to the temperature at which crystallization attains its maximum rate¹⁵⁻¹⁷. Figure 1 shows the effect of increase in cooling rate on T_{op} (where the reported T_{op} is corrected for thermal lag of the d.s.c.). This shift is a result of the fact that the time required for the formation of sufficient nuclei to produce a rate of crystallization detectable by d.s.c. is similar to the time of cooling.

All further measurements of the non-isothermal crystallization of PET and nucleated samples of PET were carried out at a cooling rate of $20^{\circ}\text{C min}^{-1}$. The T_{op} of the exotherms was found to be dependent on the concentration of the silica added to the PET as well as on the surface energy of the nucleant (Figure 2). Initially T_{op} increases at very low loadings, attains a maximum, and finally decreases with further increase in silica content. It is apparent that samples with the same silica content but containing silica with different interfacial energies do not exhibit the same crystallization kinetics. Similar behaviour, although at higher loadings of silica, has been reported by Cole and St-Pierre¹⁸ for the crystallization of isotactic poly(propylene oxide).

The increase in crystallization rate caused by the addition of silica at low loadings, reflected by an increase

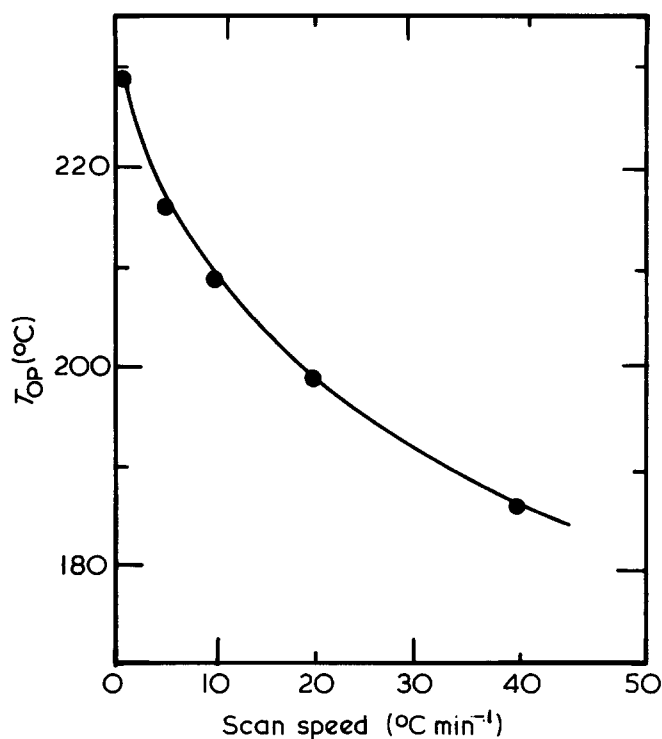


Figure 1 Dependence of the optimum crystallization temperature, T_{op} , of un-nucleated PET on the d.s.c. scan speed

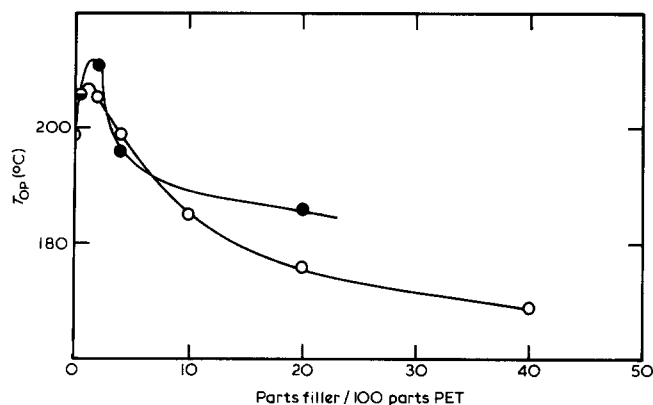


Figure 2 The effect of added silica on the optimum crystallization temperature, T_{op} , of PET (cooling rate = 20 K min^{-1}). ○, silica; ●, treated silica

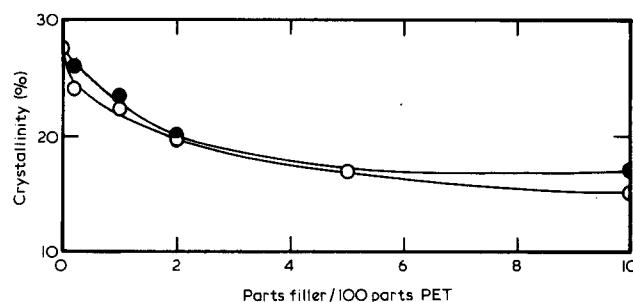


Figure 3 Effect of added silica on the crystallinity of PET crystallized at a cooling rate of 20 K min^{-1} . ○, silica; ●, treated silica

in T_{op} , can be explained by the application of classical theory for heterogeneous nucleation. Silica powder as an extraneous solid can catalyse the primary nucleation process by reducing the net free energy of formation of a unit area of nucleus interface. As silica-nucleated samples are associated with smaller free energies of nucleation, the critical number of nuclei necessary for d.s.c. detection are present at higher temperatures relative to the pure PET.

Once a maximum value of T_{op} has been obtained, small increments in the silica concentration cause the T_{op} to decrease rapidly until it levels off at approximately 20 parts silica in 100 parts PET. This behaviour is consistent with an increase in quasi-cross linking of polymer segments by interaction with the silica surface with increase in silica content. The quasi-crosslinking of the segments increases the energy value in the transport term of the nucleation rate expression² thereby lowering the overall crystallization rate with a concomitant decrease in T_{op} . This is particularly evident at loadings of more than 2 parts silica in 100 parts PET where the value of T_{op} is actually lower than that for the unnucleated PET.

The trimethylsilylated silica, which has a lower polymer melt-nucleation interfacial energy, is capable of giving a higher maximum value of T_{op} as compared to that obtained for the untreated silica (Figure 2). As the specific interactions that can occur between the free hydroxyls on the untreated silica surface and PET are less evident in the case of the treated silica, the restriction to transport of the PET segments is less, giving rise to a higher nucleation rate. However, even with the treated silica a loading of more than 2 parts per 100 parts PET causes a retardation of the overall rate of crystallization.

Figure 3 shows that the relative crystallinity (based on

heat of fusion of 117.6 J g^{-1} for fully crystalline PET¹⁹) attained during non-isothermal crystallization while cooling the sample at $20^\circ\text{C min}^{-1}$ on the d.s.c. first decreases as the nucleant concentration increases and then levels off at approximately 10 parts of silica in 100 parts PET. This is further evidence of the existence of a 'crosslinked' polymer network. The strong adsorption between the nucleant and the PET causes the amorphous sequences to be isolated between the successive particles of silica so that they are unable to participate in the crystallization process. As the silica concentration increases, the number of units available for crystallization is considerably diminished until a saturation point is attained as indicated by the smoothing of the curve in Figure 3).

Isothermal crystallization of PET

The isothermal crystallization behaviour of nucleated and un-nucleated PET was also investigated by d.s.c. Prior to crystallization, the samples were melted at 287°C for 15 min to ensure complete destruction of crystalline memory. Avrami-type isotherms for un-nucleated PET at different crystallization temperatures (Figure 4) show the change in weight fraction of crystallized PET with time. It is evident that at higher temperatures the induction time is longer and the crystallization process is slower, as predicted by theory².

A semi-quantitative analysis of the time dependence of the isothermal crystallization data in Figure 4 was attempted using the Avrami relation:

$$\alpha = 1 - X_t = \exp(-Zt^n)$$

where α is the volume fraction of crystallizable polymer not crystallized at time t , Z is a constant and n is the Avrami exponent indicative of the geometry of the growing crystalline entities^{1,2}. For un-nucleated PET an average Avrami constant of 3.3 was obtained, in agreement with previous studies of Fielding-Russel and Pillai who determined a value of 3.4 over the temperature range $230^\circ\text{--}240^\circ\text{C}$ also using d.s.c.⁴. Groeninckz *et al.*⁶ obtained $n=3.48$ from density measurements for the isothermal crystallization of PET between 100 and 113°C . The Avrami plots show a tendency to non-rectilinearity, particularly at longer crystallization times. This non-rectilinearity was particularly noticeable for nucleated samples which showed a distinct decrease in the Avrami coefficient after a major portion of the sample had been crystallized. This suggests a change in mechanism, or

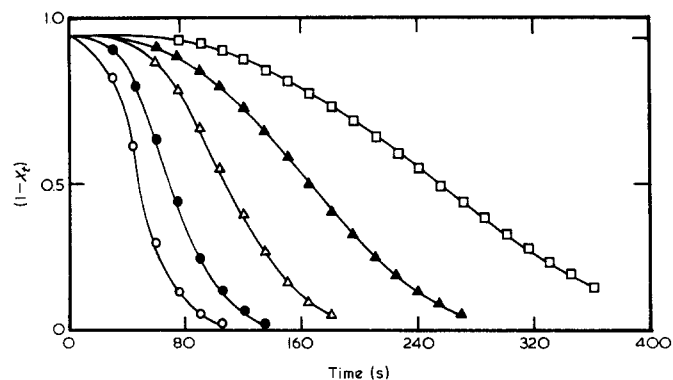


Figure 4 Crystallization isotherms for un-nucleated PET (X_t =weight fraction of crystalline PET at time t). ○, 202; ●, 207; △, 212; ▲, 217; □, 222°C

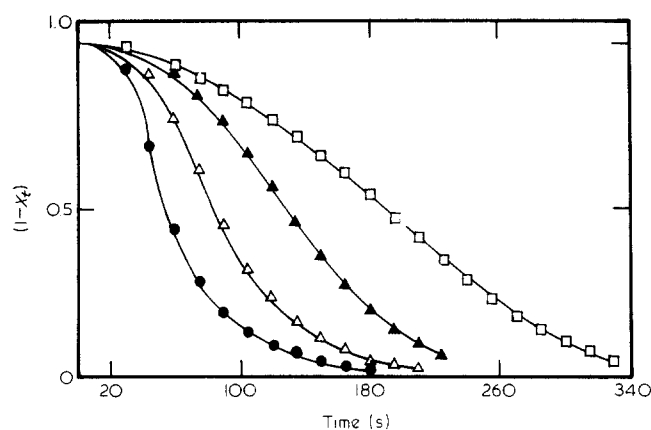


Figure 5 Crystallization isotherms for nucleated PET with 2 parts silica/100 parts PET. (X_t =weight fraction of crystalline PET at time t). ●, 207; △, 212; ▲, 217; □, 222°C

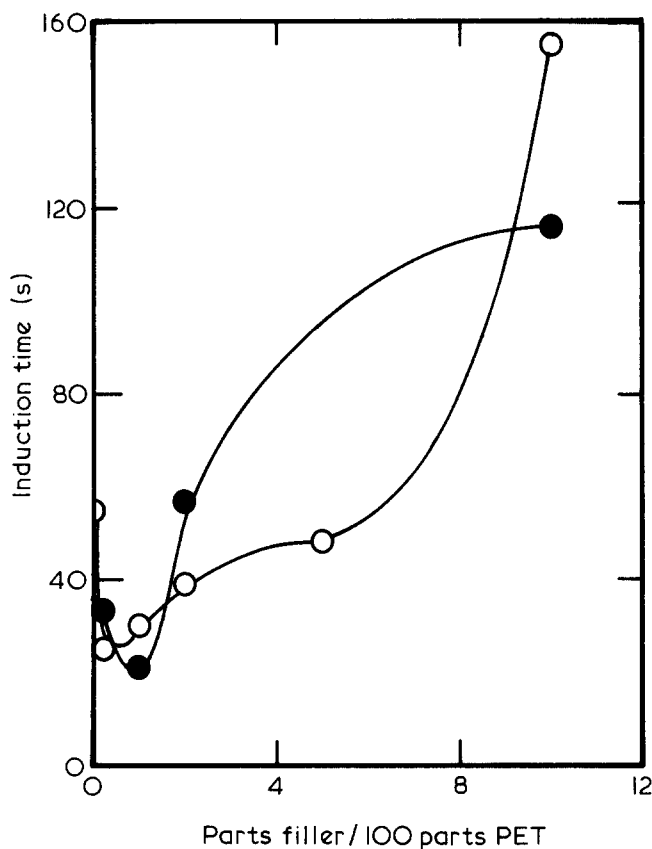


Figure 6 Effect of added silica on the induction time for the crystallization of PET at 212°C . ○, silica; ●, treated silica

growth process, at longer crystallization times. Evidently, this change is emphasized by the addition of silica nucleant.

Crystallization isotherms for a PET sample containing 2 parts silica in 100 parts PET are illustrated in Figure 5. Comparison of the initial portion of the crystallization curves in Figures 4 and 5 shows a longer induction time in the un-nucleated polymer than in the nucleated PET. The effect of added silica, both treated and untreated, on the induction time at a crystallization temperature of 212°C is shown in Figure 6. The induction time is the time period at the beginning of the crystallization process when evolved heat is too small to be detected. During this time nuclei are formed for subsequent spherulite growth. At low loadings there is a decrease in the induction time with increase in

filler content due to enhancement of primary nucleation which results upon addition of silica¹⁰. However, at higher loadings the induction periods become longer again inspite of a greater number of nuclei per unit volume. It is apparant that the retardation in secondary nucleation rate more than compensates for any increase in spherulite density.

The inhibition to crystallization by the presence of silica is also apparent in the half-times for the crystallization. Beyond ≈ 0.2 parts virgin silica per 100 parts PET the rate of crystallization is diminished at all crystallization temperatures (Figure 7). A similar pattern is obtained for PET containing surface-modified silica (Figure 8).

CONCLUSIONS

The addition of silica to PET can result in an overall decrease in crystallinity in spite of the fact that the number of nuclei increase with an increase in silica loading. This increase in number of nuclei results in an increase in the overall rate of crystallization at low concentration of filler. However, at higher silica content there is an indisputable retardation in the rate of overall crystallization which, in many cases, is sufficient to cause the rate of crystallization to become less than that of the un-nucleated sample at the same temperature.

Direct measurements, using photomicroscopy, have shown that silica also retards the rate of radial growth of spherulites of isotactic polystyrene^{9,10}. Polystyrene is

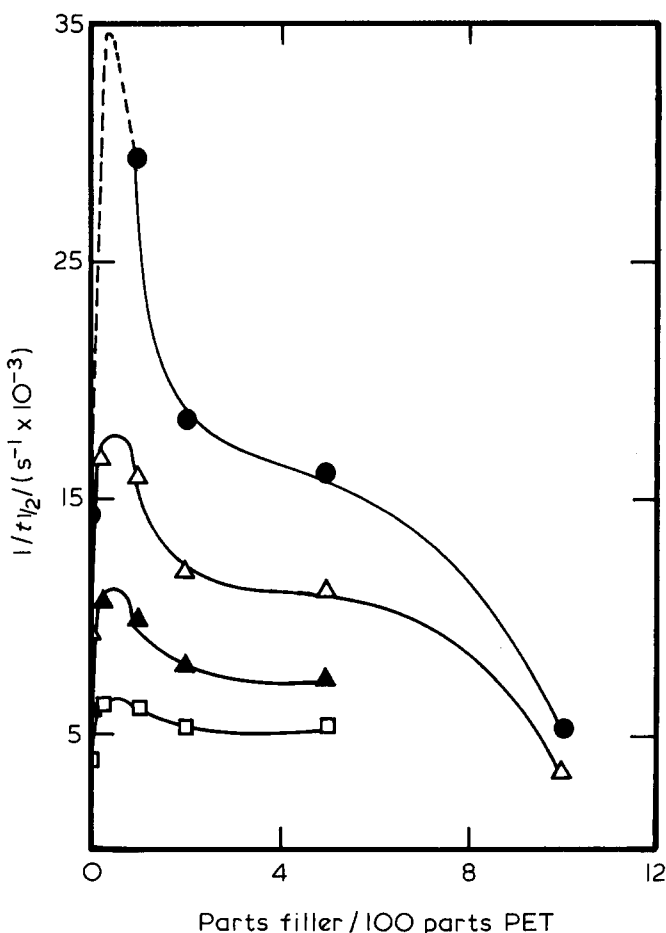


Figure 7 Effect of added silica on the reciprocal half-time, $1/t_{1/2}$, for the crystallization of PET. ●, 207; △, 212; ▲, 217; □, 222°C

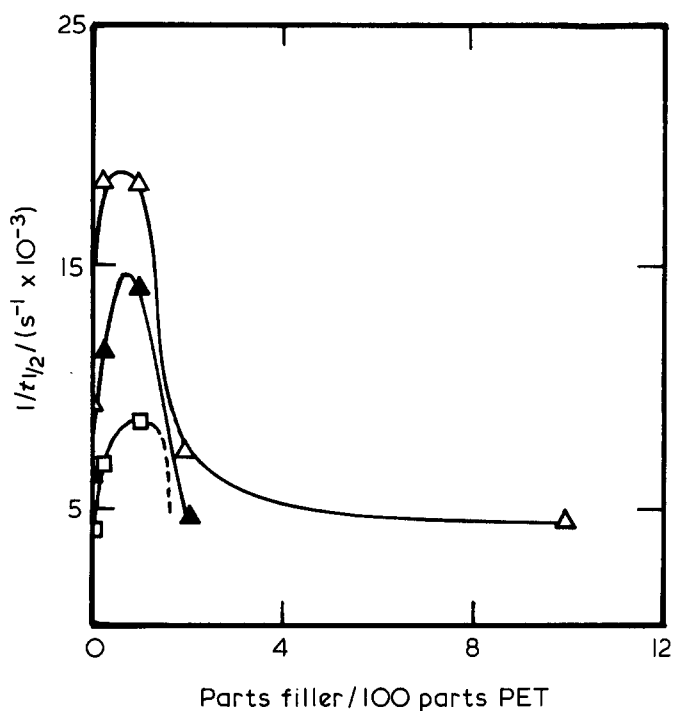


Figure 8 Effect of loading of treated silica on the reciprocal half-time, $1/t_{1/2}$, for the crystallization of PET. △, 212; ▲, 217; □, 222°C

known to adsorb strongly onto silica surfaces and the retardation in radial growth rate was attributed to this 'quasi-cross-linking' effect. Indeed, the degree of retardation was shown to be related to the heat of adsorption per polymer segment and less for 'surface treated' silica than for virgin silica.

Jopien²⁰ has shown that PET is hydrogen-bonded via almost all the carbonyl groups up to 80% of the free hydroxyl groups of the silica thus producing a 'crosslinked' polymer network. It is not unexpected then that retardation in radial growth rates would occur.

Chahal and St-Pierre²¹ showed that the relaxation modulus, E_0 , of filler-containing polymers is related to the polymer-filler interfacial energy, determined from the net heat of adsorption, ΔH , of a model compound onto the filler surface:

$$E_0 \propto \phi^{5.05} e^{b\Delta H}$$

where ϕ is the volume fraction of filler and b is a constant. The increase in modulus that results with increase in filler content was attributed to cross-link points occurring at the filler particle, either by direct interparticle chainlinks or by entangled chains adsorbed onto adjacent filler particles.

The relaxation modulus is, in turn, related to the melt viscosity, η , by:

$$E_0 = \eta/\tau$$

where τ is the relaxation time, which was found to be constant irrespective of filler treatment or concentration. Hence, a direct relation between relaxation modulus and viscosity is implied. As the modulus increases the viscosity of the melt also increases thus hindering transport of crystallizing segments. This has been confirmed by the effect of fillers on the T_g of polymer samples²²⁻²⁴. Hence, at a given temperature a polymer sample containing treated silica, which results in a lower interfacial energy, would

have less 'quasi-cross-linking' than a sample containing unmodified silica. The transport of the segments to the site of crystallization would be less restricted in the case where the treated silica was used as the nucleant.

Another effect of the nucleant presence is to be found in the slowing of the secondary stages of crystallization and a diminution of attainable percent crystallinity. The former can be in part related to transport but both are concluded to be a consequence of the lowering of the concentration of 'crystallizable' segments. With the high adsorption energies manifested in this system, adsorbed segments are considered to be excluded from the crystallization process as are segments adjacent to them. This effect is apparent in the secondary crystallization stages, *Figures 5* (PET + two parts silica) where there is a greater slowing down of crystallization in the final stages as compared to the un-nucleated PET isotherms (*Figure 4*). Thus, in the latter case, the overall crystallization will proceed for longer times before it is complete as more polymer can take part in the slower secondary process.

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