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OXYGEN INHIBITION IN DIFFERENTIAL SCANNING CALORIMETRY OF FREE RADICAL POLYMERIZATION *

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ABSTRACT

A useful analytical method of measuring reaction kinetics of polymerization is differential scanning calorimetry (DSC). One problem in DSC testing of free radical polymerization kinetics, however, is that the induction time before polymerization begins varies inversely with sample size. This paper shows that this "sample size anomaly" results from a synergistic reaction between oxygen and certain inhibitors. Two types of inhibitors were found: oxygen-inert inhibitors such as benzoquinone which do not react with oxygen and hence show little sample size anomaly, and oxygen-active inhibitors such as hydroquinone which require oxygen to be active. A model describing the effect of oxygen during inhibition was verified using isothermal DSC data for styrene homopolymerization. The inhibition time was also measured for a variety of sample pans using a commercial vinyl ester resin formulation, and observed behavior indicates the presence of both oxygen-active and oxygen-inert inhibitors. The recommended procedure for DSC sample preparation is to match the polymerization conditions during processing. In composites processing, for example, resin is saturated in air and cured in a closed mold environment, so the appropriate DSC sample procedure is to completely fill the sample pan to displace air in the headspace without changing oxygen concentration in the sample.

INTRODUCTION

Differential scanning calorimetry (DSC) is commonly used to measure the rate of polymerization, assuming that the rate of heat released is proportional to the rate of conversion. The advantages of the DSC for cure characterization are simplicity, ease of use, and the ability to monitor cure for both liquids and solids. DSC is especially useful for measuring the reaction kinetics of thermosetting polymers since other methods (such as titration, bromine absorption, and monomer extraction) are difficult or

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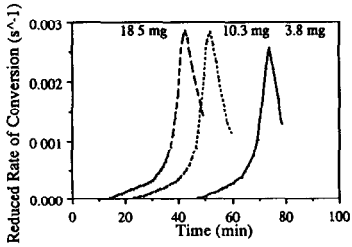


Fig. 1. Effect of sample mass on the reduced rate of conversion ($= R_p/[M]_0$) of vinyl ester resin.

impossible to apply after the gel point. In particular, crosslinking polymers which react by the free radical mechanism, such as unsaturated polyester, vinyl ester, or divinyl benzene, typically gel at monomer conversions of less than 10%, so the DSC is a very important tool for measuring kinetics.

To prevent premature polymerization of free radical monomers during shipping and handling, a free radical inhibitor is added which stabilizes free radicals which may form when exposed to light or heat. During a DSC run, the presence of inhibitor is manifested by an induction time before polymerization. Ideal inhibitors should not affect the rate of cure after the induction time.

Problems arise, however, when checking for reproducibility of DSC data. Ideally, the DSC results should be independent of sample mass barring any temperature increase during exotherm or time lags [1]. For a crosslinking vinyl ester, however, induction time varies inversely with mass (Fig. 1), though curing rate after inhibition is not affected. This sample size dependence is most likely due to oxygen, which has been shown previously to affect inhibition time in open DSC pans [2–4].

This paper will study the role of DSC sample size and oxygen in free radical polymerization kinetics. The chemistry of inhibition will provide insight into the mechanism of the oxygen effect. A proposed explanation of the DSC sample size anomaly will be tested using experimental inhibition times for various (1) inhibitor compositions, (2) sample sizes, and (3) types of DSC pans. Methods for compensation or elimination of the sample size anomaly in DSC experiments are discussed.

THEORETICAL

Kinetics of inhibition

The rate of free radical polymerization is proportional to the free radical concentration. If radical concentration is very small, owing to an inhibitor, for example, then the polymerization would be negligible, and the reaction

would be delayed until the inhibitor is consumed. Free radicals R$^{\cdot}$ may be generated by thermal decomposition of an organic peroxide initiator I

$$\mathrm{I} \xrightarrow{k_d} 2\mathrm{R}^{\cdot} \tag{1}$$

An inhibitor Z rapidly consumes free radicals as they are formed according to eqn. (1)

$$\mathrm{Z} + \mathrm{R}^{\cdot} \xrightarrow{k_z} \text{unreactive product} \tag{2}$$

The inhibitor reaction is irreversible, and after a characteristic "inhibition time" t_z, the inhibitor is completely consumed and propagation with monomer M can begin

$$\mathrm{M} + \mathrm{R}^{\cdot} \xrightarrow{k_p} \mathrm{RM}^{\cdot} \tag{3}$$

Ideally, the inhibitor should not affect k_p or R$^{\cdot}$ after t_z. From eqn. (2), the rate of consumption of inhibitor is proportional to the concentrations of radicals [R] and inhibitor [Z]

$$\frac{\mathrm{d}[\mathrm{Z}]}{\mathrm{d}t} = -k_z[\mathrm{R}][\mathrm{Z}] \tag{4}$$

where k_z is the rate constant for inhibition. The change in [R] with time is

$$\frac{\mathrm{d}[\mathrm{R}]}{\mathrm{d}t} = \underset{\substack{\text{initiation}\\ \text{rate}}}{2f[\mathrm{I}]k_d} - \underset{\substack{\text{inhibition}\\ \text{rate}}}{k_z y[\mathrm{R}][\mathrm{Z}]} - \underset{\substack{\text{termination}\\ \text{rate}}}{k_t[\mathrm{R}]^2} \tag{5}$$

where y is the number of moles of radicals consumed per mole of inhibitor. Owing to the small concentration of radicals during inhibition, the rate of termination may be neglected. When the quasi-steady state approximation ($\mathrm{d}[\mathrm{R}]/\mathrm{d}t = 0$) is applied to eqn. (5), the radical concentration [R] is given as follows

$$[\mathrm{R}] = \frac{2f[\mathrm{I}]k_d}{yk_z[\mathrm{Z}]} \tag{6}$$

Substituting eqn. (6) into eqn. (4) gives

$$\frac{\mathrm{d}[\mathrm{Z}]}{\mathrm{d}t} = -\frac{2f[\mathrm{I}]k_d}{y} \tag{7}$$

and integrating from $t = 0$ where $[\mathrm{Z}] = [\mathrm{Z}]_0$ to time t_z where $[\mathrm{Z}] = 0$, and neglecting initiator depletion ($[\mathrm{I}] = [\mathrm{I}]_0$), then the inhibition time t_z can be found

$$t_z = \frac{y[\mathrm{Z}]_0}{2f[\mathrm{I}]_0 k_d} \tag{8}$$

Hence, t_z is directly proportional to the amount of inhibitor.

Chemistry of inhibition

If the headspace contains air, then oxygen will be in contact with the sample. With a k_z/k_p of over 15 000 [5], oxygen is one of the strongest free radical inhibitors known. Paradoxically, oxygen can also be an accelerator or an initiator. The role of oxygen during polymerization depends on which initiators, monomers, and inhibitors (if any) are present.

Without other inhibitors added to the monomer, oxygen in high concentration will copolymerize with radicals of methyl methacrylate [6] or styrene [7] to form a peroxy radical

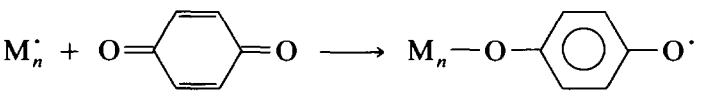
$$O_2 + M_n^{\cdot} \rightarrow M_nO_2^{\cdot} \tag{9}$$

which can then copolymerize with the monomer

$$M_nO_2^{\cdot} + M \rightarrow M_nO_2M^{\cdot} = M_{n+1}^{\cdot} \tag{10}$$

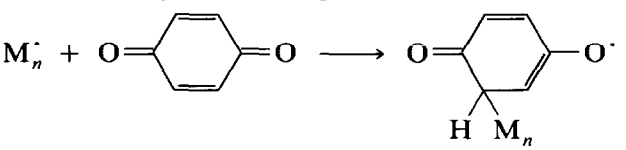
At low temperatures the peroxy radical is stable, hence eqn. (10) is slow and oxygen acts as an inhibitor. At higher temperatures, eqn. (10) is faster and oxygen accelerates curing.

The effect of inhibitors on free radical polymerization is well documented [8,9]. One inhibitor which does not react with oxygen is p-benzoquinone. The behavior of quinones are complex, and radical attack can occur either at the oxygen sites to form an ether



(11)

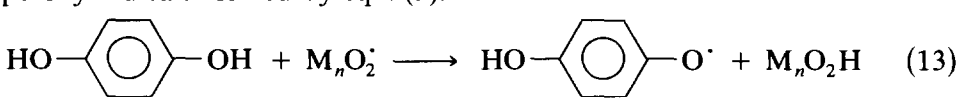
or at the ring to form a quinone



(12)

Depending on the reactivity of the products of eqns. (11) and (12), quinones may terminate either one or two free radicals.

Kurland [10] has studied the synergistic inhibition of oxygen and phenol-based inhibitors such as hydroquinone (HQ) and *p*-methoxyphenol (MMHQ). These compounds are inhibitors only in the presence of oxygen. The mechanism of oxygen inhibition is likely to be the autooxidation of peroxy radicals formed by eqn. (9).



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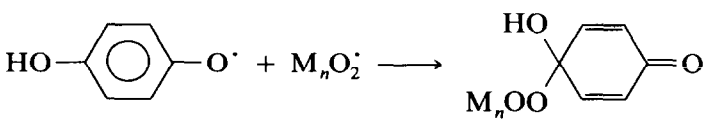

(14)

Depending on the relative rates of eqns. (13) and (14), each mole of hydroquinone may consume either one or two moles of radicals.

In eqns. (13) and (14), hydroquinone cannot inhibit the polymerization without first having oxygen to form peroxy radicals [11], hence the rate of oxygen depletion determines the inhibition time. This is proved by Kurland who polymerized acrylic acid with both high and low concentration of MMHQ, and found that inhibition time depends only on the concentration of dissolved oxygen and not on inhibitor concentration. According to Kurland, when inhibitor concentration is high, roughly one oxygen molecule is consumed per free radical. At very low inhibitor concentrations, about 10–30 oxygen molecules are consumed per radical because of formation of polyperoxide. At intermediate inhibitor concentrations, the rate of oxygen consumption depends on the relative rates of reaction of the peroxide radical $RO_2^{\cdot}$ with inhibitor and monomer.

Phenol-based inhibitors are hence sensitive to the rate of oxygen diffusion into the resin. The length of inhibition is determined by (1) the initial oxygen concentration, (2) the rate of oxygen diffusion, and (3) the rate of radical initiation. If initiation is faster than diffusion, for example, then oxygen concentration in the polymer will be low and hence inhibition time will be short. For this reason, photopolymerization in air is performed rapidly (at high UV radiation levels) to reduce the effect of oxygen [12].

Therefore, inhibitors can be divided into two classes: true inhibitors which are oxygen inert, and phenol-based inhibitors which requires oxygen. The role of oxygen in a DSC sample pan is examined next.

Oxygen inhibition in DSC samples

A DSC sample is shown schematically in Fig. 2. Typically, the sample fills only a portion of the volume in the sample pan, and the headspace above the sample will be the gas which was present when the sample was encapsulated. The DSC sample will be assumed to have a lid, and after sealing the sample pan is a closed system. If the pans were sealed in air, for example, the sample headspace will continue to be air after sealing, even though the pan is later placed in a pure nitrogen environment.

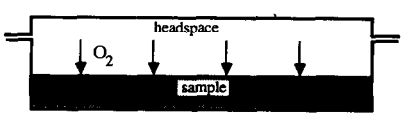

Fig. 2. Schematic diagram of DSC sample pan with oxygen in the headspace diffusing into the sample.

As shown in eqn. (8), the inhibition time t_z is proportional to the initial concentration of inhibitor, here defined to be $[Z]_{tot}$

$$t_z = \frac{[Z]_{tot}}{2f[I]_0 k_d} \tag{15}$$

When both oxygen-inert and oxygen-active inhibitors are present, $[Z]_{tot}$ can be expressed as

$$[Z]_{tot} = \underset{O_2 \text{ inert}}{y[Z_0]_0} + \underset{O_2 \text{ active}}{\frac{[O_2]_0 + \Delta[O_2]}{\nu}} \tag{16}$$

where y is the number of radicals consumed per inhibitor molecule, ν is the mean number of oxygen molecules consumed per free radical, $[Z_0]_0$ is the initial concentration of oxygen-inert inhibitor, $[O_2]_0$ is the initial concentration of oxygen in the resin sample and $\Delta[O_2]$ is the concentration of oxygen which diffuses into the sample from the headspace during inhibition. Based on the work of Kurland [10], the value of ν decreases as the concentration of oxygen-active inhibitor $[Z_1]_0$ increases, which may be approximated with an empirical expression

$$\nu = \frac{g}{[Z_1]_0} \tag{17}$$

where "g" is a proportionality factor of the order of 1 mM. Substituting eqn. (17) into eqn. (16)

$$[Z]_{tot} = y[Z_0]_0 + \frac{[O_2]_0 + \Delta[O_2]}{g}[Z_1]_0 \tag{18}$$

we can see that $[Z]_{tot}$ is proportional to both $[Z_0]_0$ and $[Z_1]_0$. Substituting eqn. (18) into eqn. (15), we find that t_z should *not* depend on sample size when *only* oxygen-inert inhibitor is present (i.e. $[Z_1]_0 = 0$).

$$t_z = \frac{y[Z_0]_0}{2f[I]_0 k_d} \tag{19}$$

Determination of t_z when oxygen-active inhibitor is present requires $\Delta[O_2]$, which may be derived from solubility data, an oxygen-monomer partition coefficient, and molar balances in both the sample and the headspace. To simplify the model considerably, however, these effects are lumped into an oxygen efficiency factor, η_{oxy}

$$\eta_{oxy} = \frac{\text{moles of oxygen which diffuse into the sample during inhibition}}{\text{moles of oxygen initially in the headspace}}$$

$$= \frac{\Delta[O_2] V_{sample}}{n_{oxy} P_{amb} V_{headspace}/(RT_{amb})} \tag{20}$$

where n_{oxy} ($= 0.21$) is the mole fraction of oxygen in the atmosphere, and R

is the gas constant, P_{amb} and T_{amb} are ambient pressure and temperature, and $V_{headspace}$ and V_{sample} are the volumes of the trapped air and the DSC sample, respectively, inside the sample pan. After rearrangement of eqn. (20) for $\Delta[O_2]$, and substitution of eqn. (18) into eqn. (15), we find that t_z depends on the ratio of the headspace to sample volumes,

$$t_z = \left[[O_2]_0 + \frac{\eta_{oxy} n_{oxy} P_{amb}}{RT_{amb}} \frac{V_{headspace}}{V_{sample}} \right] \frac{[Z_1]_0}{2f[I]_0 k_d g} \tag{21}$$

When t_z is plotted versus the volume ratio $V_{headspace}/V_{sample}$, the x-intercept from eqn. (21) is expected to be

$$x\text{-intercept} = -\frac{[O_2]_0 RT_{amb}}{\eta_{oxy} n_{oxy} P_{amb}} \tag{22}$$

After inhibition, peroxy radicals and inhibitor are assumed to be completely consumed, so neither oxygen-active or oxygen-inert inhibitors are expected to affect the rate of polymerization.

EXPERIMENTAL

Styrene (Aldrich) was polymerized with 27.5 mM 2,2′-azobisisobutyronitrile (AIBN, Kodak) initiator and with 0.42 mM *p*-benzoquinone (BQ, Aldrich) or 0.42 mM hydroquinone (HQ, Aldrich) inhibitors. Inhibitor shipped with styrene was removed by washing twice with 10% aqueous potassium hydroxide solution. Washed styrene was stored under refrigeration with molecular sieves to remove water. AIBN was recrystallized in methanol and stored at −10 °C. HQ and BQ were used directly from the manufacturer without further purification.

Kinetic measurements were performed on a Perkin–Elmer DSC7. Styrene samples of various sizes were cured in Perkin–Elmer volatile pans at 64 °C. Inhibition time was usually between 3 and 30 min, and t_z was determined by extrapolation of the heat flow data back towards the baseline, as shown in Fig. 3. Samples of various sizes were also run for styrene and AIBN

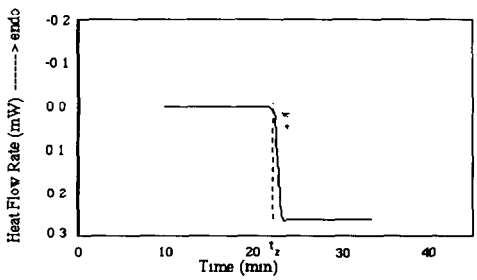

Fig. 3. Method of finding inhibition time of styrene polymerization from isothermal DSC data.

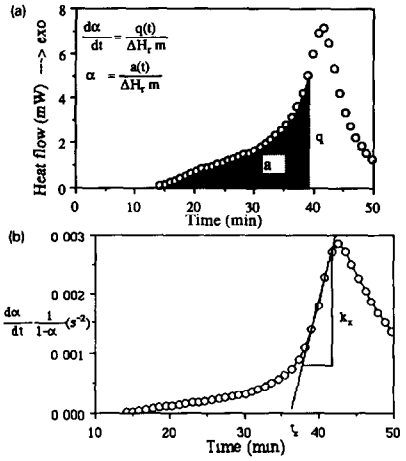

Fig. 4. Calculation procedure for finding (a) conversion $\alpha = \{([M]_0 - [M])/[M]_0\}$ and rate of conversion $d\alpha/dt$ and (b) inhibition time t_z and propagation slope k_x from isothermal DSC data.

without either HQ or BQ. The ratio $V_{headspace}/V_{sample}$ is found from the sample mass m by the conservation of volume

$$\frac{V_{headspace}}{V_{sample}} = \frac{V_{tot} - V_{sample}}{V_{sample}} = \frac{V_{tot}}{m/\rho} - 1 \tag{23}$$

where V_{tot} is the total volume of the DSC sample pan and ρ is the resin density.

The effect of sample size was also studied with a crosslinking vinyl ester resin (Derakane 411-35, Dow) with 35 wt.% styrene and an unknown mixture of inhibitors. The initiator was 2 wt.% (120 mM) *t*-butyl perbenzoate (TBPB) (93% assay, Pennwalt) at 100 °C. Resin and initiator were mixed vigorously in air for at least 1 min and air bubbles were allowed to escape (about 90 min) before DSC samples were made. The inhibition time t_z and propagation slope k_x were found by plotting the reduced rate of conversion $d\alpha/dt\ 1/(1-\alpha)$ versus time and finding the x-intercept and slope, as

TABLE 1

Specifications of several DSC sample pans

Pan	Manufacturer	Material	Volume (μl)
Standard	Perkin–Elmer	Al	$\geqslant 0$
Volatile	Perkin–Elmer	Al	25
Hermetic	Du Pont	Al	25
Hermetic (inverted)	Du Pont	Al	$\geqslant 0$
Large volume	Perkin–Elmer	SS	75

shown in Fig. 4. From dynamic DSC measurements, the heat of cure ΔH_r was found to be 325 J g^{-1}.

Experiments with vinyl ester resin used volatile, standard, hermetic, inverted, and large volume pans with sample masses between 3 and 30 mg. Values of V_{tot} for each of these pans are given in Table 1. Full volatile and hermetic pans (sample masses of 22 mg and 25 mg, respectively) were washed in chloroform or dichloromethane to remove excess resin on the outside of the pan. To further study the effect of oxygen, a 5 mg sample inside a large volume pan was covered with aluminum foil. The inhibition time of the covered sample was compared to that of an uncovered 5 mg sample in the same pan.

RESULTS AND DISCUSSION

The inhibition times for styrene are plotted for different sample masses in Fig. 5. Samples with no added inhibitor did not have any measurable inhibition time, regardless of sample size. Apparently, the startup transient for DSC (1–3 min) is longer than the inhibition time, and oxygen alone is not a strong inhibitor for styrene under these conditions. Samples with BQ, an oxygen-inert inhibitor, have roughly the same inhibition time regardless of sample size. Sample size is not an important consideration for these inhibitors. The inhibition time for HQ, however, is very dependent on sample size, ranging from about 5 min for an 18 mg sample to over 30 min for a 4 mg sample. The synergism between oxygen and HQ is apparent from this sample size dependence. Inhibition times with BQ decrease slightly with large samples perhaps because of a small synergism with oxygen, but this effect is slight.

These results agree qualitatively with the theory of oxygen-inert and oxygen-active inhibitors derived above. To test the theory quantitatively, the inhibition times are plotted versus $V_{headspace}/V_{sample}$ (Fig. 6). As predicted by eqn. (21), t_z increases linearly with volume ratio for HQ, and by eqn. (19), t_z is nearly independent of volume ratio for BQ. The x-intercept for the HQ

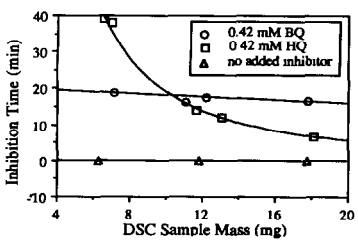

Fig. 5. Effect of sample mass on inhibition time for the polymerization of styrene.

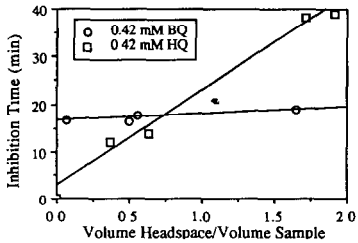

Fig. 6. Dependence of inhibition time on the ratio of pan headspace volume to sample volume for styrene.

samples is -0.195. Kurland [10] estimates $[O_2]_0$ for acrylic acid in equilibrium with air to be 1.6 mM. Assuming that η_{oxy} is unity, the x-intercept is calculated from eqn. (22) to be -0.185, which is close to the experimental value.

The effect of sample size on the reduced reaction rate data for vinyl ester samples in volatile sample pans is shown in Fig. 1. Values of t_z are plotted versus volume ratio for several pans in Fig. 7. All data for different sample sizes and pans fall on the same line, indicating that oxygen inhibition is the same for all pans.

Further evidence of oxygen inhibition is seen by comparing inhibition times on a sample in a large volume pan with and without foil. Without foil, a 6 mg sample has an inhibition time of 84 min, but when the sample is covered with foil, t_z is only 17 min. The foil acts as a vapor barrier which prevents transport of oxygen to and from the headspace.

Comparing Fig. 7 with Fig. 6, the commercial resin has characteristics of both oxygen-active and oxygen-inert inhibitors since Fig. 7 has both a nonzero y-intercept value and strong sample size dependence. The presence of both types of inhibitors has been confirmed by the resin manufacturer [13]. DSC testing of other polyester and vinyl ester resins have also shown that both types of inhibitors are present. Manufacturers perhaps use oxygen-active inhibitors to prolong shelf life while stored in air, while oxygen-inert inhibitors are used to prevent premature gelation during molding.

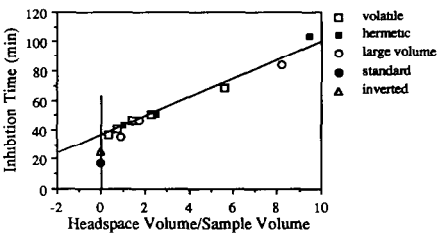

Fig. 7. Dependence of inhibition time on the ratio of headspace volume to sample volume for several types of DSC samples pans with vinyl ester resin.

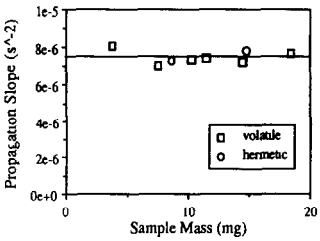

Fig. 8. Effect of sample mass on propagation slope k_x for vinyl ester resin.

Though t_z is very dependent on sample size, the propagation slope k_x (see Fig. 4b) changes little. Fig. 8 shows that values of k_x for both hermetic and volatile pans are independent of sample size. This shows that reaction kinetics *after inhibition* are unaffected by the amount of oxygen initially in the sample pan. Hence, even though inhibition is greatly affected by oxygen, the curing afterwards shows no significant effect of sample size.

In summary, sample size has no effect on the polymerization for samples with oxygen-inert inhibitors. Oxygen-active inhibitors, on the other hand, can cause an anomalous sample size dependence. Good agreement was observed between the inhibition model and the experimental data for both styrene and a vinyl ester resin. The commercial system was found to have both types of inhibitors.

PROCEDURES TO ELIMINATE OXYGEN INHIBITION

If a sample only has oxygen-inert inhibitors, no special precautions are necessary to prevent prolonged oxygen inhibition in DSC testing. However, resins with oxygen-active inhibitors require a special preparation procedure to avoid oxygen inhibition.

Oxygen is sometimes removed from the headspace by displacing air with nitrogen or argon before sealing. This technique is not recommended. Tryson and Shultz [3] found that oxygen dissolved in the resin sample is removed within minutes in an oxygen-free environment. Loss of oxygen from the sample is not encountered during processing, however, and hence DSC inhibition time in an oxygen-free headspace will be shorter than for the oxygen saturated resin during processing. Just as oxygen diffusion from the headspace prolongs inhibition, oxygen diffusion from the sample shortens inhibition, and both occurrences invalidate DSC results for process modeling.

The recommended procedure to avoid anomalous sample size effects is to seal DSC sample in a "closed-mold" environment to remove the headspace

and simulate the conditions during molding. Completely filling a sample pan is simple and it is effective in eliminating the oxygen in the headspace without losing the oxygen from the sample. Other techniques such as capping with paraffin are not recommended since the sealant may affect reactivity and gaps in the wax will allow oxygen diffusion into the sample. Aluminium foil or plastic film over the sample are also not recommended because heat transfer during cure may be restricted.

A concern about using full sample pans, however, is that they require large sample masses. Perkin–Elmer volatile pans require about 18–24 mg of sample to fill the pan. Du Pont hermetic pans require 25 mg. Large sample masses make the DSC data prone to poor temperature control and to thermal lags within the sample. If the peak heat flow is greater than 7 mW in Perkin–Elmer volatile sample pans [1], the shape of the peak may be distorted.

Distortion can be avoided in isothermal runs by curing at lower temperatures. If high temperatures are desired, however, two DSC runs can be run for each formulation: one with a full pan to measure the inhibition time in a "closed-mold" environment, and one with a smaller sample size to measure the rate of cure without the influence of peak distortion. Also, large samples are not recommended for heat flux DSCs. The two-sample procedure is perhaps the best technique when using heat flux DSCs for free radical polymerization.

OTHER SYSTEMATIC ERRORS

DSC data for free radical systems are susceptible to several systematic errors other than the sample size anomaly. Reaction during room temperature storage is significant, especially for low temperature initiators. Samples should not be stored for more than a few days for high temperature initiators, and not more than one day for low temperature initiators. Samples stored in darkness have a longer shelf life than samples left in ambient light. Refrigeration is not recommended unless precautions are taken to prevent water vapor from condensing into the sample.

Careful sample preparation procedures are advised. Oxygen will diffuse into the resin sample after mixing, so the DSC pans should be loaded a consistent time (1–5 h) after mixing the sample in air. Generally, the resin is safe to use if the bubbles entrained in the resin during mixing are gone. However, a gradient in oxygen within the sample vial is possible because of oxygen diffusion from the air.

To make sample size and oxygen concentration reproducible, samples are dropped from a disposable pipette tip (Markson Science, Inc., Del Mar, CA, part number 11803) after dipping into the resin formulation a distance of 1 cm. Consecutive drops from the pipette tip are decreasing in size, and

depending on the resin viscosity and the desired sample size, the first, second, or third drop should be used to fill the sample pan. Surface tension will hold resin above the lip of the pan, and this excess resin can be either squeezed out when closing the pan or it may be leveled off with a spatula. The lid of the pan is placed onto the sample at an angle to prevent trapping air. Excess resin which may squeeze out of the pan during crimping should be washed with methylene chloride and dried before inserting into the DSC.

Because the sample pans are full, some problem may be encountered with the pan rupturing during a run owing to expansion of the resin. If problems persist, use slightly smaller samples so that the headspace of the pan is small. Oxygen inhibition will not be significant if the pans are more than 80% full. Samples should be weighed before and after DSC testing to check for weight loss, which will be considerable (5–20%) if the pan seal has ruptured. Frequent cleaning of the DSC may be necessary by heating to 500 °C if resin spills onto the sample pan holder.

CONCLUSIONS

Oxygen inhibition has been demonstrated to lead to anomalous sample size effects when measuring free radical kinetics by DSC. When a sample contains oxygen-active inhibitors such as hydroquinone, oxygen in the headspace will diffuse into the sample to prolong inhibition, hence inhibition time is inversely proportional to sample size. The inhibition time with other oxygen-inert inhibitors, such as *p*-benzoquinone, is independent of sample size. A theory developed for inhibition time of both these inhibitors was verified with the polymerization of styrene. Inhibition time behavior of vinyl ester resin was also studied using different types of sample pans, and in all cases inhibition time increased linearly with the ratio of headspace volume to sample volume. The inhibition time behavior of commercial resins in general show evidence of having both oxygen-active and oxygen-inert inhibitors.

The recommended method for overcoming oxygen inhibition is to completely fill a volatile or hermetic sample pan. The necessary sample sizes are large (roughly 25 mg), so temperature control during cure may be a problem. When the heat flow limit (7 mW) is exceeded, two experiments are recommended for each formulation: one with a full pan to measure inhibition time without oxygen inhibition, and one with a small sample mass to reduce the amount of peak distortion.

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REFERENCES

1 G.L. Batch and C.W. Macosko, 18th North American Thermal Analysis Society Conf., San Diego, September 1989, Paper 93.
2 F.R. Wight, J. Poly. Sci., Poly. Lett. Ed., 16 (1978) 121.
3 G.R. Tryson and A.R. Shultz, J. Poly. Sci., Polym. Phys. Ed., 17 (1979) 2059.
4 C. Decker and K. Moussa, Am. Chem. Soc., Polym. Prepr., 29(1) (1988) Toronto, p. 516.
5 J. Bradrup and E.H. Immergut, (Eds.), Polymer Handbook, Wiley, New York, 2nd edn., 1975.
6 F.R. Mayo and A.A. Miller, J. Am. Chem. Soc., 80 (1958) 2493.
7 F.A. Bovey and I.M. Kolthoff, Chem. Rev., 42 (1947) 491.
8 J.W. Breitenbach and H.L. Breitenbach, Z. Phys. Chem. A190 (1942) 361.
9 K.K. Georgieff, J. Appl. Polym. Sci., 9 (1965) 2009.
10 J.J. Kurland, J. Polym. Sci., Polym. Chem. Ed., 18 (1980) 1139.
11 J.W. Breitenbach, A. Springer and K. Horeischy, Ber. Dtsch. Chem. Ges., 71B (1938) 1438.
12 N.A. Peppas and A.G. Mikos, in N.A. Peppas (Ed.), Hydrogels in Medicine and Pharmacy, Volume 1. Fundamentals, CRC Press, Boca Raton, FL, 1986.
13 L.R. Blankenship, personal communication, 1988.