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Instrumental response analysis

MTDSC AT THE GLASS TRANSITION
Quantitative use of the phase lag correction
The effects of long annealing times

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Abstract

A study of the effects of changing sample mass and purge gas on the phase lag and calculation of the out of phase (kinetic) component for polystyrene in MTDSC was undertaken. The results confirm those from an earlier study that suggested the kinetic signal is unchanged by altering these parameters thus it is probably a correct quantitative measure of this signal. The effects of long annealing times were also studied and it was shown that all the signals of MTDSC are affected in contrast to a previous study showing that for moderate annealing the reversing and kinetic signals are substantially invariant. Nevertheless the non-reversing signal remains useful for characterising relative enthalpy losses.

Keywords: annealing, glass transition, phase lag, MTDSC, TMDSC

Introduction

When Reading and co-workers introduced MTDSC [1–7] (MTDSC is also called TMDSC), in one of the first articles on the technique the use of the phase lag to obtain both the in and out of phase components of the sample's response to the perturbation was explained and demonstrated [2]. However, we also identified that there were problems in ensuring that the out of phase quantity was determined accurately [5, 9]. We noted that, while the in phase or reversing the signal and the total signal could be calibrated against known standards, this was not true for the out of phase signal. One problem that we identified was that, ideally, the phase lag should be zero when no transition was occurring, whereas the phase

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lag, in practice, was never zero. We proposed a simple baseline interpolation procedure be used to correct for this where a point was selected before and after the transition and the baseline was drawn between these two points [2, 10]. This procedure was based on the assumption that no transition was occurring at the two selected temperatures. To determine whether this was a valid procedure we formulated a rigorous mathematical model for a heat flux DSC under MTDSC conditions [10]. We concluded from our analysis that this should be a valid procedure and devised a test to determine whether this was in fact the case. According to our mathematical model this baseline correction procedure should not be influenced by the calibration constant of the calorimeter or by the sample mass. One simple way of changing the calibration constant of a heat flux DSC is to change the purge gas from nitrogen to helium. Consequently we predicted that our phase lag correction procedure should yield the same calculated value for the out of phase component regardless of whether the experiment were conducted under helium or nitrogen and regardless of sample mass. We presented the data for the glass transition of polystyrene which showed close agreement between the values for the out of phase components obtained are under these two different purge gases and for a range of masses [10]. Our results appeared to confirm that our proposed methodology for calculating the total phase component was correct.

In this article we present in more detail a further independent set of data that examines the effects of changing sample mass and the purge gas from nitrogen to helium that further supports the validity of our approach. We also present the results of a further investigation of the effects of annealing.

Nomenclature

To avoid possible confusion it is appropriate to say a few words about the nomenclature of the various signals derived from a MTDSC experiment. The first point is that all signals can be expressed either as heat capacities or as heat flows, the former quantity being the latter quantity multiplied by the average heating rate. In our original article in which we demonstrated how the phase lag can be used to calculate the in and out of phase components [2], we expressed all quantities in terms of heat flows. Subsequently it has become common practice to express quantities as heat capacities and this is the practice that we employ here. We prefer the following nomenclature:

Total heat capacity: this is obtained by dividing the average heat flow a by the average heating rate and is the equivalent of a heat capacity obtained from conventional DSC.

Complex heat capacity: This is the heat capacity determined from the response to the perturbation before any correction for the phase lag is applied a.

Reversing heat capacity or C': this is the in phase component of the heat capacity determined from the response to the perturbation.

Kinetic heat capacity or C'': this is the out of phase component of the heat capacity determined from the response to the perturbation.

The non-reversing heat capacity: this is the difference between the total heat capacity and the reversing heat capacity.

The formalism that the response to the perturbation be described as a complex quantity with a real or storage (in phase) and an imaginary or loss (out off phase) components was first proposed by Schawe [8]. We prefer the nomenclature or reversing and kinetic heat capacity (or heat flows) for the in and out of phase signals respectively, because this conveys some idea of the significance of these quantities. The use of storage and loss is misleading as heat capacity is not 'lost'. Reversing is intended to convey that this is a measurement of the energy contained (usually) in vibrational modes that can respond rapidly and reversibly, the kinetic component is a measure of any non-rapid kinetically hindered response. It is important to realise that the adoption of a complex notation in no way constitutes a change to the technique or the theoretical interpretation as has sometimes been suggested. These different terms are completely interchangeable as is the use of the heat flows or heat capacities.

Experimental

All of the results presented here are on polystyrene on a TA Instruments 2920 with a mechanical cooling accessory. We have made the assumption of that the heat capacity above and below the glass transition are the same in all of the samples. Accordingly we have applied in each case the calibration constant and the baseline shift required to ensure that the heat capacity measured above and below the transition accorded with the reference data supplied by a Wunderlich's ATHAS database. Heat capacities obtained using a reference materials such as sapphire as a calibrant could not be expected to be accurate to more than a few per cent (certainly differences in heat capacity above and below the glass transition would be smaller than the accuracy of this measurement). We concluded that the effectively random displacement of the data introduced by these measurement errors would simply confused the interpretation. Using the procedure we have adopted here all measurements are the same above and below the transition region and changes in this transition region then can be discerned with clarity.

Results

Figure 1 shows the phase lag (between derivative of temperature and heat flow) results for a series of experiments using different weights of polystyrene under both nitrogen and helium. All experiments were carried out cooling at

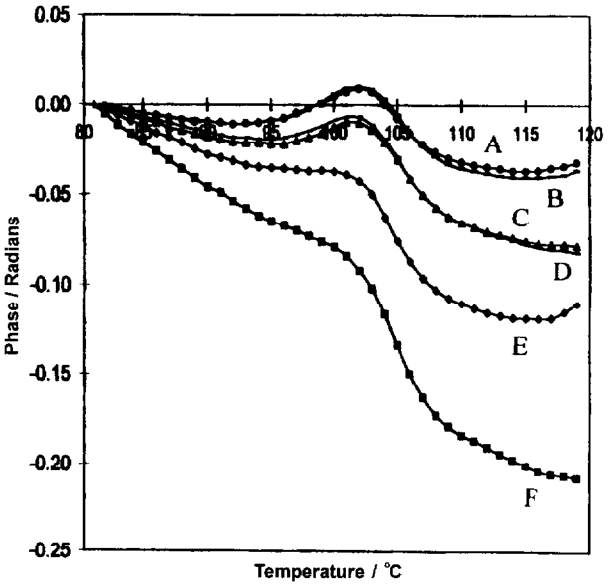

Fig. 1 Phase angle for various masses of polystyrene under nitrogen and helium; A, 7.6 mg He; B, 5.7 mg He; C, 7.6 mg N_2; D, 5.7 mg N_2; E, 3.1 mg He; F, 3.1 mg N_2

1°C min^{-1}, 60 s period with 1°C amplitude. All traces have been forced to zero at the start of the experiment (by subtracting a constant) to facilitate comparison. It can be seen that in all cases there is some baseline drift and that this becomes worse with reducing sample mass and in changing from helium to nitrogen. The origin of these drifts both within the transition region and outside is obscure. In our mathematical analysis we concluded that such drifts occurred as a consequence of the non ideal behaviour of the calorimeter [10]. However, this leaves unanswered the question of why it changes with sample mass. Figure 2 illustrates our baseline correction procedure using in both cases a sigmoidal baseline for the data set with the most and the least drift. It can be seen that, after correction, the two phase shift are similar. Figure 3 shows the reversing or *C′* results calculated using the corrected phase shifts. Reasonable agreement is seen for all sample masses in both nitrogen and helium as would be expected. Figure 4 gives the kinetic heat capacity. The variation are random and follow no real trend with either sample mass or purge gas. This variation is, therefore, probably a measure of the fundamental experimental inaccuracy. Generally the agreement is reasonable and confirms our original results [10]. The fact that the results do not change with sample mass and purge gas suggests these results can be considered a correct quantitative measure of this signal.

In previous article [11] we examined the effect of annealing for up to 45 min on the glass transition of polystyrene. Unfortunately one of the figures in this ar-

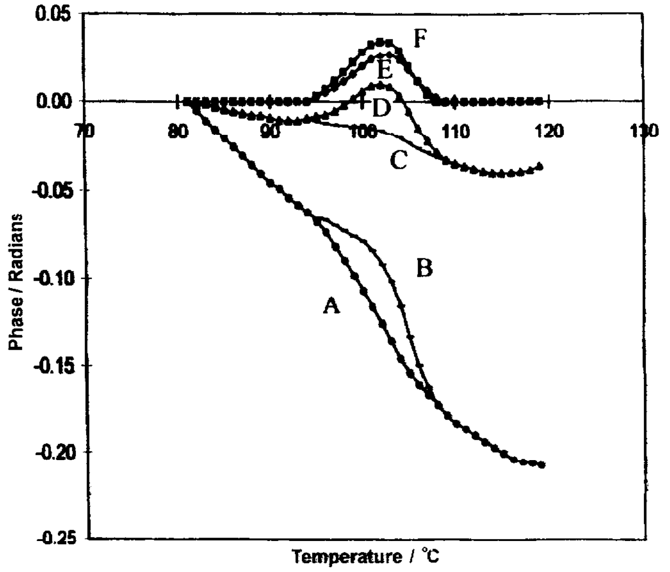

Fig. 2 Phase angle for 3.1 mg under nitrogen and 7.6 mg under helium from Fig. 1 illustrating the base-line correction procedure;
A, base-line 3.1 mg N_2; B, 3.1 mg N_2; C, base-line 7.6 mg He; D, 7.6 mg He;
E, corrected phase 7.6 mg He; F, corrected phase 3.1 mg N_2

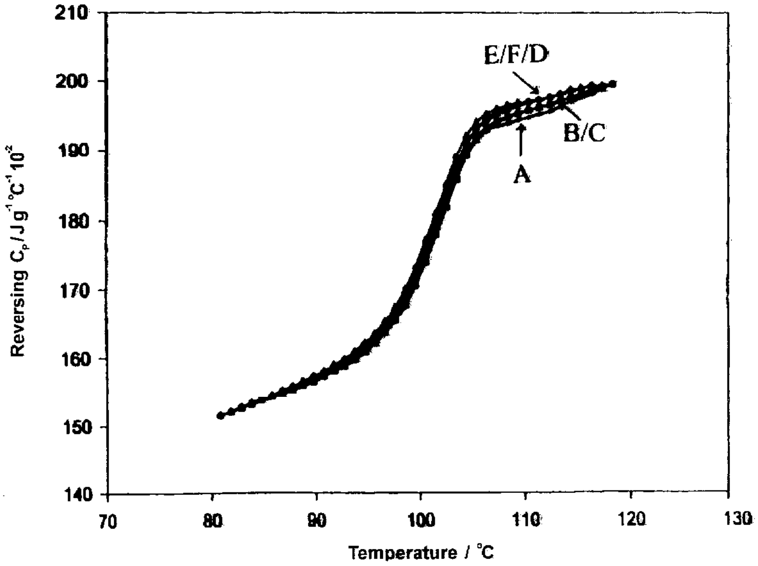

Fig. 3 Reversing heat capacity for polystyrene, various masses under nitrogen and helium; all experiments carried out at 1°C min^{-1}, ±1°C every 60 s;
A, 3.1 mg PS, helium; B, 5.7 mg PS, helium; C, 7.6 mg PS, helium;
D, 3.1 mg PS, nitrogen; E, 5.7 mg PS, nitrogen; F, 7.6 mg PS, nitrogen

ticle is incorrect. Figure 3 in [11] should be the kinetic heat capacity whereas the non-reversing signal is given (and is also given as Fig. 4). Figure 5 is the correct Fig. 3 for [11]. The conclusion of this study, supported by Fig. 5 here, is that the

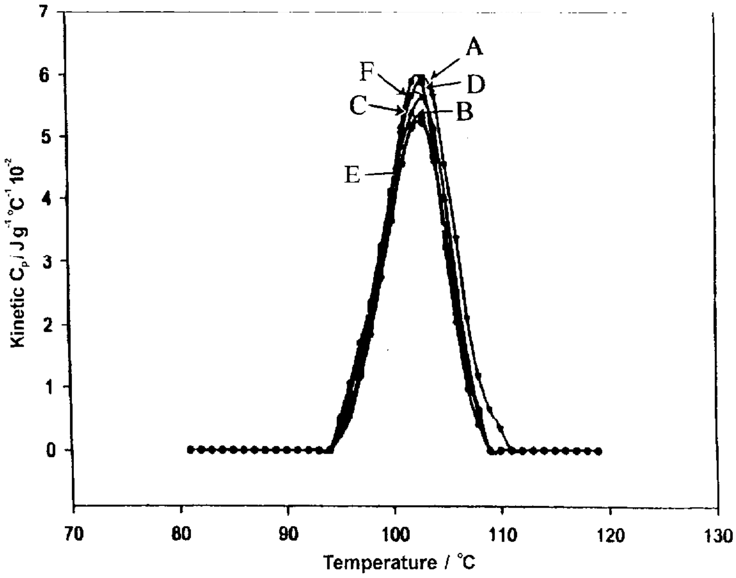

Fig. 4 Kinetic heat capacity for polystyrene, various masses under nitrogen and helium; all experiments carried out at 1°C min^{-1}, ±1°C every 60 s;
A, 3.1 mg PS, helium; B, 5.7 mg PS, helium; C, 7.6 mg PS, helium; D, 3.1 mg PS, nitrogen; E, 5.7 mg PS, nitrogen; F, 7.6 mg PS, nitrogen

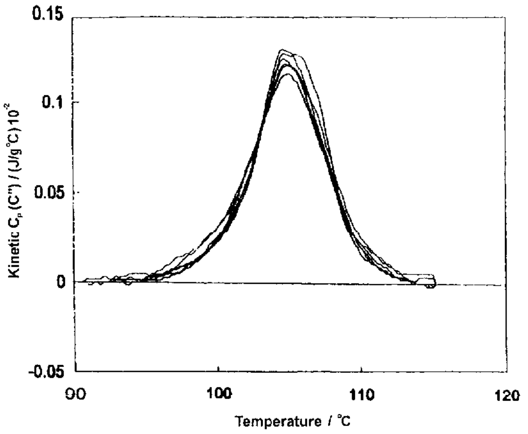

Fig. 5 Kinetic heat capacity for polystyrene annealed for various times up to 45 min (not indicated as all measurements are the same to within experimental error);
This figure should have appeared as Fig. 3 in [11]

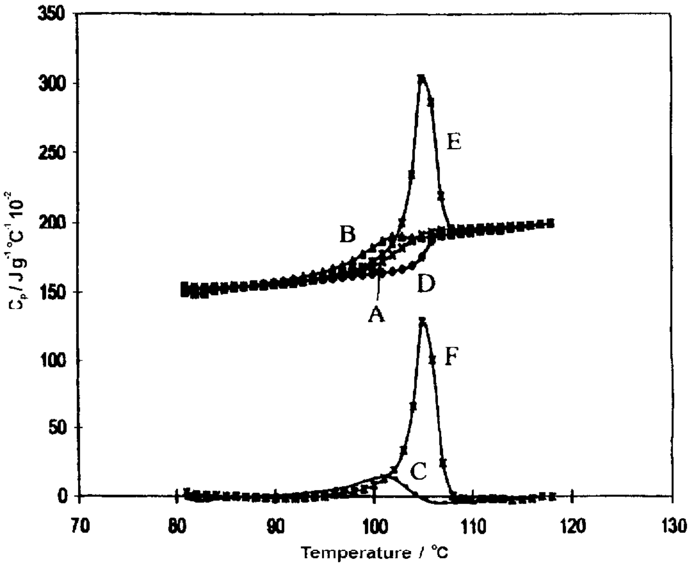

Fig. 6 Total, reversing and non-reversing heat capacities for an unannealed sample of polystyrene and one annealed for 60 h: A, C' for no annealing; B, total C_p for no annealing; C, non-reversing signal for no annealing; D, C' for 60 h annealing; E, total C_p for 60 h annealing; F, non-reversing C_p for 60 h annealing

annealing had little effect on the reversing and kinetic signals [11]. Consequently the non-reversing signal was linearly related to the enthalpy loss on annealing. Here we consider the effects of much longer annealing times.

Figure 6 shows the total, reversing and non-reversing heat capacities for an unannealed sample and one annealed at 93 degrees for 60 h. Again all experiments were carried out at 1°C min^{-1}, 60 s period with 1°C amplitude under nitrogen. The expected peak is seen in the total and non-reversing signals for the annealed sample. However, in contrast to the previous results for moderate amounts of annealing, the annealing has a noticeable affect on the reversing heat capacity. Figure 7 shows the reversing signal for a range of annealing times (all greater than in our previous study). Figure 7 gives the kinetic signal which is also noticeably affected by the annealing, in contrast to Fig. 5. Figure 8 shows the non-reversing signal.

The change in the reversing heat capacity with annealing means that the relationship between the non-reversing signal and the enthalpy loss on annealing is no longer linear. A measure of the deviation from linearity can be obtained by comparing the area under the non-reversing signal for the 60 h annealing and the area under the difference between the reversing signal for no annealing and 60 h annealing, these data are given in Fig. 9. These areas are 407 J g^{-1} and 90 J g^{-1}, respectively. Consequently the deviation is about 22%. While this deviation is significant, the nature of the change in the reversing signal with annealing means

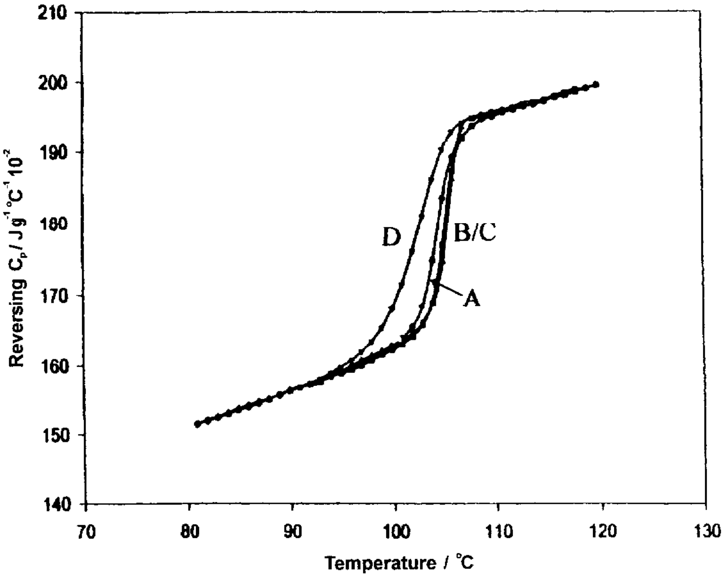

Fig. 7 Reversing heat capacity for polystyrene annealed at 93 degrees for various times; all experiments carried out at 1°C min^{-1}, ±1°C every 60 h;
A, PS (16 h annealed), nitrogen; B, PS (30 h annealed), nitrogen; C, PS (60 h annealed), nitrogen; D, PS (no annealing), nitrogen

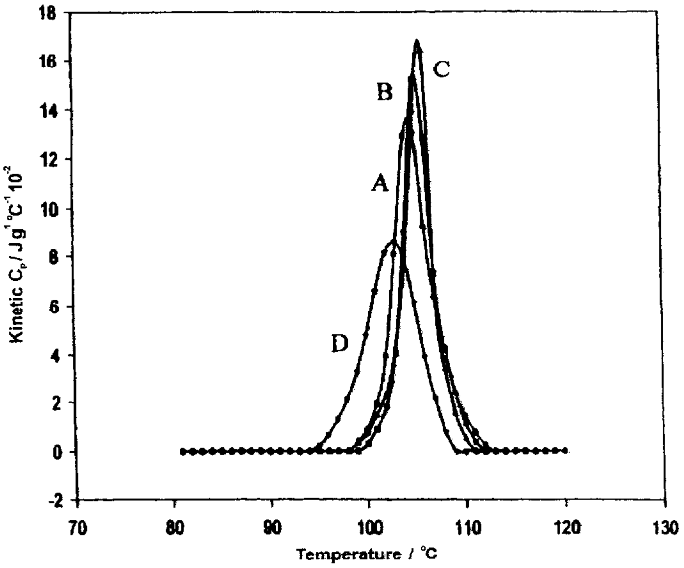

Fig. 8 Kinetic heat capacity for polystyrene annealed at 93 degrees for various times; all experiments carried out at 1°C min^{-1}, ±1°C every 60 h;
A, PS (16 h annealed), nitrogen; B, PS (30 h annealed), nitrogen; C, PS (60 h annealed), nitrogen; D, PS (no annealing), nitrogen

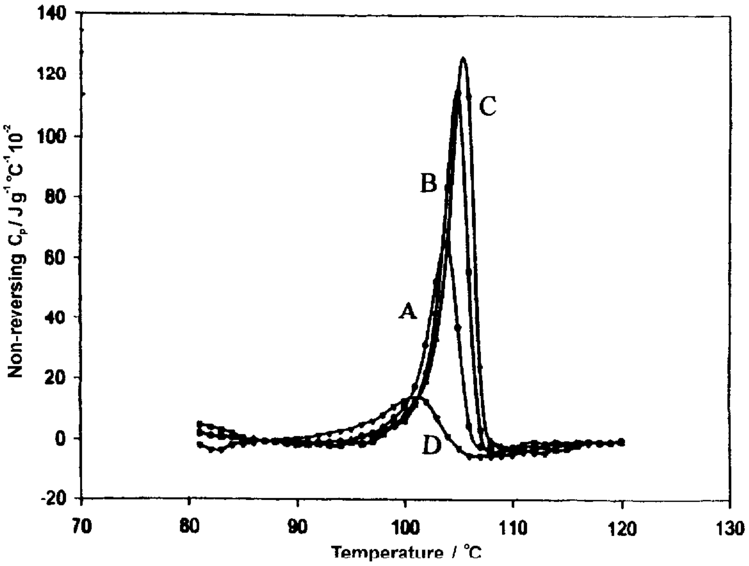

Fig. 9 Non-reversing heat capacity for polystyrene annealed at 93 degrees for various times; all experiments carried out at 1°C min^{-1}, ±1°C every 60 h;
A, PS (16 h annealed), nitrogen; B, PS (30 h annealed), nitrogen; C, PS (60 h annealed), nitrogen; D, PS (no annealing), nitrogen

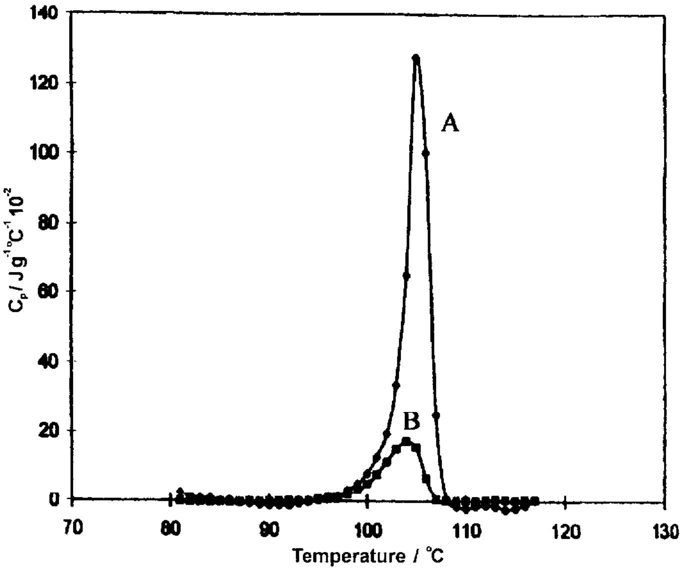

Fig. 10 Non-reversing heat capacity for polystyrene annealed at 93 degrees for 60 h coplotted with the difference between the reversing heat capacities for an unannealed sample and one annealed for 60 h; A, non-reversing signal for 60 h annealed sample; B, *C′* no annealing – *C′* 60 h annealing

that the non-reversing signal in an overestimate of the enthalpy loss thus it still increases monotonicaly with annealing time. The non-reversing signal, therefore, still remains useful for ranking systems which makes it adequate for many, particularly industrial, application. Our theoretical treatment of the glass transition [11] can be extended to account for this behaviour and we will present details of this in a future article.

Conclusions

The results obtained for different masses of polystyrene under both nitrogen and helium confirm our earlier findings and suggest that the baseline interpolation procedure we have proposed gives reasonably accurate values for the out of phase (kinetic) signal. Our earlier study showed that for small amounts of enthalpy loss on annealing the reversing signal remains substantially invariant thus the non-reversing signal is linearly related to the enthalpy loss. Here we have shown that for greater degrees of enthalpy loss both the reversing and the kinetic signals are affected thus this linear relationship is compromised. However, the non-reversing signals remains a useful comparative measure of enthalpy loss for many applications.

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